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Modelling scenarios of environmental recovery after implementation of controls on emissions of persistent organic pollutants

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5 **Modelling scenarios of environmental recovery after implementation of controls**
6 **on emissions of persistent organic pollutants**

7
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13
14 **Abstract**

15 Comparison of monitoring data with toxicologically-derived environmental quality standards
16 (EQSs) forms the basis of assessments of the quality status of the water environment. Having
17 established the status quo, the logical next step is to address instances of non-compliance
18 with EQSs by applying remedial measures, including reducing the use or at least the emission
19 of the substances of concern or by taking steps to reduce concentrations already present
20 using technological solutions such as enhanced wastewater treatment. The selection of
21 suitable remedial measures must be a compromise between cost, likely effectiveness and the
22 timescale over which improvements might be acceptable. The decision on overall
23 environmental management has also to take into account the need for demonstrable progress;
24 this might mean that it is preferable to address some more readily achievable goal rather than
25 to attempt to solve a more serious, but ultimately intractable problem. This paper describes
26 the development and application of a generic modelling tool that provides a way of assessing
27 the potential requirements for remedial actions and their likely outcomes over a timescale of
28 up to forty years taking account of sediment partitioning, environmental degradation and
29 biological accumulation. The tool was validated using a detailed UK wastewater treatment
30 works effluent discharge dataset. Examples involving several chemicals that are of current
31 concern are provided. Some substances (e.g. tributyltin, PFOS) are identified as likely to meet
32 EQS values in sediments or biota in a relatively short timescale; others (PAHs, DEHP) appear
33 to represent more intractable problems.

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

37 1. Introduction

38

39 The accumulation in the environment of substances that are persistent, bioaccumulative and
40 toxic (PBT) can represent a risk to wildlife and the human population as a result of
41 bioaccumulation and biomagnification through food chains. This issue has been identified as
42 an important global issue since organo-chlorine based pesticides and industrial chemicals
43 were found to be bioaccumulating within the food chain with demonstrable negative impacts
44 in many cases(1). In recognition of this, the Stockholm Convention on Persistent Organic
45 Pollutants (POPs) was adopted in May 2001 and entered into force in May 2004. Initially this
46 protocol identified a ban on 9 organochlorine-based POPs; it restricted the use of DDT to
47 malaria control, and curtailed inadvertent production of dioxins and furans. Subsequently,
48 further chemicals have been added to the list for control or elimination where they meet PBT
49 criteria; these include brominated diphenylethers, perfluorooctanesulphonic acid (PFOS) and
50 perfluorooctanoic acid (PFOA) additional chlorinated benzenes and phenols and chlorinated
51 paraffins. Other substances such as tributyl tin (TBT) which owing to harmful effects on dog
52 whelks was banned in antifoulant paint formulations on vessels by the International Maritime
53 Organisation in 2008(2). For other chemicals there may be local or regional controls on its use
54 such as the pyrethroid insecticide cypermethrin(3) and hexabromocyclododecane (HBCDD)
55 which is listed under the Stockholm Convention and is present in Annex 1 of Regulation (EC)
56 No 850/2004. This prohibits its production, use, import and export. Chemicals such as methyl
57 mercury have been known to be an environmental hazard for decades but are released into
58 the environment from natural as well as anthropogenic sources. This has been addressed by
59 controls being placed on concentrations in food(4).

60

61 Although world-wide policies such as the Stockholm Convention adopts a hazard-based
62 approach and identifies substances for production controls or target environmental controls
63 for unintended releases, other (often regional) legislation (e.g. EU Water Framework Directive
64 and REACH) takes a risk-based stance with the derivation of Environmental Quality Standards
65 (EQS) to protect the most vulnerable biota (e.g.(5-12)). However, measures to achieve
66 reduction in the inputs of such substances do not always produce immediate effects in terms
67 of the observed environmental concentrations (and hence of perceived risk). This can be
68 related to the residual reservoir of contaminant in the environment, uses not included in the
69 applied measures as well as unauthorised uses and to the challenges of determining
70 concentrations, often at extremely low levels, in the targeted organisms or matrix of interest.
71 Where remedial action is taken to reduce pollutant concentrations, it can therefore be difficult
72 to determine the effectiveness of control measures.

73

74 Wastewater treatment works (WwTW) represent a potential major contributor of chemicals to
75 the environment because they receive discharges from domestic, commercial and industrial
76 sources as well as legacy issues such as landfill leachate and runoff from contaminated land
77 (13). Whilst a proportion of any given trace chemical might volatilise or degrade during the
78 treatment processes, or sorb to the treatment process sludge(14), concentrations in sewage
79 effluents can be a cause for concern(15,16). Modelling of the rates of change of contaminant
80 concentrations in effluents constitutes an important regulatory tool (supplemented by
81 monitoring) in prioritising control measures and assessing their current and likely future
82 effectiveness.

83

84 The development of generic or evaluative models is not a new approach to environmental
85 impact assessment. The fate and transport of chemicals in a hypothetical, yet standard (Unit
86 World) environment has been widely used to assess general features regarding the chemical
87 fate or to screen and prioritize chemicals based on a uniform assessment metric. These
88 fugacity based models, utilise concentration and mass balance, equilibrium (between media),
89 rate controlled mass transfer, first-order decay, and advective exchange with the external
90 environment to predict fate and behaviour(17-19). These models are can either be used for
91 bespoke, site-specific applications or provide a general guide to environmental improvement.
92 Depending on specific purposes, the models have been run at both steady and non-steady
93 state (dynamic)(19,20), for general use establishing the reversibility of environmental
94 contamination with POPs in a regional setting(21), the response of environmental
95 contamination in the Arctic to the reduction in the global emissions(22), or scenarios of
96 emissions associated with industrial production, use and waste disposal(23).

97

98 Such models have been applied to POPs such as brominated diphenylethers, PCBs,
99 hexachlorobenzene, atrazine, short chain chlorinated paraffins and hexachlorocyclohexane
100 for example(24). Furthermore, such models have been developed the multi-media model
101 concept yet further to encompass chemical classification, temporal persistence, spatial range,
102 human exposure, risk, and uncertainty(25-30). Most recently this broad approach has led to
103 the development of the ChemFate model which combines four different fate and transport
104 models and was applied to chemicals in current use with radically different physico-chemical
105 characteristics, such as copper sulphate, nano copper oxide, chlorothalonil and
106 cyprodinill(31).

