



Pollutant analysis using passive samplers: principles, sorbents, calibration and applications. A review

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Abstract

Passive techniques are a constantly evolving method of monitoring water pollution, allowing the simultaneous sampling and concentration of selected chemical compounds. The most popular aqueous passive samplers are those in which sorbents are used as receiving phases, including: the Polar Organic Chemical Integrative Sampler (POCIS). Originally, POCIS contained the copolymer poly(divinylbenzene)-*co-N*-vinylpyrrolidone, which allowed the collection of analytes with $0 \leq \log K_{ow} \leq 5$. The limitation of the use of conventional samplers for sampling water pollutants only with a specific polarity has resulted in the fact that innovative sorbents are used more and more in POCIS-like samplers. In recent years, application of several innovative sorbents in POCIS-like samplers, for example: mixed-mode ion exchange polymeric sorbents, ionic liquids, molecularly imprinted polymers and carbon nanotubes has been described. This is the first review in which the usability of classical and innovative sorbents used in passive techniques principles has been collected and compared, and it has been shown that the type of sorbent can significantly affect the efficiency of sampling pollutants in the aquatic environment. The major points are the following: 1) principle of operation, of passive samplers, 2) characteristics of POCIS and sorbents used as receiving phases, 3) sampler calibration methods and environmental factors affecting their operation, 4) a detailed description of the application possibilities of conventional and innovative sorbents used in POCIS-like samplers. This review shows the growing number of works on the use of innovative sorption materials to overcome limitation of originally designed POCIS, and the published results, allow us to conclude that the type of sorbent may be a key factor in increasing the applicability of POCIS-like samplers.

Keywords Passive sampling · POCIS · Innovative sorbents · Development of POCIS-like samplers

Abbreviations

DCM	Dichloromethane
DGT	Diffusive gradients in thin films
DMLS	Discrete multilayer sampler
dSPE	Dispersive solid-phase extraction
MeOH	Methanol
MESCO	Membrane-enclosed sorptive coating
OASIS HLB	Hydrophilic–lipophilic-balanced sorbent
Pest-POCIS	Pesticide polar organic chemical integrative sampler
Pharm-POCIS	Pharmaceutical polar organic chemical integrative sampler
PIMS	Passive integrative mercury sampler

PISCES	Passive in situ concentration-extraction sampler
POCIS	Polar organic chemical integrative sampler
R_s	Sampling rate
SPMDs	Semipermeable membrane devices

Introduction

In recent years, passive techniques have been gaining more attention, especially due to researchers looking for reliable methods of monitoring inorganic and organic substances in the natural environment. Passive samplers are economic and trustworthy devices enabling the determination of the time-weighted average concentration of target compounds and thus integrating spot pollution events (Tapie et al. 2011). The advantages of passive sampling devices also include ease of use in the field without the need for electrical power

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or special equipment, and their ability to accumulate analytes and thus to measure low and very low concentrations. This is a huge advantage over spot sampling methods, in which analyte concentrations are often below the limit of quantification and limit of detection of the chosen instrumental method, thus preventing the determination of ultra-trace micropollutants in the environment (Thomatou et al. 2011). Common methods for analyte determination consist of several stages: (1) point sampling, (2) transport of samples to the laboratory, (3) extraction of analytes from the tested matrix, (4) purification and concentration of target compounds and (5) instrumental analysis. The use of such dynamic methods for monitoring environmental pollution has many shortcomings. The main disadvantage is that the sampled spot represents only those impurities that are present at the time of sampling. Episodic events, such as storm water leaks or runoff, are often overlooked because pollution can disperse before the next sampling period. Sampling several times to take into account episodic events may be difficult to perform physically, organizationally and financially, especially in remote areas (Zhang et al. 2016). Without sufficient sampling repeatability, it may not be possible to determine the time-weighted average concentrations of target compounds. In addition, passive sampling devices take samples of labile fractions, which are probably more toxicologically relevant than total concentrations in terms of bioavailability assessment (Silvani et al. 2017). For this reason, passive dosimeters are an attractive alternative to traditionally used sampling methods.

The ideal model of a passive sampler has a simple design, is cheap and easy to prepare, apply and analyze and is selective and sensitive for a wide range of chemical compounds, regardless of the medium being tested. In practice, the sampler design is developed for several purposes and no single device is suitable for all applications. The simplest passive sampling devices are single-phase polymer samplers, in which the polymer formula and surface area-to-volume ratio can be selected to increase sampler performance. In contrast, two-phase passive samplers consist of a receiving phase and diffusion membranes. The use of membranes is to lengthen the kinetic phase by slowing down the diffusion between the water phase and the receiving phase (Wennrich et al. 2003; Vrana et al. 2005; Terzopoulou and Voutsas 2016; Criquet et al. 2017; Yang et al. 2017). A wide range of devices is available for the passive sampling of pollutants in the aquatic environment, namely: semipermeable membrane devices (SPMDs) (Huckins et al. 1999, 2000; Harman et al. 2008a, b; Creusot et al. 2013), polymer sheets (Puls and Paul 1997; Vroblesky 2001), ceramic dosimeters (Bopp et al. 2005), diffusive gradients in thin-film (DGT) technique (Denney et al. 1999; Larner et al. 2006; Schintu et al. 2008), discrete multilayer sampler (DMLS) (Larner et al. 2006), membrane-enclosed sorptive coating (MESCO)

sampler (Vrana et al. 2006), passive integrative mercury sampler (PIMS) (Brumbaugh et al. 2000), passive in situ concentration–extraction sampler (PISCES) (Barranger et al. 2014), Chemcatcher (Vrana et al. 2006, 2007; Aguilar-Martínez et al. 2008; Booij and Chen 2018) or passive organic chemical integrative sampler (POCIS) (Rujiralai et al. 2011; Černoch et al. 2011; Pesce et al. 2011; Charlestra et al. 2012; Miège et al. 2012; Creusot et al. 2013; Belles et al. 2014a; Kaserzon et al. 2014b; Aisha et al. 2017; Yabuki et al. 2018; Guibal et al. 2018; Rosen et al. 2018). POCIS-like samplers are some of the most frequently used passive devices in environmental analytics. Conventionally used sorbents in POCIS allow for effective sampling of chemical compounds with $0 \leq \log K_{ow} \leq 5$. These samplers were used at least 196 times to sampling water pollutants such as pharmaceuticals, pesticides, endocrine-disrupting substances, personal care products and phenols (“Hydrophilic–lipophilic-balanced sorbent (Oasis HLB)” and “Triphasic sorbent admixture” sections). However, one of the basic restrictions of commercial POCIS is the inefficient uptake of strongly hydrophilic and ionic organic compounds from water. Therefore, scientists are constantly looking for increasingly more efficient, less costly and more reliable devices for monitoring environmental micropollutants. Numerous studies, in which various constructional solutions of samplers and different types of membranes were used, or innovative sorption materials were sought, contributed to the rapid development of passive techniques. In recent years, there has been a successful application of several innovative sorbents in POCIS-like samplers, for example: Strata-X (Balaam et al. 2010), Oasis MAX (Fauvelle et al. 2012), Chromabond HRX (Fauvelle et al. 2012), Strata XAW or Oasis WAX (Kaserzon et al. 2014; Gobelius et al. 2019), Septra ZT (Booij et al. 2013), Strata X-CW (Carpinteiro et al. 2016), ionic liquids (Caban et al. 2016), Bond-Elute Plexa sorbent (Mijangos et al. 2018a, b), molecularly imprinted polymers (Berho et al. 2017), carbon nanotubes (Jakubus et al. 2016) (Table 1).

In this paper, a review of the literature from the last 16 years, i.e., since the appearance of POCIS-like samplers in environmental analysis, has been carried out to summarize the latest knowledge on the development of passive samplers. Studies using POCIS-like samplers, depending on the sorbent used, from 2004 to 2020 have been chronologically compiled and are presented in Tables 2, 3 and 4. The work describes in detail the basics of passive techniques, sampler calibration methods and their limitations, and types of passive devices depending on the way the probe works. The possibilities of using specific sorbents in POCIS-like samplers are described in detail, as well as their advantages and disadvantages. This review proves that the use of innovative sorption materials, and various types of POCIS modifications have allowed the application of this type of passive

Table 1 Properties, advantages and disadvantages of innovative sorbents used in polar organic chemical integrative samplers

Sorbent type	Characterization	Particle size [μm]	Pore size [\AA]	Surface area [$\text{m}^2 \text{g}^{-1}$]	Advantages	Disadvantages	References
Strata-X	A reversed phase functionalized polymeric sorbent, which allows the sorption of neutral, acid and basic compounds due to the formation of π - π bonds, hydrogen bonds and hydrophobic interactions with the analyte. ¹	33 ¹	85 ¹	800 ¹	Strata-X has been shown to be more efficient at extracting a wider range of analytes than Oasis HLB The possibility of using Strata-X-sampler extracts for bioassays to assess ecological risk The possibility of obtaining time-weighted average concentrations	No selectivity	Balaam et al. (2010), Rotter et al. (2011), Kaserzon et al. (2014b)
Oasis MAX	Mixed-mode anion-exchange polymeric sorbent that provides additional sites for strong anion-exchange interactions due to the formation of π - π bonds, strong anion-exchange and hydrophobic interactions with the analyte. ²	30	85	810	Oasis MAX has been shown high extraction efficiency and satisfactory sampling rates for both inert and acidic chemicals	Oasis MAX has been shown low extraction efficiency and unsatisfactory sampling rates for the most hydrophilic chemicals	Fauvelle et al. (2012)
Chromabond HRX	Hydrophobic polystyrene-divinylbenzene polymer with an extensive specific surface area. ³	85	55-60 ³	1100	–	Chromabond HRX has been shown low sampling rates of the tested neutral compounds and a complete lack of uptake for some acidic pesticides	Fauvelle et al. (2012)

Table 1 (continued)

Sorbent type	Characterization	Particle size [μm]	Pore size [\AA]	Surface area [$\text{m}^2 \text{g}^{-1}$]	Advantages	Disadvantages	References
Strata XAW	A weak anion-exchange functionalized polymer sorbent that ensures complete sorption of acidic chemicals due to the formation of π - π bonds, weak anion-exchange and hydrophobic interactions with the analyte ^a	33 ¹	85 ¹	800 ¹	Oasis WAX has been shown to be more efficient at extracting a wider range of perfluorinated compounds than Oasis HLB The possibility of obtaining time-weighted average concentrations	–	Kaserzon et al. (2012, 2013, 2014a)
Sepra ZT	Pyrrolidone modified styrenedivinylbenzene polymer. ¹	30	85	800 ¹	Sepra-ZT-sampler has been shown to be more efficient at extracting a wider range of chemicals than spot sampling The possibility of obtaining time-weighted average concentrations	–	Booij et al. (2013)
Oasis WAX	Mixed-mode weak anion-exchange reserved-phase sorbent for strong acidic chemicals due to the formation of π - π bonds, weak anion-exchange and hydrophobic interactions with the analyte. ²	30 ²	80 ²	–	Comparable analyte concentration values obtained from Oasis WAX-sampler with concentration values obtained by spot sampling	–	Y. Li et al. (2016a), Gobelius et al. (2019)
Strata X-CW	A weak cation-exchange functionalized polymer sorbent that ensures complete sorption of basic chemicals due to the formation of π - π bonds, weak cation-exchange and hydrophobic interactions with the analyte. ¹	33 ¹	85 ¹	800 ¹	–	Strata-X-CW-sampler has been shown lower the extraction efficiency of tested analytes than Oasis HLB-sampler	Carpinteiro et al. (2016)

Table 1 (continued)

Sorbent type	Characterization	Particle size [μm]	Pore size [\AA]	Surface area [$\text{m}^2 \text{g}^{-1}$]	Advantages	Disadvantages	References
Ionic Liquid	Ionic chemical compounds that are characterized melting point below 100°C .	–	–	–	Ionic liquids have been shown to be more efficient at extracting a wider range of perfluorinated compounds than Oasis HLB Comparable analyte concentration values obtained from ionic liquid-passive sampler with concentration values obtained by spot sampling The ability to design ionic liquids to achieve desired chemical properties	High price of ionic liquids High toxicity of some ionic liquids	Caban et al. (2016), Męczykowska et al. (2017b, 2018, 2019), Wang et al. (2017)
Strata XAW mixed with Bond-Elute Plexa sorbents	Bond-Elute Plexa is polymer sorbent with hydroxylated, amide-free surface and non-polar polystyrene-divinylbenzene polymer core.	33 (Strata XAW), 45 (Bond-Elute Plexa)	85 (Strata XAW), –	800 (Strata XAW), –	The possibility of using modified sampler extracts for bioassays to assess ecological risk The possibility of obtaining time-weighted average concentrations	–	Mijangos et al. (2018a, b), Solagaistua et al. (2018)
Molecularly imprinted polymers	Synthesized in the laboratory.	–	–	–	Sampler with molecularly imprinted polymers has a specific selectivity for perfluorinated compounds and can overcome matrix interference	The need for a multi-step synthesis High price of molecularly imprinted polymers	Berho et al. (2017), Cao et al. (2018), Xiong et al. (2019)

Table 1 (continued)

Sorbent type	Characterization	Particle size [μm]	Pore size [\AA]	Surface area [$\text{m}^2 \text{g}^{-1}$]	Advantages	Disadvantages	References
Carbon nanotubes	Non-modified multi-walled carbon nanotubes with outer diameter < 8.	–	–	500	Sampler with carbon nanotubes has been shown high sampling rates using only 100 mg of sorbent The possibility of multiple regeneration of carbon nanotubes and re-use as a sorbent The ability to modify the surface of carbon nanotubes to obtain the desired sorption properties	High price of carbon nanotubes	Jakubus et al. (2016)

¹Information from <https://www.phenomenex.com/>

²Information from <https://www.waters.com/>

³Information from <https://www.mn-net.com/>

sampler to be extended (“Innovative sorbents” section and Table 1).

