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Chemical calibration, performance, validation and applications of the polar organic chemical integrative sampler (POCIS) in aquatic environments

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16

17
18 **POCIS (Polar Organic Chemical Integrative Sampler) is a relatively recent integrative**
19 **sampler developed to trap hydrophilic organic micropollutants in aquatic environments.**
20 **Nevertheless, at present, there is no review dealing specifically with this tool.**

21 **The aim of this paper was to compile information from numerous references based on**
22 **POCIS in order to discuss on the evaluation of time-weighted average concentrations**
23 **(calibration methods, sampling rates, performance and reference compounds...) and to**
24 **critically review the different in situ applications (screening or quantifying micropollutants,**
25 **coupling with toxicity tests), application domains (molecules analyzed, sampling media) and**
26 **analytical protocols for POCIS (processing, analysis, exposure duration).**

27

28 *Keywords:* Calibration; Environmental monitoring; Performance and reference compound; POCIS; Polar organic
29 contaminants; Sampling rate; Surface water; Time-weighted average concentration

30

31 *Abbreviations:* Bio-EEQ, Biological estradiol equivalent; BLYES, Bioluminescent yeast estrogen screen; Cal-EEQ,
32 Calculated estradiol equivalent; EROD, 7-ethoxyresorufin-O-deethylase; GC, Gas chromatography; LC, Liquid
33 chromatography; LDPE, Low-density polyethylene; MS, Mass spectrometer; MSFD, Marine strategy framework
34 directive; POCIS, Polar organic chemical integrative sampler; PRC, Performance and reference compound; PSE,
35 Pressurized solvent extraction; QA, Quality assurance; QC, Quality control; R_s, sampling rate; RSD, Relative standard
36 deviation; SD, Standard deviation; SPE, Solid phase extraction; SPMD, Semi-permeable membrane device; TWA, Time-
37 weighted average; WFD, Water framework directive; WWTP, Waste water treatment plant; YAS, Yeast androgen
38 screen; YES, Yeast estrogen screen

39

40 **1 Introduction**

41

42 Passive samplers (including integrative or kinetic and equilibrium samplers) are relatively new
43 emerging tools for sampling micropollutants in waters. Since the apparition of the first passive
44 sampler for surface waters [1], these tools have been quickly widespread and several associated
45 monitoring approaches have been proposed. The principle of these techniques is based on the
46 accumulation of contaminants by passive diffusion in the devices. In most cases, these tools consist
47 of a receiving phase (i.e., a liquid absorbant, a solid adsorbant or a chelatant gel) having an affinity
48 for a specific class of pollutants, separated from the sampled solution by a diffusion-limiting layer
49 (i.e., a porous or non porous membrane or a gel).

50 Passive samplers have several advantages. In the case of equilibrium samplers, equilibrium
51 pollutant concentrations from the medium can be derived if exposure time is long enough, if
52 response times are shorter than fluctuations of water concentrations and if phase-water partition
53 coefficients of the studied compounds are known [2-4]. In the case of kinetic samplers, they can
54 provide time-weighted average (TWA) concentrations if the receiving phase acts as a “zero sink” (no
55 release of trapped molecules) and if sampling rates are constant during the exposure time [4]. In
56 addition, passive samplers concentrate analytes directly in-situ, which can reduce quantification and
57 detection limits. Furthermore, they make sampling preparation easier and allow to limit degradation
58 of trapped molecules during transport and storage. Also, they do not need power requirements, and
59 they are relatively simple to operate, generally small and light. They can be coupled with bioassays
60 for effect monitoring. However, these tools have some drawbacks. Firstly, it is difficult to determine
61 the accuracy of TWA concentrations obtained in situ with kinetic samplers, because sampling rates,
62 which are specific for each compound and which represent the quantity of water cleared by the
63 sampler per time unit, depend on water flow velocities, temperature, biofouling and possibly
64 concentration fluctuations. Moreover, the comparison with grab sampling, often used to determine
65 the accuracy of TWA concentrations, is not really reliable since grab samples do not supply exact
66 average concentrations. For instance, short concentration variations can be missed with grab
67 sampling. Alternatively, automated samplers collecting weekly average samples may be used but
68 chemical conservation is not ensured for all analytes. Secondly, there is a need to study response
69 time of passive samplers in order to know if they are able to detect small concentration variations
70 over time. Thirdly, the fraction sampled vary according to the passive sampler (and the membrane
71 used), and do not represent strictly the free dissolved fraction.

72 Since 2000, fourteen reviews have presented a state-of-the-art in passive sampling [2-15].
73 Concerning passive sampling for polar compounds, among the fourteen reviews presented, eight of
74 them discussed POCIS briefly [9, 15] or more in depth [2-4, 10-11, 14]. All of these reviews
75 reported data on several different tools and therefore do not focus specifically on POCIS.

76 The main subjects approached in these reviews are:

- 77 - the presentation of passive samplers and their history,
- 78 - the estimation of TWA concentrations using kinetic samplers. Among the fourteen reviews,
79 there is no discussion about the calibration method (advantages and drawbacks of laboratory
80 or in situ calibrations). Only Zabiegala et al. [4] suggested that passive samplers should be
81 validated in situ since laboratory conditions are generally too different than in the field.
82 Moreover, authors did not describe calibration systems used to obtain laboratory sampling
83 rates. Only one article reported sampling rate values from the literature for POCIS
84 exclusively for several hormones and pharmaceuticals [3]. Sampling rate values were
85 classified by molecule as a function of agitation, sampling time and temperature. However,
86 this review was not exhaustive as only 4 references were cited.
- 87 - the applications of passive samplers: screening, evaluation of TWA concentrations, coupling
88 with bioassays or with biomonitors, family of molecules analyzed, sampling media. These
89 applications are presented for several different tools, but they are not exhaustive nor detailed

90 enough for POCIS. Mills et al. [11] and Söderstrom et al. [3] interestingly provided details of
91 the molecules themselves rather than only the families of molecules sampled for POCIS.
92 However, there are only 4 references cited by Mills et al. [11] and Söderstrom et al. [3].
93 Furthermore, Söderstrom et al. [3] discussed applications for POCIS, but from only 5
94 references.

95 - the protocols for the analytical method of extraction of passive samplers [2, 5]. However,
96 there are no details about the storage, type of solvent used to perform the extraction (when
97 the tool requires a solvent extraction) or analysis. These points are detailed in articles but not
98 in reviews.

99 Hence, the present review proposes to study in a detailed way numerous publications relative
100 to POCIS since its early development in 1999 until 2012. The general aim of this review is to study
101 POCIS: its performances, its applications and its validity in the field. The aspects detailed are the
102 following:

- 103 - the evaluation of TWA concentration (calibration methods, quantitative aspects of the POCIS
104 in terms of sampling rates and performance reference compounds),
- 105 - the POCIS applications (screening, evaluation of TWA concentrations, comparison with grab
106 sampling, coupling with toxicity tests) and application domains (molecules sampled, media
107 studied),
- 108 - the protocols for using POCIS (processing, analysis, exposure durations).

109

110 **2 Principle of POCIS**

111

112 **2.1 Presentation of POCIS**

113

114 POCIS is composed of a solid sorbent receiving phase sandwiched between two microporous
115 polyethersulfone diffusion-limiting membranes with 100 nm pore sizes [16]. The sorbent appears to
116 be more specific for pesticide compounds and some hormones when it is a triphasic mixture (Isolute
117 ENV+ and Ambersorb 1500 dispersed on SX-3 Bio Beads; “pesticide” POCIS) or more specific for
118 pharmaceutical compounds when it is the OASIS® HLB phase [17]. However, Mazzella et al. [18]
119 reported better recoveries for herbicides in the OASIS® HLB phase (“pharmaceutical” POCIS) than
120 as a triphasic mixture. In contrast, Li et al. [19] indicated that uptake rates of pharmaceuticals were
121 higher with “pesticide” POCIS. In fact, generally, the “pharmaceutical” POCIS is more often used
122 because it has some advantages as, for example, the elution solvent which is less toxic with
123 “pharmaceutical” POCIS than with “pesticide” POCIS [19] or the ease of utilization of the OASIS®
124 HLB phase compared with the triphasic mixture.

125 Whatever the phase used, POCIS has been designed to catch polar organic compounds ($\log K_{ow} < 4$)
126 [16].

127 POCIS has to be immersed in water during few days or weeks. It is then recuperated and
128 transported to the laboratory to be dismantled to collect the receiving phase. Analytes are extracted
129 from the solid sorbent by solvent(s) with solid phase extraction (SPE), sonication or pressurized
130 solvent extraction (PSE). The eluate is then analyzed generally by liquid chromatography coupled
131 with mass spectrometer (LC/MS) or by gas chromatography coupled with mass spectrometer
132 (GC/MS).

133 Figure 1 shows the disassembled view of POCIS.

134

135 (figure 1)

136

137 **2.2 Accumulation in POCIS**

138

139 Accumulation in POCIS is based on the passive diffusion of analytes from water into the POCIS
140 receiving phase. There are 3 different accumulation regimes of pollutants (as a function of time): a
141 linear (or kinetic/integrative) regime, a pseudolinear regime and an equilibrium regime (figure 2).
142 POCIS is generally used in the linear regime to conduct to TWA concentrations. Alternatively, it can
143 be immersed in water for the screening of micropollutants or coupling with bioassays. In these
144 cases, POCIS can be used in any regime, since the final information is qualitative (quantity of
145 pollutant(s) in POCIS or effect for bioassays) and not quantitative as for TWA concentrations.

146

147 (figure 2)

148

149 **2.3 Evaluation of TWA concentration**

150

151 *2.3.1 Introducing the sampling rate*

152

153 In order to obtain TWA concentrations of the studied molecules, laboratory or in situ calibration of
154 POCIS is necessary. The calibration permits to link the quantity of a compound accumulated in the
155 tool to its concentration in the medium sampled, thanks to the determination of its sampling rate
156 (R_s). To be correctly calibrated, POCIS must be used in the kinetic regime. The concentration of a
157 compound in the tool is linked to its concentration in the medium via the equation (1):

158

$$159 \quad (1) \quad C_s = C_w k_u t$$

160

161 where C_s is the concentration of the analyte in the sorbent at time t ($\mu\text{g/g}$), C_w the TWA
162 concentration of the analyte in the water ($\mu\text{g/L}$), k_u the uptake rate of the analyte in POCIS (L/g/d)
163 and t the time (d).

164 When using equation (1), it is possible to introduce the sampling rate:

165

$$166 \quad (2) \quad C_s = \frac{C_w R_s t}{M_s}$$

167

168 where R_s is the sampling rate (L/d) and M_s is the mass of sorbent in POCIS (g).

169 The sampling rate is the volume of water cleared by unit of time for a given molecule. It depends
170 on water flow, temperature and biofouling [2]. Since these parameters are not the same in the
171 laboratory or in situ, corresponding sampling rates will be different. Thus, to obtain accurate in situ
172 TWA concentrations, it is necessary to correct laboratory sampling rates with performance and
173 reference compounds or to perform in situ calibration.

174

175 *2.3.2 Performance reference compounds and corrected sampling rates*

176

177 When laboratory calibrations are performed, corrected laboratory sampling rates are needed because
178 laboratory and in situ sampling rates are different. For that, performance and reference compounds
179 (PRCs) are used as internal standards. PRCs permit to correct R_s from varying environmental
180 conditions.

181 A PRC is a compound not present in the environment (e.g., a deuterated molecule), which is
182 spiked in the sorbent phase of POCIS before its exposure. In principle, the quantification of the
183

184 PRC's elimination constant in the laboratory and in situ permits to obtain corrected sampling rates, if
185 isotropic exchange is checked. The determination of such corrected sampling rates is explained in
186 equations 3 and 4.

187 First of all, it is necessary to determine the elimination rate constant of the PRC in the laboratory
188 and in situ:

$$189 \quad (3) \quad \frac{C_s}{C_{s0}} = e^{-k_e t}$$

192 with C_{s0} : the initial concentration of the PRC in the sorbent before its exposure, and k_e : the
193 elimination rate constant of the PRC.

194 Then, it is possible to calculate corrected sampling rates, as follows:

$$196 \quad (4) \quad R_{s(\text{corr})} = \left(\frac{k_{e\text{PRC}(\text{insitu})}}{k_{e\text{PRC}(\text{lab})}} \right) \times R_{s(\text{lab})}$$

199 with $R_{s(\text{corr})}$: the corrected sampling rate, $k_{e\text{PRC}(\text{insitu})}$: the elimination constant of the PRC measured in
200 situ, $k_{e\text{PRC}(\text{lab})}$: the elimination constant of the PRC measured in the laboratory, and $R_{s(\text{lab})}$: the
201 laboratory sampling rate.

202 The desorption of the PRC from the sorbent has to be quantifiable during of the entire POCIS
203 exposure time. Nevertheless, it is complicated to identify suitable PRCs with POCIS because
204 interactions of molecules with the receiving phase are based on adsorption phenomena (i.e.,
205 anisotropic exchange); whereas in semi-permeable membrane device (SPMD), for example,
206 interactions are based on partition (i.e., isotropic exchange) [20]. At last, it is necessary to identify
207 the molecules corrected by a specific PRC. For that, further research is needed.

209 2.3.3 Calculation of sampling rates

211 In practice, sampling rates are generally obtained from equation 2 using laboratory or in situ
212 calibration. So, authors have to quantify the concentration of analyte(s) in POCIS (C_s) and in water
213 (C_w). It is also possible to calculate laboratory sampling rates using only the analyte concentrations
214 remaining in the water following each period of POCIS exposure with equation 5 [17, 21]:

$$216 \quad (5) \quad R_s = \frac{C_i - C_t}{C_i} \times \frac{V_T}{t}$$

221 with C_i : the initial analyte concentration ($\mu\text{g/L}$), C_t : the analyte concentration at time t ($\mu\text{g/L}$) and
222 V_T : the total volume of the laboratory calibration tank. In this case, it must be assumed that analyte
223 loss by degradation is negligible.