107 With improved access to databases and ever more sophisticated computing software there is
108 a range of other available models and decision support tools available for environmental
109 modelling of chemicals. These include (1) domain knowledge modelling which has been

110 applied to wastewater management via the environmental decision support tools (EDSS) and
111 ontology-based wastewater environ-mental decision-support systems (OntoWEDSS)(32);
112 water quality modelling applied to eutrophication in Hong Kong(33) and river water
113 assessment(34); (2) data mining using remote sensing data for surface waters(35) and in
114 groundwater assessment(36); (3) Bayesian Networks for urban pollution prediction(37) and
115 emergent water pollution accidents risk analysis(38); or (4) a combination of these approaches
116 for water quality assessment(39). Water quality models are common and are available as
117 open source or commercially supported packages but are largely stochastic such as SIMCAT
118 which provides probability based estimates at any given instance in time (typically 1 to 3 year
119 periods⁽¹³⁾ or time series models such as INCA which can predict processes and trends but
120 require significant flow and land use data(40). Trends in POPs concentrations have been
121 monitored and modelled in biota from Polar regions(41). However, there is no 'off the shelf'
122 modelling tool available to fulfil the needs of being able to simply predict the length of time
123 required to achieve any given environmentally safe concentration for PBT chemicals at a local
124 level for meeting legislation such as the WFD.

125

126 Models are often developed as bespoke tools for meeting a defined purpose, whether for
127 industrial, regulatory or academic purposes. Consequently there is rarely an off-the-shelf
128 model available that fulfils all of the requirements of any given situation. The discharge of
129 wastewater into receiving waters is the main 'industrial' input of contaminants into the aquatic
130 environment of many countries including the UK. To be able to predict the impact of regulation
131 of POPs on long term concentrations in the aquatic environment as a result of WwTW
132 discharges and to be able to assess compliance with EQS is of vital importance to regulatory
133 agencies and sewage treatment operatives alike. This paper describes a novel prototype tool
134 that has been developed to specifically allow a user to predict the likely future effect of
135 measures to control environmental inputs from WwTW, based on current data that provide an
136 estimate of continual year-on-year percentage reduction.

137

138 This approach addresses the situation primarily where EQS style standards have been set for
139 biota or for surface waters where sediment concentrations might be an additional important
140 factor. A key feature is to determine the likely time taken to comply with an EQS and thereby
141 to prioritise action on substances for which measures are likely to be fruitful within a desired
142 timescale. The tool makes it possible to estimate (and visualise) the effect of a proposed
143 change in contaminant input on the likely environmental outcome over a 20-40-year planning
144 horizon. The tool is capable of being applied to all chemicals, even those of emerging concern
145 with lower Kow values, where it might be shown that bioconcentration via sediment and/or
146 biota is not a threat to compliance with EQS. However owing to the established PBT properties

147 of many established chemicals concern, the modelling tool was primarily developed to address
148 persistent contaminants that: a) are of concern in biota and b) are taken up by biota primarily
149 through exposure (through feeding or otherwise) to contaminated sediments. The initial
150 approach explained here outlines the development and examples of outputs, subsequent
151 developments have involved extensive improvements to the user interface and the output
152 visualisations, not discussed here. The tool is intended to be used in regulatory screening
153 scenario testing for generic risk assessment, not a site specific application. By taking this
154 approach it is possible to prioritise possible remedial action for regulated substances in biota
155 in relation to the likelihood that prompt action might feasibly be rewarded by worthwhile
156 progress towards compliance and to manage expectations for refractory substances that
157 would be likely to pose difficulties in meeting current standards.

158 2. Methods

159 2.1 Choice of test chemicals

160

161 The development of his tool, therefore, focused on an exposure pathway relating to
162 substances that are of interest because of their environmental persistence and their tendency
163 to adsorb to sediments. To demonstrate the efficacy of the approach an array of chemicals
164 from different sources and with differing physico-chemical characteristics was selected from a
165 longer list of priority chemicals (ESI, Table S1). Brominated diphenyl ethers,
166 diethylhexylphthalate (DEHP), tributyltin (TBT), hexabromocyclododecane, and the
167 fluorocarbons (PFOS and PFOA) have been subject to significant controls or bans to prevent
168 or minimise release to the environment. Their PBT properties, however, means that
169 environmental regulators need to be able to predict the time period that will be required to
170 meet compliance with set objectives. Two polynuclear aromatic hydrocarbons
171 (benzo(a)pyrene and fluoranthene) were selected as they are also PBT chemicals but are
172 capable of being generated naturally and the significant legacy contamination of the
173 environment means any die-away may be much slower than anthropogenic PBT chemicals.
174 Cypermethrin offered a contrast, as it is less persistent, is still being used under more
175 restricted circumstances than previously, but is of concern from a toxicity point of view.

176

177 Substances, having different chemical properties, for which the above modelling approach
178 might not be applicable, or for which the conceptual model might need to be modified, include
179 metals which do not decompose, and substances such as many pharmaceuticals that have a
180 lower affinity for particulate matter. In these cases, different approaches would be appropriate
181 to the estimation of exposure routes to biota and their ultimate environmental fate.

182

183

184 2.2 The approach

185

186 The development of the estimator tool itself is intended to provide an assessment of the effects
187 of pollution control interventions for different trace substances with an output visualising
188 change and indicating the likely time taken (for any chosen magnitude of reduced input) to
189 result in compliance with the EQS or other critical concentration values. Mechanistically, the
190 tool concentrates on the net overall outcome of the concurrent processes of contaminant
191 addition to the environment and of removal by processes of natural purification (degradation
192 and sorption to particulates). The tool is not an attempt to model specific conditions at any
193 particular location. To do this would require information on the nature, size and configuration

194 of the receiving environment and specific detail of local inputs and environmental processes
195 that are neither readily available nor in many cases even understood.

196

197 In order to make the outputs meaningful and to facilitate comparisons between substances
198 and different control measures a notional receiving environment is set up as part of the tool.
199 This comprises a nominal discharge for a WwTW corresponding to 50,000 population
200 equivalent, discharging to a watercourse that provides a nominal threefold dilution. Such a
201 dilution represents a reasonable worst case that takes account of the dilution for discharges
202 that for more than 98% of sewage treatment load in the UK for example(13). These
203 assumptions effectively determine the respective sewage effluent and river flow regimes. This
204 specified dilution/flow regime is then used in conjunction with the likely settling time of
205 discharged particulate matter to establish the width and length of the impacted watercourse
206 and hence the receiving sediment mass. In all outputs discussed here, this notional “sediment
207 target” is held constant, although the possibility to make alterations to the preceding
208 assumptions remains an option.