Characteristic of selected passive samplers

The polar organic chemical integrative sampler was developed at the Columbia Environmental Research Center (US Geological Survey) and the patent was granted in the United States in November 2002 (# 6478961). POCIS was first used in the field in 2004 (Alvarez et al. 2004b) to monitor hydrophilic pollution of the aquatic environment ($\log K_{ow} < 4$). Polar organic chemical integrative sampler (POCIS) can be both a kinetic and equilibrium sampler and consists of three parts: (1) sorbent, (2) polyethersulfone membranes and (3) two stainless steel rings (Fig. 1) (Alvarez et al. 2004a). The original configuration consisted of 100 mg of sorbent sandwiched between two microporous (pore size 100 nm, thickness 130 μm) polyethersulfone membranes that were held together by two stainless steel washers (thickness 3.2 mm, internal diameter 3.3 cm, outer diameter 7.0 cm) (Booij and Chen 2018). Polyethersulfone microporous membranes act as semipermeable barriers between an effective receiving phase (solid sorbent) and the external environment (aqueous phase). The pores in the membranes prevent the accumulation of solid particles, colloids, and fauna and flora with cross sections of a diameter larger than the pore size, simultaneously allowing the accumulation of target compounds (environmental micropollutants). As sorbents, Oasis HLB (hydrophilic–lipophilic-balanced copolymer [poly(divinylbenzene)-co-*N*-vinylpyrrolidone]) or 80:20 (m/m) ISOLUTE[®] ENV + (hydroxylated polystyrene–divinylbenzene copolymer) and Amborsorb 1500 (carbon lightly dispersed on S-X3 Biobeads) are used (Alvarez et al. 2004b). The latter sorbent mixture is commonly referred to as “Triphasic sorbent admixture.” Since 2004, the original POCIS and modified POCIS (e.g., containing a different type of sorbent or membranes) have been successfully used for the monitoring of pollutants in sediment (Alvarez et al. 2012), atmosphere (Kot-Wasik et al. 2007), soil (Pignatello et al. 2010) and water (Alvarez et al. 2008). Ahrens et al. (2015) compared the usefulness of five types of passive samplers for monitoring selected chemical compounds in aquatic environments. The obtained results indicated that POCIS was characterized by the highest extraction efficiency among the tested samplers. It is not surprising then that POCIS-like samplers are some of the most frequently used passive devices in environmental analytics. The introduction and testing of new sorption materials in passive techniques are aimed both at increasing the range of chemicals that can be sampled by the sampler but also at increasing the sampling rate (R_s) and extraction efficiency. During the selection of an innovative sorbent, scientists are often

Table 2 Application of polar organic chemical integrative sampler containing hydrophilic–lipophilic-balanced sorbent (Oasis HLB) to monitor contaminants level in different matrices