224 Other authors, such as MacLeod et al. [22], proposed to calculate laboratory sampling rates using
225 the slope of the decrease in water concentration over the exposure time. A positive control (beaker
226 with no POCIS) is present in order to take into account possible analyte degradation. Then, assuming
227 that the uptake of contaminants is only controlled by the aqueous boundary layer [16-17], R_s is equal
228 to:

$$232 \quad (6) \quad R_s = k_u V_T$$

235 With the assumption of aqueous boundary layer control, R_s is also equal to:

$$237 \quad (7) \quad R_s = \left(\frac{D_w}{L_w} \right) \times A$$

241

242 with D_w : aqueous diffusion coefficient of the compound, L_w : thickness of the stagnant film water and
243 A: the surface area of the sampler.

244 Bartelt-Hunt et al. [23] calculated an average L_w value with laboratory R_s given by MacLeod et al.
245 al. [22] and they estimated D_w for each of their compounds (pharmaceuticals) using the Hayduk-
246 Laudie model [24]. Then, they were able to calculate sampling rates for each compound without any
247 calibration.

248

249 **3 Discussion**

250

251 **3.1 Calibration method and system – determination of sampling rates and influence of** 252 **experimental parameters**

253

254 **3.1.1 Laboratory calibration**

255

256 In the laboratory, POCIS are immersed in water spiked with the molecules of interest. The exposure
257 media has to be controlled (temperature, agitation, contaminant concentrations, physicochemical
258 parameters).

259 The advantages of laboratory calibration are:

- 260 - all sampling rates (R_s) can be obtained since all molecules are present,
- 261 - laboratory R_s are “reliable” since they are based on constant and controlled micropollutant
262 concentrations.

263 However this method has some drawbacks:

- 264 - it is necessary to find PRCs to correct laboratory R_s for all studied molecules. Until now,
265 there are very few PRCs for POCIS. Only Mazzella et al. [18, 25] successfully used DIA-d5
266 to correct laboratory R_s for herbicides with “pharmaceutical” POCIS in river waters,
- 267 - this laboratory calibration is costly and time consuming.

268 From literature, we found various calibration systems for POCIS. They are described in table 1
269 as a function of the calibration methods and the parameters applied.

270 To maintain constant micropollutant contaminations, three calibration methods can be used:
271 static calibration (closed system, with molecule spiking at the beginning of the experiment), static
272 renewal calibration (closed system, with molecule spiking at constant interval times) or continuous
273 flow calibration (open system with continuous molecule spiking). The static calibration is suitable
274 when the molecules studied are neither quickly degraded nor adsorbed (e.g., on the microcosm inner
275 surface) during the time of the sampler deployment [18, 26-27] or when the calibration duration is
276 short, i.e., less than one week [28]. The static renewal calibration is the most commonly used
277 calibration system as it is simpler to run [16-17, 20, 22, 29-33]. Only 2 authors realized a continuous
278 flow calibration system with POCIS [34-37]. But, in almost all references, the stability of water
279 concentrations was not showed.

280 Various exposure media containers can be used: beakers (1 to 3 L), bottles (3 L) and aquaria (8
281 to 300 L). These different containers lead to different adsorption phenomena (due to various ratio
282 volume over surface) and also different agitation methods.

283 Calibration systems employ various agitation and temperature conditions and various types of
284 exposure media. An agitation system like that used by Mazzella et al. [18, 25, 38], with flow directed
285 in front of POCIS, seems to be more representative of environmental turbulences than magnetic
286 agitation or helix agitation. But some exposure media are not agitated at all [16-17, 22, 30-31].
287 Stirred bar agitation, often used with beakers or bottles, can vary from 60 rpm to 900 rpm [28].
288 Agitation can be expressed either in rpm or in cm/s making comparison difficult. Nevertheless, Li et
289 al. [19], underlined that the influence of agitation on uptake of polar compounds (pharmaceuticals

290 and endocrine disrupting compounds) did not exceed twofold for most of the studied compounds
291 during a 21 day in situ exposure experiment, with flow rates varying from 2.6 to 37 cm/s.

292 The temperature of the exposure media can vary from 5°C [28] to 28 °C [22]. The increase of
293 temperature can lead to a maximum of a twofold increase in R_s for pharmaceuticals and endocrine
294 disrupting compounds [28, 33].

295 Generally, the pH during laboratory calibrations is unchanged and is supposed to be around 7.
296 But some authors tested the influence of pH on R_s . Li et al. [39], using “pharmaceutical” POCIS,
297 found that R_s for acidic pharmaceuticals were higher at low pH (i.e., under their neutral form) than at
298 high pH (i.e., under their ionized form), whereas R_s for basic compounds were higher at high pH
299 (neutral form) than at low pH (ionized form). For neutral compounds, R_s were unchanged for the
300 range of pH tested (3 to 9). These results would suggest that uptake rates are higher for neutral
301 molecules than for ionized molecules. In addition, Zhang et al. [37] stated that RSD on R_s were
302 below 5% for neutral endocrine disrupting compounds (hormones, plasticizer) in the range of pH
303 tested (4 to 10) with “pharmaceutical” POCIS.

304 Exposure media can be distilled water [16-17, 20-22, 27-30, 33, 37], tap water [18, 20, 25, 31],
305 river water [34] or seawater [26, 32-33, 35-36]. The influence of salinity has been demonstrated in
306 some cases. Indeed, R_s of atrazine was 0.240 L/d and 0.239 L/d in distilled water [20] and in tap
307 water [18] respectively, whereas it was 0.042 L/d with seawater (salinity not specified) [26].
308 Moreover, Togola and Budzinski [33] tested the effect of salinity in 2 L beakers in stirred conditions.
309 For basic pharmaceuticals, lower R_s were obtained (up to 64%) for POCIS exposed in salted water
310 (35 practical salinity unit) than those exposed in unsalted water. In contrast, for acid
311 pharmaceuticals, there was no difference between the R_s obtained in salted or unsalted water.
312 Similarly, Zhang et al. [37] also tested the influence of salinity (from 0.18 to 35 PSU) with endocrine
313 disrupting compounds and pharmaceuticals (which can be acid or basic) and demonstrated that R_s
314 did not vary significantly (RSD<12%).

315 Another parameter which can influence R_s is biofouling. Though curiously, it seems to increase
316 accumulation for alkylphenols. Indeed, Harman et al. [35] calculated R_s of 0.13 L/d for 2,4-
317 dimethylphenol in unfouled “pesticide” POCIS and 0.20 L/d for the same compound in fouled
318 “pesticide” POCIS. They explained this by a possible reduction of interactions of POCIS analytes
319 with fouled membranes.

320 Furthermore, calibration can be performed with various micropollutant concentrations and
321 various exposure durations. Concentrations vary according to the study and to the molecules from
322 0.001 µg/L for colourings, detergents, fragrances and preservatives [34] to 1000 µg/L for hormones
323 [27]. It seems that the concentration has no influence on R_s for pharmaceuticals and endocrine
324 disrupting compounds, as tested at 2 concentration levels: 0.5 and 5 µg/L [29, 33]. In order to study
325 the optimal kinetic regime of the molecules accumulation into POCIS, exposure times vary from 1
326 day [31-32, 37] to 56 days [16, 30]. It was showed that linear uptake could be as long as 56 days for
327 some pesticides and pharmaceuticals with concentrations up to 5 µg/L [16]. In general, laboratory
328 calibrations are performed during 21 or 28 days for cyanotoxins [31], alkylphenols [36], hormones
329 [29], pesticides [18] and pharmaceuticals [22] in order to ensure staying within the kinetic regime.
330 Nonetheless, some compounds show evidence of a curvilinear accumulation into POCIS before 21
331 days of exposure; as for example, pesticides such as DIA, DEA, sulcotrione and mesotrione, which
332 are very polar or anionic compounds [18].

333 Sampling rates may also vary according to the type of POCIS: Hernando et al. [26], found R_s of
334 0.011 L/d and 0.023 L/d for benzothiazole with “pharmaceutical” and “pesticide” POCIS
335 respectively, using the same calibration system. In addition, R_s vary with the size of POCIS: Zhang
336 et al., [37] tested 3 different exposure areas (5.72, 11.33 and 22.89 cm²) and obtained positive
337 relationships between R_s and the exposure surface area of the sampler, with a correlation coefficient
338 from 0.82 (ethynilestradiol) to 1.0 (bisphenol A).

339 Furthermore, calculation methods for R_s determination can be different from one author to
340 another leading to different results. Most authors determined R_s using equation (2), by measuring the
341 mass of the analyte in POCIS and the mean water concentrations (several grab samples per week)
342 [16, 18, 20, 25, 33-37]. However, two authors calculated laboratory R_s for hormones and pesticides
343 by measuring only grab water concentrations using equation (5): Alvarez [17] did perform water
344 renewal each day, placing POCIS into a freshly spiked beaker; but Rujiralai [21] did not perform any
345 water renewal; this last method does not take into account possible degradation of compounds in
346 water. MacLeod et al. [22] and Li et al. [28] calculated R_s using equation (6). This method permits to
347 take into account possible analyte degradation, while avoiding daily renewals of the aqueous
348 solution as performed Alvarez [17]; but it seems to supply higher R_s than those calculated using
349 equation (2). Indeed, some R_s reported by MacLeod et al. [22] and Li et al. [28] were higher than 1
350 L/d, although such high levels were never reported by other authors. Therefore, we recommend that
351 R_s should be estimated preferentially using equation (2).

352 To conclude, laboratory R_s are difficult to obtain as they imply costly and time-consuming
353 laboratory calibration experiments. Calculated R_s may vary with physico-chemical parameters
354 (temperature, pH, salinity, biofouling...), agitation of exposure media, as well as the type and size of
355 POCIS. They are possibly also influenced by the level of micropollutant concentration, the exposure
356 duration, the calibration systems, and the calculation methods.

358 3.1.2 *In situ calibration*

359
360 In situ, POCIS are exposed to aquatic environments. Agitation, temperature, physicochemical
361 parameters, biofouling and micropollutant concentrations are not controlled; they can only be
362 measured using grab or automated sampling.

363 The advantage of in situ R_s is that, in principle, PRCs are not needed anymore. Indeed, in situ R_s
364 are reliable and constant for a specific site if environmental parameters do not vary too much during
365 the calibration. Thus, if POCIS are immersed at a given site and if environmental parameters are
366 close to those observed during the in situ calibration performed at the same site, POCIS can supply
367 accurate TWA concentrations. However, it is clearly too costly and time-consuming to perform an in
368 situ calibration for each studied site and sampling date. So, it could be interesting to determine
369 average in situ R_s with associated variability, as a function of different sites and different
370 environmental conditions. As of today, there are no published data on the variability of in situ R_s
371 linked to environmental parameters (e.g., water flow, temperature...). Therefore, when applying the
372 in situ R_s strategy, it is necessary to determine in situ R_s and the associated variability for each field
373 campaign.

374 In situ R_s are also evaluated using average micropollutant concentrations obtained from grab or
375 automated sampling, which can be biased due to possible concentration variation and insufficient
376 sampling frequency.

377 To date, very few values of in situ R_s have been published [25, 37, 40]. Zhang et al. [37],
378 analyzed triplicates of "pharmaceutical" POCIS every day during 2 weeks at 2 different sites (a
379 wastewater treatment plant [WWTP] effluent and river water) in order to validate POCIS
380 performance in situ. The studied molecules were an antibiotic, anticonvulsives, anti-inflammatories,
381 an antipsychotic, a betablocker, estrogens, an inhibitor and a plasticizer. In situ R_s were higher than
382 laboratory R_s , since flow velocity was higher in effluent and river water than in the laboratory.
383 Mazzella et al. [25] performed an in situ calibration in 2 rivers in order to compare laboratory R_s ,
384 corrected laboratory R_s and in situ R_s for selected herbicides. Exposure time was 22 days with
385 duplicate "pharmaceutical" POCIS analyzed at 6, 13 and 22 days. It appeared that in situ R_s were
386 closer to corrected R_s than to laboratory R_s . The authors concluded that in situ calibrations are
387 preferable, but too costly and time-consuming. Jacquet et al. [40] exposed "pharmaceutical" POCIS
388 in a river at 3 sites located near a WWTP outflow, in order to evaluate in situ R_s variability for

389 betablockers and estrogens. At each site, POCIS were immersed in triplicate during 7, 14 and 21
390 days at 3 different stations (upstream, downstream and effluent from the WWTP). Taking into
391 account all measured in situ R_s , RSD were between 33 and 71%; these results were considered
392 satisfactory in view of the various environmental conditions tested.

393 Moreover, an interesting flow-controlled field experiment was performed by Li et al. [19]; this
394 approach could be useful in order to better estimate influencing parameters on R_s directly in situ.
395 Indeed, although the authors did not calculate R_s , they exposed POCIS directly in effluent of a
396 WWTP controlling agitation in order to measure pharmaceuticals and estrogens. So, this system
397 could be considered an intermediate between the laboratory and the field.

398 To conclude, in situ R_s seem to be more reliable than laboratory R_s because they take into
399 account environmental conditions. But in situ calibration is still an exploratory approach which
400 needs more data and field campaigns to evaluate its performance and applicability to measure TWA
401 concentrations in various waters.