209

210 The operation of the estimator tool is to input different nominal control measures (the reduction
211 in concentration achieved is entered - the mechanisms of control are not considered) and to
212 determine the effect of these measures on resultant sediment and biota concentrations. Key
213 assumptions are that:

214 a) Contaminants can be discharged from a) the conceptual WwTW discussed above, or
215 b) from other point or diffuse sources in the area under consideration. A measured
216 concentration in sewage effluent is the basis of the former inputs. Estimation of the
217 latter contribution from non-WwTW sources is considered as a multiple of the WwTW
218 load. This is based on data provided by recent UKWIR catchment monitoring
219 programmes⁽⁴²⁾. These studies compared the in-river concentrations with known
220 sewage effluent sources. Any contributions to the former that were not assignable to
221 the latter were considered to be “non-WwTW” sources;

222 b) The pathway of a contaminant is via adsorption to sediment, settlement and then by
223 transfer (by exposure or through the food chain to aquatic or benthic organisms
224 (biota)). The implication of this is that dissolved contaminants are not taken into
225 account. This assumption is proposed as a workable proposition for PBT substances
226 because of their affinity for sediments; its adoption for more hydrophilic substances
227 where exposure of biota in the water column might not be appropriate.

228 Knowledge of the concentration of contaminants in the effluent discharge and their
229 characteristics regarding partitioning to particulate matter then makes it possible to calculate
230 the load discharged and the extent to which this will contaminate the sediment target referred
231 to above. This resulting sediment concentration is then used to estimate a concentration in
232 biota using the convention of a biota-sediment concentration factor (BSCF)(43).

233

234 **2.3 Calculations**

235

236 Further information on the calculations and in particular the units used are provided in the
237 Electronic supporting information (ESI Tables S2 and S3). Contaminants in the environment
238 are in a constant state of flux. Processes of addition and removal combine to determine
239 whether or not concentrations will tend to increase, decrease or, if these processes are in
240 balance, stay the same. Determination of the fate and behaviour of chemicals in the
241 environment is essentially a question of understanding rates of change. The rate of change in
242 concentration of an environmental contaminant is determined by two factors. Firstly, there is
243 the rate of disappearance of the substance; this can be assumed to be related to how much
244 substance is present at any given time. This has been considered to follow a so-called first
245 order exponential decay curve. The second factor is the rate at which the substance is added
246 by the processes that raised the concentration in the first place, in this case, discharges from
247 wastewater treatment works (WwTW) and release from other unspecified sources
248 (categorised as non-WwTW inputs).

249

250 The rate of change of concentration may therefore be given by equation (1):

252

$$251 \frac{dy}{dx} = -k \times y + S \times x \quad (1)$$

253

254 Where y is concentration, x is time (e.g. years); S is the amount of substance added to
255 sediment per unit time and k is the decay rate constant = $[\ln(2)/(\text{the half-life})]$. Hence:

256

$$257 \frac{dy}{dx} + k \times y = S \times x \quad (2)$$

258

259 This is a first order differential equation of a standard form that can be solved for y to give the
260 solution below:

261

$$262 y_x = c_1 \times e^{-kx} + c_2 \quad (3)$$

263

264 where c_1 and c_2 are constants of integration. The constant c_2 is calculated as $-s/k$; c_1 relates
265 to conditions at time x ($S_x/-k$), hence:

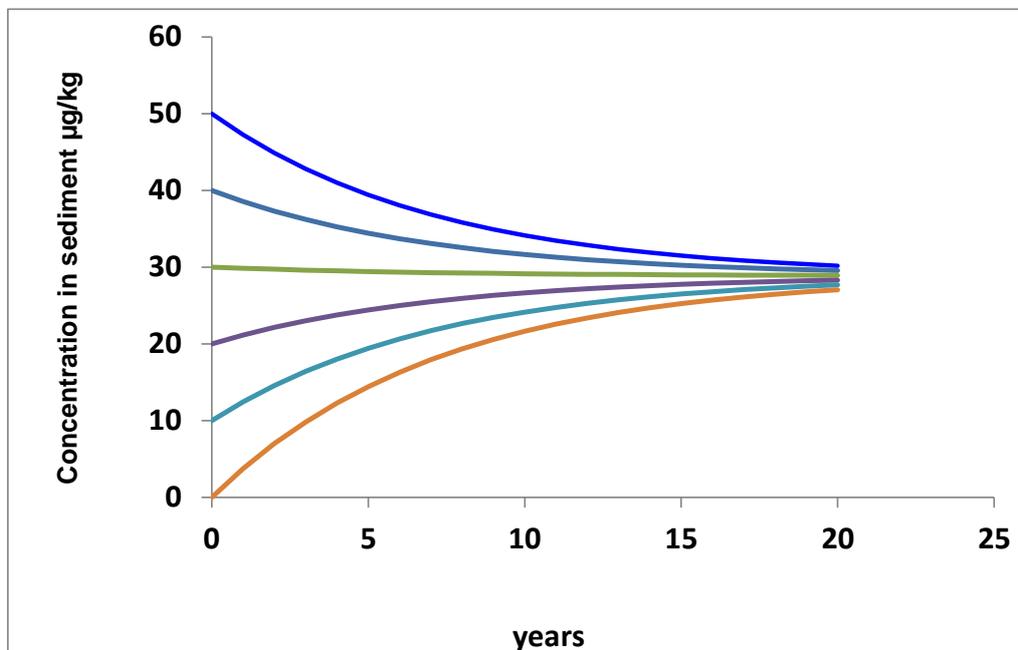
266

$$267 \quad y_x = \frac{S_x}{-k} \times e^{-kx} + \frac{S_0}{k} \quad (4)$$

268

269 S_0 , the rate of contaminant addition to sediment is considered in the first instance to be related
270 to a wastewater effluent discharge and hence is dependent on the concentration in the
271 effluent, the flow of effluent in unit time and the mass of the receiving sediment target. The
272 last two of these quantities can be taken (for any given situation) to be constants since sewage
273 flow is largely dependent on the population equivalent of the WwTW and the sediment target
274 (the quantity of sediment in the receiving river reach that is available to be contaminated) is
275 fixed. Hence S ($\mu\text{g}/\text{kg}/\text{yr}$) is assumed to be the concentration of contaminant in the particulate
276 phase in the effluent ($\mu\text{g}/\text{l}$) multiplied by a constant expressed ($Const_{flow/sed}$, see below) as
277 $\text{l}/\text{yr}/\text{kg}$.

278 The above equation (1) will generate a series of curves showing the change in concentration
279 based on what the starting conditions are. This concept is demonstrated in Figure 1 which
280 illustrates that whatever the starting condition the concentration will tend to the same
281 equilibrium value which is equal to S_0/k . How long it takes to reach equilibrium depends on the
282 value of k .