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pharmaceuticals	200	PES	MeOH, 20 mL	River water	Renewable static, renewable semi-static	R_s calculation Time-weighted average concentrations Comparison pest-POCIS and pharm-POCIS	Alvarez et al. (2004b)
Pharmaceuticals	200	PES	MeOH, 20 mL	Wastewater, river water	Renewable static	R_s calculation Time-weighted average concentrations	Jones-Lepp et al. (2004)
Pesticides, personal care products, fragrances, fire retardants, plasticizers, domestic	–	PES	–	Wastewater	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS to standard water-column sampling	Alvarez et al. (2005)
Estrogens	100	PES	MeOH, 40 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison pest-POCIS and pharm-POCIS Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Vermeirssen et al. (2005)
Personal care products	200	PES	–	River water	Flow-through	R_s calculation Time-weighted average concentrations	Macleod et al. (2007)
Herbicides	200	PES	MeOH, 5 mL	Tap water	Semi-static	R_s calculation using performance reference compounds Performance reference compounds validation Comparison pest-POCIS and pharm-POCIS	Mazzella et al. (2007)
Pharmaceuticals	200	PES	Ethyl acetate/acetone (50/50; v/v),/	Estuarine water	Renewable semi-static	R_s calculation Evaluation of impact of temperature, salinity, pharmaceuticals concentration on R_s values Time-weighted average concentrations	Togola and Budzinski (2007)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Endocrine disrupting substances	200	PES	Acetone, 50 mL	River water, wastewater	Renewable semi-static	R_s calculation Time-weighted average concentrations Comparison pest-POCIS and pharm-POCIS	Arditsoglou and Voutsas (2008)
Microcystins	200, 156.5, 78.3, 38.8	Polycarbonate, nylon, PES, polyester	2 × MeOH and water (9:1 v/v acidified with 0.1% TFA), 20 mL	Surface water	Renewable semi-static	Membrane evaluation Sorbent mass evaluation Uptake curves	Kohoutek et al. (2008)
Pharmaceuticals, endocrine disrupting substances, personal care products	100	PES, PE	3 × MeOH, 10 mL	River water	Flow-through	R_s calculation Comparison between PE and PES membranes Evaluation of impact of environmental condition on R_s values Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Zhang et al. (2008)
Contaminants	200	PES	MeOH, 50 mL	Laboratory water	Flow-through	R_s calculation	Harman et al. (2008a)
Organo-tin compounds, halogenated compounds, polycyclic aromatic hydrocarbons and alkylphenols	200	PES	MeOH, 50 mL	Laboratory water	Flow-through	R_s calculation	Harman et al. (2008b)
Pharmaceuticals, illicit drugs	200	PES	MeOH, 20 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Bartelt-Hunt et al. (2009)
Alkylated phenols	200	PES	MeOH, 20 mL	–	Flow-through	R_s calculation Determination of the impact of various fouling treatments on the sampling of contaminants in POCIS	Harman et al. (2009)
Herbicides	200	PES	MeOH, 5 mL	Tap water	Semi-static, in situ	R_s calculation Assessment of the suitability of the performance reference compounds	Mazzella et al. (2010)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Microcystins	38.8, 200	Polycarbonate, PES	2 × Aqueous MeOH (90% v/v acidified with 0.1% TFA), 5 mL	Surface water	Renewable semi-static, renewable static	R_s calculation Field exposure Comparison of the uptake efficiency of the pharmaceuticals (200 mg) to POCIS configuration prepared in-house (38.8 mg)	Kohoutek et al. (2010)
Herbicides	200	PES	MeOH, 3 mL then 75% MeOH/25% ethyl acetate (v/v), 3 mL	River water	–	Estimation of Time-weighted average concentrations R_s estimation using performance reference compounds (from other authors)	Pesce et al. (2010)
Pharmaceuticals	200	PES	MeOH, 40 mL	Surface water, groundwater	–	Coupling of POCIS extracts with short-term photosynthesis bioassays	Dougherty et al. (2010)
Synthetic organic compounds	200	PES	MeOH	Lake	–	Monitoring of micropollutants	Rosen et al. (2010)
Pharmaceuticals, personal care products, endocrine disrupting substances	200	PES	MeOH, 50 mL	Treated wastewater	In-situ	Uptake curves Water flow effects on POCIS uptake	Li et al. (2010b)
Herbicides	200	PES	MeOH, 3 mL then 75% MeOH/25% ethyl acetate (v/v), 3 mL	River water	In-situ	R_s estimation using performance reference compounds	Vercaene-Eairmal et al. (2010)
Pesticides, polycyclic aromatic hydrocarbons	200	PES	MeOH, 40 mL	Groundwater	–	Estimation of Time-weighted average concentrations R_s estimation using performance reference compounds (from other authors)	Fox et al. (2010)
Endocrine disrupting substances	200	PES	MeOH	Lake	–	Estimation of Time-weighted average concentrations using POCIS and SPMDs Monitoring of endocrine disrupting substances	Writer et al. (2010)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Alkylphenols, polycyclic aromatic hydrocarbons	240	PES	MeOH, 20 mL	Sea water	–	R_s estimation using performance reference compounds (from other authors) Comparison of currently used biological methods to POCIS for measuring in situ exposure to polycyclic aromatic hydrocarbons and alkylphenols	Harman et al. (2011a)
Pesticides	200	PES	MeOH, 3 mL then 75% MeOH/25% ethyl acetate (v/v), 3 mL	River water	In-situ	Coupling of POCIS extracts with Yeast Estrogen Screen bioassays R_s estimation using performance reference compounds Estimation of time-weighted average concentrations	Pesce et al. (2011)
Pharmaceuticals, personal care products, endocrine disrupting substances	200	PES	MeOH, 50 mL	River water, tap water	Semi-static	Evaluation the effect of solution pH and dissolved organic matter on the R_s Comparison the uptake efficiency of the pharmaceuticals to two POCIS configurations prepared in-house	Li et al. (2011)
Pharmaceuticals	200	PES	MeOH, 20 mL	Wastewaters	Semi-static	Calculation of R_s Estimation of time-weighted average concentrations Comparison of calculated R_s with literature R_s	Bartel-Hunt et al. (2011)
Pharmaceuticals, polycyclic aromatic hydrocarbons, hormones, phenols, pesticides	200	PES	DCM/MeOH (50:50 v/v), 30 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Coupling of POCIS extracts with in vivo and in vitro bioassays	Tapie et al. (2011)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Atrazine	200	PES	MeOH and water (9:1 v/v acidified with 0.1% TFA),/	River water	–	Monitoring of atrazine	Černoch et al. (2011)
Pharmaceuticals	200	PES	MeOH and water (9:1 v/v acidified with 0.1% TFA),/	River water	–	Monitoring of pharmaceuticals	Černoch et al. (2012)
Alkylphenols, phenolated polymers, hormones, pharmaceuticals	200	PES	–	Tap water	Static, in situ	R_s calculation Comparison $R_{s(\text{lab})}$ with $R_{s(\text{in situ})}$	Miège et al. (2012)
Perfluorinated chemicals	200	PES	0.1% (v/v) ammonia solution in MeOH, 6 mL then MeOH, 6 mL	Estuarine water	Renewable static	R_s calculation Time-weighted average concentrations Comparison sampling efficiency between Oasis WAX and Oasis HLB sorbents	Kaszeron et al. (2012)
Pharmaceuticals	200	PES	–	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Vystavna et al. (2012)
Pharmaceuticals, hormones	200	PES	MeOH, 10 mL then MeOH/methylene chloride 50/50 (v/v), 10 mL	Wastewater	In-situ	Comparison of POCIS and water samples R_s calculation Time-weighted average concentrations Study of candidate performance reference compounds for the POCIS sampling	Jacquet et al. (2012)
Pharmaceuticals, antidepressants, personal care products	200	PES	MeOH, 50 mL	Lake	–	R_s estimation (from other authors) Estimation of time-weighted average concentrations using POCIS and SPMDs	Helm et al. (2012)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Synthetic organic compounds	200	PES	DCM/methyl-tert-butyl ether, 8:2 (v/v), 25 mL	Lake	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison sampling properties between the POCIS and SPMDs Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Alvarez et al. (2012)
Pesticides	200	PES	–	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Coupling of POCIS extracts with short-term photosynthesis bioassays	Morin et al. (2012b)
Pesticides	200	PES	MeOH, 40 mL	Synthesized river water	Static, flow-through	R_s calculation Evaluation of the effect of organic matter and hydrodynamics on the R_s	Charlestra et al. (2012)
Pharmaceuticals, alkylphenols and pesticides	200	PES	MeOH, 10 mL, then MeOH/DCM (v/v: 50/50), then DCM, 10 mL	Surface water	–	R_s estimation (from other authors) Time-weighted average concentrations	Munaron et al. (2012)
Pesticides	–	PES	MeOH, 5 mL, then MeOH/ethyl acetate 5: 5 (v/v), 5 mL	Drinking water, river water	Renewable static	R_s calculation using performance reference compounds Comparison between two innovative sorbents and Oasis HLB	Fauvelle et al. (2012)
Pharmaceuticals	200	PES	MeOH, 15 mL	Wastewater	Renewable semi-static	R_s calculation Time-weighted average concentrations	Bailly et al. (2013)
Perfluorinated chemicals	200	PES	MeOH, 40 ml	Wastewater	In-situ	R_s calculation Comparison R_s between pharm-POCIS and pest-POCIS	Fedorova et al. (2013)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides	230	PES	ACN, 8 mL	Surface water	In-situ	R_s calculation Comparison between $R_{s(\text{lab})}$ and $R_{s(\text{in situ})}$ Time-weighted average concentrations Evaluation the effectiveness of POCIS compared with the classical spot sampling method	Ibrahim et al. (2013)
Alkylphenols, hormones, pesticides, pharmaceutical, UV filter	200	PES	2 × MeOH, 5 mL, then 2 × MeOH/DCM (5/5, v/v), 5 mL	Tap water	Flow-through	R_s calculation Comparison $R_{s(\text{lab})}$ with literary R_s	Morin et al. (2013)
Nutrients, pharmaceuticals, pesticides	200	PES	MeOH, 15 mL	Wastewater	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Bailey et al. (2013)
Pesticides	200	PES	ACN, 8 mL	Tap water	Flow-through	R_s calculation	Ibrahim et al. (2013)
Pesticides	450	PES	MeOH	Groundwater	–	R_s estimation (from other authors) Time-weighted average concentrations	Bertho et al. (2013)
Pesticides	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate (75:25, v/v), 3 mL	River water	–	Comparison sampling properties between the POCIS and passive stir bare sorptive extraction (SBSE)	Assoumani et al. (2013)
Illicit drugs	200	PES	–	Wastewater	–	Monitoring of illicit drugs	Boles and Wells, (2014)
Trace organic compounds	200	PES	DCM/methyl-tert-butyl ether (8:2, v:v)/	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Coes et al. (2014)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticide	200	PES	MeOH, 5 mL	River water	In-situ	R_s calculation using performance reference compounds Time-weighted average concentrations	Dalton et al. (2014)
Pharmaceuticals	200	PES	ACN, 3 mL, then ACN: MeOH, 50:50 (v/v), 3 mL	Wastewater	Semi-static	R_s calculation Time-weighted average concentrations	Amdany et al. (2014)
Perfluorinated chemicals, pharmaceuticals, pesticides	200	PES	Acetone, 50 mL	River water, tap water	Flow-through	R_s calculation Time-weighted average concentrations Evaluation the effect of water flow rates and analytes concentration on the R_s	Di Carro et al. (2014)
Pharmaceuticals, hormones, sucralose	220	PES	MeOH, 100 mL	Drinking water	Semi-static	R_s calculation Time-weighted average concentrations Comparison of POCIS with the spot sampling method Ecological risk assessment	Metcalf et al. (2014)
Herbicides	200, 600	PES	MeOH, 5 mL, then MeOH/ethyl acetate 50: 50 (v/v), 5 mL	Ultrapure water	Flow-through	R_s calculation Utility assessment of performance reference compounds Sorbent mass evaluation	Fauvelle et al. (2014)
Pesticides	200	PES	MeOH, 10 mL, then MeOH/DCM (v/v: 50/50), then DCM, 10 mL	Seawater	–	R_s estimation (from other authors) Time-weighted average concentrations The risk assessment to chemical contamination	Barranger et al. (2014)
Pesticides	200	PES, Nylon	MeOH, 10 mL, then DCM/MeOH (50:50; v/v), 10 mL, then DCM, 10 mL	Laboratory water	Flow-through	R_s calculation performance reference compounds evaluation Comparison between nylon and PES membranes	Belles et al. (2014a)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides	200	PES	MeOH, 10 mL, then DCM/MeOH (50:50; v/v), 10 mL, then DCM, 10 mL	Tap water	Renewable static, in situ	R_s calculation using performance reference compounds performance reference compounds validation Comparison $R_{s(\text{lab})}$ with $R_{s(\text{cor})}$	Belles et al. (2014b)
Pesticides	200	PES	–	River water	–	Coupling of POCIS extracts with short-term photosynthesis bioassays The risk assessment to chemical contamination	Kim Tiam et al. (2014)
Pharmaceuticals, endocrine disrupting substances	200	PES	MeOH, 40 mL	River water, lake	Static, semi-static	R_s calculation Evaluation of the effect of water phase stirring on the R_s	Bayen et al. (2014)
Contaminants of emerging concern	200	PES	DCM/methyl-tert-butyl ether (8:2, v:v), 25 mL	Coastal water	–	Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Alvarez et al. (2014)
Pesticides	200	PES	MeOH, 3 mL then MeOH/ethyl acetate, 75:25 (v/v), 3 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Monitoring of micropollutants Comparison of accumulation in sorbent and PES membranes Performance reference compounds evaluation Comparison between active and passive sampling	Lissalde et al. (2014)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides	200	PES	MeOH/ethyl acetate (75:25 v/v), l	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS and Water Agency data in the framework of operational monitoring	Poullier et al. (2014)
Herbicides	200	PES	MeOH, 6 mL	River water	–	R_s calculation using performance reference compounds Time-weighted average concentrations	Schopfer et al. (2014)
Fungicides, germicides, flame retardants and pharmaceuticals	200	PES	MeOH, 50 mL	River water	–	Coupling of POCIS extracts with Yeast Estrogen Screen bioassays Comparison between the pest-POCIS, pharm-POCIS, LDPE (low density polyethylene membrane) and silicone strips in terms of their sampling properties	Liscio et al. (2014)
Munitions constituents	200	PES	Ethyl acetate, 20 mL	Seawater	Flow-through	R_s calculation Time-weighted average concentrations	Belden et al. (2015)
Pesticides	220	PES	MeOH, 1.5 mL, then DCM/MeOH (8/2, v/v), 8 mL	River water	Flow-through	Comparison R_s between pharm-POCIS and pest-POCIS R_s calculation Time-weighted average concentrations Comparison R_s values between pharm-POCIS, pest-POCIS, silicone rubber, Chemcatcher®SDB-RPS and Chemcatcher®C18	Ahrens et al. (2015)
Pesticides	–	–	–	River water	–	Coupling of POCIS extracts with enzymatic assay	Kim Tiam et al. (2015)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pharmaceuticals	200	PES	MeOH, 50 mL	Wastewater	In-situ	R_s calculation Time-weighted average concentrations	Brown et al. (2015)
Pharmaceuticals	200	PES	MeOH, 50 ml	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Jaimes-Correa et al. (2015)
Pharmaceuticals, Pesticides	200	PES	MeOH, 10 mL, then DCM/MeOH (50:50; v/v), 10 mL, then DCM, 10 mL	River water	–	R_s estimation (from other authors) using performance reference compounds Time-weighted average concentrations	Gonzalez-Rey et al. (2015)
Pesticides	200	PES	MeOH, 3 mL then MeOH: ethyl acetate, 75:25 (v/v), 3 mL	River water	Flow-through	R_s calculation Time-weighted average concentrations Comparison between active and passive sampling	Poulier et al. (2015)
Endocrine disrupting substances	200	PES	MeOH, 50 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Brown et al. (2015)
Pesticides	200	PES	MeOH, 3 mL then MeOH: ethyl acetate, 75:25 (v/v), 3 mL	Laboratory water	–	R_s estimation (from other authors) Time-weighted average concentrations using performance reference compounds	Guibal et al. (2015b)
Pesticides and their metabolites	200	PES	MeOH, 3 mL then MeOH: ethyl acetate, 75:25 (v/v), 3 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Guibal et al. (2015a)
Microcystins	300	PES	2 × MeOH and water (9:1 v/v acidified with 0.1% TFA), 5 mL	Ultrapure water	Flowthrough	R_s calculation Comparison sampling properties between the POCIS, Chemcatcher and silicone membrane sampler	Nyoni et al. (2015)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides	220	PES	EtOH	Laboratory water	Renewable semi-static	R_s calculation Evaluation of the effect of water temperature on R_s values	Yabuki et al. (2016)
Corrosion inhibitors, pesticides, pharmaceuticals	200	PES	MeOH, 8 mL	River water	In-situ	R_s calculation Time-weighted average concentrations Comparison between Oasis HLB and Strata X-CW sorbents Performance reference compounds evaluation	Carpinteiro et al. (2016)
Pharmaceuticals	200	PES	2 × MeOH, 2 mL	Seawater	Renewable static	R_s calculation Time-weighted average concentrations	Martinez Bueno et al. (2016)
Pesticides, carbamate, triazine, urea, pharmaceuticals, phenols, and industrial chemicals	200	PES	Hexane/DCM (5:5, v/v), 5 mL and DCM/ethyl acetate (5:5, v/v), 3 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Terzopoulou and Voutsas (2016)
Endocrine disrupting substances	–	–	MeOH, 10 mL, then DCM/MeOH (50:50; v/v), 10 mL, then DCM, 10 mL	River water	–	Coupling of POCIS extracts with in vivo and in vitro bioassays	Sonavane et al. (2016)
Pesticides, pharmaceuticals, hormones, fluorinated surfactants, bisphenol A, triclosan	200	PES	–	Treated wastewater	–	R_s estimation (from other authors) An interlaboratory study on passive sampling of emerging water pollutants	Vrana et al. (2016)
Pesticides, polycyclic aromatic hydrocarbons, personal care products	200	Nylon	Acetone, 1.5 mL, then DCM, 10 mL	Tap water	Renewable static	R_s calculation Water flow effects on POCIS uptake Comparison between nylon and PES membranes Comparison between Oasis HLB and Dowex Optipore L493 sorbents	Morrison and Belden (2016a)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pharmaceuticals	200	PES	–	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Li et al. (2016b)
Ciprofloxacin	200	PES	ACN, 10 mL	Hospital effluent	–	R_s estimation (from other authors) Time-weighted average concentrations	Ory et al. (2016)
Pharmaceuticals	200	PES	–	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Bayen et al. (2016)
Pharmaceuticals, endocrine disrupting substances, pesticides, herbicides, drugs of abuse	–	PES	MeOH, 5 mL	Ultrapure water	Renewable static	R_s calculation	Miller et al. (2016)
Emerging pollutants	200	PES	Acetone, 50 mL	Drinking water	Flow-through	R_s calculation Time-weighted average concentrations	Mirasole et al. (2016)
Rodenticide, hormones, antiparasitic, cardiovascular agent, pharmaceuticals, pesticides and their metabolites	200	PES	ACN, 8 mL, then MeOH, 8 mL	Groundwater	–	Screening for micropollutants Comparison of POCIS with the spot sampling method	Soulier et al. (2016)
Fungicides, herbicides, pharmaceuticals	200	PES	MeOH, 50 mL	Lake water	Semi-static	R_s calculation Time-weighted average concentrations	Metcalf et al. (2016)
Pharmaceuticals, steroid hormones, the artificial sweetener, sucralose, fungicides, herbicides, biocides	–	PES	MeOH, 100 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Diamond et al. (2016)
Pesticides	200	PES	3 × ethyl acetate, 10 ml	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Zhang et al. (2016)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Hormones	200	PES	DCM, then acetone, then MeOH	Wastewater	In-situ	R_s calculation Comparison POCIS sampler, a variant of the Chemcatcher sampler containing SDB-RPS Empore disks and the Empore disk-based sampler	Škodová et al. (2016)
Pesticides, polycyclic aromatic hydrocarbons, personal care products	200	Nylon	Acetone, 1.5 mL, then DCM, 10 mL	Tap water	Static	R_s calculation using performance reference compounds Performance reference compounds validation Water flow effects on POCIS uptake	Morrison and Belden, (2016b)
Pharmaceuticals, artificial sweeteners, personal care product, fragrances, sugar substitutes, steroid hormone	220	PES	MeOH, 100 mL	Wastewater	Static	R_s calculation using performance reference compounds Performance reference compounds validation Time-weighted average concentrations	Sultana et al. (2016)
Pesticides	200	PES	MeOH, 25 mL	Surface water	–	Monitoring of pesticides	Van Metre et al. (2017)
Alkylphenols	200	PES	Acetone/heptane (4:1 v/v), 20 mL	Ultrapure water	Renewable static	R_s calculation Investigation the role of the PES membranes in the uptake of the pollutants	Silvani et al. (2017)
Pharmaceuticals, illicit drugs	220	PES	5% ammonium hydroxide in MeOH, 5 mL and 5% acetic acid in MeOH, 5 mL	Wastewater	In-situ	R_s calculation Time-weighted average concentrations	Baz-Lomba et al. (2017)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Organophosphate flame retardants	200	PES	Acetone, 6 mL	River water, drinking water	Renewable semi-static	Assessment of the usability of PES membranes with a larger pore diameter (0.45 μm) than those available in commercial POCIS (0.1 μm pore size) R_s calculation Impact study of pH, dissolved organic matter concentration, and flow rates/turbulence on the R_s values Time-weighted average concentrations Ecological risk assessment	Yang et al. (2017)
Pharmaceuticals and their metabolites	200	PES	2 \times MeOH, 5 mL	River water	–	Time-weighted average concentrations Comparison of POCIS with the spot sampling method R_s estimation (from other authors)	Zha et al. (2017)
Pesticides	200	PES	MeOH	Surface water	–	Time-weighted average concentrations Comparison of POCIS with the spot sampling method Ecological risk assessment R_s estimation (from other authors)	Aisha et al. (2017)
Pharmaceuticals	200	PES	MeOH, 100 mL	Surface water	–	Time-weighted average concentrations Monitoring of pharmaceuticals	Vystavna et al. (2017)
Pharmaceuticals	200	PES	MeOH, 5 mL, then MeOH/DCM (1:1, v/v), 5 mL, then MeOH, 5 mL	–	–	Time-weighted average concentrations Monitoring of pharmaceuticals	Lhotský et al. (2017)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Perfluorinated substances	30	PES	MeOH containing 5% ammonium hydroxide, 6 mL	Wastewater	Flow-through	R_s calculation Impact study of flow rate and water temperature, dissolved organic matter and pH on R_s Time-weighted average concentrations Comparison between Oasis HLB and immobilized ionic liquid	Wang et al. (2017)
Pesticides and their metabolites, fungicides, herbicides, insecticides, pharmaceuticals, caffeine, sucralose	200	PES	MeOH, 5 mL, then MeOH/ethyl acetate (50/50 v/v) 5 mL, then ethyl acetate, 5 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Evaluation of the effectiveness of POCIS compared with the classical spot sampling method	Criquet et al. (2017)
Pesticides and their metabolites	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Guibal et al. (2017)
Pesticides	220	PES	MeOH, 15 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Yabuki et al. (2018)
Pharmaceuticals, perfluorinated compounds, caffeine	200	PES	Acetone, 50 mL	Drinking water	Semi-static	R_s calculation Time-weighted average concentrations	Magi et al. (2018)
Pesticides	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	Tap water	Flow-through	R_s calculation Time-weighted average concentrations	Bernard et al. (2018)
Organophosphate flame retardants	200	PES	2 × Acetone, 10 mL	River water	Renewable semi-static	R_s calculation using performance reference compounds Performance reference compounds validation	Li et al. (2018a)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides	200	PES	MeOH, 5 mL, then MeOH/ethyl acetate (1:1, v/v), 5 mL, then ethyl acetate/hexane (1:4, v/v), 5 mL	River water	In-situ	R_s calculation using performance reference compounds Performance reference compounds validation Time-weighted average concentrations Ecological risk assessment Comparison of active and passive sampling R_s calculation	Lehmann et al. (2018)
Alkylphenols and phenols, pharmaceuticals, hormones, pesticides, UV filter	200	PES	2 × MeOH, 5 mL, then 2 MeOH/DCM (50/50, v/v), 5 mL	Tap water	Flow-through	R_s calculation	Morin et al. (2018)
Munition constituents	–	PES	Ethyl acetate	Underwater	Flow-through	R_s calculation Water flow effects on POCIS uptake	Lotufo et al. (2018)
Pharmaceuticals	200	PES	MeOH/water (1:2, v/v), 30 mL	River water	–	Monitoring of pharmaceuticals	Camotti Bastos et al. (2018)
Flame retardants	200	PES	Acetone, 6 mL	River water	In-situ	R_s calculation Time-weighted average concentrations	Zha et al. (2018)
Pesticides	230	PES	ACN, 8 mL	Surface water	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Branchet et al. (2018)
Contaminants	200	PES	DCM/isopropanol/TFA (80:20:0.1 v/v/v), 10 mL	Seawater	–	R_s estimation (from other authors) Time-weighted average concentrations	Di Carro et al. (2018)
Pesticides, pharmaceuticals	54.5	PES	3 × MeOH, 10 mL	Ultrapure water	Semi-static	R_s calculation Comparison sampling properties between the POCIS and mixed polymer sampler Water flow effects on POCIS uptake	Jeong et al. (2018a)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides	220	PES	MeOH, 100 mL	Lake	Renewable static	R_s calculation using performance reference compounds Performance reference compounds validation Time-weighted average concentrations	Sultana et al. (2018)
Munitions constituents	200	PES	–	Seawater, estuarine water	Flow-through	R_s calculation Time-weighted average concentrations	Rosen et al. (2018)
Pesticide	200	PES	–	River water	–	Time-weighted average concentrations	Fauvelle et al. (2018)
Pesticides	220	PES	2 × MeOH, 20 mL	River water	Renewable semi-static	R_s calculation Time-weighted average concentrations Comparison of active and passive sampling	Berton et al. (2018)
Contaminants of emerging concern	200	PES	MeOH, 20–25 mL	River water	–	Monitoring micropollutants	Jorgenson et al. (2018)
Pesticides	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of active and passive sampling	Guibal et al. (2017)
Pharmaceuticals	200	PES	DCM/ACN (8/2, v/v), 8 mL, then DCM, 10 mL	Seawater	–	Screening for pharmaceuticals	Björlenius et al. (2018)
Pesticides	200	PES	2 × ACN, 20 mL	Deionized water	Flow-through	R_s calculation Effects study of temperature and hydrodynamic conditions on R_s values	Djomte et al. (2018)
Pesticides	220	PES	Ethyl acetate, 5 mL	Surface water	In-situ	R_s calculation using performance reference compounds Performance reference compounds validation Comparison between passive and active sampling Ecological risk assessment	Ahrens et al. (2018)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Endocrine disrupting substances	200	PES	3 × Ethyl acetate, 10 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS with the spot sampling method Ecological risk assessment	Zhang et al. (2018)
Pharmaceuticals	200	PES	–	Wastewater	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Chaves-Barquero et al. (2018)
Pharmaceuticals, human tracers	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	River water	Semi-static	R_s calculation Time-weighted average concentrations Ecological risk assessment	Guibal et al. (2018)
Pesticides, pharmaceuticals, and perfluorinated chemicals	200	PES	0.1% (v/v) ammonia solution in MeOH, 6 mL then MeOH, 6 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Challis et al. (2018a)
Pharmaceuticals and their metabolites	200	PES	2 × MeOH, 5 mL	Wastewater	Renewable static, in situ	R_s calculation using performance reference compounds Performance reference compounds validation Comparison $R_{s(\text{lab})}$ with $R_{s(\text{cor})}$ and $R_{s(\text{in situ})}$	Li et al. (2018a)
Pesticides and pharmaceuticals	200	PES	MeOH, 30–40 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS, DGT sampler and the spot sampling method	Challis et al. (2018b)
Pharmaceuticals, pesticides	220	PES	MeOH, 10 mL	River water	Semi-static	R_s calculation Time-weighted average concentrations	Jeong et al. (2018b)
Pesticides	230	PES	ACN, 8 mL	Coastal water	–	R_s estimation (from other authors) Time-weighted average concentrations	Mhadhbi et al. (2019)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Endocrine disrupting substances	200	PES	DCM/methyl-tert-butyl ether, 80:20 (v/v), 25 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Iwanowicz et al. (2019)
Pharmaceuticals, endocrine disrupting substances, pesticides	230	PES	MeOH, 40 mL	River water	–	Screening for micropollutants	Jones et al. (2019)
Perfluorinated chemicals	200	PES	MeOH, 8 mL	Drinking water	Flow-through	R_s calculation Time-weighted average concentrations Comparison between POCIS-HLB, POCIS-WAX and spot sampling method	Gobelius et al. (2019)
Pesticides	200	PES	MeOH, 100 mL	Lake	Renewable static	R_s calculation Time-weighted average concentrations	Metcalf et al. (2019)
Insecticides	200	PES	ACN, 10 mL	Surface water	Flow-through	Monitoring of pesticides R_s calculation Time-weighted average concentrations Ecological risk assessment Comparison Oasis HLB sorbent with polymer sorbent synthesized in-house	Xiong et al. (2019)
Pesticides, pharmaceuticals, hormones, polycyclic aromatic hydrocarbons, polychlorinated biphenyls	200	PES	2 × MeOH/DCM, (1:1 v/v), 3 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Coupling of POCIS extracts with in vitro bioassay	Toušová et al. (2019)
Pesticides	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	River water	–	R_s calculation Time-weighted average concentrations Coupling of POCIS and grab sampling method for monitoring of micro-pollutants	Bernard et al. (2019)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Microcystin-LR	220	PES	3 × MeOH, 10 mL	Lake	Flow-through	R_s calculation Time-weighted average concentrations	Brophy et al. (2019)
Microcystins	–	–	–	Drinking water	Static	R_s calculation Time-weighted average concentrations	Jaša et al. (2019)
Pharmaceuticals	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	Ultrapure water	–	Ecological risk assessment R_s estimation (from other authors)	Buzier et al. (2019)
Pharmaceuticals, pesticides, hormones	200	PES	MeOH, 20 mL	River water	–	Time-weighted average concentrations Performance reference compounds validation Comparison of POCIS and DGT R_s estimation (from other authors)	Rico et al. (2019)
Pharmaceuticals, pesticides, hormones	–	PES	–	River water	–	Screening for micropollutants Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Arenas-Sánchez et al. (2019)
Contaminants	220	PES	3 × Acetone, 3 mL	Surface water	–	Monitoring of micropollutants Ecological risk assessment R_s estimation (from other authors) using performance reference compounds	De Baat et al. (2019)
Explosive substances	200	PES	2 × MeOH, 3 mL	Lake	Flow-through	Time-weighted average concentrations Coupling of POCIS extracts with in vitro bioassay R_s calculation Time-weighted average concentrations Determination of transfer kinetics through PES membrane	Estoppey et al. (2019)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Contaminants	200	PES	2 × DCM/ACN (1:1, v/v)	Wastewater	–	Monitoring of micropollutants	Gallé et al. (2019a)
Endocrine disrupting substances	54.5	PES	–	River water	Renewable static	R_s calculation Time-weighted average concentrations Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Müller et al. (2019)
Contaminants	220	PES	2 × DCM/ACN (1:1, v/v)	River water	–	R_s estimation (from other authors) Monitoring of micropollutants Time-weighted average concentrations	Gallé et al. (2019b)
Munitions constituents	–	PES	Ethyl acetate	Flume water	–	R_s estimation (from other authors) Time-weighted average concentrations	Lotufo et al. (2019)
Pharmaceuticals	200	PES	MeOH, 6 mL, then ACN, 6 mL	Laboratory water	Semi-static	R_s calculation Estimation of impact of salinity and water pH on R_s values	Lis et al. (2019)
Pesticides	–	PES	–	Lake	–	R_s estimation (from other authors) Time-weighted average concentrations	Corcoran et al. (2020)
Pesticides	200	PES	MeOH	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS with the spot sampling method	de Castro Lima et al. (2020)
Pharmaceuticals	200	PES	MeOH, 25 mL	River water	–	Monitoring of pharmaceuticals	Neher et al. (2020)
Pesticides	200	PES	2 × ACN, 20 mL	Deionized water	Flow-through	Effects study of sediment on POCIS uptake	Djomte et al. (2020)