402

403 (table 1)

404

405 3.2 Literature sampling rates and evaluation of TWA concentrations

406

407 3.2.1 Comparison of literature sampling rates

408

409 Sampling rates for POCIS gathered from literature are presented in table 2. Almost 200
410 molecules have been studied for the determination of R_s . They are classified by family and by
411 calibration type. Then, they are ordered by separating R_s obtained with “pharmaceutical” or
412 “pesticide” POCIS. Moreover, laboratory R_s were classified according to “standard conditions” (i.e.,
413 most used in the literature): typical POCIS (45.8 cm², 200 mg of receiving phase) calibrated in
414 freshwater between 15 and 25°C in stirred conditions. We specified when laboratory R_s were
415 obtained in different conditions. This classification permitted to better identify the factors leading to
416 a variation of R_s .

417

418 (table 2)

419

420 Sampling rates for POCIS vary from 0.001 L/d for leucomalachite green [32] to 2.459 L/d for 4-
421 *n*-nonylphenol [28]. Generally, R_s are lower than 1 L/d, except for 4-*n*-nonylphenol, triclosan and
422 fluoxetine [22, 28].

423 Differences in R_s between molecules could be due to their physico-chemical properties (log K_{ow} ,
424 pKa, molar mass, size and shape...). But, as stated previously, several factors can also modify the
425 value of R_s : the type and size of POCIS, agitation and physico-chemical parameters (temperature,
426 pH, total and dissolved organic compounds, conductivity...) [28], as well as biofouling [35].
427 Furthermore, seawater could decrease the uptake rates of basic pharmaceuticals [33] in comparison
428 with freshwater. Also, the calibration system itself, the duration of the experiment, the analyte
429 concentrations and the calculation methods are suspected to impact the R_s values.

430 Hence, for a single molecule, laboratory R_s can vary significantly between studies when
431 conditions vary. For estrone, R_s ranged from 0.1199 L/d [29] to 0.699 L/d [28]. Indeed, agitation
432 used by Arditoglou and Voutsas [29] was lower than that of Li et al. [28] (Cf. table 1). Similar
433 hypothesis can be proposed for bisphenol A, β -estradiol, ethynilestradiol or 4-*n*-nonylphenol. It is
434 not possible to compare R_s obtain by Hernando et al. [26] with these two authors for estrone since
435 agitation and water concentrations were not indicated. For diuron, R_s obtained by Mazzella et al.
436 [18] is almost 3 times higher than the one determined by Martinez Bueno et al. [32]: 0.247 and 0.086

437 L/d, respectively. This difference is probably due to the seawater used during the calibration by
438 Martinez Bueno et al. [32]. The same assumption can be made for simazine, since R_s obtained by
439 Mazzella et al. [18] is almost 5 times the one determined by Hernando et al. [26]: 0.210 and 0.045
440 L/d respectively. But curiously, R_s obtained by Martinez Bueno et al. [32] for this molecule (0.223
441 L/d) is similar to that reported by Mazzella et al. [18].

442 Generally, when comparing laboratory R_s with the same POCIS (“pharmaceutical” and 45.8 cm²
443 surface) calibrated in “standard” conditions, literature data are similar, i.e., the ratio between the
444 highest and the lowest R_s is less than a factor of 2. This is the case for 6 pharmaceuticals
445 (trimethopim, carbamazepine, fluoxetine, paroxetine, metoprolol and propranolol) and one
446 detergent (4-tert-butylphenol) between MacLeod et al. [22] and Li et al. [28]; and for 2 pesticides
447 (desethylatrazine and simazine) between Mazzella et al. [18] and Alvarez et al. [20]. Nevertheless,
448 dispersion can be higher for some molecules. Indeed, ratios of 3.4 and 9.1 are observed for naproxen
449 and sulfapyridin R_s respectively, between MacLeod et al. [22] and Li et al. [28]. It is possible that,
450 for these 2 pharmaceuticals, which are polar and under anionic form in water, MacLeod et al. [22]
451 exceeded the optimal duration for linear uptake, since analyses of POCIS were performed after 25
452 days of exposure, leading to a bias in R_s data; as compared with an experimental exposure of 8 days
453 for Li et al. [28]. It is interesting to specify that the same calculation method was used to obtain R_s in
454 both studies.

455 Unfortunately, it is difficult to compare laboratory R_s between studies because they are obtained
456 using different calibration systems and different conditions which, most of the time, are not fully
457 described. Moreover, different calculation methods can increase the dispersion of R_s data. Therefore,
458 to obtain comparable and reliable laboratory R_s , it is necessary to standardize and to control
459 laboratory calibration protocols. Furthermore, the optimal duration for linear uptake of the studied
460 compounds should be systematically verified. For that, it is necessary to perform a calibration curve
461 with multiple points taken at different time (for example 0, 7, 14 days). With these conditions, a
462 reference laboratory sampling rates database would be available, which could be useful to calculate
463 corrected reliable laboratory R_s with PRC(s). Concerning R_s obtained in situ, it is uneasy to compare
464 them with laboratory R_s as experimental conditions are too different.

465

466 3.2.2 *Sampling rates vs log K_{ow}*

467

468 Some authors tried to link their measured laboratory R_s with the log K_{ow} of molecules. The interest
469 of such correlations would be to predict R_s and avoid laboratory calibrations for every studied
470 molecule.

471 According to Togola and Budzinski [33], R_s followed a linear relationship ($R^2=0.69$) with log
472 K_{ow} (from -0.07 to 4.80) for 7 basic compounds (3 anticonvulsives, 2 antidepressants, 1
473 antihistaminic, 1 stimulant). Li et al. [28] also found a linear relationship ($R^2=0.84$) for 14 basic
474 compounds (antibiotic, antidepressants and betablockers) with log K_{ow} between 0 and 4. It was also
475 the case for 8 neutral compounds (1 antibiotic, 1 anticonvulsive, 1 antidepressant, 1 stimulant, 3
476 estrogens and 1 phenol) [28]. However, MacLeod et al. [22] indicated that for 3 basic compounds
477 (betablockers) and 4 acid compounds (anti-inflammatories), R_s followed a Gaussian model as a
478 function of log K_{ow} (between 0 and 4.5), with the highest R_s for log K_{ow} around 3 or 4 ($R^2=0.99$ for
479 betablockers). In Mazzella et al. [25], R_s for 6 herbicide compounds (basic and neutral with log K_{ow}
480 between 1.15 and 3.13) seemed to follow a curvilinear model versus log K_{ow} . The maximum log K_{ow}
481 was around 3. If POCIS had no membranes, the R_s would increase with increasing log K_{ow} , since log
482 K_{sw} , which reflects the affinity of each chemical with the receiving phase of the POCIS, increases
483 with hydrophobicity. When the membrane is polar, it is expected to limit R_s of compounds with log
484 $K_{ow}>3$, explaining why a curvilinear model is observed. It is possible that the membrane be
485 “transparent” (rapid diffusion equilibrium) for some neutral and basic pharmaceutical compounds,
486 driving to a linear pattern between R_s vs log K_{ow} . In contrast, Arditoglou et al. [29], found no

487 correlation between $\log K_{ow}$ and R_s for 6 hormones and 8 alkylphenols or phenols, which are all
488 neutral in distilled water.

489 It would be interesting to obtain more R_s for herbicides with $\log K_{ow} > 3$ in order to check if the
490 curvilinear model is still valid or not. This suggestion can also be extended for pharmaceuticals.
491 Perhaps the ionized characteristics of some molecules should be taken into account. Indeed, when
492 molecules are ionized, the $\log K_{ow}$ (which is then called $\log D$) can dramatically decrease or increase
493 as a function of the pKa and the pH values [39]. That could explain why ionized molecules show
494 linear patterns for R_s vs $\log K_{ow}$ even with high $\log K_{ow}$.

495 Up to now, it is not possible to predict a R_s solely from $\log K_{ow}$. Other parameters (size, shape
496 and ionizability of molecules) would have to be taken into account.

497 498 3.2.3 *Evaluating of the reliability of TWA concentrations*

500 In order to evaluate the reliability of POCIS R_s , several authors compared concentrations from
501 POCIS with concentrations from grab or automated sampling and calculated in situ TWA
502 concentrations.

503 504 3.2.3.1 *TWA concentrations calculated with laboratory R_s*

505 Fifteen different studies compared TWA concentrations of analytes calculated from POCIS exposed
506 in situ using laboratory R_s , with mean concentrations measured from grab sampling [16, 20-22, 25,
507 28-29, 31, 33, 38, 41-45]. Mean water concentrations are generally obtained (when indicated)
508 calculating an average value of grab samples concentrations. The sampling frequency is different
509 from one study to another. It can vary from one sample per day [33], to one sample per month [21].
510 Some authors used average grab concentrations from literature [21, 28]. Only Mazzella et al. used an
511 automatic sampler in order to obtain highly representative weekly composite samples made with
512 hourly sampling frequency to study herbicides [25]. The stability of molecules was checked for 10
513 days.

514 These studies demonstrated that for almost all the molecules studied (alkylphenols, herbicides,
515 hormones, pharmaceuticals, phenols), TWA and average concentrations from grab or automated
516 sampling were in good agreement. However, Li et al. [28], for betablockers and caffeine, and
517 Mazzella et al. [38], for herbicides, indicated that TWA concentrations were sometimes lower (up to
518 90%) or systematically higher (from 11 to 49%) respectively, than those from average grab
519 sampling. Mazzella et al. [25], indicated that TWA concentrations for herbicides (without correction
520 by PRC) were sometimes lower (about 3 to 4 times) than those from weekly composite samples.
521 Rujiralai et al. [21] indicated that concentrations of estrogens were higher (about 4 times) or lower
522 (about 3 times) when comparing TWA and grab concentrations. Authors stated that differences
523 between the two methods might come from grab samples since the comparison is done between a
524 specific sampling time and a TWA concentration measured over the exposure period [16, 21], from
525 differences in temperature between laboratory and field experiments [22], or due to the presence of
526 dissolved organic carbon in the water at the studied site [29].

527 In conclusion, it is difficult to evaluate the reliability of TWA concentrations obtained in situ
528 using laboratory R_s because a reference TWA concentration value is generally not available. One
529 method to obtain a reliable reference TWA concentration value is to use automated sampling
530 performed at short time intervals (e.g., daily or weekly composite samples made with high sampling
531 frequency). But it is not feasible at all sites and could be applied at a reasonable cost only for stable
532 molecules. Another method could be to perform laboratory experiments with fluctuating and
533 controlled conditions (agitation, temperature, physico-chemical parameters of water, concentrations
534 of micropollutants...) in order to mimic field conditions. Then, it would be possible to validate TWA
535 concentration using laboratory R_s obtained previously against the defined concentration (nominal
536 concentration checked by grab samples).

537

538 3.2.3.2 TWA concentrations calculated with in situ R_s

539 To determine the reliability of in situ R_s , TWA concentrations (ng/L) could be compared with
540 average grab concentrations (ng/L), which were obtained manually [37, 40] or with an automated
541 sampler [25, 40].

542 Zhang et al. [37] used specific in situ R_s . Indeed, the effluent R_s , obtained via previous in situ
543 calibrations, were then applied to calculate TWA concentrations of pollutants in the same effluent.
544 They found good correlations between TWA and grab concentrations for pharmaceuticals but not for
545 endocrine disrupting compounds (hormones and bisphenol A). The authors concluded on the need to
546 perform appropriate field validation. Jacquet et al. [40] used in situ R_s for betablockers to measure
547 TWA concentrations in the Seine River, which were in good agreement with average grab
548 concentrations (performed two times per week). Mazzella et al. [25] found that when no PRC are
549 applicable, in situ R_s supply TWA data that are probably more reliable than TWA using laboratory
550 R_s .

551 It is clear that the reliability of TWA concentrations is difficult to evaluate in situ. In situ R_s seem
552 to be more reliable than laboratory R_s . But in situ calibration for each field campaign is a costly and
553 a time-consuming method. Thus, there is a need to obtain more data in order to estimate variability
554 on mean in situ R_s with environmental conditions and to avoid systematic in situ calibrations.
555

556 3.3 POCIS applications

557

558 3.3.1 Molecules and media studied

559

560 POCIS was designed to trap polar organic contaminants with $\log K_{ow}$ lower than 4 [16]. This
561 parameter is not fixed since pollutants with higher octanol-water partition coefficients can also be
562 accumulated. However, for these compounds, other types of integrative samplers are more
563 appropriate, like low-density polyethylene (LDPE) or SPMD [46].

564 More than 300 chemicals have already been detected or quantified in POCIS in laboratory or in
565 situ (table 3): anesthetics (2 molecules), anthelmintic (1), antianginal (1), antibiotics (22),
566 anticonvulsives (7), anticorrosive (1), antidepressants (14), antifoaming (1), antihistaminics (2), anti-
567 inflammatories (11), antipsychotic (1), antiulcerous (1), bactericides (6), betablockers (5), colourings
568 (3), cosmetics (2), cyanotoxins (2), decongestant (1), detergents/surfactants (50), diuretic (1), drug
569 for viral infection (1), hormones (14), flame retardants (4), fragrances (17), fungicides (9), herbicides
570 (62), inhibitors (6), insecticides (35), lipid (1), odorant (1), plasticizers (5), preservatives (4),
571 repellents (2), stimulants (7) and UV filters (4).

572 Among these accumulated molecules, numerous have $\log K_{ow} > 4$ (circa 70 molecules)
573 demonstrating that the validity field of POCIS needs further investigation. For example, POCIS can
574 trap molecules such as azythromycin ($\log K_{ow} = 4.02$), diclofenac ($\log K_{ow} = 4.51$), alkylated phenols
575 like 4-*tert*-octylphenol ($\log K_{ow} = 5.28$) and 4-*n*-octylphenol ($\log K_{ow} = 5.50$) and traseolide (\log
576 $K_{ow} = 6.14$).

