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

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

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

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

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

1 Introduction

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

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

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

The main subjects approached in these reviews are:

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

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

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

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

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

2 Principle of POCIS

2.1 Presentation of POCIS

POCIS is composed of a solid sorbent receiving phase sandwiched between two microporous polyethersulfone diffusion-limiting membranes with 100 nm pore sizes [16]. The sorbent appears to be more specific for pesticide compounds and some hormones when it is a triphasic mixture (Isolute ENV+ and Ambersorb 1500 dispersed on SX-3 Bio Beads; “pesticide” POCIS)) or more specific for pharmaceutical compounds when it is the OASIS® HLB phase [17]. However, Mazzella et al. [18] reported better recoveries for herbicides in the OASIS® HLB phase (“pharmaceutical” POCIS) than as a triphasic mixture. In contrast, Li et al. [19] indicated that uptake rates of pharmaceuticals were higher with “pesticide” POCIS. In fact, generally, the “pharmaceutical” POCIS is more often used because it has some advantages as, for example, the elution solvent which is less toxic with “pharmaceutical” POCIS than with “pesticide” POCIS [19] or the ease of utilization of the OASIS® HLB phase compared with the triphasic mixture.
Whatever the phase used, POCIS has been designed to catch polar organic compounds (log K_{ow}<4) [16].

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

Figure 1 shows the disassembled view of POCIS.

(figure 1)

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2.2 Accumulation in POCIS

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

(figure 2)

2.3 Evaluation of TWA concentration

2.3.1 Introducing the sampling rate

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

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

where C_s is the concentration of the analyte in the sorbent at time t (µg/g), C_w the TWA concentration of the analyte in the water (µg/L), k_u the uptake rate of the analyte in POCIS (L/g/d) and t the time (d).

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

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

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

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

2.3.2 Performance reference compounds and corrected sampling rates

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

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

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

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

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

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

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

$$R_{s(corr)} = \left(\frac{k_{ePRC(insitu)}}{k_{ePRC(lab)}}\right) \times R_{s(lab)} \quad (4)$$

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

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

2.3.3 Calculation of sampling rates

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

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

with C_i: the initial analyte concentration (µg/L), C_t: the analyte concentration at time t (µg/L) and V_T: the total volume of the laboratory calibration tank. In this case, it must be assumed that analyte loss by degradation is negligible.

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

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

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

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

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

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

3 Discussion

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

3.1.1 Laboratory calibration

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

The advantages of laboratory calibration are:

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

However this method has some drawbacks:

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

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

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

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

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

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

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

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

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

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

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

Sampling rates may also vary according to the type of POCIS: Hernando et al. [26], found R_s of 0.011 L/d and 0.023 L/d for benzothiazole with "pharmaceutical" and "pesticide" POCIS respectively, using the same calibration system. In addition, R_s vary with the size of POCIS: Zhang et al., [37] tested 3 different exposure areas (5.72, 11.33 and 22.89 cm^2) and obtained positive relationships between R_s and the exposure surface area of the sampler, with a correlation coefficient from 0.82 (ethynilestradiol) to 1.0 (bisphenol A).

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

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

3.1.2 In situ calibration

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

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

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

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

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

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

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

(table 1)

3.2 Literature sampling rates and evaluation of TWA concentrations

3.2.1 Comparison of literature sampling rates

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

(table 2)

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

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

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

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

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

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

3.2.2 Sampling rates vs log K_{ow}

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

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

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

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

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

3.2.3 Evaluating of the reliability of TWA concentrations

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

3.2.3.1 TWA concentrations calculated with laboratory R_s

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

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

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

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3.2.3.2 TWA concentrations calculated with in situ R_s

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

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

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

3.3 POCIS applications

3.3.1 Molecules and media studied

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

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

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

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

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

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

3.3.2 The 3 main uses of POCIS

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

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

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

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

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

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

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

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

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

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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 inducted (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 immerged 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

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3.4 General issues for using POCIS

3.4.1 Exposure duration

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

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

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

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

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

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3.4.2 Transport and conservation of POCIS

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

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

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

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

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

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

3.4.3 Processing and analysis techniques

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

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

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

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

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

3.4.4 Quality assurance

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

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

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

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

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

4 Conclusion

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

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

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

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

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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	Herbicids	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	Herbicids	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]

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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, fungicid, 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	Anesthesic, antibiotics, colouring, fungicide, herbicids, 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