Table 2 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Pesticides, pharmaceuticals	200	PES	DCM/ACN (1:1, v/v), 10 mL	Wastewater	Flow-through	R_s calculation Time-weighted average concentrations	Gallé et al. (2020)
Pharmaceuticals	200	PES	–	Wastewater	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS, DGT and spot sampling method	Challis et al. (2020)

R_s sampling rate; PES polyethersulfone; PE polyethylene; POCIS polar organic chemical integrative sampler; pest-POCIS pesticide POCIS; pharm-POCIS pharmaceutical POCIS; DGT diffusive gradients in thin films; SPMDs semi-permeable membrane devices; DCM dichloromethane; MeOH methanol; THF tetrahydrofuran; ACN acetonitrile; EtOH ethanol; TFA trifluoroacetic acid

guided by the results of traditional extraction methods (e.g., solid-phase extraction). Kaserzon et al. (2012) based their selection of sorbent on the results that showed that the weak anion-exchange material Oasis WAX is a suitable sorbent in solid-phase extraction for anionic perfluorinated compounds, thanks to the modification of the Oasis HLB sorbent with piperazine groups. Based on the results that confirm similar solid-phase extraction performance when using Oasis HLB and Oasis WAX for the extraction of perfluorinated compounds (with Oasis WAX being a better sorbent for short-chain compounds) (Taniyasu et al. 2005), Kaserzon et al. (2012) decided to use this sorbent also in POCIS-like samplers. Similarly, Caban et al. (2016) based their experiments on promising studies on the use of ionic liquids in liquid–liquid extraction (Vičkačkaitė and Padarauskas 2012) and interesting properties of ionic liquids (they can act as solvents for compounds that differ significantly in polarity.) They decided to use ionic liquids as the receiving phase in POCIS-like sampler for collection of a diverse range of chemical compounds (pharmaceuticals, hormones, phenols). Scientists are also guided by their own earlier research when choosing an innovative sorbent in passive techniques. Berho et al. (2017) conducted tests on the use of synthesized molecular imprinted polymer as a sorbent in solid-phase extraction to isolate aminomethylphosphonic acid and glyphosate. Due to the fact that they obtained satisfactory results, they decided to use molecularly imprinted polymers as a sorbent also in POCIS-like sampler. Similarly, Jakubus et al. (2016), who were initially interested in using carbon nanotubes as the sorbent in dispersive solid-phase extraction (dSPE) (Paszkiwicz et al. 2018; Jakubus et al. 2019a, b) because of their adsorption properties, ability to π – π interaction, and good thermal and chemical stability also decided to determine the effectiveness of carbon nanotubes as sorbents in POCIS-like sampler. Thanks to the use of innovative sorbents, effective sampling of analytes belonging to chemical groups such as: endocrine-disrupting substances, pesticides, perfluorinated chemicals, pharmaceuticals, corrosion inhibitors, phenols, hormones, musk compounds, personal care products and polycyclic aromatic hydrocarbons, was carried out. The characteristics of innovative sorbents used in POCIS-like samplers are presented in Table 1.

Calibration of passive samplers

During the exposure of the sampler in water, depending on the compounds present in the tested matrix, the environmental conditions and the exposure time of the passive device, the concentration of the analyte in the sampler increases linearly during phase I (kinetic). In phase II (intermediate), the accumulation kinetics are curvilinear. In contrast, phase III (equilibrium) corresponds to the equilibrium separation

Table 3 Applications of polar organic chemical integrative sampler containing triphasic sorbent admixture to monitor contaminants level in different matrices

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Herbicides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 15 mL	River water	Renewable static, renewable semi-static	R_s calculation Time-weighted average concentrations Comparison pest-POCIS and pharm-POCIS	Alvarez et al. (2004b)
Pesticides, hormones, pharmaceuticals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 30 mL	River water	In-situ	R_s calculation Time-weighted average concentrations Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Petty et al. (2004)
Estrogens	100	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison pest-POCIS and pharm-POCIS Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Vermeirssen et al. (2005)
Herbicides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 5 mL	tap water	Semi-static	Comparison of both efficiencies and accuracies between pharm-POCIS and pest-POCISs Calculation of R_s	Mazzella et al. (2007)
Pesticides	–	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 30 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations	Sharpe and Nichols (2007)
Pesticides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL, then ethyl acetate, 20 mL	Surface river	–	R_s estimation (from other authors) Time-weighted average concentrations Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Alvarez et al. (2008)
UV filters	200	PES	MeOH, 2 mL, then DCM/MeOH/Toluene (8:1:1, v:v:v), 7 mL	Lake, wastewater	–	Monitoring of UV filters	Zenker et al. (2008)

Table 3 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Endocrine disrupting substances	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	River water, wastewater	Renewable semi-static	R_s calculation Time-weighted average concentrations Comparison pest-POCIS and pharm-POCIS	Arditsoglou and Voutsas (2008)
Herbicides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	Surface water, ground-water	–	Monitoring of herbicides	Dougherty et al. (2010)
Synthetic organic compounds	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v)/	Lake	–	Monitoring of micropollutants	Rosen et al. (2010)
Endocrine disrupting substances	200	PES	THF/MeOH/Acetone (4:3:3 v/v/v), 50 mL	Drinking water	–	Monitoring of endocrine disrupting substances	Magi et al. (2010)
Pharmaceuticals, personal care products, endocrine disrupting substances	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 100 mL	Treated wastewater	In-situ	Uptake curves Water flow effects on POCIS uptake	Li et al. (2010b)
Hormones	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	Wastewater, river water	Semi-static	R_s calculation Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Rujiralai et al. (2011)
Pesticides, hormones	200	PES	–	Deionized water	Semi-static	Calculation of R_s Comparison of calculated R_s with literature R_s	Bartelt-Hunt et al. (2011)
Pesticides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 30 mL	Lake	Renewable static	R_s calculation Time-weighted average concentrations Monitoring of pesticides Comparison of POCIS with the spot sampling method	Thomatou et al. (2011)
Atrazine	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v)/	River water	–	Monitoring of atrazine	Čermoch et al. (2011)
Pharmaceuticals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v)/	River water	–	Monitoring of pharmaceuticals	Čermoch et al. (2012)