577 Most commonly, sampling sites are situated in rivers near WWTPs. POCIS were exposed
578 upstream and downstream of WWTPs in several studies [22-23, 28, 37, 41, 47-60]. Quantities of
579 micropollutants were also measured in POCIS exposed in WWTP influent [53, 61-63] and effluents
580 [19-20, 22-23, 29-30, 37, 41-42, 53, 57, 61-64]. POCIS applied to study contaminants around
581 WWTPs (influent, effluent, upstream, downstream) were located in several countries: USA,
582 Switzerland, Canada, UK, Italy, Czech Republic and Greece.

583 Alternatively, POCIS was studied in river waters not directly influenced by WWTPs [16, 20, 22,
584 25, 38, 43-44, 50, 54, 65-70]. POCIS was also studied in lakes [28, 31, 47, 55, 71-73], estuaries [29,
585 33, 74], marine waters [26, 29, 32, 35-36, 75], upstream and downstream farms [27, 45] and waters

586 from constructed wetlands [17, 76]. These studies were performed in the USA, France, Switzerland,
587 Spain, the Czech Republic and Greece.

588

589 3.3.2 The 3 main uses of POCIS

590

591 The 3 main applications of POCIS, detailed in table 3, are:

- 592 - the coupling of POCIS with chemical analysis for micropollutants screening *in situ*,
- 593 - the coupling of POCIS with chemical analysis to assess TWA concentrations of
- 594 micropollutants *in situ*,
- 595 - the coupling of POCIS with bioassay analysis to analyze toxicity *in situ*.

596 Table 3 presents also the different aims of the studies, the family of molecules studied, the types of
597 water studied, the maximal exposure duration of POCIS and if bioassays were performed using
598 POCIS extracts.

599 The use of POCIS for screening and for evaluation of TWA concentrations allows to evaluate
600 chemical quality of aquatic environments spatially and temporally.

601 Screening is generally performed to evaluate a contamination source [50, 53-54, 56, 60-62, 69-
602 70, 72-73, 76], to determine a gradient of concentrations [50, 52-53, 55, 60, 62, 70, 72, 74, 77] or to
603 study the influence of seasons on the aquatic environment's contamination [47, 52-53, 72, 74]. This
604 application is performed in different media (rivers, groundwaters, lakes, marine waters, WWTP
605 influents and effluents) with exposure durations of about 3 to 4 weeks. However, accumulation of
606 different compounds can take longer: for instance, Liedtke et al. [72] exposed POCIS for 169 days to
607 study a detergent, a plasticizer and hormones, in lake inflows and outflow.

608 TWA concentrations were obtained for numerous organic molecules (colouring, cyanotoxines,
609 detergents, plasticizers, hormones, pesticides, pharmaceuticals, stimulants) in different media (rivers,
610 lakes, estuaries, marine waters, WWTP effluents, farms) [16-20, 22-23, 25-45, 47, 63, 65, 68, 71,
611 75]. Exposure durations vary generally from 2 to 4 weeks. Only 3 authors calculated "corrected"
612 TWA concentrations of herbicides in rivers using a PRC [18, 25, 43, 45]. Jones-Lepp et al. [30] and
613 Alvarez et al. [47] studied the seasonal evolution of micropollutants concentrations. The evaluation
614 of TWA concentrations is more time-consuming than the use of POCIS for screening since previous
615 calibrations are required. Obtaining accurate TWA concentrations represents a real issue for using
616 POCIS for water quality monitoring. For further details, this point is discussed in section 3.2.2.

617

618 POCIS can also be coupled with bioassays. In this case, POCIS are generally exposed in
619 contaminated sites that could induce positive responses with bioassays (i.e., in or near WWTPs). The
620 most commonly used is the yeast estrogen screen (YES) test, indicating a disrupting endocrine effect
621 on estrogen receptors [27, 49, 51, 57-59, 62, 65-66, 72, 76]. The YES test allows to "biodelect"
622 endocrine disruptor molecules such as hormones, detergents, plasticizers, etc. Alvarez et al. [47]
623 used the bioluminescent YES (BLYES), which appeared to be more rapid than the classical YES
624 test. The unit of these bioassays is the estradiol equivalent (bio-EEQ). In most cases, POCIS extracts
625 induced a response with YES test in WWTPs influent or effluents [57, 59, 62], constructed wetlands
626 [76], river waters (watersheds, upstream or downstream of WWTPs) [27, 47, 49, 51, 58-59, 65, 76].
627 Disrupting endocrine effect was also tested on extracts from POCIS immersed in lakes thanks to the
628 yeast androgen screen (YAS) test [66]. No response was found with this bioassay.

629 Another bioassay tested is the Microtox test revealing aquatic ecotoxicological effect based on
630 inhibition of bioluminescence from a bacteria [65]. This bioassay was tested on POCIS extracts
631 immersed in river waters located downstream of WWTPs and all the responses were negative.

632 A new bioassay called HG5LN-hPXR cells was tested on extracts from POCIS immersed in
633 river water [67]. The responses of this bioassay were positive, especially for semi-polar compounds.
634 These authors used other bioassays on POCIS extracts to test estrogenic, PAH-like, dioxin-like,

635 androgenic and anti-androgenic activities. The 2 former were positive, whereas the 3 latter bioassays
636 were negative.

637 At last, Harman et al. [77] tested 3 bioassays on POCIS extracts from an off-shore oil production
638 in the North Sea. The first one measured the 7-ethoxyresorufin-O-deethylase (EROD) activity which
639 is a biomarker for the aryl-hydrocarbon. The second one was the vitellogenin analysis in order to
640 determine the biological response to mimic estrogens. The third one measured the acute toxicity
641 (cytotoxicity) of the extract. Results indicated that EROD activity was induced (positive result) at
642 10 km of the off-shore station, the vitellogenin was inhibited at this distance (positive result) and that
643 there was no metabolic toxicity (third test). This indicates that arylhydrocarbon receptor agonists
644 may inhibit estrogen receptor-mediated vitellogenin production with no cytotoxicity.

645
646 Some authors compared results from POCIS with those from grab sampling, bioassays or
647 biological organisms (concentrations or effects).

648 For example, the nature of micropollutants trapped by POCIS was compared with the nature of
649 micropollutants found in grab water sample [48, 73-74]. Alvarez et al. [48] underlined that POCIS
650 permitted to detect more compounds than classical grab sampling downstream a WWTP located in
651 the Delaware River. Indeed, they found 32 organic molecules from POCIS extracts and only 9 to 24
652 organic molecules from grab sampling.

653 Quantities or TWA concentrations from POCIS can also be compared with bioassays performed
654 on POCIS extracts [47, 64-65, 67, 76-77] or with biological organisms (concentrations [52, 60] or
655 effects [50, 54, 56, 62, 69-70, 72-73]).

656 To compare TWA concentrations and bioassays, authors use Calculated estradiol equivalents
657 (cal-EEQ) and Biological estradiol equivalents (bio-EEQ). Cal-EEQ are obtained with classical
658 chemical analysis performed on POCIS extracts, using a correction factor on all estrogens measured
659 (for example 0.33 for estrone, 1 for estradiol...). Bio-EEQ are obtained with the response from YES
660 test performed on POCIS extracts. Vermeirssen et al. [58] and Liscio et al. [62] found a good
661 correlation between cal-EEQ and bio-EEQ exposed upstream and downstream of WWTPs or in
662 WWTP influent and effluent, respectively. However, differences can be found because some
663 chemical compounds which are not estrogens can be estrogen mimicking chemicals. Indeed,
664 Matthiessen et al. [27] and Liedtke et al. [72] did not find matching results when comparing cal-EEQ
665 and bio-EEQ immersed in upstream and downstream farms or in tributaries or outflow of a lake,
666 respectively.

667 Some authors also compared bio-EEQ from POCIS extracts with bio-EEQ from grab samples.
668 Balaam et al. [49] realized this comparison downstream a WWTP. Results from POCIS extracts and
669 spot samples were different. Nevertheless, bio-EEQ from POCIS extracts fitted well with predicted
670 (modeled) monthly average steroid estrogen concentrations. Moreover, bio-EEQ can be compared
671 with effects [51, 58, 62, 72] on biological organisms.

672
673 In summary, screening, TWA concentrations and coupling of POCIS extracts with bioassays are
674 performed in order to obtain respectively a chemical qualitative, a chemical semi-quantitative or a
675 biological information about water quality of the medium studied. Complementary studies are
676 necessary to improve the determination of average TWA concentrations in order to obtain
677 quantitative chemical information; and also to better understand differences between results of
678 bioassays performed on POCIS extracts with TWA concentrations. Hence, POCIS can be used, at
679 present, for investigative monitoring programmes as a chemical or a biological screening tool. It
680 might also be used for operational monitoring programmes (instead of usual grab sampling), and is
681 particularly useful in remote areas (far from laboratory facilities), although more studies are still
682 needed for quantitative applications.

683

684 3.4 General issues for using POCIS

685

686 3.4.1 Exposure duration

687

688 Exposure durations of a POCIS in a particular medium can be variable. To provide TWA
689 concentrations, the tool has to be in the kinetic regime. Thus, POCIS must be exposed long enough
690 to ensure that accumulation of compounds is sufficient to be detectable (after few days of exposure),
691 but not more than the optimal exposure duration (i.e., the longer exposure duration possible but
692 lower than the maximum time of the kinetic regime).

693 In the laboratory, minimal exposure duration was 1 day to analyze cyanotoxins with
694 “pharmaceutical” POCIS [31, 71]. The maximal exposure duration was 56 days [16, 30] for
695 analyzing hormone, pesticides, pharmaceuticals and stimulants with “pesticide” or “pharmaceutical”
696 POCIS. Alvarez et al. [16] showed linear uptake for pesticides ($r^2=0.993$ and 0.994 for diuron and
697 isoproturon, respectively) and pharmaceuticals ($r^2=0.944$ and 0.988 for levothyroxine and
698 azithromycin, respectively) during 56 days of exposure with “pesticides” configuration (exposure
699 surface of 18 cm^2) of POCIS. Jones-Lepp et al. [30] did a calibration over 56 days with
700 “pharmaceutical” configuration of POCIS (exposure surface of 18 cm^2) in the same conditions as
701 Alvarez [16], but data on R_s and determination coefficients were not detailed. Thus, it is not possible
702 to conclude if the analytes were still in the linear uptake or not. Kohoutek et al. [31] also performed
703 a calibration with “pharmaceutical” POCIS configuration (exposure surface of 14.1 cm^2) with
704 polycarbonate membranes (instead of polyethersulfone) over a period of 42 days. It appeared that,
705 after 28 days, the tool was still in linear uptake for sampling cyanotoxins. From 28 to 42 days, it
706 seemed that the accumulation entered in a pseudolinear regime, as mentioned by Vrana et al. [2]. In
707 addition, with “pharmaceutical” configuration (exposure surface of 41 cm^2), linear uptake was
708 observed during 28 days of exposure with detergents ($r^2=0.810$ for octylphenol, 0.985 for
709 nonylphenol, 0.988 for tert-octylphenol, 0.990 for BPA, OP1EO, NP2EO, 0.995 for OP2EO and
710 0.996 for NP1EO) and estrogenic hormones ($r^2=0.994$ for E1 and MeEE2, 0.995 for β -E2 and 0.999
711 for α -E2, E3 and EE2) [29]. Other authors showed that polar organic compounds (colourings,
712 detergents, flame retardant, fragrances, pesticides and preservatives) were still accumulated
713 proportionally with time, during 28 days with POCIS in “pesticide” configuration [78] or
714 “pharmaceutical” configuration [25, 34, 36].

715 In situ, minimal exposure durations for POCIS exposed near or within WWTPs was 5 days in
716 order to analyze an estrogenic hormones, pharmaceuticals and a plasticizer with “pharmaceutical”
717 POCIS [37] or to analyze a detergent, estrogenic hormones and a plasticizer with “pesticide” POCIS
718 [62]. The maximal exposure duration for these types of water was 54 days to analyze a colouring, a
719 cosmetic, detergents, flame retardants, fragrances, an odorant, pesticides, a plasticizer,
720 pharmaceuticals, a repellent and stimulants with “pesticide” and “pharmaceutical” POCIS [48].

721 POCIS exposed in water with lower micropollutants concentrations (river waters with no source
722 of contamination, estuaries or marine waters) are usually deployed for a longer time. Maximal
723 exposure durations varied from 7 days [29, 70] to 169 days [72]. Liedtke et al. [72] did not indicate
724 if POCIS was still in the kinetic regime after 169 days of exposure. They analyzed a detergent,
725 hormones and a plasticizer. Their study determined if tributaries and outflow of a lake had an
726 endocrine effect in coupling extracts of POCIS with the YES test.

727

728 It is important to consider that the duration of the kinetic regime depends in part on the molecule
729 studied and also on the type of POCIS applied (membrane, type and size). Therefore, calibration
730 experiments (in laboratory or in situ) are necessary to estimate the optimal exposure duration of the
731 integrative sampler for each new molecule and for the chosen POCIS configuration.

732

733 3.4.2 *Transport and conservation of POCIS*
734

735 Very few authors discussed about the conservation and transport of POCIS before its exposure. For
736 conservation, Alvarez et al. [16] inserted prewashed POCIS at -20°C in containers filled with argon.
737 Bidwell et al. [50] also placed POCIS under argon atmosphere in containers, but they did not provide
738 any indication on temperature. Jacquet et al. [40], wrapped POCIS in aluminium foil and a freezer
739 bag and stored them at -20°C. Li et al. [28] only indicated that POCIS were inserted in air-tight
740 (stainless steel) containers. Liedtke et al. [72] also indicated that POCIS were conserved in their
741 original stainless-steel containers (from manufacturer). The transport before exposure was carried
742 out at -20°C for Alvarez et al. [16, 20], at 4°C [40] or at room temperature [50, 72], but there was no
743 information about a possible temperature effect.

