Wydział Chemii Uniwersytetu Gdańskiego

mgr Klaudia Godlewska

NANORURKI WĘGLOWE JAKO INNOWACYJNE SORBENTY W EKSTRAKCJI PASYWNEJ MIKROZANIECZYSZCZEŃ ŚRODOWISKA WODNEGO

Promotor:
dr hab. Monika Paszkiewicz, prof. UG

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P1 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Application of the polar organic chemical integrative sampler for isolation of environmental micropollutants - a review, *Critical Reviews in Analytical Chemistry* (2020), 50 (1), 1-28, DOI:10.1080/10408347.2019.1565983, IF_{2020} 6,54

P2 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Pollutant analysis using passive samplers: principles, sorbents, calibration and applications. A review, *Environmental Chemistry Letters* (2021), 19 (1), 465-520, DOI:10.1007/s10311-020-01079-6, IF_{2020} 9,03

P3 K. Godlewska, A. Jakubus, P. Stepnowski, M. Paszkiewicz, Impact of environmental factors on the sampling rate of β-blockers and sulfonamides from water by a carbon nanotube-passive sampler, *Journal of Environmental Sciences* (2021), 101, 413-427, DOI:10.1016/j.jes.2020.08.034, IF_{2020} 5,57

P4 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Carbon nanotubes, activated carbon and Oasis HLB as sorbents of passive samplers for extraction of selected micropollutants - comparison of sampling rates and extraction efficiency, *Microchemical Journal* (2022), 172, 1-12, DOI:10.1016/j.microc.2021.106975, IF_{2020} 4,82

P5 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Carbon nanotube-passive samplers as novel tools for sampling and determining micropollutants in the aquatic environment, *Science of the Total Environment* (2022), 836, 155551, DOI:10.1016/j.scitotenv.2022.155551, IF_{2020} 7,96

Sumaryczny IF[1] prac wchodzących w skład rozprawy doktorskiej – 33,92, sumaryczna liczba cytowań[2] prac wchodzących w skład rozprawy doktorskiej – 26.

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[2] Liczba cytowań publikacji według bazy Web of Science (WoS)

Spis treści

Wykaz skrótów

3,5-DCP - 3,5-dichlorofenol
8-CNT - niemodyfikowane wielościenne nanorurki węglowe o średnicy zewnętrznej < 8 nm, ang. *unmodified multi-walled carbon nanotubes with an outside diameter of < 8 nm*
50-CNT - niemodyfikowane wielościenne nanorurki węglowe o średnicy zewnętrznej > 50 nm, ang. *unmodified multi-walled carbon nanotubes with an outside diameter of > 50 nm*
ACE – acebutolol
ACN – acetonitryl
ATE – atenolol
CBZ - karbamazepina
CEC – zanieczyszczenia wzbudzające coraz większe obawy, ang. *contaminants of emerging concern*
CNT - nanorurki węglowe, ang. *carbon nanotubes*
CNT-PSD – urządzenia do pasywnego pobierania próbek zawierające nanorurki węglowe jako sorbent, ang. *passive sampling device containing carbon nanotubes as a sorbent*
COOH8-CNT - wielościenne nanorurki węglowe modyfikowane grupami –COOH o średnicy zewnętrznej < 8 nm, ang. *multi-walled carbon nanotubes modified with the –COOH groups with an outer diameter of < 8 nm*
C_{TWA} - średnie ważone w czasie stężenie, ang. *time-weighted average concentration*
DEZ – dezypramina
DIC – diklofenak
DOM - rozpuszczona materia organiczna, ang. *dissolved organic matter*
E2 - 17-β-estradiol
EDC - związki zaburzające gospodarkę hormonalną, ang. *endocrine disrupting compounds*
EE2 - 17-α-etynyloestradiol
ESI – jonizacja przez elektrorozpraszanie ang. *electrospray ionization*
hCNT - helikalne wielościenne nanorurki węglowe o średnicy zewnętrznej 100-200 nm, ang. *helical multi-walled carbon nanotubes with an outer diameter 100-200 nm*
HPLC-DAD - wysokosprawna chromatografia cieczowa z detektorem fotodiodowym, ang. *high performance liquid chromatography with diode array detector*
IMI - imipramina
KET - ketoprofen
LC-MS/MS - wysokosprawna chromatografia cieczowa sprzężona ze spektrometrią mas ang. *high performance liquid chromatography coupled with tandem mass spectrometry*
LOD - granica wykrywalności, ang. *limit of detection*
LOQ - granica oznaczalności, ang. *limit of quantification*
LQp - granica oznaczalności próbnika pasywnego, ang. *limit of quantification of passive sampler*
LQg - granica oznaczalności punktowego pobierania próbek (ang. *limit of quantification of grab sampling)*
MeOH - metanol
MET - metoprolol
MTX - metotreksat
MWCNT - wielościenne nanorurki węglowe, ang. *multi-walled carbon nanotubes*
NAD - nadolol
NAP - naproksen
NLPZ - niesteroidowe leki przeciwzapalne
NW – nie wykryto
Oasis HLB – ang. *hydrophilic-lipophilic balanced copolymer [poly(di-vinylbenzene)-co-N-vinylpyrrolidone]*
Oasis-PSD - urządzenia do pasywnego pobierania próbek zawierające Oasis HLB j ako sorbent, ang. *passive sampling device containing Oasis HLB as a sorbent*
OH8-CNT - modyfikowane grupami –OH wielościenne nanorurki węglowe o średnicy zewnętrznej < 8 nm, ang. *multi-walled carbon nanotubes modified with the –OH groups with an outer diameter of < 8 nm*
PBA – bisfenol A
PES - polieterosulfonowe
PIN - pindolol
PNP – p-nitrofenol
POCIS – ang. *polar organic chemical integrative sampler*
PRO - propranolol
PSD - urządzenia do pasywnego pobierania próbek, ang. *passive sampling devices*
R_s – współczynnik szybkości pobierania, ang. *sampling rate*
s8-CNT - krótkie niemodyfikowane wielościenne nanorurki węglowe o średnicy zewnętrznej < 8 nm, ang. *short unmodified multi-walled carbon nanotubes with an outside diameter of < 8 nm*
SCP – sulfachloropirydazyna
SDD – sulfadimidyna
SDZ - sulfadiazyna
SDX - sulfadimetoksyna
SMP – sulfametoksypirydazyna
SMT – sulfametizol
SMX – sulfametoksazol
SMZ – sulfamerazyna
SPD – sulfapirydyna
SPMD - półprzepuszczalne urządzenia membranowe, ang. *semi permeable membrane devices*
STZ - sulfatiazol
TLPD - tricykliczne leki przeciwdepresyjne
QqQ – potrójny kwadrupol, ang. *triple quadrupole*