Table 3 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Herbicides, pharmaceuticals and industrial chemicals	–	PES	MeOH, 2 ml, then DCM/MeOH/Toluene (8:1:1, v:v:v), 7 mL	River water	Flow-through	Determination of the partitioning coefficients of the analytes between water and PES membrane Comparison between the POCIS and Chemcatcher in terms of their sampling properties	Vermeirssen et al. (2012)
Perfluorinated chemicals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 ml	Wastewater	In-situ	R_s calculation Comparison R_s between pharm-POCIS and pest-POCIS	Fedorova et al. (2013)
Endocrine disrupting substances	100	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 30 ml	River water	Flow-through	R_s calculation using performance reference compounds Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Vallejo et al. (2013)
Fungicides, germicides, flame retardants and pharmaceuticals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 ml	River water	–	Coupling of POCIS extracts with Yeast Estrogen Screen bioassays Comparison between the pest-POCIS, pharm-POCIS, LDPE (low density polyethylene membrane) and silicone strips in terms of their sampling properties	Liscio et al. (2014)
Antimicrobials	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 40 ml	River water	Renewable semi-static	R_s calculation Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Gautam et al. (2014)

Table 3 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Analgesics, psycholeptics, antidepressants and illicit drugs	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 ml	River water	In-situ	R_s calculation Time-weighted average concentrations Evaluation of effect of environmental conditions on R_s	Fedorova et al. (2014)
Munitions constituents	200	PES	–	Seawater	Flow-through	R_s calculation Time-weighted average concentrations Comparison R_s between pharm-POCIS and pest-POCIS	Belden et al. (2015)
Pesticides	220	PES	MeOH, 1.5 mL, then DCM/MeOH (8/2, v/v), 8 mL	River water	Flow-through	R_s calculation Time-weighted average concentrations Comparison R_s values between pharm-POCIS, pest-POCIS, silicone rubber, Chemcatcher®SDB-RPS and Chemcatcher®C18	Ahrens et al. (2015)
Pesticides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 30 ml	Laboratory water	Renewable semi-static	R_s calculation	Thomatou et al. (2015)
Endocrine disrupting substances	–	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 15 mL	Surface water	–	Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Pickford et al. (2015)
Perfluorinated chemicals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	River water	–	Monitoring of perfluorinated chemicals Comparison of POCIS data and the data from analysis of fish muscle and liver tissue	Cervený et al. (2016)
Pesticides, carbamate, triazine, urea, pharmaceuticals, phenols, and industrial chemicals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 5 mL	River water	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Terzopoulou and Voutsas, (2016)

Table 3 (continued)

Class of analytes	Sorbent mass [mg]	Membrane type	Eluent type and volume	Water type	Calibration method	Aims	References
Tonalide	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	River water	–	Monitoring of tonalide Comparison of POCIS and biota for monitoring of micropollutant	Tumova et al. (2017)
Perfluorinated chemicals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	River water	–	Monitoring of perfluorinated chemicals	Cervený et al. (2018)
Pesticides	–	PES	MeOH, 10 mL, then MeOH/DCM (v/v), 10 mL, then DCM, 10 mL	River water	–	Monitoring of pesticides	Spirhanzlova et al. (2019)
Pharmaceuticals	228	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	River water	–	Monitoring of pharmaceuticals	Grabicová et al. (2020)

R_s sampling rate; PES polyethersulfone; POCIS polar organic chemical integrative sampler; pest-POCIS pesticide POCIS; pharm-POCIS pharmaceutical POCIS; DCM dichloromethane; MeOH methanol; THF tetrahydrofuran; ACN acetonitrile; EtOH ethanol; TFA trifluoroacetic acid

of the relationship between the receiving phase (in the sampler) and the medium surrounding the dosimeter (Kot-Wasik et al. 2007) (Fig. 2).

There are two main types of passive samplers:

- equilibrium passive sampling devices,
- kinetic passive sampling devices.

Equilibrium samplers are kept in the exposure environment until equilibrium is achieved between the analyte concentration in the receiving phase and the analyte concentration in the matrix surrounding the sampler. The principle of operation of such a device determines that when the concentration of the analyte in the exposure medium becomes constant (no further accumulation of the analyte in the receiving phase), and after reaching equilibrium the concentration of the analyte in the receiving phase will not change, the concentration of the target compound in the environment can be determined using phase–water partition coefficients (K_{sw}) according to the following equation (Yates et al. 2007; Pintado-Herrera et al. 2016; Smedes 2018):

$$C_s = C_w K_{sw} \quad (1)$$

where C_s is the analyte concentration in the receiving phase at a known exposure time and C_w is the analyte concentration in the aqueous phase. The suitability of equilibrium passive sampling devices depends on the size and variability of the test compound concentration in the aqueous phase and the sampler response time, which must be shorter than the mentioned changes in analyte concentration (Huckins et al. 2000).

Kinetic passive sampling devices are designed in such a way that the accumulation of target compounds is complete over time and responds to changes in the concentration of analytes in water. These devices are used to measure the time-weighted average concentrations of tested chemicals in the environment according to the following formula (Arditsoglou and Voutsas 2008; Harman et al. 2011b; Thomatou et al. 2011; Tanwar et al. 2015):

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

where R_s [$L \text{ day}^{-1}$] is the sampling rate of the analyte, M_s [kg] is the mass of sorbent, t [d] is the sampling period and C_s [$g \text{ kg}^{-1}$] and C_w [$g \text{ L}^{-1}$] are the concentrations of the target compound in the receiving phase and in the aquatic phase, respectively. To determine the time-weighted average concentration of the target compound, it is necessary to determine the R_s value (meaning the amount of water purified from a tested chemical compound per unit of time). To determine the R_s values of the analytes, the passive samplers used must be calibrated in the laboratory or in situ (Vrana

Table 4 Applications of polar organic chemical integrative sampler (POCIS)-like samplers containing innovative sorbents to monitor contaminants level in different matrices

Sorbent type	Sorbent mass [mg]	Membrane type	Eluent type and volume	Class of analytes	Water type	Calibration method	Aims	References
Strata-X	300	PES	Ethyl acetate, 5 mL, then MeOH, 10 mL, then 3 × ultra-pure water, 5 mL	Endocrine disrupting substances	River water	–	R_s calculation Time-weighted average concentrations Coupling of POCIS extracts with Yeast Estrogen Screen bioassays	Balaam et al. (2010)
Strata-X	300	PES	MeOH, 50 mL	Prometryn	River water	Flow-through	R_s calculation Time-weighted average concentrations Ecological risk assessment	Rotter et al. (2011)
Chromabond HRX and Oasis MAX	–	PES	MeOH, 5 mL, then MeOH/ethyl acetate 5: 5 (v/v), 5 mL	Pesticides	Drinking water, river water	Renewable static	R_s calculation using performance reference compounds Comparison sampling efficiency between Chromabond HRX, Oasis MAX and Oasis HLB sorbents Performance reference compounds validation	Fauvelle et al. (2012)
Strata XAW	600	PES	0.1% (v/v) ammonia solution in MeOH, 6 mL then MeOH, 6 mL	Perfluorinated chemicals	Estuarine water	Renewable static	R_s calculation Time-weighted average concentrations Comparison sampling efficiency between Oasis WAX and Oasis HLB sorbents	Kaserzon et al. (2012)
Strata XAW	600	PES	0.1% (v/v) ammonia solution in MeOH, 6 mL then MeOH, 6 mL	Perfluorinated chemicals	River water	Flow-through	R_s calculation using performance reference compounds Evaluation the effect of water flow rate on the uptake kinetics	(Kaserzon et al. (2013)

Table 4 (continued)

Sorbent type	Sorbent mass [mg]	Membrane type	Eluent type and volume	Class of analytes	Water type	Calibration method	Aims	References
Sepra ZT	300	PES	MeOH, 12 mL	Pesticides	Estuarine and coastal waters	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison sampling efficiency between POCIS, silicone rubber sheet and spot sampling method	Booij et al. (2013)
Strata XAW	600	PES	0.1% (v/v) ammonia solution in MeOH, 6 mL then MeOH, 6 mL	Perfluorinated chemicals	Laboratory water	In-situ	R_s calculation Evaluation the effect of water flow rate on R_s	Kaserzon et al. (2014a)
Strata-X	600	PES	MeOH, 5 mL, then ACN, 3 mL, then acetone 3 mL	Pesticides, personal care products, pharmaceuticals	Estuarine water	Renewable static	R_s calculation Comparison sampling efficiency between POCIS and Chemcatcher Evaluation of impact of PES membrane on R_s values	Kaserzon et al. (2014b)
Oasis WAX	200	PES	0.1% (v/v) ammonia solution in MeOH, 4 mL then MeOH, 4 mL	Perfluorinated chemicals	Surface water	Renewable static	R_s calculation Time-weighted average concentrations Evaluation of impact of water temperature, dissolved organic matter concentrations and pH on R_s values	Li et al. (2016a)
Strata X-CW	200	PES	MeOH, 8 mL	Corrosion inhibitors, pesticides, pharmaceuticals	River water	In-situ	R_s calculation Time-weighted average concentrations Comparison between Oasis HLB and Strata X-CW sorbents Performance reference compounds evaluation	Carpinteiro et al. (2016)

Table 4 (continued)

Sorbent type	Sorbent mass [mg]	Membrane type	Eluent type and volume	Class of analytes	Water type	Calibration method	Aims	References
Ionic liquids, ionic liquid mixed with C18-silica sorbent	200	PES	5 × ACN, 10 mL	Pharmaceuticals, phenols, hormones	Seawater	Static, semi-static	R_s calculation Comparison sampling efficiency between ionic liquid and ionic liquid mixed with C18-silica sorbent	Caban et al. (2016)
Dowex Optipore L493	200	Nylon	Acetone, 1.5 mL, then DCM, 10 mL	Pesticides, polycyclic aromatic hydrocarbons, personal care products	Tap water	Renewable static	R_s calculation Water flow effects on POCIS uptake Comparison between nylon and PES membranes Comparison between Oasis HLB and Dowex Optipore L493 sorbents	Morrison and Belden, (2016a)
Dowex Optipore L493	200	Nylon	Acetone, 1.5 mL, then DCM, 10 mL	Pesticides, polycyclic aromatic hydrocarbons, personal care products	Tap water	Renewable static	R_s calculation using performance reference compounds Performance reference compounds validation	Morrison and Belden, (2016b)
Molecularly imprinted polymers	200	PES, nylon	2 × HCl (0.1 M), 4 mL	Pesticides	Laboratory water	Flow-through	R_s calculation Comparison between PES membranes and nylon membranes	Berho et al. (2017)
Carbon nanotubes	100	PES	ACN/MeOH/DCM (40:40:20; v/v), 20 mL	Pharmaceuticals, pesticides, phenols	Laboratory water	Semi-static	R_s calculation	Jakubus et al. (2016)

Table 4 (continued)

Sorbent type	Sorbent mass [mg]	Membrane type	Eluent type and volume	Class of analytes	Water type	Calibration method	Aims	References
C18 sorbent mixed with triphasic sorbent admixture	200	PES	DCM/ethyl acetate/MeOH (4:4:2, v/v), 8 mL	Alachlor, trifluralin, herbicides, alkylphenols, hormones, musk compounds	Wastewater	Flow-through, In-situ	R_s calculation using performance reference compounds Performance reference compounds validation Time-weighted average concentrations Comparison $R_{s(\text{lab})}$ with $R_{s(\text{cor})}$ and $R_{s(\text{in situ})}$	Iparraguirre et al. (2017)
Ionic liquids	30	PES	MeOH containing 5% ammonium hydroxide, 6 mL	Perfluorinated substances	Wastewater	Flow-through	R_s calculation Impact study of flow rate and water temperature, dissolved organic matter and pH on R_s Time-weighted average concentrations Comparison between Oasis HLB and immobilized ionic liquid	Wang et al. (2017)
Ionic Liquid	200	PES, Nylon, Teflon	ACN, 50 mL	Pharmaceuticals	Wastewater, surface water	Semi-static	R_s calculation Comparison between PES, Teflon and nylon membranes	Męczykowska et al. (2017b)
Strata XAW mixed with Bond-Elute Plexa sorbents	200	Nylon	2.5% ammonia in MeOH, 6 mL then MeOH, 6 mL	Contaminants	Estuarine water	Flow-through	R_s calculation using performance reference compounds Performance reference compounds validation Time-weighted average concentrations	Mijangos et al. (2018a)
Ionic Liquid	200	PES	ACN, 10 mL	Pharmaceuticals	Seawater, stream water	Semi-static	R_s calculation Evaluation of impact of water salinity and pH on R_s values	Męczykowska et al. (2018)

Table 4 (continued)

Sorbent type	Sorbent mass [mg]	Membrane type	Eluent type and volume	Class of analytes	Water type	Calibration method	Aims	References
Molecularly imprinted polymers	30	PES	Acetic acid/MeOH (1:6, v/v),/	Perfluorinated substances	Laboratory water	Flow-through	R_s calculation Evaluation of impact of water pH, flow velocity, and dissolved organic matter concentrations on R_s values	Cao et al. (2018)
Strata XAW mixed with Bond-Elute Plexa sorbents	200	Nylon	–	Contaminants	Wastewater	Static-renewable	R_s calculation Time-weighted average concentrations Coupling of POCIS extracts with in situ bioassays	Solagaistua et al. (2018)
Strata XAW mixed with Bond-Elute Plexa sorbents	200	Nylon	MeOH with 2.5% ammonium, 6 mL, then MeOH, 6 mL	Contaminants	Estuarine water	–	R_s estimation (from other authors) Time-weighted average concentrations Ecological risk assessment	Mijangos et al. (2018b)
Oasis WAX	200	PES	MeOH, 8 mL	Perfluorinated chemicals	Drinking water	Flow-through	R_s calculation Time-weighted average concentrations Comparison between POCIS-HLB, POCIS-WAX and spot sampling method	Gobelius et al. (2019)
Synthesized adsorbent (polymer)	200	PES	ACN, 10 mL	Insecticides	Surface water	Flow-through	R_s calculation Time-weighted average concentrations Ecological risk assessment Comparison Oasis HLB sorbent with polymer sorbent synthesized in-house	Xiong et al. (2019)

Table 4 (continued)

Sorbent type	Sorbent mass [mg]	Membrane type	Eluent type and volume	Class of analytes	Water type	Calibration method	Aims	References
Ionic liquids	200	PES	ACN,/	Pharmaceuticals	River water	Semi-static	R_s calculation Evaluation of impact of water temperature, dissolved organic matter concentrations and stirring of water on R_s values	Męczykowska et al. (2019)

R_s sampling rate; PES polyethersulfone; POCIS polar organic chemical integrative sampler; DCM dichloromethane; MeOH methanol; ACN acetonitrile

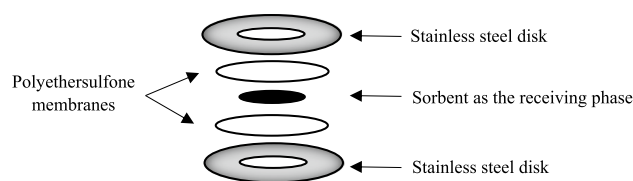


Fig. 1 Polar organic chemical integrative sampler (POCIS) consisting solid sorbent, polyethersulfone membranes and two stainless steel rings—schematic illustration

et al. 2006; Macleod et al. 2007; Aguilar-Martínez et al. 2008; Ibrahim et al. 2013).