283

284 **Figure 1 Representation of decay curves generated for different chemical starting**
285 **concentrations, but tending towards the same equilibrium value which is**
286 **equal to S_0/k**

287

288 The assumptions made here are that the notional WwTW pe is 50,000, the volume discharged
 289 per person is 290 l/d (giving a total of 7.25 Ml/d) and that the sediment target corresponds to
 290 a river reach that provides a dilution of approximately 3 fold (the length and width of the river
 291 are used to determine a stretch of river that would allow sediment to settle based on Stokes
 292 Law. In this case the river is 2.5m wide and the mixing length is 620m(44). The resulting
 293 sediment target for an accessible depth of sediment of 5 cm is 200,000 kg based on a density
 294 of 1.6 g/cm³. The dissolved component of the effluent discharge is assumed to travel
 295 downstream and is not considered further.

296 Hence, the initial rate of contaminant input is calculated as:

297

$$298 \quad S_0 = C_{particulate\ effl} \times Const_{flow/sed} \quad (5)$$

299

300 Where $Const_{flow/sed}$ is explained above and $C_{particulate\ effl}$ is the concentration of
 301 contaminant in the particulate phase

302

$$303 \quad C_{particulate\ effl} = 1 - \left[\frac{C_{total}}{1 + (K_p \times SPM)} \right] \quad (6)$$

304

305 C_{total} is the total contaminant concentration (µg/l), K_p is the partition coefficient of the
 306 contaminant for sewage solids (l/kg) and SPM is the concentration of suspended particulate
 307 matter in the effluent/river (kg/l) – assumed to be 0.000005 (5 mg/l).

308 K_p can be a measured value if a credible one is available, or it can be derived from the
 309 octanol/water partition coefficient K_{ow} as:

310

$$311 \quad \log K_p = foc \times (0.72 \times \log K_{ow} + 0.42) \quad (7)$$

312

313 foc , the fraction of organic carbon in the sediment and for sewage solids is assumed to be 1.0,
 314 but can be adjusted to a more realistic value such as 0.33 where necessary⁽⁴⁵⁾. Matters
 315 become more complicated when a reduction (as a result of pollution control measures) in the
 316 input concentration is considered. This has been expressed as an annual percentage rate of
 317 reduction (APR) which is converted to a rate of reduction constant, k_{red} , that is applied to the
 318 values of S for each succeeding year of the simulated decay in overall concentration. This
 319 leads to the input at year [x] being estimated as:

320

$$321 \quad S_x = S_0 \times (1 - k_{red})^x \quad (8)$$

322

323 In summary, the sediment concentration in year [x] is given by the sum of

- 324 • What remains of the initial concentration in year [x]; and,
325 • The combined effect of what has been added up to year [x] and of this what has
326 decomposed.

327 In mathematical terms this is:

328

329
$$y_x = \frac{S_0}{k} \times e^{-kx} + \frac{S_x}{-k} \times e^{-kx} + \frac{S_x}{k} \quad (9)$$

330

331 The above representation is one of a system undergoing equilibration between the constant
332 addition of a contaminant and its tendency to decay (decompose) with time. The situation
333 becomes more complicated when the rate of addition itself changes during the modelling
334 period under consideration. At this point it is necessary to consider some practical examples
335 that require certain enabling or simplifying assumptions. Clearly, it is important to keep these
336 assumptions in mind.

337

338 **2.4 Testing**

339 The text below lists the main considerations relating to the construction of a realistic depiction
340 of the behaviour of a contaminant to the competing effects of decomposition and addition.

341

342 Firstly, there is the question of where the simulation starts, i.e. what is the state of
343 contamination at year zero? It is accepted that that historical emissions for many of the test
344 substances were considerably higher in the past when they were used without control or
345 mitigation. However, gaining accurate data for historic concentrations is challenging owing to
346 advances in analytical capabilities and the fact that observed concentrations were highly
347 variable and often localised. An extreme case would be to assume starting with a pristine,
348 uncontaminated sediment, except that is unrealistic and as can be seen from Figure 1 (orange
349 curve) there would be a period over which the equilibrium concentration is established within
350 the sediment. Beginning with a concentration at the equilibrium value is the simplest approach
351 (and the one most often chosen) because it represents contamination over the longer term,
352 thereby is a way of accounting for historic emissions and avoids the complication of this initial
353 phase of equilibration. Other options have been explored but are not dealt with here.

354

355 There are several approaches to using the illustrative tool:

356

357 **Starting conditions are likely to:**

- 358 a) use the known inputs as the determinant of equilibriums starting conditions. This might
359 be valuable when inputs are known and there is then the ability to check whether or
360 not the predicted equilibrium value is of the same order as any observed values;
- 361 b) be based on the observed values and to examine the likely direction of travel when
362 current inputs are entered into the tool. This might indicate either a discrepancy
363 between the two sets of observations or errors in other inputs. In particular, if the
364 sewage effluent inputs lead to underestimation of environmental levels, it might be the
365 case that there are additional inputs from other sources.

366 The approach used here for illustrative purposes was to use an estimate of the equilibrium
367 concentration (calculated from the estimated inputs) and to proceed to assess the likely effects
368 of any possible remedial measures.

369

370 **The nature of projected changes.**

371 Linear reductions at constant rate should be ruled out as they would imply the attainment of
372 zero or negative concentrations. The two most worthwhile approaches are to assume a
373 constant percentage rate of decline (effectively an exponential decay curve) with (possibly)
374 the option at some point in the future of a further step change in input rate, which could come
375 about from the cessation of a discharge, via for example, further effluent treatment. The use
376 of a single decay curve can be unproductive as these tend to flatten out leading to a potential
377 “no progress” situation, the option of further measures leading to a future boost to decline
378 might be of value (provided of course that there is reason to believe that such measures might
379 be applied). Such a second phase of remediation was also included.

380

381 **2.5 Scenario testing**

382 Scenario modelling is essentially an approach whereby a model is used to examine the likely
383 effect of a series of actions or, more simply, to answer “what if” type questions.

384 Consequently, the estimator tool was used to evaluate the likely outcome of five different level
385 of reduction in inputs:

- 386 1) Scenario 1: an annual percentage rate of reduction (APR) of 10% in the WwTW
387 input;
- 388 2) Scenario 2: an APR of 10% in the WwTW input, accompanied an APR of 10% in
389 non-WwTW sources;
- 390 3) Scenario 3: an APR of 7% in the WwTW input, accompanied an APR of 5% in non-
391 WwTW sources. The rationale behind that is that these reductions were agreed to be

392 both realistically achievable and not so small as not to be measurable. Two more
393 ambitious scenarios were also explored:

394 4) Scenario 4: an APR of 14% in the WwTW input, accompanied an APR of 5% in non-
395 WwTW sources. is likely to be more realistic than that scenarios 1 and 2 insofar as
396 these reductions are more likely to be achieved; and,

397 5) Scenario 5: an APR of 21% in the WwTW input, accompanied an APR of 5% in non-
398 WwTW sources.