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Table 2. Sampling rates (R_s) for POCIS with "pharmaceutical" or "pesticide" (underlined) configuration, POCIS with a 45.8 cm^2 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	**Anesthesics**	0.329 (±0.133)	Laboratory	[22]
		0.090 (±0.067)[c]	Laboratory	[22]
Mepivacaine		0.202[h]	Laboratory	[32]
Thiabendazole	**Anthelmintics**	0.27[b]	/	[23]
Albendazole	**Antibiotics**	0.055[h]	Laboratory	[32]
Azithromycin		0.06[b]	/	[23]
		0.120 (±0.075)[a]	Laboratory	[16]
		0.021 (±0.006)[a, 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[h]	Laboratory	[32]
		0.911 (±0.403)	Laboratory	[22]
		0.183 (±0.111)[c]	Laboratory	[22]
Oxytetracycline		0.023[h]	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[h]	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]

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n-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]
o-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] 0.012 (±0.007)[a, c] 0.200 0.027[c]	Laboratory 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) 0.030 (±0.008)[a] 0.007 (±0.004)[a, c] 0.068 0.016	Laboratory Laboratory Laboratory Laboratory Laboratory	[22] [16] [16] [20] [20]

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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)[e]	Laboratory	[31]
Microcystine RR		0.022[c, e]	Laboratory	[71]
		0.022 (±0.007)[c, e]	Laboratory	[31]
		0.090 (±0.019)[e]	Laboratory	[31]
4-*n*-Butylphenol	**Detergents/Surfactants**	0.036[h]	Laboratory	[36]
		0.03[h]	Laboratory	[35]
		0.01[d, h]	Laboratory	[35]
4-*tert*-Butylphenol		0.120	Laboratory	[34]
		0.170[h]	Laboratory	[36]
		0.09[h]	Laboratory	[35]
		0.12[d, h]	Laboratory	[35]
2,6-di-*tert*-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-Diiospropylphenol		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]

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6-*tert*-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-*tert*-butyl-4-Ethylphenol		0.161[h] 0.08[h] 0.09[d, h]	Laboratory Laboratory Laboratory	[36] [35] [35]
2-*tert*-butyl-4-Methylphenol		0.218[h] 0.08[h] 0.11[d, h]	Laboratory Laboratory Laboratory	[36] [35] [35]
4-*tert*-butyl-2-Methylphenol		0.191[h] 0.09[h] 0.12[d, h]	Laboratory Laboratory Laboratory	[36] [35] [35]
2,6-di-*tert*-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-*n*-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-*n*-Octylphenol (OP)		0.0100 (±0.0081) 0.0062 (±0.0033)	Laboratory Laboratory	[29] [29]
4-*tert*-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-*tert*-Octylphenol		0.06[h] 0.04[d, h]	Laboratory Laboratory	[35] [35]
2-*n*-Propylphenol		0.075[h] 0.06[h] 0.06[d, h]	Laboratory Laboratory Laboratory	[36] [35] [35]
4-*n*-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 47 (PBDE 47)	**Flame retardants**	0.069	Laboratory	[34]
Pyrene	**Fragrances**	0.024	Laboratory	[34]
Fenpropimorph	**Fungicides**	0.088	Laboratory	[20]
p-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]

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Benzothiazole (TCMTB)		0.006[h] 0.011[h] 0.023[h]	Laboratory Laboratory Laboratory	[32] [26] [26]
Acetochlor	**Herbicides**	0.2252	Laboratory	[18]
Atrazine		0.240 0.214[h] 0.042[h] 0.239 (±0.008) 0.240 (±0.056)[a] 0.050 (±0.014)[a, c] 0.042[h] 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]
Desethylterbuthylazine		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[h] 0.2473 0.045 (±0.016)[a] 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[h] 0.032[h] 0.041[h]	Laboratory Laboratory Laboratory	[32] [26] [26]
Ioxynyl		0.112 0.1768	Laboratory Laboratory	[20] [18]
Isoproturon		0.218 (±0.001) 0.086 (±0.008)[a] 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]