To calibrate a passive sampler in the laboratory, it is necessary to build an appropriate exposure system. In the literature, there are usually three methods of obtaining $R_{s(\text{lab})}$:

1. static calibration (Lotufo et al. 2018; Magi et al. 2018),
2. renewable static calibration (Thomatou et al. 2011; Belden et al. 2015; Li et al. 2016a; Silvani et al. 2017),
3. flow-through calibration (Harman et al. 2008a, b; Zhang et al. 2008).

Static calibration is carried out in a closed system, spiked with analytes at the beginning of the experiment. This method can be used when the tested compounds are stable (do not degrade quickly) and/or when the duration of the calibration is short (i.e., a few days) (Lotufo et al. 2018). Renewable static calibration is performed in a closed system, spiked with analytes at constant intervals. This is the most commonly used method for calibrating passive samplers due to its simplicity (Morin et al. 2012a). Flow-through calibration is performed in an open system with the continuous enrichment of analytes. This method is much more labor intensive than the others (Martínez Bueno et al. 2009). In order to better reflect environmental conditions, a modification of static sampling calibration methods is introduced. Namely, the aqueous phase is mixed during the experiment, most often by means of a magnetic stirrer. Such calibration methods are called quasi-static or semi-static (Caban et al. 2016; Jakubus et al. 2016; Męczykowska et al. 2017a; Lotufo et al. 2018; Lis et al. 2019).

The calibration links the quantity of a compound accumulated to its concentration in the studied environment by determining its sampling rate. To properly calibrate the device, it must be used in the kinetic variant, and then R_s values can be determined according to formula (2). High R_s values are required because organic pollutants in the environment occur at low concentration levels. The sampling rate of analytes is increased by means of various design variants of the sampler. It is important to know which layer limits the uptake rate of the tested compound. There are four limiting layers: the receiving phase, membranes, possible biotic

Fig. 2 Kinetic and equilibrium uptake phases as a function of time—kinetic (phase I), intermediate (phase II) and equilibrium (phase III)

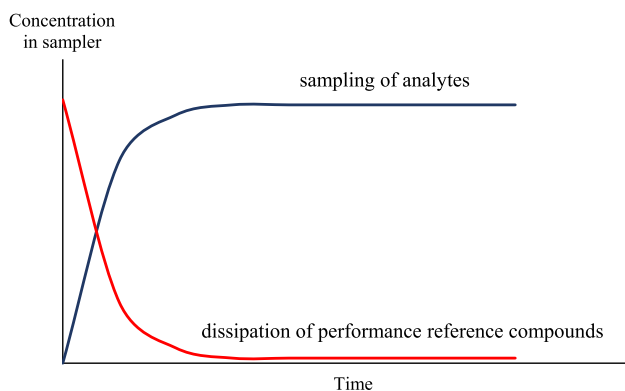
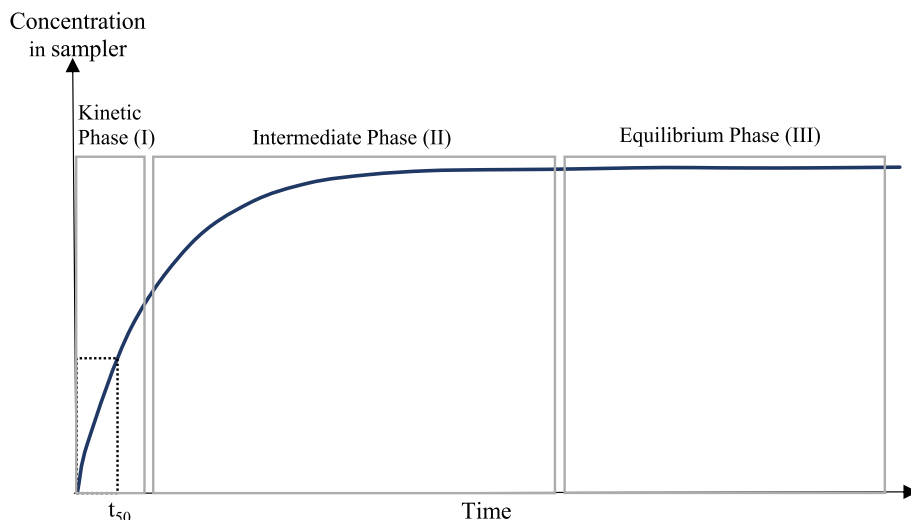


Fig. 3 Simultaneous sampling of analytes by a passive sampler and dissipation of performance reference compounds (PRCs) from the receiving phase during its exposure in the environment

contamination of the membrane and the aqueous boundary layer (Ibrahim et al. 2013; Vallejo et al. 2013; Berho et al. 2017). In addition, the R_s values may also depend on environmental conditions such as water salinity (Togola and Budzinski 2007; Bayen et al. 2014; Męczykowska et al. 2018), pH of the donor phase (Li et al. 2011, 2016a; Lis et al. 2019), temperature (Ibrahim et al. 2013; Yabuki et al. 2016) and dissolved organic matter concentration (Li et al. 2011; Ibrahim et al. 2013). For this reason, many scientists propose to use performance reference compounds to make the obtained R_s values more reliable.

Performance reference compounds are compounds added to the receiving phase in the sampler before its exposure which do not affect the process of sampling analytes from water. During the exposure of the passive device, the performance reference compounds are released from the sampler into the external environment. The

sampling of analytes and the release of performance reference compounds are caused by the same molecular process (Fig. 3). Changes in the sampling rates of analytes due to environmental conditions (e.g., decrease in temperature, increase in salinity, decrease in pH) should be reflected by the same changes in the release of performance reference compounds from the samplers (Harman et al. 2012).

The release of performance reference compounds is required to follow first-order kinetics (Carpinteiro et al. 2016):

$$\ln \frac{C_t}{C_0} = k_e t \quad (3)$$

where C_t and C_0 are the concentrations in the receiving phase [$\mu\text{g g}^{-1}$] during t [day] and before introduction, respectively, and k_e is the elimination rate constant [day^{-1}]. The elimination rate constant is used to determine the corrected R_s ($R_{s(\text{cor})}$). Therefore, $R_{s(\text{cor})}$ can be determined by the following equation (Morin et al. 2012a):

$$R_{s(\text{cor})} = \frac{k_{e(\text{in situ})}}{k_{e(\text{lab})}} R_{s(\text{lab})} \quad (4)$$

where $k_{e(\text{lab})}$ is the calculated elimination rate constant in the laboratory and $k_{e(\text{in situ})}$ is the elimination rate constant obtained in the field. The ratio of $k_{e(\text{in situ})}$ to $k_{e(\text{lab})}$ is called the environmental adjustment factor. According to theory, the environmental adjustment factor reflects changes in uptake rates (relative to laboratory data) due to differences in analyte properties, environmental conditions, membrane biofouling and the water phase flow rate. For instance, if the environmental adjustment factor values are relatively constant for analytes with a $\log K_{ow}$ value in the range of 4–8, then these factors will be appropriate for most hydrophobic chemicals (Męczykowska et al. 2017a).

Performance reference compounds are compounds that are not present in the environment and may be, for example, isotopically labeled compounds (^2H -, ^{13}C -labeled reference compounds can be used). The ideal solution would be if each compound had its own performance reference compounds (e.g., anthracene-d10 as the performance reference compound for anthracene). However, for practical reasons this is not possible. Performance reference compounds are usually hydrophobic compounds, successfully used in SPMDs or Chemcatcher techniques, in which hydrophobic analytes are sampled ($\log K_{\text{ow}}$ 4.5–6). In the case of hydrophilic analytes, the selection of the appropriate performance reference compounds is not easy. For instance, for pharmaceuticals, several studies used diclofenac-d4 and ibuprofen-d3 as performance reference compounds, but the results obtained were not satisfactory (Camilleri et al. 2012; Carpinteiro et al. 2016; Lissalde et al. 2016), whereas Carpinteiro et al. (2016) conducted research to assess the usefulness of selected performance reference compounds for the determination of two corrosion inhibitors, seven pesticides and four pharmaceuticals in river water using POCIS. Of the seven potential performance reference compounds, only deisopropylatrazine-d5 and 4-methylbenzotriazol-d3 showed a significant release that was consistent with the first-order kinetic model. It was proved that these two performance reference compounds allow a significant reduction in the effect of water flow on R_s , and 4-methylbenzotriazol-d3 can be used to determine time-weighted average concentrations estimated using deisopropylatrazine-d5. Moreover, Mazzella et al. (2010) used deisopropylatrazine-d5 as a performance reference compound in the determination of polar herbicides in water using POCIS. They calibrated the samplers in situ and in the laboratory using the performance reference compound. Comparing the obtained $R_{s(\text{in situ})}$ and $R_{s(\text{cor})}$ values, they noticed no significant differences between the sampling rate values. These results confirm the potential use of deisopropylatrazine-d5 as a performance reference compound for some polar herbicides. The authors concluded that in situ calibrations are a better solution, but too costly and time-consuming. Therefore, calibration using performance reference compounds but, in the laboratory, seems to be a promising method for obtaining reliable R_s values. However, research into the selection of the appropriate performance reference compounds for the sampling of polar compounds by POCIS is still in its early stages.

Impact of environmental conditions on sampling rate

R_s values depend on the physicochemical properties of the analytes (molecular weight, hydrophobicity, solubility) and environmental conditions such as water flow, salinity, sample pH, temperature, biofouling and dissolved organic matter

concentration (Gong et al. 2018). The amount of research on determining the impact of specific external factors on the sampling rate and the efficiency of extraction of passive samplers is constantly growing.

The first environmental factor that significantly affects the sampling rate of analytes, which should be mentioned, is the pH of the water. Many environmental contaminants, including some pharmaceuticals and hormones, have functional groups that can be ionized at various pH values of water. Additionally, the water pH may have an effect on changing the hydrophobicity and/or solubility of the target chemicals. Avdeef et al. (2000) showed that the hydrophobicity of some drugs varies depending on the pH of the solution. For this reason, Li et al. (2011) conducted research on the effect of the dissolved organic matter concentration and pH of the solution on R_s values for POCIS (Oasis HLB as a sorbent). The sampling rates for acid pharmaceuticals were shown to decrease with increasing pH from 3 to 9, while the sampling rates for basic chemicals (e.g., β -blockers) increased with increasing pH from 3 to 9. More importantly, R_s values for inert drugs and phenolic compounds with high pK_a values (e.g., bisphenol A) remained unchanged in the pH range of 3–9. Zhang et al. (2008), in their studies, also showed that R_s values for target compounds with a pK_a greater than 10 remain relatively similar at pH 4–10 with an relative standard deviation less than 5% when using POCIS.

Another external factor that can negatively affect the sampling rate of chemicals is the presence of dissolved organic matter in the water because it can:

1. bind to target molecules,
2. dominate at adsorption sites and inhibit the adsorption capacity for some target analytes,
3. induce interference and time-consuming preparation.

Due to complexing with dissolved organic matter, the available concentration of target chemicals may decrease, and the complexes formed are difficult to disperse in the sampler. The measure of the total dissolved organic matter concentration is the dissolved organic carbon concentration, which in the aquatic environment is usually 2–10 mg L^{-1} (Yang et al. 2017). Most dissolved organic carbon in natural waters is fulvic and humic. Li et al. (2011) examined the relationship between the R_s values of selected drugs and hormones and the dissolved organic carbon concentration (3.33, 3.86 and 4.92 mg L^{-1}) in the sample. It was shown that there is a tendency for the accumulation rate of acid, neutral and alkaline analytes to increase in POCIS with an increasing dissolved organic matter concentration in water, but these differences were not statistically significant. Charlestra et al. (2012) also investigated the impact of dissolved organic matter on the rate of pesticide uptake from water by POCIS. They proved that the dissolved organic matter concentration

in the water phase in the range of 0.1–5 mg L⁻¹ does not significantly affect the R_s values of the target compounds. At the same time, the authors emphasize the need for further research using higher dissolved organic matter concentrations to completely exclude the effect of dissolved organic matter on R_s values.

Salinity is an environmental factor that can strongly affect the sampling rate of compounds, especially from seawater. Salinity values of environmental waters are in a wide range of 0–35 PSU (1 practical unit of salinity corresponds to 1 g of salt per kg of solution), depending on the type of water reservoir, but also on temperature, precipitation, melting glaciers, etc. Many literature sources indicate that the solubility of most organic pollutants in water decreases with increasing salt concentration due to the so-called salting effect. This effect should theoretically increase their sorption efficiency in the sampler. On the other hand, complexing organic chemicals with polyvalent cations can inhibit and delay the sampling of target organic pollutants. Togola and Budzinski (2007) proved that water salinity showed little effect on the accumulation of acid compounds in POCIS, while the R_s values of basic compounds decreased with increasing salinity. Shi et al. (2014) conducted POCIS calibrations to determine antibiotics and hormones in coastal waters. The effect of sample salinity (0‰, 14‰, 35‰) on the R_s values of target analytes was investigated. It was shown that an increase in water salinity caused an increase in the sampling rate of all the tested compounds excluding estriol, with the highest R_s values observed at 14‰ salinity. This complex relationship indicates that POCIS should be thoroughly tested for various environmental conditions before use in the field.