744 For calibration, Alvarez [17], Mazzella et al. [18] and Li et al. [28] wet POCIS by putting them
745 in distilled water 24h before exposure. This permits to reduce the possibility of a greater flux across
746 the membrane during the wetting stage at the beginning of the experiments.

747 After retrieval, POCIS were sometimes washed in the field to remove attached debris [17, 29,
748 32-33, 58, 61-64, 68] then transported to the laboratory. They could be wrapped in aluminium foil
749 [27-29, 40, 44, 52, 59-64, 68, 72] and transported in a container. Sometimes POCIS are directly
750 inserted in containers without aluminium protection. The transport could be done in frozen
751 conditions [16, 19-20, 64], at 0 to 4°C [22, 28-29, 32, 40-42, 50] or at room temperature [52, 58, 60,
752 62-63, 68, 72].

753 Back in the laboratory, POCIS were frozen (between -15 to -20°C) until processing. Sometimes
754 they were rinsed with ultrapure water just before processing.

755 Many authors only indicated transport conditions and not the conservation conditions or *visa*
756 *versa*. Sometimes the two were not mentioned at all.

757 We recommend that before exposure and if POCIS was spiked by PRC, conservation and
758 transport should be done in cold conditions (0 to 4°C). Back in the laboratory, POCIS have to be
759 stored at -20°C.
760

761 3.4.3 *Processing and analysis techniques*
762

763 The extraction of POCIS was obtained by transferring the sorbent in most cases into a SPE glass
764 cartridge or into an ASE cell [26] or by sonification [31, 71].

765 The solvent extraction of “pesticide” POCIS was generally carried out with a mixture of
766 methanol/toluene/dichloromethane (1/1/8). The solvent extraction of “pharmaceutical” POCIS was
767 done with methanol for most of the authors. There were also extractions with other solvents
768 depending of the molecules studied.

769 Sometimes an additional step of purification was carried out, such as filtration [30, 41, 47-48,
770 65], column cleanup with Florisil [26, 56, 73], size exclusion chromatography followed by column
771 cleanup with Florisil [65] or dilution of the final POCIS extract [40]. For Sellin et al. [56], the
772 purification allowed to decrease ion suppression observed for hormones in POCIS extracts.

773 Most authors used LC-MS/MS or GC-MS systems depending of the molecules, although there
774 were other analytical methods cited in literature (i.e., FIA-MS, GPC-UV, LC-DAD, GC-ECD).

775 For bioassay tests, POCIS underwent the same sample preparation than samples intended for
776 chromatographic analysis. However, the solvent had to be exchanged based on the bioassay: ethanol
777 for yeast estrogen screen (YES) test [58, 62, 65, 72]; methanol for BLYES test [47]; and DMSO for
778 Microtox test [65], EROD activity test, vitellogenin test or cytotoxicity test [77].
779

780 3.4.4 *Quality assurance*
781

782 Quality assurance (QA) for passive samplers deployment in laboratory or in situ requires blank
783 POCIS controls (laboratory and field blanks), spike controls and replicates [79]. But these
784 recommendations are seldom described in literature.

785 The following quality controls (QCs) are the most commonly used: POCIS field blank controls
786 (POCIS deployed in the field but not immersed in the medium); and/or POCIS laboratory blank
787 controls (POCIS constructed concurrently with the deployed POCIS but never transported to the
788 field and stored in the laboratory) [20].

789 Analyte recovery should be verified. Several authors determined recovery [16, 18, 28-29, 36,
790 54]. If the analyte recovery is not performed, it can have an impact on final results; that would need
791 to be taken into account, especially when comparing results between POCIS and grab sampling, or
792 between different molecules at a given site.

793 When the PRC strategy was used, authors checked for the initial concentration of the PRC (DIA-
794 d5 in all cases) [18, 25]. Replicates of the unexposed spiked sorbent [18, 25, 45] or field spiked
795 blanks [43] were analyzed by using the same elution protocol as for exposed spiked POCIS.
796 Mazzella et al. [18, 25] reported an accuracy for DIA of 99% of the expected value (25 $\mu\text{g/g}$) with a
797 relative standard deviation (RSD) of 3% (n=3), and of 84% for DIA-d5 with RSD of 8% (n=3),
798 respectively.

799 Replicate POCIS were generally exposed in order to obtain more robust values (in laboratory and
800 in situ). Generally authors used duplicate or triplicate POCIS. For R_s determination, resulting
801 standard deviations (SD) could vary greatly as indicated in table 2. They apparently depend on the
802 type of calibration, the type of POCIS used, and the molecule studied.
803

804 **4 Conclusion**

805

806 This review, focalized on POCIS, points out the crucial questions of calibration and possible bias in
807 the evaluation of TWA concentrations; it also details the different applications of this passive
808 sampler and the available information on analytical protocols to use it. These aspects are studied
809 throughout the detailed examination of data collected from 62 references covering a period from
810 1999 to 2012.

811 Laboratory sampling rates per molecule can vary significantly as a function of the different
812 calibration methods (in terms of calibration system and physico-chemical parameters of water) and
813 the type of POCIS used. It would be necessary to standardize calibration protocols in order to reduce
814 dispersion and to obtain a reference data base on laboratory R_s . For instance, “standard conditions”
815 as cited in table 2, could be used. Moreover, the evaluation of reliable in situ TWA concentration
816 still needs further research. Indeed, better knowledge is required on the PRC strategy, with a real
817 challenge at identifying candidate molecules able to be desorbed from the solid phase of POCIS and
818 to be used as internal surrogates of the exposure step. Besides, in situ calibration is an alternative
819 strategy to explore. Indeed, in situ R_s would allow to remove the problem of environmental
820 conditions. Furthermore, the definition of in situ R_s variability as a function of environmental
821 conditions could be useful to avoid systematic calibrations.

822 In the context of the Water Framework Directive (WFD) and Marine Strategy Framework
823 Directive (MSFD), POCIS is a very useful tool for screening of pollutants, measuring trends in level
824 of pollutants, and also for the identification of pollution sources or the evaluation of toxicological
825 effects in aquatic environments. However, in order to obtain quantitative and representative TWA
826 data, several aspects still require more research, such as the use of PRC; the influence of seasons,
827 biofouling and physico-chemical characteristics of aquatic systems on the pollutant accumulation in
828 POCIS; optimum exposure duration; and, finally the capacity of the tool to detect short variation
829 concentrations (estimation of lag time). Moreover, in order to improve the reliability and the

830 comparability of results obtained with POCIS, there is a need to define standardized protocols for
831 deployment, quality assurance/quality control procedures (with certified materials) and validation of
832 calibration procedures (e.g., intercomparison exercises).

833

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835

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839

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965

Tables

Table 1. Laboratory calibration methods and experimental parameters for POCIS.

Calibration method	Type of POCIS Size of POCIS (cm ²)	Family of molecules	Container used	Type of water	Concentrations of analytes (µg/L)	Water concentration analysis	Water temperature (°C)	Agitation	POCIS analysis (days)	Reference
Static	Pesticide and pharmaceutical 45.8	Colouring, fungicide, herbicides, hormones, insecticides, repellent	Aquarium (20L)	Seawater	0.17	?	18	?	t=18 and 24	[26]
?	Pharmaceutical 45.8	Hormones	Beaker (1L)	Distilled water	1) 1 2) 10 3) 100 4) 1000	Yes Mean water concentrations	20	?	?	[27]
Static	Pesticide and pharmaceutical 41	Herbicides	Aquarium (80L)	Tap water	1-2	Yes Mean water concentrations	17	Yes (2-3 cm/s)	Duplicates at t=5, 10, 15 and 21	[18]
Static	Pharmaceutical 41	Herbicides	Aquarium (80L)	Tap water	1-2	Yes Mean water concentrations	?	Yes (2-3 cm/s)	Duplicates at t=7, 14, 21 and 28	[25]
Static	Pharmaceutical 45.8	Antibiotics, anticonvulsive, antidepressants, anti-inflammatories, bactericide, betablockers, detergent, fungicide, hormones, plasticizer	Bottle (3L)	Distilled water	2-10	Yes Mean water concentrations	5, 15 and 25 in stirred condition 25 in unstirred condition	Yes (800-900 rpm) No (60 rpm)	Triplicates at t=8	[28]
?	Pesticide ? (7 cm diameter)	Hormones	Beaker (1.5L)	Distilled water	0.1	Yes Determined at 7, 14 and 28 days	Ambient temperature	Yes (? rpm)	Triplicates at t=7, 14 and 28	[21]
Static renewal (every day in stirred conditions, every 4 days in unstirred conditions)	Pesticide 18	Herbicide, hormone, insecticide	Beaker (1L)	Distilled water	1-1.5	Yes Mean water concentrations	?	Yes (? rpm) No	28	[17]
Static renewal (every day in stirred conditions, every 4 days in unstirred conditions)	Pesticide and pharmaceutical 18	Antibiotic, antidepressant, antiulcerous, herbicides, hormone	Beaker (1L)	Distilled water	5	Yes Mean water concentrations	27 in stirred condition 23 in unstirred condition	Yes (? rpm) No	Triplicates at t=7, 14, 28 and 56	[16]
Static renewal (every day in stirred conditions, every 4 days in unstirred)	Pharmaceutical 18	Antibiotic, antidepressant, antiulcerous, hormone, stimulants	Beaker (1L)	Distilled water	5	?	27 in stirred condition 23 in unstirred condition	Yes (? rpm) No	Triplicates at t=7, 14, 28 and 56	[30]

0

conditions)										
Static renewal (every day in stirred conditions)	Pesticide and pharmaceutical 45.8	Fungicides, herbicides, insecticides	Aquarium (8L)	Water	10	Yes Mean water concentrations	?	Yes (? cm/s)	5	[20]
Static renewal (every 6 days in stirred conditions, every 10 days in unstirred conditions)	Pharmaceutical 45.8	Analgesics, antibiotics, anticonvulsive, antidepressants, antidiabetic, anti-inflammatories, bactericides, benzodiazepine, betablockers, diuretic, herbicide, inhibitors, stimulant	Beaker (3L)	Distilled water	1	Yes Mean water concentrations	28 in stirred condition 22 in unstirred condition	Yes (3-12 cm/s) No	25 in stirred condition 29 in unstirred condition	[22]
Static renewal (every day in stirred conditions)	Pharmaceutical 45.8	Anticonvulsive, antidepressants, anti-histaminic, anti-inflammatories, benzodiazepines, fungicide, inhibitors	Beaker (2L)	1) Distilled water 2) Distilled water 3) Distilled water 4) Distilled salted water	1) 5 2) 5 3) 0.5 or 5 or 10 4) 5	Yes Mean water concentrations	1) 15 2) 27 3) 21 4) 21	Yes (? rpm)	1) 1 POCIS at t=7, 14 and 21 2) 1 POCIS at t=7, 14 and 21 3) 3 POCIS at 7 or 3 POCIS at 2 when 10 µg/L 4) 3 POCIS at 7	[33]
Static renewal (every day in stirred conditions)	Pesticide and pharmaceutical 45.8	Detergents, hormones, plasticizer	Beaker (1L)	Distilled water	1) 0.5 2) 5	?	23.5	Yes (350 rpm)	1) 3 POCIS at t=7, 14 and 28 2) 1 POCIS at 7	[29]
Static renewal (every day in stirred conditions)	Pharmaceutical 45.8	Anesthetic, antibiotics, colouring, fungicide, herbicides, insecticides	Beaker (2L)	Seawater	0.5	?	21	Yes (? rpm)	Duplicates at t=1, 3 and 7	[32]
Static renewal (every other day in stirred conditions, every half-week in unstirred conditions)	Pharmaceutical 14.1	Cyanotoxins	Beaker (1L)	Water	0.2-5	?	22	Yes (? rpm) No	Triplicates at t=1, 7, 14, 21, 28, 35 and 42	[31]
Continuous flow	Pharmaceutical 45.8	Colourings, detergents, fragrances, preservatives	Aquarium (300L)	River water	0.001-0.01	Yes Mean water concentrations	18	Yes (2 cm/s)	Triplicates at t=7, 14, 21 and 28	[34]
Continuous flow	Pharmaceutical 45.8	Colourings, detergents, fragrances, preservatives	Aquarium (200L)	Seawater	0.05-0.12	Yes Mean water concentrations	10	Yes (4 cm/s or 100 rpm)	Triplicates at t=7, 14, 21 and 28	[36]
Continuous flow	Pesticide 45.8	Detergents	Aquarium (200L)	Seawater	0.05-0.12	Yes Mean water concentrations	10	Yes (4 cm/s or 100 rpm)	Triplicates at t=7, 14, 21 and 28	[78]
Continuous flow	Pharmaceutical 45.8	Antibiotic, anticonvulsives, anti-inflammatories, antipsychotics, betablocker, hormones, inhibitor, plasticizer	Aquarium (30L)	Distilled water	1) 0.01 2) 0.02 3) 0.05 4) 0.1 5) 0.25 6) 0.5 7) 1	Yes Mean water concentrations	15	Yes (? cm/s)	Triplicates every day during 10 days	[37]

?: not specified

Table 2. Sampling rates (R_s) for POCIS with “pharmaceutical” or “pesticide” (underlined) configuration, POCIS with a 45.8 cm² exposure surface except when specified. Standard conditions: unsalted water, stirred, between 15 and 25°C except when specified.