399 In scenarios 3-5 the reduction on non-WwTW sources was kept at 5% because it was judged
400 that these might be more difficult to establish and to address owing to their diffuse nature.

401 Physico-chemical data utilised for input data are summarised in Table 1 based on data
402 obtained from the literature (ESI, Table S4). It is acknowledged that the measurement and
403 reporting of these key physico-chemical properties varies considerably as seen in Table S4,
404 depending on the ambient environmental and/or test conditions, temporal and spatial
405 variability, as well as sampling and sample pretreatment methodologies. Consequently values
406 often range over more than an order of magnitude. However, the benefits of a model are that
407 this variability may be tested via a full sensitivity analysis.

408

409 **Table1 Inputs used in scenario modelling**

Input	Input concentration – WwTW source	Input load to sediment – non-point source as multiplier of WwTW input	Half-life (t ½) of substance in sediment	BSCF to biota	Log Kp value	Biota EQS	Sediment critical value
Units	µg/l	µg/year	years		l/kg	µg/kg	µg/kg
Substance							
TBT	0.00023	0.4	1.6	10	4.7	n/a	1.1 (a)
Methyl-Mercury	0.0029	1.6	0.0041	100	6.46	20	
HBCDD	0.011	0.8	0.27	1	6	167	
Cypermethrin	0.00034	1.3	0.027	0.2	5.5	n/a	0.2 (b)
PFOS	0.0075	1.0	3	1.5	3.15	9.1	
PFOA	0.0085	10.1	3	1.6	2.70	9.1 c)	
Benzo(a)pyrene	0.0049	6.1	1.94	1.3	4.81	5	
Fluoranthene	0.013	0.9	1.14	0.5	4.23	30	
DEHP	0.76	0.4	0.04	1	5.9	n/a	180 (c)
BDE47	0.000018	0.4	0.45	4	6	0.0085	

410 Notes: Sediment critical values inserted on the bases shown below where no biota EQS has been set

411 a) TBT 9 µg Sn/kg dry weight, corrected for 1% TOC in sediment(46).

412 b) Cypermethrin sediment EQS of 0.2 µg/kg dry weight(47).

413 c) For PFOA the EQS value for PFOS has been inserted to facilitate compliance estimation

414 d) USEPA sediment screening benchmark value 180 µg/kg dry weight for DEHP(48).

415

416

417

418 **2.6 Validation**

419 Limited validation was possible using recent UK data obtained for WwTW effluent
420 concentrations between 2013 and 2019 inclusive. The UKWIR CIP is a monitoring programme
421 sponsored and designed by the UK Water Industry with the aim of prioritising any possible
422 required action on effluent quality required in order to assist compliance with current regulation
423 on surface water quality (further details are provided in (42)). In this context, data have been
424 obtained from approximately annual tranches of monitoring undertaken at in 2013, 2016, 2017,
425 2018 and (more or less completed) 2019. For each tranche of analyses effluent quality data
426 were obtained for between 140 and 180 different WwTW. This constitutes a six-year period of
427 testing from which it is possible to estimate a monitoring-based value for an annualised
428 percentage rate of change accumulated over more than 700 sites of effluent concentration for
429 a range of trace contaminants. Of the substances of interest here data are available for DEHP,
430 TBT, triclosan, benzo(a)pyrene and (as a representative of BDEs) BDE 47.

431 **2.7 Limitations**

432 The purpose of this model is to take readily available physico-chemical data combined with
433 release scenarios to be able to establish compliance against sediment and/or biota standards.
434 As it stands the development and application of the tool does not allow for site-specific cases
435 nor allows the input of ambient environmental parameters such as salinity, temperature and
436 pH as it was outside of the scope of the research and the aims of the tool's development.
437 However, it should be noted that parameters included in the tool such as partition coefficients
438 and decay rate constants do reflect ambient pH, T and salinity. Consequently, the tool may be
439 applied to other scenarios where ambient conditions significantly differ from typical UK
440 environments, for example hotter climates or more acidic waters by amending the decay rate
441 constant (likely to be higher in warmer environments) or partition coefficient (based on
442 chemical pka) respectively.

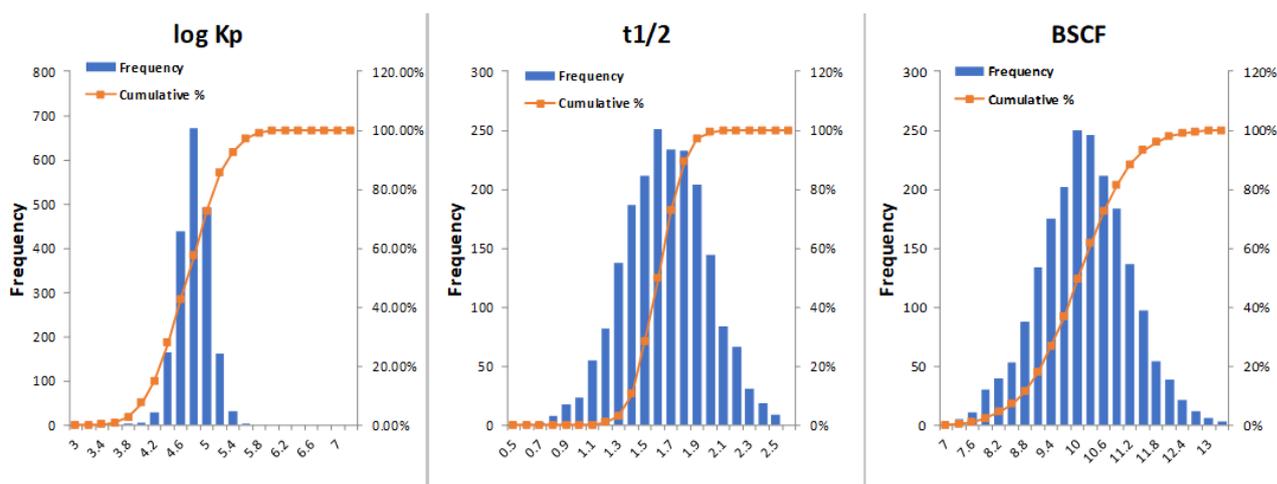
443 3. Results and discussion

444 3.1 Sensitivity analysis

445 Reliable regression-correlation based sensitivity measures are key to ranking water quality
446 model parameters(49). Environmental modelling exercises usually initially yield a single figure
447 (estimate) of the desired output. In this case the figure is time in years to reach compliance
448 with a quality standard. There is a risk that an output of this kind can be taken to be an absolute
449 prediction. In order to avoid this mistake, it is important to provide some indication of the
450 uncertainty that might reasonably be associated with the output value, of its sensitivity to
451 different inputs and also to rank the input values in order of importance to the overall reliability
452 of the calculations that have been made. As part of the scenario analysis of the estimator tool,
453 the effect on the output of variation of the key input parameters, i.e. the substance partition
454 coefficient (K_p), the half-life in sediment ($t_{1/2}$) and the BSCF was undertaken. This took the
455 form of a set of 1000 calculations for each substance, in each of which, the values of these
456 three inputs were varied within a plausible range that might reflect uncertainty in the value
457 chosen. The range and variability of the resulting output of this semi partial correlation were
458 then examined.