In addition to the factors mentioned above, the water flow also has an important impact on the sampling rate. In the case of an integral (kinetic) passive sampler, there is a strong relationship between sampling and the boundary layer with water on the membrane. Therefore, increasing the flow rate of the solution should reduce the thickness of the water/membrane boundary, which is equivalent to increasing the sampling rate of analytes by the passive kinetic sampler. Di Carro et al. (2014) examined the relationship between the water flow (2, 5.1, 10.2 and 15.3 cm s⁻¹) and the sampling rate during flow-through calibration. POCIS passive samplers were used with Oasis HLB sorbent as the receiving phase, and the analytes were pesticides, pharmaceuticals and perfluorinated compounds. It was proved that increasing the flow rate of the water phase affects the R_s values, although increasing the flow velocity was not always synonymous with an increase in R_s values. However, in the research of Charlestra et al. (2012) both water flow and mixing were shown to significantly increase the uptake rate of target analytes, which is closely related to the reduction of the diffusion boundary layer.

Temperature is another important factor that can affect the sampling rate of analytes by passive samplers. In theory, an increase in the temperature of the aqueous phase should increase the mobility of the analyte and accelerate the mass transfer from the water to the receiving phase in the sampler. Moreover, in membrane processes, the solvent flow through the membrane depends on its chemical potential, which grows with increasing temperature (Djomte et al. 2018). Yabuki et al. (2016) studied the relationship between temperature (18, 24 and 30 °C) and the sampling rate of 48 pesticides by POCIS. The results confirmed that for most analytes, the uptake rate increases with increasing temperature. Similar conclusions were drawn by Li et al. (2010a), who studied the effect of temperature (5, 15 and 25 °C) on the sampling rate for 29 different pharmaceuticals. They also showed that the highest R_s values of analytes were obtained for the highest temperature – 25 °C. However, it should be remembered that the presented examples do not confirm that the temperature increase–increase R_s relationship will take place for all types of pollution.

The last environmental factor which should be taken into consideration when calibrating passive samplers is biofouling. Biofouling is a membrane growth caused by microorganisms, animals, plants or algae and the formation of a biofilm layer on the membrane or directly in the receiving phase. The growing biofilm at the top of the membrane reduces the surface for the passive extraction of water pollutants. The permeability of the membrane becomes less, which reduces the efficiency of the passive process (Męczykowska et al. 2017a). An idea to minimize the effect of biofouling is to cover the receiving phase with membranes. Schäfer et al. (2008) proved that biofouling on a naked disk (in a passive Chemcatcher® sampler) causes a decrease in the sampling rate. Polyethersulfone membranes, used in POCIS, are characterized by a higher resistance to biofouling due to their polarization. Lissalde et al. (2014), in their research on the sampling of pesticides from water by POCIS, proved that biofouling is not a factor which limits the accumulation of analytes in the sampler sorbent.

Considering the fact that so many environmental factors can (in many ways) affect the sampling rate of analytes from water reservoirs, in situ calibration or laboratory calibration using performance reference compounds, with a simultaneous assessment of the impact of environmental conditions is justified.

Sorbents used in passive organic chemical integrative samplers

Hydrophilic–lipophilic-balanced sorbent (Oasis HLB)

Oasis HLB sorbent (specific surface area $\sim 800 \text{ m}^2 \text{ g}^{-1}$) is one of the most commonly used sorption materials in both active and passive methods of extracting water pollutants. The HLB polymer contains both hydrophobic (i.e., benzene and aliphatic chains) and hydrophilic (i.e., pyrrolidone) fragments. This unusual structure contributes to the good water wettability and high sorption capacity of hydrophobic and hydrophilic compounds. Commercially available pharmaceutical POCIS devices containing Oasis HLB (200 or 220 mg/POCIS) as the receiving phase are provided by companies such as Environmental Sampling Technologies, Exposmeter AB and E&H Services. However, many scientists buy the sorbent separately and create home-made samplers to reduce or increase the amount of sorbent used in POCIS (Table 2). Researchers are constantly striving to reduce the costs of the sampling, preparation and final analysis of environmental samples. For this reason, the most common attempts to reduce the weight of the receiving phase while maintaining good sampling efficiency are of an economic nature. On the other hand, scientists who increase the amount of Oasis HLB used in the sampler aim at increasing the sampling rate and the efficiency of collecting aqueous pollutants, and the use of Oasis HLB sorbent can be a cost-effective approach in environmental analysis.

Fauvelle et al. (2014) performed a laboratory calibration of passive samplers to compare the uptake of both polar and acid herbicides for 20 days in POCIS devices containing 200 and 600 mg Oasis HLB (POCIS-200 and POCIS-600). A significant increase in R_s values between POCIS-200 and POCIS-600 was observed for the uptake of compounds in the kinetic phase. Moreover, Kohoutek et al. (2008) conducted research to develop and evaluate the use of a passive sampler for microcystins and to compare the ability of different configurations (membranes and sorbent mass) to effectively accumulate these analytes. They applied three ratios of the sorbent mass to the membrane surface area (2.75, 5.55 and $11.10 \text{ mg (cm}^2\text{)}^{-1}$), using an Oasis HLB sorbent sampling device and a polycarbonate membrane. The obtained results proved that the sampling rate decreased along with an increase of the sorbent mass-to-surface area ratio. The researchers stated that this could be related to changes in diffusion velocity. The lower effective thickness (at a lower sorbent mass) caused a higher speed of the water sample through the sorbent layer, which leads to a more efficient accumulation of microcystins. Other researchers also obtained high extraction efficiency and satisfactory sampling rates, using, e.g., 100 mg (Vermeirssen et al. 2005; Zhang

et al. 2008), 30 mg (Wang et al. 2017) or 54.5 mg (Jeong et al. 2018a; Müller et al. 2019) Oasis HLB. Considering the above, it can be concluded that the increase in sorbent mass will not always increase the uptake rate of the target chemical compounds.

In research conducted by Kohoutek et al. (2008), polyethersulfone, polyester, nylon and polycarbonate membranes were tested, between which Oasis HLB sorbent (200 mg) was placed. It was determined that chemicals can migrate to the sorbent layer through the membrane in two ways, i.e., dissolution and migration through the polymer matrix of the membrane, and migration through the pores filled with water. These two modes control the accumulation of analytes to the passive sampler. Assuming the constant exposure conditions used in the experiments of Kohoutek et al. (2008), the most important features affecting accumulation were the effective membrane thickness and the open pore volume. Among the tested membranes, the polycarbonate membrane showed the highest microcystin uptake rate as well as similar uptake frequencies for two different microcystin variants (microcystin-RR and microcystin-LR). The polycarbonate membrane is a thin membrane (5–25 μm), ensuring rapid diffusion and analyte collection at medium flow rates. They also obtained very similar results for polyethersulfone membranes, which are durable, resistant and tensile and have a large volume of open pores. However, the relatively large thickness of this microporous membrane (110–150 μm) can lead to the stagnation of the water boundary layer, which extends the diffusion pathway for target compounds. Less effective accumulation was found for the hydrophilic nylon-66 membrane, which is relatively thick (65–125 μm) with an average pore volume. In contrast, the polyester membrane, which is naturally hydrophilic, resistant and of small thickness (5–11 μm), accumulated only microcystin-RR and no microcystin-LR was found. Belles et al. (2014a, b) proposed replacing polyethersulfone membranes with nylon membranes in POCIS (Oasis HLB as a sorbent) in order to be able to collect hydrophobic compounds and improve the accumulation of other pollutants. The R_s values of each hydrophobic analyte were higher in the POCIS-Nylon configuration than in POCIS-Polyethersulfone. This is mainly due to the fact that the pores in nylon membranes are larger than in polyethersulfone membranes, which contributes to a reduction in the mass transfer resistance and increases the accumulated amounts of various chemical compounds in the sampler. Nonetheless, for very polar compounds, changing the membrane type did not affect the amount of compound in the receiving phase.

However, regardless of the sorbent mass or membrane type used, each passive sampler should be calibrated before use in the field. For pharm-POCIS, all known sampler calibration methods are used (Table 2). Interestingly, the most common are the flow-through or in situ methods, despite

them being time-consuming and complicated. As previously mentioned, *in situ* calibration is the most reliable method for determining R_s values. However, by using other methods, many researchers focus on developing the performance reference compounds-based approach to improve the accuracy of passive sampler calibration. Jacquet et al. (2012), in their studies, tested three deuterated beta-blockers and four deuterated hormones as potential performance reference compounds. Unfortunately, only deuterated atenolol showed significant dispersion from the POCIS sorbent. Sultana et al. (2016) also tested four deuterated beta-blockers (atenolol-d7, metoprolol-d6, sotalol-d6 and propranolol-d7) as performance reference compounds in POCIS-Oasis HLB during laboratory and *in situ* calibration. Of the tested compounds, metoprolol-d6 and propranolol-d7 showed significant and comparable elimination rates from sorbent in laboratory and field experiments and therefore were used as performance reference compounds in the further calibration of POCIS. But Li et al. (2018a, b) tested several different deuterated compounds (acetaminophen-d3, antipyrine-d3, sulfamethoxazole-d4, carbamazepine-d10, diclofenac acid-d4, clofibrac acid-d4, bezafibrate-d6, ibuprofen-d3 and naprofen-d3) as potential performance reference compounds. In this case, only antipyrine-d3, carbamazepine-d10 and sulfamethoxazole-d4 showed dispersion with POCIS according to first-order kinetics. As can be seen, finding the right performance reference compounds that could be used successfully in pharm-POCIS is not easy, but more and more work is being done on this subject (Table 2) to provide the necessary knowledge for a better understanding of the performance reference compounds-based approach.

An important step in the procedure for determining pollutants using POCIS is the extraction of analytes retained on the surface of the sorbent. According to Table 2, methanol (MeOH) is the most common elution solvent used in POCIS-Oasis HLB. It is also a widely used eluent in active extraction methods; thus, it is not surprising that MeOH has been successfully used for the desorption of compounds from Oasis HLB, such as pharmaceuticals (Alvarez et al. 2004b; Jones-Lepp et al. 2004), hormones (Vermeirssen et al. 2005), pesticides (Mazzella et al. 2007), endocrine disrupting products (Zhang et al. 2008), personal care products (Li et al. 2010b), polycyclic aromatic hydrocarbons (Harman et al. 2008), alkylphenols (Harman et al. 2009), nutrients (Bailly et al. 2013), flame retardants (Liscio et al. 2014), artificial sweeteners (Diamond et al. 2016) and explosive substances (Estoppey et al. 2019). MeOH, despite the ability to elute many organic compounds, is not always sufficient to obtain an effective extraction. Therefore, scientists create various types of elution mixtures by adding e.g. ethyl acetate, acetone, dichloromethane (DCM), methylene chloride, etc. to methanol to increase the elution efficiency of analytes from Oasis HLB (Table 2). In addition, the literature provides

information on the use of different volumes of selected eluents ranging from 4 mL of MeOH (Martínez Bueno et al. 2016) to 100 mL of MeOH (Metcalf et al. 2014). For the sampling of chemicals that differ significantly in hydrophobicity, step elution is often used with two or more solvents (Morin et al. 2018).

In some papers, scientists compare the sampling properties of different types of passive samplers (Table 2). Škodová et al. (2016) carried out calibrations of POCIS-Oasis HLB, Chemcatcher-SDB-RPS (styrene divinylbenzene-reversed phase sulfonated) Empore disk and an Empore disk-based sampler to determine the R_s values and the efficiency of hormone extraction from water. The results showed that only POCIS containing Oasis HLB was able to integrate sampling for up to one month. For Chemcatcher, kinetic sampling was only possible for one week. In addition, the authors emphasized that the practical advantage of POCIS over the Chemcatcher design used is its low pollution during manipulation. Liscio et al. (2009) compared the sampling properties of POCIS, low-density polyethylene sampler and silicone strips. Their results also confirm the best suitability of POCIS for the sampling of endocrine disrupting compounds.

Although pharm-POCIS was mainly developed for the accumulation of pharmaceuticals, this sampler has been used so far to monitor: pharmaceuticals, pesticides (biocides, herbicides, insecticides, fungicides), personal care products, fragrances, fire retardants, plasticizers, domestics, microcystins, endocrine-disrupting substances, polycyclic aromatic hydrocarbons, phenols, UV filters, stimulants, anticorrosive substances, antidepressants, perfluorinated chemicals, surfactants, drugs of abuse, artificial sweeteners, sucralose, munition constituents and more (Table 2). According to the collected data, pharm-POCIS is most often exposed in rivers but also in wastewater, seawater, groundwater, drinking water and lakes (Table 2). Interestingly, pharm-POCIS has been used in many pesticide-monitoring studies for which POCIS containing another sorbent was originally developed (pest-POCIS containing a triphasic sorbent admixture). Mazzella et al. (2007) conducted a study in which they compared the herbicide uptake efficiency of two commercially available POCIS configurations (pharm-POCIS and pest-POCIS). They noticed that pharm-POCIS is more efficient and more accurate for sampling most analytes. It should be mentioned that their experiments lasted only 5 days and it is not certain whether the same effect would be obtained during long-term exposure. On the other hand, Vermeirssen et al. (2005) showed that the use of pest-POCIS and pharm-POCIS allowed the determination of very similar time-weighted average concentrations values for estrogen concentrations in river waters (excluding one sampling site, where pest-POCIS showed better sampling properties than pharm-POCIS). In addition, they proved that pest-POCIS is more suitable for combining with bioassays than

pharm-POCIS. This shows that despite the fact that Oasis HLB is widely used as a sorbent in POCIS, it is not always the best choice, which leads to a constant search for innovative sorption materials.