Molecules	Family	$R_s \pm SD$ (L/d)	Type of calibration	Reference
Codeine	Anesthetics	0.329 (± 0.133)	Laboratory	[22]
		0.090 (± 0.067) ^c	Laboratory	[22]
Mepivacaine		0.202 ^b	Laboratory	[32]
Thiabendazole	Anthelmintics	0.27 ^b	/	[23]
Albendazole	Antibiotics	0.055 ^b	Laboratory	[32]
Azithromycin		0.06 ^b	/	[23]
		0.120 (± 0.075) ^d	Laboratory	[16]
		0.021 (± 0.006) ^{b, c}	Laboratory	[16]
		0.270	Laboratory	[20]
		0.048 ^c	Laboratory	[20]
Clarithromycin		0.668 (± 0.233)	Laboratory	[22]
		0.090 (± 0.118) ^c	Laboratory	[22]
Erythromycin		0.0163 ^b	Laboratory	[32]
		0.911 (± 0.403)	Laboratory	[22]
		0.183 (± 0.111) ^c	Laboratory	[22]
Oxytetracycline		0.023 ^b	Laboratory	[32]
Roxithromycin		0.723 (± 0.430)	Laboratory	[22]
		0.134 (± 0.138) ^c	Laboratory	[22]
Sulfachloropyridazine		0.20 ^b	/	[23]
Sulfadimethoxine	0.17 ^b	/	[23]	
	0.091 (± 0.042)	Laboratory	[22]	
	0.021 (± 0.071) ^c	Laboratory	[22]	
Sulfamethazine	0.18 ^b	/	[23]	
	0.114 (± 0.029)	Laboratory	[22]	
	0.049 (± 0.040)	Laboratory	[22]	
Sulfamerazine	0.20 ^b	/	[23]	
Sulfamethiazole	0.21 ^b	/	[23]	
Sulfamethoxazole	0.21 ^b	/	[23]	
	0.339 (± 0.057)	Laboratory	[28]	
	0.348 (± 0.049)	Laboratory	[28]	
	0.291 (± 0.004) ^f	Laboratory	[28]	
	0.202 (± 0.019) ^c	Laboratory	[28]	
	0.43	In situ (river downstream)	[37]	
0.22	In situ (WWTP effluent)	[37]		
Sulfathiazole	0.22 ^b	/	[23]	
Tetracycline	0.071 ^b	Laboratory	[32]	
Trimethoprim	0.436 (± 0.006)	Laboratory	[28]	
	0.411 (± 0.073)	Laboratory	[28]	
	0.213 (± 0.035) ^f	Laboratory	[28]	
	0.215 (± 0.003) ^c	Laboratory	[28]	
	0.360 (± 0.210)	Laboratory	[22]	
	0.090 (± 0.074) ^c	Laboratory	[22]	
Virginiamycin	0.09 ^b	/	[23]	
Carbamazepine	Anticonvulsives	0.20 ^b	/	[23]
		0.561 (± 0.024)	Laboratory	[28]
		0.397 (± 0.018)	Laboratory	[28]
		0.230 (± 0.016) ^f	Laboratory	[28]
		0.235 (± 0.046) ^c	Laboratory	[28]
		0.348 (± 0.116)	Laboratory	[22]
		0.112 (± 0.023) ^c	Laboratory	[22]
		0.100	In situ (river downstream)	[37]
0.210	In situ (WWTP effluent)	[37]		
Citalopram	Antidepressants	0.758 (± 0.033)	Laboratory	[28]
		0.735 (± 0.015)	Laboratory	[28]
		0.354 (± 0.020) ^f	Laboratory	[28]
		0.314 (± 0.086) ^c	Laboratory	[28]
Desmethyl citalopram		0.707 (± 0.024)	Laboratory	[28]
		0.598 (± 0.044)	Laboratory	[28]
		0.401 (± 0.082) ^f	Laboratory	[28]
		0.355 (± 0.035) ^c	Laboratory	[28]
Desmethyl sertraline		0.962 (± 0.047)	Laboratory	[28]
		0.839 (± 0.056)	Laboratory	[28]
		0.761 (± 0.029) ^f	Laboratory	[28]
		0.477 (± 0.039) ^c	Laboratory	[28]

<i>n</i> -Desmethyl venlafaxine		0.408 (±0.014) 0.298 (±0.052) 0.133 (±0.016) ^f 0.187 (±0.001) ^c	Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28]
<i>o</i> -Desmethyl venlafaxine		0.396 (±0.026) 0.158 (±0.060) 0.159 (±0.001) ^f 0.179 (±0.082) ^c	Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28]
Fluoxetine		0.974 (±0.045) 0.694 (±0.009) 0.484 (±0.012) ^f 0.433 (±0.058) ^c 1.37 (±0.35) 0.223 (±0.130) ^c 0.086 (±0.023) ^a <u>0.012 (±0.007)^{a, c}</u> 0.200 0.027 ^c	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28] [22] [22] [16] [16] [20] [20]
Paroxetine		0.987 (±0.082) 0.942 (±0.044) 0.905 (±0.023) ^f 0.605 (±0.023) ^c 0.883 (±0.545)	Laboratory Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28] [22]
Sertraline		0.868 ±0.054) 0.622 (±0.026) 0.602 (±0.036) ^f 0.471 (±0.044) ^c	Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28]
Venlafaxine		0.521 (±0.033) 0.388 (±0.038) 0.167 (±0.065) ^f 0.104 (±0.039) ^c	Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28]
Diphenhydramine	Antihistaminics	0.15 ^b	/	[23]
Acetaminophen	Anti-inflammatories	0.30 ^b 0.145 (±0.033) 0.111 (±0.016) 0.139 (±0.011) ^f ^c	/ Laboratory Laboratory Laboratory Laboratory	[23] [28] [28] [28] [28]
Celecoxib		0.669 (±0.142) 0.169 (±0.093)	Laboratory Laboratory	[22] [22]
Diclofenac		0.166 (±0.052) 0.092 (±0.055) ^c 0.120 0.160	Laboratory Laboratory In situ (river downstream) In situ (WWTP effluent)	[22] [22] [37] [37]
Fenoprofen		0.230 (±0.066) 0.167 (±0.058) ^c	Laboratory Laboratory	[22] [22]
Ibuprofen		0.348 (±0.052) 0.254 (±0.019) 0.204 (±0.004) ^f 0.197 (±0.013) ^c	Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28]
Indomethacine		0.300 0.160	In situ (river downstream) In situ (WWTP effluent)	[37] [37]
Ketoprofen		0.135 (±0.035) 0.083 (±0.078) ^c	Laboratory Laboratory	[22] [22]
Naproxen		0.392 (±0.024) 0.298 (0.016) 0.239 (±0.009) ^f 0.200 (±0.037) ^c 0.116 (±0.053) 0.083 (±0.055) ^c	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28] [22] [22]
Sulfapyridin		0.462 (±0.025) 0.319 (±0.026) 0.267 (±0.030) ^f 0.201 (±0.008) ^c 0.051 (±0.038) 0.041 (±0.053)	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28] [22] [22]
Omeprazole	Antiulcerous	2.46 (±0.61) <u>0.030 (±0.008)^a</u> <u>0.007 (±0.004)^{a, c}</u> 0.068 0.016	Laboratory Laboratory Laboratory Laboratory Laboratory	[22] [16] [16] [20] [20]

Sulfisoxazole	Bactericides	0.536 (± 0.377)	Laboratory	[22]
Temazepam	Benzodiazepines	0.421 (± 0.101)	Laboratory	[22]
		0.128 (± 0.062) ^c	Laboratory	[22]
Acebutolol	Betablockers	0.210 (± 0.069)	In situ	[40]
Atenolol		0.094 (± 0.015)	Laboratory	[28]
		/	Laboratory	[28]
		0.087 (± 0.003) ^f	Laboratory	[28]
		0.073 (± 0.013) ^c	Laboratory	[28]
		0.040 (± 0.070)	Laboratory	[22]
		0.037 (± 0.064) ^c	Laboratory	[22]
		0.090 (± 0.064)	In situ	[40]
Bisoprolol		0.160 (± 0.085)	In situ	[40]
Metoprolol		0.465 (± 0.039)	Laboratory	[28]
		0.309 (± 0.106)	Laboratory	[28]
		/	Laboratory	[28]
		0.156 (± 0.034) ^c	Laboratory	[28]
		0.599 (± 0.270)	Laboratory	[22]
		0.097 (± 0.066) ^c	Laboratory	[22]
	0.270 (± 0.140)	In situ	[40]	
Nadolol	0.447 (± 0.036)	Laboratory	[28]	
	0.178 (± 0.009)	Laboratory	[28]	
	0.118 (± 0.014) ^f	Laboratory	[28]	
	0.309 (± 0.022) ^c	Laboratory	[28]	
Propranolol	0.917 (± 0.084)	Laboratory	[28]	
	0.646 (± 0.029)	Laboratory	[28]	
	0.484 (± 0.063) ^f	Laboratory	[28]	
	0.271 (± 0.066) ^c	Laboratory	[28]	
	0.980 (± 0.345)	Laboratory	[22]	
	0.147 (± 0.129) ^c	Laboratory	[22]	
	0.060	In situ (river downstream)	[37]	
	0.120	In situ (WWTP effluent)	[37]	
	0.250 (± 0.133)	In situ	[40]	
Sotalol	0.151 (± 0.021)	Laboratory	[28]	
	0.172 (± 0.001)	Laboratory	[28]	
	0.076 (± 0.008) ^f	Laboratory	[28]	
	0.099 (± 0.012) ^c	Laboratory	[28]	
	0.110 (± 0.059)	In situ	[40]	
Leucomalachite green	Colourings	0.001 ^h	Laboratory	[32]
Malachite green		0.002 ^h	Laboratory	[26]
		0.003 ^h	Laboratory	[26]
Microcystine LR	Cyanotoxines	0.017 ^{c, e}	Laboratory	[71]
		0.017 (± 0.005) ^{c, e}	Laboratory	[31]
		0.087 (± 0.019) ^c	Laboratory	[31]
Microcystine RR		0.022 ^{c, e}	Laboratory	[71]
		0.022 (± 0.007) ^{c, e}	Laboratory	[31]
		0.090 (± 0.019) ^c	Laboratory	[31]
4- <i>n</i> -Butylphenol	Detergents/Surfactants	0.036 ^h	Laboratory	[36]
		0.03 ^h	Laboratory	[35]
		0.01 ^{d, h}	Laboratory	[35]
4- <i>tert</i> -Butylphenol		0.120	Laboratory	[34]
		0.170 ^h	Laboratory	[36]
		0.09 ^h	Laboratory	[35]
		0.12 ^{d, h}	Laboratory	[35]
2,6-di- <i>tert</i> -Butylphenol		0.03 ^h	Laboratory	[35]
		0.05 ^{d, h}	Laboratory	[35]
2,5-Diisopropylphenol		0.065 ^h	Laboratory	[36]
		0.08 ^h	Laboratory	[35]
		0.07 ^{d, h}	Laboratory	[35]
2,6-Diisopropylphenol		0.225 ^h	Laboratory	[36]
		0.07 ^h	Laboratory	[35]
		0.07 ^{d, h}	Laboratory	[35]
2,4-Dimethylphenol	0.111 ^h	Laboratory	[36]	
	0.13 ^h	Laboratory	[35]	
	0.20 ^{d, h}	Laboratory	[35]	
2,5-Dimethylphenol	0.104 ^h	Laboratory	[36]	
	0.17 ^h	Laboratory	[35]	
	0.25 ^{d, h}	Laboratory	[35]	
3,5-Dimethylphenol	0.105 ^h	Laboratory	[36]	
	0.19 ^h	Laboratory	[35]	
	0.27 ^{d, h}	Laboratory	[35]	

6- <i>tert</i> -butyl-2,4-Dimethylphenol		0.254 ^h 0.06 ^h 0.08 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
4-Ethylphenol		0.159 ^h 0.16 ^h 0.21 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
2- <i>tert</i> -butyl-4-Ethylphenol		0.161 ^h 0.08 ^h 0.09 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
2- <i>tert</i> -butyl-4-Methylphenol		0.218 ^h 0.08 ^h 0.11 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
4- <i>tert</i> -butyl-2-Methylphenol		0.191 ^h 0.09 ^h 0.12 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
2,6-di- <i>tert</i> -butyl-4-Methylphenol		0.10 ^h 0.11 ^{d, h}	Laboratory Laboratory	[35] [35]
4-isopropyl-3-Methylphenol		0.150 ^h 0.09 ^h 0.11 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
4- <i>n</i> -Nonylphenol (NP)		0.1167 (±0.0124) 2.459 (±0.131) 1.654 (±0.181) 1.199 (±0.032) ^f 0.923 (±0.155) ^c 0.1050 (±0.0115)	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[29] [28] [28] [28] [28] [29]
Nonylphenol diethoxylate (NPEO2)		0.1173 (±0.0179) 0.1006 (±0.0040)	Laboratory Laboratory	[29] [29]
Nonylphenol monoethoxylate (NPEO1)		0.0899 (±0.0071) 0.0961 (±0.0160)	Laboratory Laboratory	[29] [29]
4- <i>n</i> -Octylphenol (OP)		0.0100 (±0.0081) 0.0062 (±0.0033)	Laboratory Laboratory	[29] [29]
4- <i>tert</i> -Octylphenol (t-OP)		0.1204 (±0.0110) 0.058 ^h 0.1097 (±0.0113) 0.13 ^h 0.10 ^{d, h}	Laboratory Laboratory Laboratory Laboratory Laboratory	[29] [36] [29] [35] [35]
Octylphenol diethoxylate (OPEO2)		0.0922 (±0.0095) 0.0956 (±0.0131)	Laboratory Laboratory	[29] [29]
Octylphenol monoethoxylate (OPEO1)		0.1037 (±0.0134) 0.1105 (±0.0172)	Laboratory Laboratory	[29] [29]
2-methyl-4- <i>tert</i> -Octylphenol		0.06 ^h 0.04 ^{d, h}	Laboratory Laboratory	[35] [35]
2- <i>n</i> -Propylphenol		0.075 ^h 0.06 ^h 0.06 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
4- <i>n</i> -Propylphenol		0.094 ^h 0.05 ^h 0.05 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
2,3,5-Trimethylphenol		0.193 ^h 0.06 ^h 0.08 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
2,4,6-Trimethylphenol		0.189 ^h 0.10 ^h 0.15 ^{d, h}	Laboratory Laboratory Laboratory	[36] [35] [35]
Triclosan	Disinfectants	1.929 (±0.232) 1.442 (±0.105) 1.006 (±0.037) ^f 0.753 (±0.081) ^c 1.920 (±0.620) 0.184 (±0.132) ^c	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28] [22] [22]
Hydrochlorothiazide	Diuretics	0.053 (±0.061) 0.016 (±0.045) ^c	Laboratory Laboratory	[22] [22]
Polybromodiphenylether (PBDE 47)	Flame retardants	0.069	Laboratory	[34]
Pyrene	Fragrances	0.024	Laboratory	[34]
Fenpropimorph	Fungicides	0.088	Laboratory	[20]
<i>p</i> -Nitrophenol,		0.196	Laboratory	[20]
Prochloraz		0.098	Laboratory	[20]
Propiconazole		0.300	Laboratory	[20]
Propyzamide		0.280	Laboratory	[20]
Tebuconazole		0.240	Laboratory	[20]