459 The measures of the variation in inputs can be described in terms of the coefficient of variation
460 (CoV), the standard deviation of value divided by the mean. After due consideration, the
461 following CoV values were selected: log K_p 0.05, half-life 0.2 years and BSCF 0.1. Figure 2
462 shows the ranges of variation for nominal inputs of log K_p =4.7, $t_{1/2}$ = 1.6 years and BSCF =10
463 fold. Clearly, in practice, the nominal values that are relevant to the substance of interest would
464 be entered.

465



467

468 **Figure 3** Ranges of input variations for nominal inputs of $\log K_p = 4.7$, $t_{1/2} = 1.6$ years and
 469 **BSCF = 10** fold assuming CoV values of $\log K_p$ 0.05, half-life 0.2 years and
 470 **0.1**

471 The effect of this variation in inputs on the output time to compliance was assessed from the
 472 1000 output values and expressed as a 25th – 75th percentile range (which was found to be
 473 symmetrical about the mean value).

474 The relative importance of the three inputs was also evaluated via a multiple linear regression
 475 on the outputs. The outcome of this depended on the actual value of the inputs in a complex
 476 way:

- 477 • BSCF, being merely a multiplier, was found to be of the least importance for the six
 478 substances for which there were biota EQS values;
- 479 • Where the value of $\log K_p$ was in the range 4.5 – 6, $\log K_p$ tended to be the most
 480 influential factor. This is because over this range of $\log K_p$ values, the value of $\log K_p$
 481 has a marked controlling influence over the proportion of substances that is associated
 482 with the particulate phase. For a $\log K_p$ of 4.5 at a typical total suspended solids
 483 concentration of river water (5 mg/l), approximately 13% of the substance will be
 484 associated with particulates (and therefore be part of the load to sediment), whereas
 485 for $\log K_p$ of 6 over 90% of the substance load is in particulate form (at equilibrium).
 486 Consequently $\log K_p$ had significant impact on TBT, Me-Hg, HBCDD, cypermethrin,
 487 BaP, fluoranthene, DEHP and BDE47. The persistence and hydrophobic nature of
 488 many POPs, in particular PCBs has been extensively studied and the slow rate of
 489 disappearance from the environment well characterised(50,51).

490 • If the value of $\log K_p$ is outside this critical range the half-life value can become the
491 most important factor, particularly if it is low, where variation makes a larger difference.
492 Reported environmental half lives for chemicals are notoriously variable (even when
493 using standardised tests such as OECD308) owing to varying ambient conditions
494 which tests have been typically carried out including, temperature, sediment type,
495 chemical concentration, redox conditions, water quality, microbial assemblages and
496 acclimatization etc(52).

497 Modelling uptake of PCBs and dioxins into biota (including human) key factors were identified
498 as half-lives of the chemicals, body weight variability, lipid fraction, food assimilation efficiency,
499 physiological processes (uptake/elimination rates), environmental exposure concentrations
500 (sediment, water, food) and eating behaviours⁽⁵³⁾. One thing that is important to stress is that
501 this sensitivity analysis does not reflect the likely outcome or insure against serious error
502 caused by using a completely inappropriate/wrong value for an input to the estimator tool. The
503 implicit assumption is that a reasonably representative estimate of $\log K_p$, BSCF or half-life is
504 available in the first place.

505 **3.2 Scenario modelling**

506 The outputs of the estimator tool for the five scenarios are summarised in Table 2.

507

508

509 **Table 2 Scenario modelling outputs**

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Bespoke scenario
	Time in years to meet EQS value at 0.1 APR reduction of WwTW emissions without control of diffuse sources 10% APR WwTW only	Time in years for reduction of both types of inputs 10% APR both	Time in years for reduction of both types of inputs APR: WwTW 7% Non-WwTW 5%	APR: WwTW 14% Non-WwTW 5%	APR: WwTW 21% Non-WwTW 5%	See below for definition of bespoke scenario Estimated uncertainty range in brackets
TBT	12 ± 7	6 ± 3	10 ± 5	6 ± 3	5 ± 3	6 (5-11)
Methyl-Mercury	47 ± 8	9 ± 1	17 ± 3	13 ± 2	12 ± 2	16 (13-18)
HBCDD	Complies	Complies	Complies	Complies	Complies	Complies
Cypermethrin	0 to 3	0 to 2	0 to 2	0 to 1	0	Complies (0-5)
PFOS	4 ± 11	3 ± 3	3 ± 5	2 ± 4	2 ± 4	5 (0-7)
PFOA	Complies	Complies	Complies	Complies	Complies	Complies
Benzo(a)pyrene	1110 ± 61	45 ± 3	88 ± 5	84 ± 5	84 ± 5	96 (90-100)
Fluoranthene	144 ± 52	9 ± 3	18 ± 6	16 ± 6	16 ± 6	19 (12-26)
DEHP	45 ± 5	15 ± 1	25 ± 3	18 ± 2	16 ± 2	22 (18-24)
BDE47	86 ± 3	42 ± 2	67 ± 2	43 ± 1	38 ± 1	68 (64-70)