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

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Carbofuran		0.260	Laboratory	[20]
Chlorfenvinphos		0.200	Laboratory	[20]
4,6-Dinitro-*o*-cresol		0.090	Laboratory	[20]
Cypermethrin		0.011[h] 0.012[h]	Laboratory Laboratory	[26] [26]
o-p'-DDE		0.032	Laboratory	[20]
p-p'-DDE		0.032	Laboratory	[20]
o-p'-DDT		0.018	Laboratory	[20]
p-p'-DDT		0.018	Laboratory	[20]
Deltamethryn		0.003[h] 0.004[h]	Laboratory Laboratory	[26] [26]
Diazinon		0.186 (±0.025)[a] 0.056 (±0.008)[a, c]	Laboratory Laboratory	[17] [17]
Dichlorvos		0.006 0.021[h] 0.021[h] 0.013[h]	Laboratory Laboratory Laboratory Laboratory	[20] [32] [26] [26]
Dieldrin		0.086	Laboratory	[20]
Diflubenzuron		0.004[h]	Laboratory	[32]
Dimethoate		0.220	Laboratory	[20]
Diphenyl sulfone (DPS)		0.319[h]	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 0.204	Laboratory Laboratory	[20] [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) 0.835 (±0.058) 0.740 (±0.036) 0.531 (±0.063)[f] 0.482 (±0.066)[c] 0.040 (±0.008)[g] 0.0877 (±0.0072) 0.660 0.580	Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory Laboratory In situ (river downstream) In situ (WWTP effluent)	[29] [28] [28] [28] [28] [37] [29] [37] [37]
Quinoline	**Preservatives**	0.027	Laboratory	[36]
2,6-Dimethylquinoline		0.017	Laboratory	[36]
DEET	**Repellents**	0.19[b]	/	[23]
Permethryn		0.013[h] 0.017[h]	Laboratory Laboratory	[26] [26]
Caffeine	**Stimulants**	0.27[b] 0.127 (±0.021) 0.151 (±0.018) 0.096 (±0.008)[f] /[c]	/ Laboratory Laboratory Laboratory Laboratory	[23] [28] [28] [28] [28]
Cotinine		0.24[b]	/	[23]
D-amphetamine		0.26[b]	/	[23]
1,7-Dimethylxanthine		0.33[b]	/	[23]
Methamphetamine		0.22[b] 0.089	/ Laboratory	[23] [20]
MDMA		0.170	Laboratory	[20]

[a]: POCIS with 18 cm^2 surface; [b]: calculated sampling rates; [c]: unstirred condition; [d]: fouled POCIS; [e]: POCIS with 14,1 cm^2 surface; [f]: temperature ≤ 10°C; [g]: POCIS with 11.5 cm^2 surface; [h]: salted water

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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 micropolluants - 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, ozination byproduct, plasticizer, preservatives, repellent, stimulants, UV filters	Downstream of WWTPs	54	/	[48]
Screening	- Screening of micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - Evaluation of a contamination source - Comparison of POCIS quantities with fish responses	Hormones	River waters	7	/	[70]
Screening	- Screening of micropolluants - 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 micropolluants - Determination of POCIS quantities and evaluate if they have an impact on the response of cells synthetising a xenobiotic receptor	Anticonvulsive, anti-inflammatory, detergents, herbicides, hormone, insecticides, plasticizer	River water	30	/	[67]
Screening	- Screening of micropolluants - Evaluation of a contamination source	Detergent, hormones, plasticizer	WWTP influent WWTP effluent	14 or 28	/	[61]
Screening	- Screening of micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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 micropolluants - 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]

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	- 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-inflammatories, 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-inflammatories, 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-inflammatories, 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-inflammatories, antipsychotic, betablocker, hormones, inhibitor, plasticizer	WWTP effluent Upstream WWTP Downstream WWTP	5	/	[37]

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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	Anesthesic, 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, fungicid, 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 *in situ* - 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]

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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 MolDarT test Sediment contact assay 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	?	YES test	[49]

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Figures

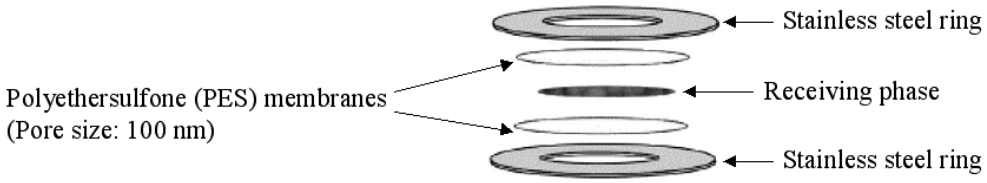

Figure 1. Disassembled view of the POCIS.

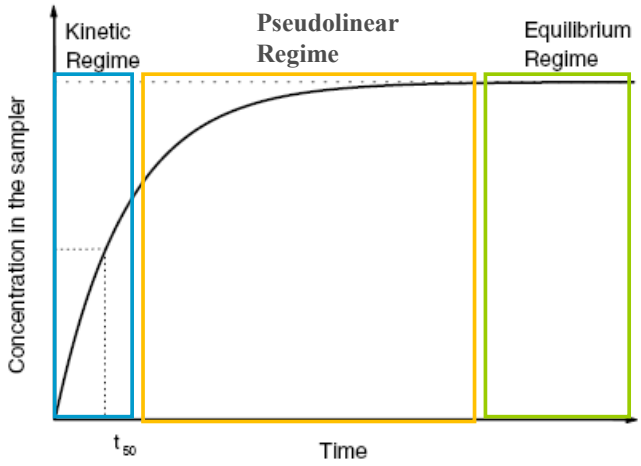

Figure 2. The 3 different accumulation regimes: kinetic, pseudolinear and equilibrium of a POCIS as a function of the time [2].