Benzothiazole (TCMTB)		0.006 ^b 0.011 ^b 0.023 ^b	Laboratory Laboratory Laboratory	[32] [26] [26]
Acetochlor	Herbicides	0.2252	Laboratory	[18]
Atrazine		0.240 0.214 ^b 0.042 ^b 0.239 (±0.008) 0.240 (±0.056) ^d 0.050 (±0.014) ^{a, c} 0.042 ^b 0.059 (±0.008)	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory In situ	[20] [32] [26] [18] [17] [17] [26] [25]
Bentazon		0.092	Laboratory	[20]
Bromoxynil		0.102	Laboratory	[20]
Chloridazon		0.240	Laboratory	[20]
Chlorsulfuron		0.106	Laboratory	[20]
Clopyralid		0.020	Laboratory	[20]
Cyanazine		0.340	Laboratory	[20]
Deetherbutylazine (DET)		0.205 (±0.006) 0.075 (±0.009)	Laboratory In situ	[18] [25]
2,6-Dichlorbenzamide		0.280	Laboratory	[20]
2,4-Dichlorophenoxyacetic acid (2,4-D)		0.092	Laboratory	[20]
DCPMU		0.2669	Laboratory	[18]
Desethylatrazine (DEA)		0.260 0.167 (±0.027) 0.061 (±0.005)	Laboratory Laboratory In situ	[20] [18] [25]
Desethylterbutylazine		0.300	Laboratory	[20]
Deisopropylatrazine (DIA)		0.220 0.106 (±0.017) 0.025 (±0.002)	Laboratory Laboratory In situ	[20] [18] [25]
Desmethylisoproturon (IPPMU)		0.2269	Laboratory	[18]
Dichlobenil		0.146	Laboratory	[20]
Dichlorprop		0.116	Laboratory	[20]
Dinoseb		0.110	Laboratory	[20]
Diuron		0.086 ^b 0.2473 0.045 (±0.016) ^d 0.005 (±0.002) ^{a, c} 0.100 0.011 ^c	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[32] [18] [16] [16] [20] [20]
Ethofumesate		0.280	Laboratory	[20]
Fluroxypyr		0.086	Laboratory	[20]
Hexazinone		0.260	Laboratory	[20]
Hydroxyatrazine		0.100	Laboratory	[20]
Hydroxysimazine		0.054	Laboratory	[20]
Irgarol		0.129 ^b 0.032 ^b 0.041 ^b	Laboratory Laboratory Laboratory	[32] [26] [26]
Ioxynyl		0.112 0.1768	Laboratory Laboratory	[20] [18]
Isoproturon		0.218 (±0.001) 0.086 (±0.008) ^d 0.015 (±0.003) ^{a, c} 0.200 0.034 ^c	Laboratory Laboratory Laboratory Laboratory Laboratory	[18] [16] [16] [20] [20]
Lenacil		0.340	Laboratory	[20]
Linuron	0.2359	Laboratory	[18]	
MCPA	0.072	Laboratory	[20]	
Mechlorprop	0.122	Laboratory	[20]	
Mesotrione	0.0355	Laboratory	[18]	
Metabenzthiazuron	0.200	Laboratory	[20]	
Metamitron	0.220	Laboratory	[20]	
Metazachlor	0.260	Laboratory	[20]	
Metoxuron	0.240 0.1977	Laboratory Laboratory	[20] [18]	
Metribuzin	0.168	Laboratory	[20]	
Metsulfuron-methyl	0.078	Laboratory	[20]	
Metolachlor	0.225 (±0.016) ^b	Laboratory	[25]	
Nicosulfuron	0.0439	Laboratory	[18]	
Pendimethalin	0.260	Laboratory	[20]	
Propachlor	0.240	Laboratory	[20]	

Simazine		0.220 0.223 ^h 0.045 ^h 0.210 (±0.001) 0.049 ^h 0.063 (±0.009)	Laboratory Laboratory Laboratory Laboratory In situ	[20] [32] [26] [18] [26] [25]
Sulcotrione		0.0457	Laboratory	[18]
Terbuthylazine		0.280 0.2507	Laboratory Laboratory	[20] [18]
Terbutryn		0.141 ^h 0.043 ^h 0.045 ^h	Laboratory Laboratory Laboratory	[32] [26] [26]
Estrone (E1)	Hormones	0.1199 (±0.0177) 0.15 ^h 0.699 (±0.087) 0.636 (±0.068) 0.601 (±0.022) ^f 0.363 (±0.065) ^c 0.040 (±0.012) ^g 0.1292 (±0.0121) 0.160 ^h 0.018 (±0.009) 0.800 0.280	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory In situ (river downstream) In situ (WWTP effluent)	[29] [26] [28] [28] [28] [28] [37] [29] [26] [21] [37] [37]
α-Estradiol (α-E2)		0.1216 (±0.0031) 0.1451 (±0.0141)	Laboratory Laboratory	[29] [29]
β-Estradiol (β-E2)		0.1145 (±0.0139) 0.693 (±0.092) 0.596 (±0.040) 0.580 ±0.104 ^f 0.334 (±0.053) ^c 0.129 0.090 ^f 0.037 (±0.007) ^g 0.1144 (±0.0150) 0.025 (±0.014) 0.600 0.540	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory In situ (river downstream) In situ (WWTP effluent)	[29] [28] [28] [28] [28] [27] [27] [37] [29] [21] [37] [37]
Estriol (E3)		0.1571 (±0.0041) 0.1305 (±0.0098) 0.033 (±0.019)	Laboratory Laboratory Laboratory	[29] [29] [21]
Ethinylestradiol (EE2)		0.2217 (±0.0525) 0.18 ^h 0.853 (±0.143) 0.751 (±0.047) 0.747 (±0.082) ^f 0.379 (±0.006) ^c 0.051 (±0.007) ^g 0.302 (±0.034) ^a 0.070 (±0.006) ^{a, c} 0.2137 (±0.0456) 0.21 ^h	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[29] [26] [28] [28] [28] [28] [37] [17] [17] [29] [26]
Levothyroxine		0.053 (±0.028) ^a 0.009 (±0.008) ^{a, c} 0.120 0.021 ^c	Laboratory Laboratory Laboratory Laboratory	[16] [16] [20] [20]
Mestranol (MeEE2)		0.1064 (±0.0074) 0.1068 (±0.089)	Laboratory Laboratory	[29] [29]
Gemfibrozil	Inhibitor	0.350 (±0.012) 0.306 (±0.031) 0.257 (±0.005) ^f 0.222 (±0.014) ^c 0.192 (±0.034) 0.112 (±0.118) ^c	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory	[28] [28] [28] [28] [22] [22]
Sildenafil		0.665 (±0.171)	Laboratory	[42]
Tadalafil		0.806 (±0.186)	Laboratory	[42]
Vardenafil		0.312 (±0.180)	Laboratory	[42]
Aldrin	Insecticides	0.032	Laboratory	[20]
Azinphos ethyl		0.180	Laboratory	[20]
Azinphos methyl		0.178	Laboratory	[20]
Carbaryl		0.130 ^h 0.019 ^h 0.014 ^h	Laboratory Laboratory Laboratory	[32] [26] [26]

Carbofuran		0.260	Laboratory	[20]
Chlorfenvinphos		0.200	Laboratory	[20]
4,6-Dinitro- <i>o</i> -cresol		0.090	Laboratory	[20]
Cypermethrin		0.011 ^b	Laboratory	[26]
		0.012 ^b	Laboratory	[26]
<i>o</i> - <i>p</i> '-DDE		0.032	Laboratory	[20]
<i>p</i> - <i>p</i> '-DDE		0.032	Laboratory	[20]
<i>o</i> - <i>p</i> '-DDT		0.018	Laboratory	[20]
<i>p</i> - <i>p</i> '-DDT		0.018	Laboratory	[20]
Deltamethryn		0.003 ^b	Laboratory	[26]
		0.004 ^b	Laboratory	[26]
Diazinon		0.186 (±0.025) ^d	Laboratory	[17]
		0.056 (±0.008) ^{a, c}	Laboratory	[17]
Dichlorvos		0.006	Laboratory	[20]
		0.021 ^b	Laboratory	[32]
		0.021 ^b	Laboratory	[26]
		0.013 ^b	Laboratory	[26]
Dieldrin		0.086	Laboratory	[20]
Diiflubenzuron		0.004 ^b	Laboratory	[32]
Dimethoate		0.220	Laboratory	[20]
Diphenyl sulfone (DPS)		0.319 ^b	Laboratory	[32]
Endrin		0.094	Laboratory	[20]
Fenitrothion		0.090	Laboratory	[20]
Hydroxycarbofuran		0.006	Laboratory	[20]
Isodrin		0.034	Laboratory	[20]
Lindane		0.092	Laboratory	[20]
		0.204	Laboratory	[34]
Malathion		0.005	Laboratory	[20]
Mevinphos		0.060	Laboratory	[20]
Parathion-ethyl		0.142	Laboratory	[20]
Parathion-methyl		0.122	Laboratory	[20]
Pirimicarb		0.300	Laboratory	[20]
Bisphenol A	Plasticizers	0.1171 (±0.0192)	Laboratory	[29]
		0.835 (±0.058)	Laboratory	[28]
		0.740 (±0.036)	Laboratory	[28]
		0.531 (±0.063) ^f	Laboratory	[28]
		0.482 (±0.066) ^c	Laboratory	[28]
		0.040 (±0.008) ^g	Laboratory	[37]
		0.0877 (±0.0072)	Laboratory	[29]
		0.660	In situ (river downstream)	[37]
		0.580	In situ (WWTP effluent)	[37]
Quinoline	Preservatives	0.027	Laboratory	[36]
2,6-Dimethylquinoline		0.017	Laboratory	[36]
DEET	Repellents	0.19 ^b	/	[23]
Permethryn		0.013 ^b	Laboratory	[26]
		0.017 ^b	Laboratory	[26]
Caffeine	Stimulants	0.27 ^b	/	[23]
		0.127 (±0.021)	Laboratory	[28]
		0.151 (±0.018)	Laboratory	[28]
		0.096 (±0.008) ^f	Laboratory	[28]
		/ ^c	Laboratory	[28]
Cotinine		0.24 ^b	/	[23]
D-amphetamine		0.26 ^b	/	[23]
1,7-Dimethylxanthine		0.33 ^b	/	[23]
Methamphetamine		0.22 ^b	/	[23]
		0.089	Laboratory	[20]
MDMA		0.170	Laboratory	[20]

^a: POCIS with 18 cm² surface; ^b: calculated sampling rates; ^c: unstirred condition; ^d: fouled POCIS; ^e: POCIS with 14,1 cm² surface; ^f: temperature ≤ 10°C; ^g: POCIS with 11.5 cm² surface; ^h: salted water

Table 3. Different applications performed with POCIS.