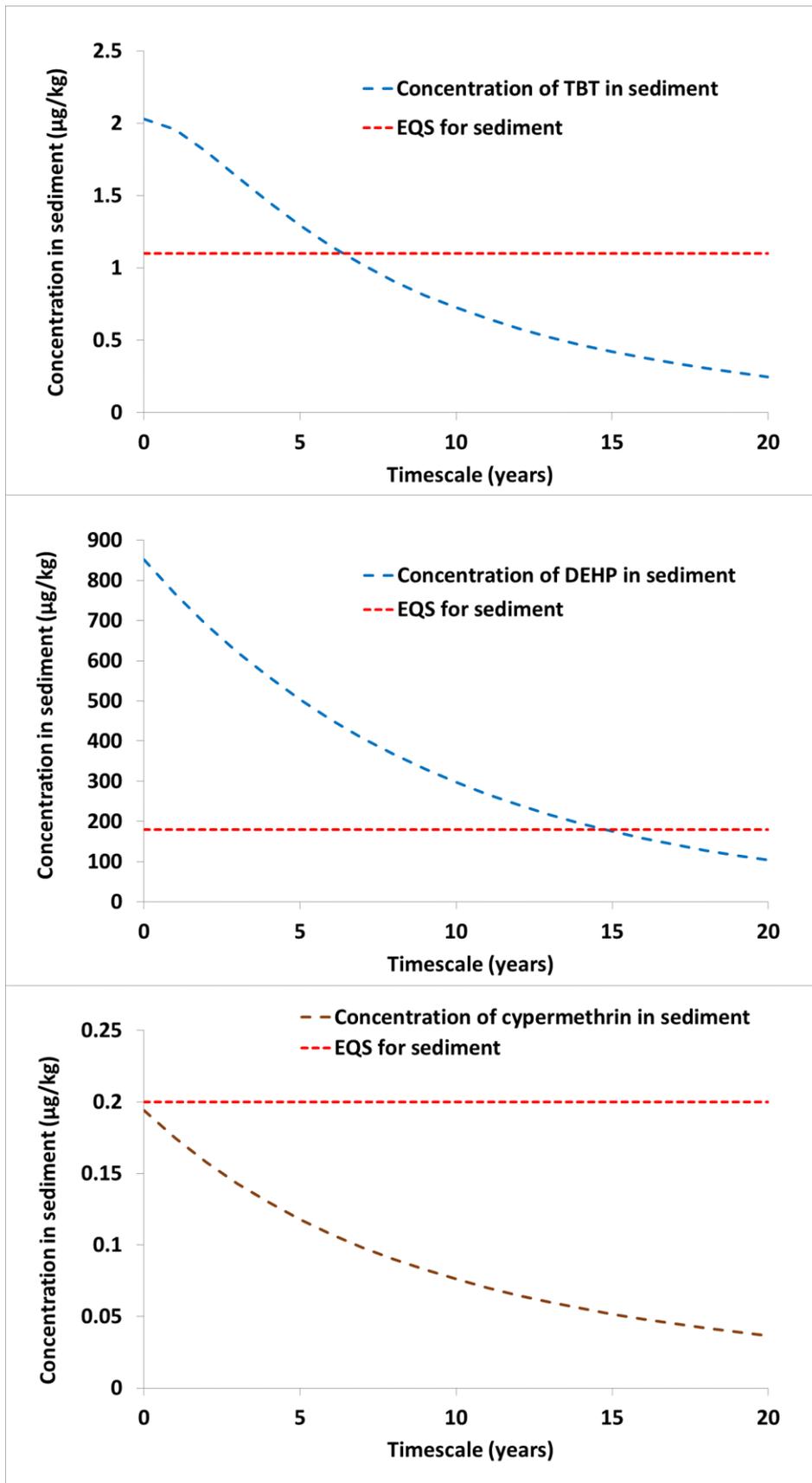
510 Notes

- 511 • APR is annual percentage reduction – the percentage reduction in inputs to the environment achieved in
512 each successive year
- 513 • Negative times indicate that the estimator tool inputs result in an output showing compliance is already
514 achieved (see below for illustrations)
- 515 • The ± values in the table are 25th to 75th percentile ranges based on simulated variations of the three main
516 estimator inputs (partition coefficient K_p, half-life in sediment t_{1/2} and BSCF) applying respective coefficient
517 of variation of 0.5, 0.2 and 0.1 respectively, – see section 2.4 for discussion)

518

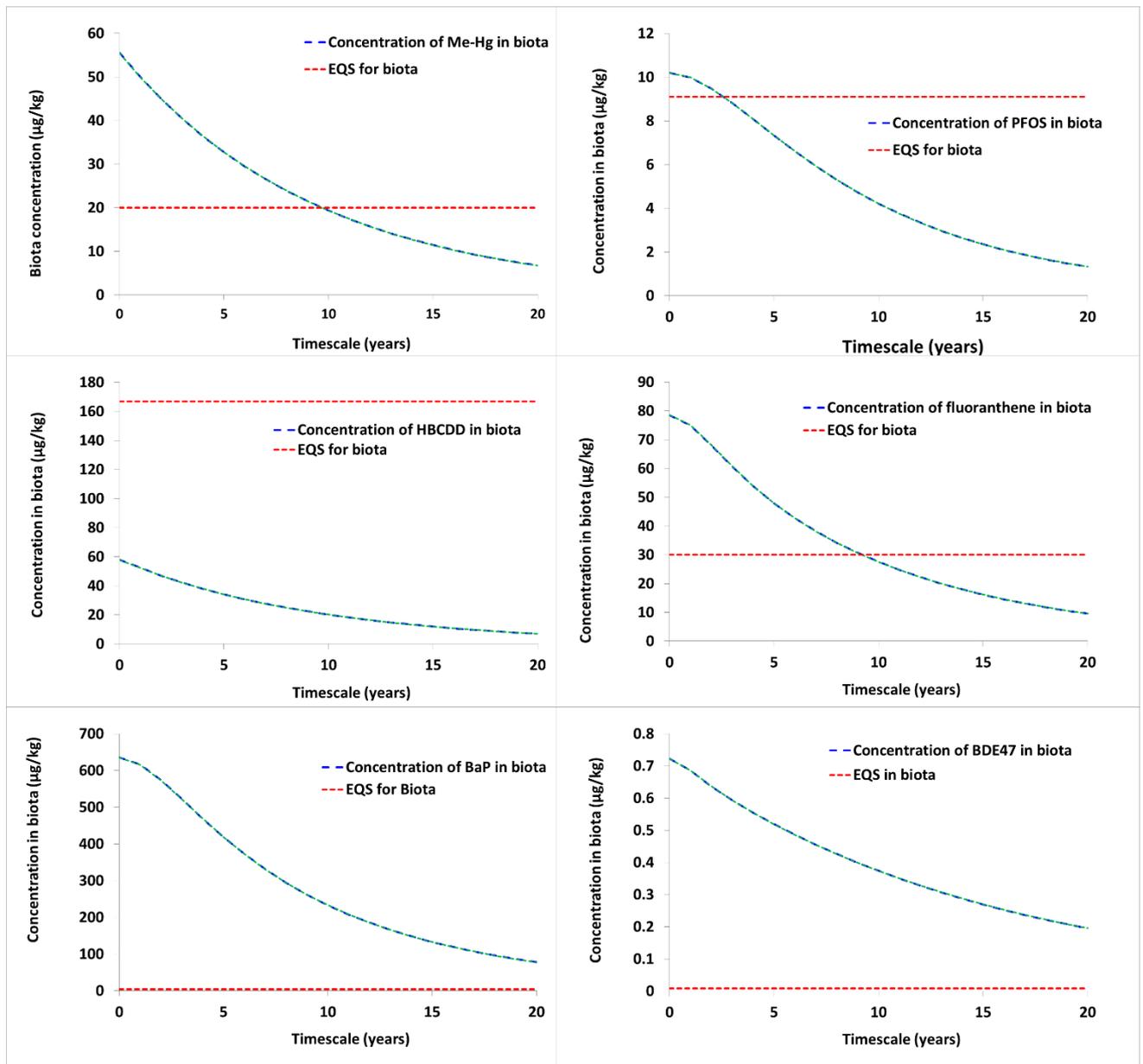
519 Illustrations of the rates of change of environmental concentrations shown in Figures 3 and 4
520 are for APR reductions of 10% in both types of inputs (scenario 2). The purpose of these
521 figures is to provide a visualisation of the different cases. The decay curves displayed in these
522 figures are for chemicals for which reliable sediment and biota EQS are available. There is a
523 bias towards biota standards owing to them being considered the sensitive environmental
524 receptors, often associated with the risk of secondary poisoning on higher organisms,
525 including humans. Plots for the other substances are provided in ESI Figures S1 and S2.