Triphasic sorbent admixture

ISOLUTE® ENV+ is a polymer polystyrene sorbent used to isolate a wide range of polar pollutants from water. Commercially available pesticide POCIS devices containing a triphasic sorbent admixture (200 or 220 mg/POCIS) as the receiving phase are supplied by companies such as: Exposmeter AB and E&W Services. Pest-POCIS was originally created to monitor pesticides in the aquatic environment, but scientists successfully used this sampler to also collect such compounds as pharmaceuticals (Černoch et al. 2012), hormones (Rujiralai et al. 2011), UV filters (Černoch et al. 2012), phenols (Terzopoulou and Voutsas 2016), perfluorinated compounds (Cervený et al. 2018), personal care products (Li et al. 2010b), endocrine disrupting substances (Magi et al. 2010), flame retardants (Liscio et al. 2014), munitions constituents (Belden et al. 2015) (Table 3). According to the collected data, POCIS containing ISOLUTE® ENV+ is most often exposed in rivers (as well as POCIS-Oasis HLB) but also in sewage, seawater, groundwater, drinking water and lakes. The mass of the triphasic sorbent admixture used as the sorbent is usually 200 mg. However, Vermeirssen et al. (2005) proved that by using half the weight of this sorbent, it is also possible to sample analytes from water. Comparing the concentrations of pollutants obtained after POCIS exposure with those obtained from spot sampling, no significant differences were observed. Similar results were obtained by Vallejo et al. (2013), who successfully used 100 mg of the triphasic sorbent admixture in POCIS to sample endocrine-disrupting substances from the aquatic environment, and the time-weighted average concentrations obtained were similar to those obtained from spot sampling. This proves the potential of the triphasic sorbent admixture to be termed an economic sorbent.

In the same studies, the use of equilin-d4, estradiol-d3, prostaglandin-d9 and bisphenol A-d12 as performance reference compounds was evaluated. Linear elimination was noted only for equilin-d4 and estradiol-d3, and it was these compounds that were successfully used as performance reference compounds when determining the time-weighted average concentrations of endocrine-disrupting substances in water. These are the only studies, summarized in Table 3, that used the performance reference compound approach in pest-POCIS.

Considering the eluent used to extract the retained analytes from the sorbent, it was most often a mixture of dichloromethane, methanol and toluene. This elution mixture was

successfully used to elute pesticides, hormones, pharmaceuticals, endocrine-disrupting substances, industrial chemicals, perfluorinated chemicals and phenols, retained on the surface of the triphasic sorbent admixture. Interestingly, no studies used only MeOH as the eluent, which often occurred during the extraction of analytes from Oasis HLB. Several literature reports mention the use of step elution to increase the extraction efficiency of target compounds (Zenker et al. 2008; Ahrens et al. 2015; Spirhanzlova et al. 2019). In contrast, the volumes used in the elution from pest-POCIS ranged from 5 to 70 mL (Table 3).

In the research of Fedorova et al. (2013), for the first time, the calibration of pest-POCIS and pharm-POCIS, used for the sampling of perfluorinated compounds from water, was performed. After an instrumental analysis of POCIS extracts, ten of the 15 target chemicals were found. Perfluorinated compounds with the longest alkyl chains have not yet been detected in any type of POCIS, which highlights the need to look for alternative sorbents that will increase the range of POCIS applicability. Absorption curves were plotted and sampling rates calculated for the compounds that could be detected. The results indicate that pest-POCIS has a better ability to accumulate perfluorinated compounds compared to pharm-POCIS. On the other hand, Arditoglou and Voutsas (2008) studied the efficiency of endocrine-disrupting substances extraction from water for pest-POCIS and pharm-POCIS. They proved that both types of POCIS had similar extraction efficiency and sampling rates.

Innovative sorbents

According to Table 4, Balaam et al. (2010), as the first in 2010, used a different sorbent in POCIS-like samplers than those used for years, i.e., a functionalized polymeric sorption material that contains *N*-vinylpyrrolidone (Strata-X), which allows stronger interactions to be achieved between the analyte and the sorbent. The researchers were inspired by active extraction research where Strata-X has been shown to be more effective in retaining a wider range of chemicals than Oasis HLB. They created samplers similar to those described by Alvarez et al. (2004b), where they used 300 mg Strata-X. The modified and calibrated POCIS was used to determine the time-weighted average concentrations of endocrine distributing substances in river water. After the exposure of the probes in the environment, the analytes retained on the sorbent surface were eluted and the extracts obtained were combined with bioassays to assess the environmental risk. Comparing the results, it was proved that Strata-X is more effective at sampling endocrine-disrupting substances than Oasis HLB.

Two years later, Fauvelle et al. (2012) proposed testing two sorbents: Chromabond HRX and Oasis MAX. Chromabond is a polystyrene–divinylbenzene polymer with an

extensive specific surface area and Oasis MAX is a mixed-mode anion-exchange sorbent that provides additional sites for strong anion-exchange interactions. They introduced passive samplers into drinking water and rivers to monitor pesticides. The classic POCIS-Oasis HLB was also used to compare the sampling efficiency between samplers. It turned out that despite the large specific surface area, Chromabond HRX showed low sampling rates of the tested inert compounds and a complete lack of uptake for some acidic pesticides, which may be closely related to the hydrophobic nature of this sorbent. In the case of POCIS-Oasis HLB, a high efficiency of uptake of moderately polar compounds, and some restrictions on the sampling of highly polar and acid analytes were demonstrated. In contrast, the samplers containing Oasis MAX were characterized by high extraction efficiency and satisfactory sampling rates of both neutral and acidic chemicals, except for the most hydrophilic, inert pesticides. The obtained results confirmed the usefulness of the Oasis MAX sampler for sampling acidic compounds from water.

In 2012, Kaserzon et al. (2012) used 600 mg of Oasis WAX (weak anion-exchange sorbent) to increase the uptake of perfluorinated compounds by passive samplers. Comparing the extraction efficiency of POCIS-Oasis HLB and POCIS-Oasis WAX, they were similar, but POCIS-Oasis WAX sampled short-chain perfluorinated compounds more efficiently. This shows that classic POCIS can be used in monitoring perfluorinated compounds, but with a more limited range of analytes than a POCIS-like sampler containing a weak anion-exchange sorbent. Later studies also confirm the usefulness and advantages of Oasis WAX over Oasis HLB used in samplers for the uptake of perfluorinated compounds (Kaserzon et al. 2013, 2014a). In 2016, Li et al. (2016a, b) successfully managed to use only 200 mg of this sorbent for the effective extraction of perfluorinated compounds from surface water, which makes WAX sorbents even more attractive from an economic point of view.

Another sorbent proposed in the literature was Strata X-CW-cation-exchange mixed-mode sorbent, which was placed in a POCIS-like sampler. Carpinteiro et al. (2016) used this probe to determine the sampling rates of corrosion inhibitors, pesticides and pharmaceuticals in river water. Comparative studies showed that the extraction efficiency of the tested analytes was always higher (with one exception) for traditional POCIS-Oasis HLB than for POCIS-Strata X-CW, which excluded the usefulness of this ion exchange sorbent in passive techniques.

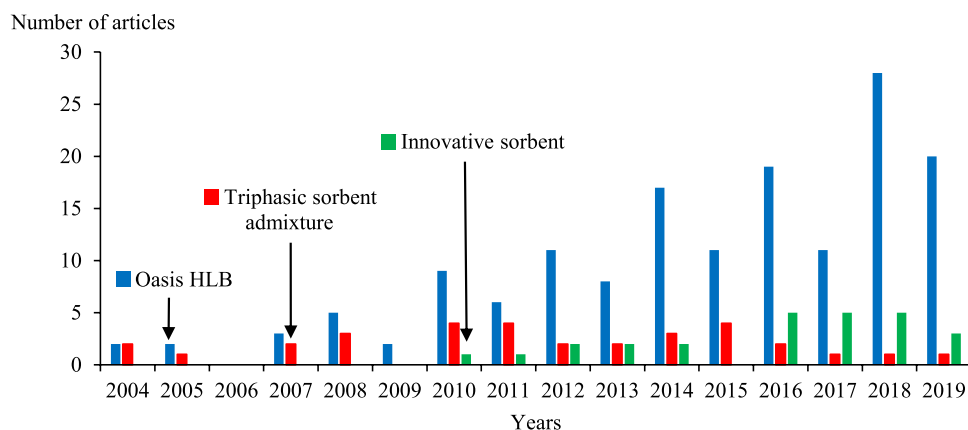
In 2016, ionic liquids were closed between polyether-sulfone membranes for the first time and an innovative POCIS-like sampler was created. Caban et al. (2016) used the following ionic liquids in their research: 1-hexyl-3-methylimidazolium bis[(tri-fluoromethyl)sulfonyl]amide ([C6MIM][TFN]), trihexyl(tetradecyl)phosphonium

dicyanamide ([P666-14][N(CN)₂]), tributyl(tetradecyl)phosphonium *p*-dodecylbenzenesulfonate ([P444-14][DDBS]) and tributyl(ethyl)phosphonium diethylphosphate ([P2444][(2O)₂PO₂]). They compared the sampling efficiency of pharmaceuticals, hormones and phenol derivatives between samplers containing only ionic liquids and samplers containing, as a sorbent, a mixture of an ionic liquid and C₁₈-silica sorbent. The mixture of the ionic liquid ([P666-14][N(CN)₂]) and C₁₈ sorbent used in the sampler was characterized by the highest extraction efficiency of the tested analytes and the best behavior in a developed sampler. The presented research proved the possibility of using ionic liquids as the receiving phase in passive techniques for the sampling of compounds with a wide range of polarity. These conclusions were also confirmed in later studies by Wang et al. (2017) who used only 30 mg of an imidazole ionic liquid in a POCIS-type sampler to accumulate perfluorinated compounds. Comparative studies showed that probes containing ionic liquids displayed a higher extraction capacity for short-chain perfluorinated compounds than POCIS-Oasis HLB and ensured kinetic uptake within 21 days. The calculated time-weighted average concentration for most analytes was consistent with that obtained from active sampling. The obtained results contributed to the creation of further studies on the development of POCIS-like samplers with ionic liquids (Męczykowska et al. 2017b, 2018, 2019).

In 2017 Berho et al. (2017) successfully used molecularly imprinted polymers as a sorbent in a POCIS-like sampler for sampling glyphosate and aminomethylphosphonic acid. A year later, Cao et al. (2018) also used such a modified sampler, this time to accumulate perfluorinated compounds, and compared its extraction efficiency with the previously developed POCIS-WAX. It was proved that POCIS with molecularly imprinted polymers used as a sorbent has a specific selectivity for the tested perfluorinated compounds and can overcome matrix interference. However, such a sampler has not yet been used directly in the aquatic environment to monitor pollution.

In 2017, carbon nanotubes were also used for the first time as a promising sorption material in passive samplers. Jakubus et al. (2016), in their research, proved that the use of carbon nanotubes as the receiving phase allows higher R_s values of the tested analytes (pharmaceuticals, hormones, phenols) to be achieved than when using conventional sorbents. The weight of the sorbent in traditional POCIS is generally 200 mg. But, Jakubus et al. (2016) successfully developed POCIS-like sampler, which used half the amount of sorbent (100 mg). In addition, the carbon nanotubes can be reused as a sorption material. Based on the work of López-Feria et al. (2009), carbon nanotubes can be used as a sorbent at least 100 times with the same efficiency. Considering the facts mentioned above, carbon nanotubes are

Fig. 4 Summary of the number of studies in 2004–2019 years on the POCIS-like sampler depending on the type of sorbents used



an interesting sorbent in POCIS, not only in analytical but also economic terms.

Conclusion

This review describes in detail the possibilities and restrictions on the use of traditional sorbents in POCIS. Since the introduction of the POCIS sampler in 2004, these devices have gained more and more popularity and interest, which is clearly shown in Fig. 4, which shows the amount of research on POCIS over the past 17 years. As can be seen, the huge advantage of the Oasis HLB sorbent over the triphasic sorbent admixture is that it was used in POCIS-like samplers between 2004 and 2020 at least 160 times, compared to 33 times for the admixture (according to the collected literature).

The following uses of POCIS have been identified in the existing literature (Tables 2, 3 and 4):

1. Carrying out the calibration and performance testing of the sampler,
2. Determining the impact of environmental factors (temperature, water pH, dissolved organic matter concentration, mixing the receiving phase, water flow, salinity) on the sampling rate of target compounds,
3. Determining the impact of the type of membrane and/or sorbent used on the sampling efficiency of analytes,
4. Comparing the extraction efficiency of different passive samplers,
5. Screening/monitoring water pollution,
6. Calculating time-weighted average concentrations,
7. Testing various chemical compounds that can perform the function of performance reference compounds in POCIS,
8. Comparing the concentrations of analytes obtained from POCIS with those obtained from spot sampling,

9. Combining POCIS extracts with bioassays to assess environmental risk.

As Fig. 4 shows, the current number of studies that are performed using POCIS-like samplers is about six times greater than the number of tests performed in the first years since the appearance of POCIS in environmental analysis. The amount of literature collected in this review confirms the huge potential of these samplers as potentially reliable devices for monitoring the aquatic environment, and for other important applications. Scientists are constantly developing this extraction technique to minimize its disadvantages and expand its applicability. Attempts to modify the type of sorbent and/or its amount in POCIS-like samplers have repeatedly ended in success and the possibility of using this device to collect strongly polar and ionic compounds, by increasing the extraction efficiency (Table 4). However, Oasis HLB, which is easily available and inexpensive, is still the most popular sorption material. In contrast, the use of a triphasic sorbent admixture has been, over the last few years, small, even smaller than the use of POCIS-like samplers with innovative sorbents (Fig. 4).

One of the basic restrictions of commercial POCIS is the inefficient uptake of strongly hydrophilic and ionic organic compounds from water. The growing number of works on the use of innovative sorption materials to overcome this limitation and the published results allow us to conclude that the type of sorbent may be a key factor in increasing the applicability of POCIS-like samplers. It should be emphasized that the majority of research into new sorption materials for POCIS is in the early stages and further tests, ideas and solutions are needed to develop a reliable sorbent that will allow the sampling of a wide range of chemical compounds.

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