Application(s)	Aim(s)	Family of molecules	Type(s) of water	Maximal exposure duration (days)	Bioassay(s)	Reference
Screening	- Screening of micropollutants - Comparison of POCIS quantities with grab sampling concentrations	Analgesics, antacid, antianginal, antibiotics, anticonvulsive, antiasthmatic, anticoagulant, anticorrosive, antifoaming, antifungal, antilipemic, antioxidant, antirheumatic, benzodiazepine, colouring, cosmetic, decongestant, degreaser, deodorizer, detergents, disinfectant, flame retardants, fragrances, fungicides, herbicides, insecticides, odorants, ozonation byproduct, plasticizer, preservatives, repellent, stimulants, UV filters	Downstream of WWTPs	54	/	[48]
Screening	- Screening of micropollutants - Determination of POCIS quantities - Evaluation of a contamination source - Comparison of POCIS quantities with the response of fish concentrations	Hormones	Downstream of WWTP River waters	21	/	[54]
Screening	- Screening of micropollutants - Evaluation of a contamination source - Determination of a gradient of concentration - Comparison of POCIS quantities with fish concentrations	UV filters	Upstream of WWTPs Downstream WWTPs	28	/	[60]
Screening	- Screening of micropollutants - Evaluation of a contamination source - Determination of a gradient of concentration - Comparison of POCIS quantities with fish responses	Hormones, stimulant	Upstream of WWTP Downstream WWTP	7	/	[56]
Screening	- Screening of micropollutants - Evaluation of a contamination source - Comparison of POCIS quantities with fish responses	Hormones	River waters	7	/	[70]
Screening	- Screening of micropollutants - Evaluation of a contamination source - Determination of a gradient of concentration	Antibiotic, detergents, flame retardants, fragrances, herbicides, inhibitor, lipid, plasticizers, repellent, stimulant	Downstream WWTP Cave waters River water	28 to 35	/	[50]
Screening	- Screening of micropollutants - Determination of POCIS quantities and evaluate if they have an impact on the response of cells synthesising a xenobiotic receptor	Anticonvulsive, anti-inflammatory, detergents, herbicides, hormone, insecticides, plasticizer	River water	30	/	[67]
Screening	- Screening of micropollutants - Evaluation of a contamination source	Detergent, hormones, plasticizer	WWTP influent WWTP effluent	14 or 28	/	[61]
Screening	- Screening of micropollutants - Determination of a gradient of concentration - Seasonal influence on POCIS quantities - Comparison of POCIS quantities with grab sampling concentrations	Anticonvulsive, antidepressant, anti-inflammatories, betablocker, flame retardant, herbicides, inhibitor, repellent, stimulant	Estuary	61 or 62	/	[74]
Screening	- Determination of a gradient of concentration - Seasonal influence on POCIS quantities - Comparison of POCIS quantities with organisms concentrations	UV filters	Upstream of WWTPs Downstream WWTPs	28	/	[52]
Screening	- Screening of micropollutants - Determination of POCIS quantities - Evaluation of a contamination source - Determination of a gradient of concentration - Seasonal influence on POCIS quantities	Perfluorated organic compounds, pesticides, pharmaceuticals	WWTP influent WWTP effluent Downstream WWTPs River waters	21 to 28	/	[53]

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Screening	- Screening of micropollutants - Determination of a gradient of concentration - Comparison of POCIS quantities with bioassays performed on POCIS extracts	Detergents	Seawaters	42	EROD test Vtg test CuSO4 test	[77]
Screening	- Screening of micropollutants - Determination of a gradient of concentration	Anticorrosive, bactericides, osmetic, detergent, flame retardant, fragrances, herbicide, plasticizers, preservatives, stimulant	Upstream WWTP Downstream WWTP River water Lake	30	/	[55]
Screening	- Screening of micropollutants - Evaluation of a contamination source - Comparison of POCIS quantities with fish responses	Hormones	River water (in laboratory) River water with sediment (in laboratory) Laboratory water (in laboratory)	7	/	[69]
Screening	- Screening of micropollutants - Evaluation of a contamination source - Comparison of POCIS quantities with grab sampling concentrations, sediment concentrations and fish concentrations	Anticorrosive, detergents, hormones, lipids, plasticizer, repellent, stimulant	Lakes	21	/	[73]
Screening TWA concentrations	- Screening of micropollutants - Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Antibiotic, antiulcerous, herbicides, hormone, insecticides, stimulants	4 studies: 1) WWTP effluents 2) Downstream WWTPs 3) Downstream WWTPs and river water 4) WWTP effluents	4 studies: 1) 30 2) 54 3) 30 4) 28	/	[20]
Screening Coupling with bioassay	- Screening of micropollutants - Evaluation of a contamination source - Coupling of POCIS extracts with YES test	anticonvulsives, antidepressants, anti-inflammatory, decongestant, detergent, fragrance, herbicides, insecticide, stimulants	Wastewaters Downstream WWTPs	28	YES test	[76]
Screening Coupling with bioassay	- Screening of micropollutants - Evaluation of a contamination source - Determination of a gradient of concentration - Comparison of POCIS quantities with YES test performed on POCIS extracts and with fish responses	Detergent, hormones, plasticizer	WWTP Influent WWTP effluent	5 to 14	YES	[62]
Screening Coupling with bioassay	- Screening of micropollutants - Evaluation of a contamination source - Determination of a gradient of concentration - Seasonal influence on POCIS quantities - Comparison of POCIS quantities with YES test performed on POCIS extracts and with fish responses	Detergent, hormones, plasticizer	Lake inflows Lake outflow	60 to 169	YES	[72]
Screening Coupling with bioassay	- Screening of micropollutants - Coupling of POCIS extracts with algal assay or bioluminescence inhibition assay	Anti-inflammatory, antibiotics, fungide, herbicides, insecticides, stimulant	WWTP effluents	35	Algal assay Bioluminescence inhibition assay	[64]
Screening TWA concentrations, Coupling with bioassay	- Screening of micropollutants - Seasonal influence on POCIS concentrations - TWA concentrations - Coupling of POCIS extracts with BLYES test - Comparison of POCIS concentration with response of BLYES test performed on POCIS extracts	Antifoaming, colouring, cosmetic, , flame retardants, fragrances, herbicides, plasticizers, repellent	Upstream WWTPs Downstream WWTPs	1) 31 2) 49	BLYES test	[47]
TWA concentrations	- Rs determination in laboratory - TWA concentrations	Herbicide, hormone, insecticide	Wastewaters Downstream WWTPs	28	/	[17]
TWA concentrations	- Rs determination in laboratory - TWA concentrations	Antibiotic, antidepressant, antiulcerous, herbicides, hormone	River waters	30	/	[16]

	- Comparison of POCIS concentrations with grab sampling concentrations					
TWA concentrations	- Rs determination in laboratory - TWA concentrations	Antibiotic, antidepressant, antiulcerous, detergents, hormone, stimulants	WWTP effluents	28 to 30	/	[30]
TWA concentrations	- Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Analgesics, antibiotics, anticonvulsive, antidepressants, antidiabetics, anti-inflammatory, antiulcerous, bactericides, betablockers, benzodiazepines, diuretic, inhibitors,	WWTP effluents Downstream WWTPs River water	21 to 28	/	[22]
TWA concentrations	- Rs estimation (from previous references from them) - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations from other authors	Analgesics, antibiotics, anticonvulsive, antidepressants, antidiabetics, anti-inflammatory, antiulcerous, bactericides, betablockers, benzodiazepines, diuretic, inhibitors,	WWTP effluents	41 or 51	/	[42]
TWA concentrations	- Rs determination in laboratory - PRC determination	Herbicides	/	/	/	[18]
TWA concentrations	- Rs estimation (from previous reference from them) - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Herbicides	Spiked river water (in laboratory)	9	/	[38]
TWA concentrations	- Rs estimation (from previous reference from them) - TWA concentrations thanks to a PRC - Comparison of POCIS concentrations with grab sampling concentrations	Herbicides	River waters	14	/	[25]
TWA concentrations	- Rs estimation (from other author) - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Herbicides, insecticide	River waters	21	/	[44]
TWA concentrations	- Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Anticonvulsive, antidepressants, antihistaminic, anti-inflammatory, benzodiazepines, inhibitors	Estuary	34	/	[33]
TWA concentrations	- Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Detergents, hormones, plasticizer	WWTP Effluents Estuary Seawater	7	/	[29]
TWA concentrations	- Rs determination in laboratory	Biocides, detergents, flame retardant, fragrances, insecticides, plasticizer	/	/	/	[34]
TWA concentrations	- Rs determination in laboratory	Colouring, detergents, fragrances, preservatives	/	/	/	[36]
TWA concentrations	- Rs determination in laboratory	Detergents	/	/	/	[78]
TWA concentrations	- TWA concentrations	Bactericides, detergents	Seawater	42	/	[75]
TWA concentrations	- Rs determination in laboratory	Cyanotoxins	/	/	/	[71]
TWA concentrations	- Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Cyanotoxins	Lake	7 to 21	/	[31]
TWA concentrations	- Rs optimisation in laboratory - Rs determination in situ - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Antibiotic, anticonvulsives, anti-inflammatory, antipsychotic, betablocker, hormones, inhibitor, plasticizer	WWTP effluent Upstream WWTP Downstream WWTP	5	/	[37]

TWA concentrations	- Rs estimation (calculated or from other authors) - TWA concentrations	Analgesic, anthelmintic, antibiotics, antihistaminic, repellent, stimulants	Upstream of WWTPs Downstream WWTPs WWTP effluent	7	/	[23]
TWA concentrations	- Rs determination in laboratory - TWA concentrations	Anesthetic, antibiotics, colouring, fungicide, herbicides, insecticides	Fish farm	15	/	[32]
TWA concentrations	- Rs estimation (from other authors) - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations - Comparison of POCIS concentrations with mussel concentrations	Antidepressant	Upstream WWTP Downstream WWTPs WWTP effluent	14 to 21	/	[41]
TWA concentrations	- Rs determination in laboratory	Colouring, fungicide, insecticides, herbicides, hormones, repellent	/	/	/	[26]
TWA concentrations	- Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Analgesics, antibiotics, anticonvulsive, antidepressants, anti-inflammatories, bactericide, betablockers, fungicide, inhibitor, stimulant	Downstream WWTPs Lakes	26 to 29	/	[28]
TWA concentrations	- Estimate the flow velocity on sampling rates	Analgesics, antibiotics, anticonvulsive, antidepressants, anti-inflammatories, bactericide, betablockers, fungicide, inhibitor, stimulant	WWTP effluents	21	/	[19]
TWA concentrations	- Rs determination in laboratory	Analgesics, antibiotics, anticonvulsive, antidepressants, anti-inflammatories, bactericide, betablockers, fungicide, inhibitor, stimulant	/	/	/	[39]
TWA concentrations	- Rs estimation (from other authors) - TWA concentrations	Detergent, hormones, plasticizer	River waters	28	/	[68]
TWA concentrations	- Rs estimation (from other authors) - TWA concentrations	Detergent, hormones, plasticizer	WWTP influent WWTP effluent	14 to 28	/	[63]
TWA concentrations	- Rs estimation (from other author) - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Herbicides	River waters	10	/	[45]
TWA concentrations	- Rs determination <i>in situ</i> - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Betablockers, hormones	WWTP effluents Upstream WWTPs Downstream WWTPs River water	24	/	[40]
TWA concentrations	- Rs determination in laboratory - TWA concentrations - Comparison of POCIS concentrations with grab sampling concentrations	Hormones	WWTP effluent Upstream WWTP Downstream WWTP	28	/	[21]
TWA concentrations Coupling with bioassay	- TWA concentrations - Coupling of POCIS extracts with YES test and Microtox test	Herbicides, insecticides	River waters	More than 60	YES test Microtox test	[65]
TWA concentrations Coupling with bioassay	- Rs determination in laboratory - TWA concentrations - Coupling of POCIS extracts with YES test - Comparison of POCIS concentrations with YES tests performed on POCIS extracts	Hormones	Upstream farms Downstream farms	21 to 70	YES	[27]
TWA concentrations Coupling with bioassay	- Rs estimation (from other author) - TWA concentrations thanks to a PRC - Coupling of POCIS extracts with photosynthesis bioassay - Comparison of POCIS concentrations with grab sampling concentrations	Herbicides	Upstream river water Middle river water Downstream river water	14	Photosynthesis bioassay	[43]

Coupling with bioassay	- Coupling of POCIS extracts with YES test - Comparison of YES test performed on POCIS extracts and grab sampling	EEQ	WWTP effluent Upstream WWTP Downstream WWTP	21	YES	[59]
Coupling with bioassay	- Coupling of POCIS extracts with YES test - Comparison of YES test performed on POCIS extracts and grab sampling concentrations	Detergent, hormones, plasticizers	WWTP effluent Upstream WWTPs Downstream WWTPs	22	YES	[57]
Coupling with bioassay	- Coupling of POCIS extracts with YES test - Comparison of YES test performed on POCIS extracts and fishes	EEQ	Upstream WWTP Downstream WWTP	30	YES test	[51]
Coupling with bioassay	- Coupling of POCIS extracts with YES test, YAS test, E-screen test, MolDarT test, sediment contact assay test	Hormones	Lake	?	YES test YAS test E-screen test	[66]
Coupling with bioassay	- Coupling of POCIS extracts with YES test and Microtox test - Comparison of YES test performed with POCIS extracts and with grab sampling	Hormones	Upstream WWTP Downstream WWTPs WWTP effluent	?	MolDarT test Sediment contact assay test YES test	[49]

Figures

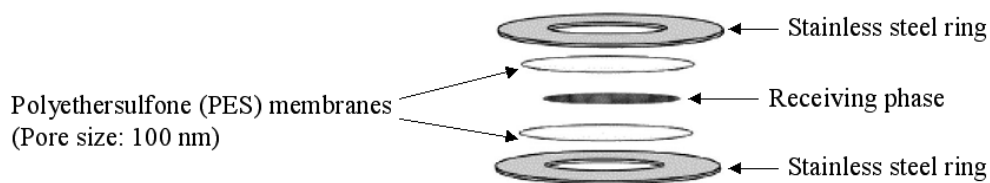


Figure 1. Disassembled view of the POCIS.

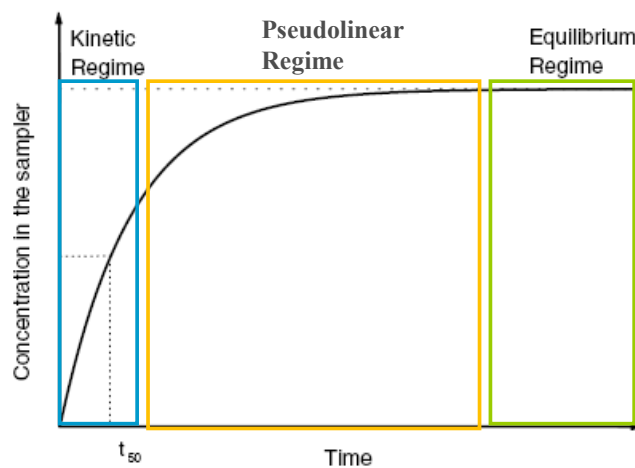


Figure 2. The 3 different accumulation regimes: kinetic, pseudolinear and equilibrium of a POCIS as a function of the time [2].