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Figure 3 Illustrations of decline in sediment contaminant concentrations for APR reductions of 10% in both types of inputs (scenario 2)



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Figure 4 Illustrations of decline in biota contaminant concentrations for APR reductions of 10% in both types of inputs (scenario 2)

539

540 Reported estimations of trends in POP concentrations in water/sediment/biota are, as noted
541 above, often based on site specific case studies for individual contaminants. These studies
542 frequently result in markedly different estimates in trends. This, in turn, makes it difficult to
543 compare between studies and with the generic approach derived here. However, at least for
544 the wastewater inputs to the aquatic environment, data required for such a comparison are
545 now available from the extensive, multi-determinand survey of wastewater treatment works'
546 quality provided by the UKWIR Chemicals Investigation Programme (CIP)⁽⁴²⁾. This would
547 provide a baseline for a modelling approach that took input data and projected its likely effect
548 on biota concentrations and the extent to which regulatory compliance might be achieved in
549 the future.

550 The UKWIR CIP is a monitoring programme provided data between 2013, 2016, 2017, 2018
551 and 2019(42). Effluent quality data were obtained for more than 700 sites and provided the
552 opportunity to estimate a monitoring-based value for an annualised percentage rate of change
553 of POP levels in effluent. Table 3 summarises the rates of changes (as annualise percentage
554 rate (APR)) observed for the substances of interest with additional data provide for
555 benzo(a)pyrene and fluoranthene as examples of contaminants that would not have changed
556 in concentration because unlike the other substances they had not been subjected to control
557 measures in the period concerned.

558 The table shows that, given the observed variability of measurements, an APR over six years
559 as large as approximately 5% would be likely to have been detected as statistically significant.

560 **Table 3. Measured variability of concentrations over a six year period (2013-2019)**

Substance	Annualised % rate of change	P value for trend	Stat sig? p=0.05
Triclosan	-18	0.0005	sig
DEHP	-7	0.02	sig
TBT	-17	0.002	sig
BDE47	-15	0.0005	sig
Benzo(a)pyrene	-4	0.26	ns
Fluoranthene	2.4	0.3	ns

561

562 Figures for the fluorocarbons, cypermethrin and HCBDD are not shown because monitoring
563 data were not obtained in the earliest year of the programme, resulting in the assessment
564 period being too short for meaningful analysis.

565 These results indicate that the scenarios for which the decay tool was tested are not unrealistic
566 in relation to the magnitudes of environmental change that might be achieved by current
567 control measures. This prompts the conclusion that, provided these APR values can be
568 sustained over the next five to ten years, current measures will indeed succeed in effluent
569 concentration at the great majority of WwTW sites that are below the regulated values. Clearly,
570 this will need to be confirmed by monitoring, although other European countries have also
571 reported declining concentrations of PFOS over the past decade, although the picture is never
572 completely clear as in heavily urbanised or industrialised areas trends may be masked by
573 legacy pollution(54).

574 This tool represents a plug flow environment with finite spatial (downstream) extent, with
575 dynamic accumulation or loss occurring in the sediment due to wastewater (and other)
576 loadings, equilibrium biosorption to sediments, and first-order decay. Similar to previous
577 models(17-19) the formulation allows for a simple exponential approach to a new “steady
578 state”, as the loading input is modified. Although the Mackay models include more
579 environmental compartments (typically water, air, soil, sediments, and biota), they also require
580 some form of adaptation to represent the 1-D fate and transport of a river because the media
581 compartments are based on the premise of a continuous stirred tank reactor (CSTD). The
582 CSTD approach have been applied to the environmental fate in terms of spatial range and
583 temporal persistence of lindane, hexachlorobenzene, dieldrin and dioxins for example, in
584 compartments such as soil(27).

585 The development and use of the tool described here takes account of a combination of
586 modelling and monitoring to provide support for current control strategies and for the use of
587 the tool for new substances of interest in the future. This predictive model therefore allows the
588 opportunity to identify the required reduction in any given chemical source (point or diffuse) to
589 meet a required EQS within a given time period. Any potential mitigation measures can then
590 be assessed on a cost-benefit basis to identify the most appropriate solutions. Furthermore,
591 the model will show whether a biota EQS is achievable and the relative importance of diffuse
592 versus point sources.

593

594 4. Conclusions

595 This investigation has examined an approach to comparing the impact of control strategies of
596 different effectiveness for environmental contamination by trace substances.

597

598 Comparisons made on the same basis suggest that:

599

600 1. Some substances of current interest (HBCDD, cypermethrin, PFOA) appear not to
601 present generic compliance problems – based on current estimates of mean WwTW
602 effluent concentrations.

603 2. Concentrations of other substances (methyl-mercury, TBT, PFOS) are above the
604 relevant quality criterion, but given a 10% annual percentage reduction that is evident
605 in current data, these substances might be compliant with regulations in a relatively
606 short time.

607 3. The remaining substances of those examined (BDEs, benzo(a)pyrene, fluoranthene
608 and DEHP) appear to present more intractable longer-term compliance problems.

609

610 **Conflicts of interest**

611 There are no conflicts of interest to declare.

612

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617

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