1. Streszczenie

W niniejszej pracy przedstawiono wyniki badań nad oceną możliwości zastosowania nanorurek węglowych jako sorbentu w urządzeniach do pasywnego pobierania próbek (CNT-PSD). Załączony dorobek publikacji prezentuje przeprowadzone eksperymenty, których wynikiem było opracowanie kinetycznego próbnika pasywnego zawierającego nanorurki węglowe (CNT) jako fazę odbierającą.

W pierwszym etapie badań opracowano i poddano walidacji metody analityczne pozwalające na oznaczenie wybranych mikrozanieczyszczeń w wodzie z wykorzystaniem wysokosprawnej chromatografii cieczowej oraz wysokosprawnej chromatografii cieczowej sprzężonej ze spektrometrią mas. Następnie przeprowadzono semi-statyczną kalibrację przygotowanych próbników pasywnych zawierających wielościenne nanorurki węglowe. Zastosowane CNT różniły się między sobą średnicą zewnętrzną, długością, powierzchnią właściwą czy też rodzajem grup funkcyjnych. Na podstawie otrzymanych wyników wybrano wielościenne nanorurki węglowe modyfikowane grupami –COOH o średnicy zewnętrznej < 8 nm (COOH8-CNT), jako najbardziej efektywne do ekstrakcji β-blokerów i sulfonamidów z fazy wodnej. Natomiast niemodyfikowane wielościenne nanorurki węglowe o średnicy zewnętrznej < 8 nm (8-CNT) wybrano jako najlepsze do pobierania leków cytostatycznych, niesteroidowych leków przeciwzapalnych, tricyklicznych leków przeciwdepresyjnych, pochodnych fenolu oraz hormonów. Krzywe pobierania związków docelowych z wody przy zastosowaniu wybranych nanorurek węglowych jako sorbentów charakteryzowały się liniowością, stąd określono opracowane próbniki pasywne jako kinetyczne.

Kolejnym etapem był wybór odpowiedniego eluentu do desorpcji analitów zatrzymanych na powierzchni nanorurek węglowych. Przeprowadzono badania z wykorzystaniem kilku rodzajów rozpuszczalników oraz ich mieszanin w celu uzyskania jak najwyższych efektywności elucji. Wykazano, iż przy zastosowaniu mieszaniny ACN:MeOH:CH_3COOH (1:1:1) uzyskano najwyższe efektywności ekstrakcji dla wszystkich badanych związków chemicznych.

Następnie określono wpływ czynników środowiskowych na szybkości pobierania (R_s) analitów przez CNT-PSD. W tym celu, przeprowadzono eksperymenty, w których woda otaczająca próbnik charakteryzowała się różnymi parametrami fizykochemicznymi, mianowicie: różnymi wartościami pH, stężeniami rozpuszczonych kwasów humusowych oraz wartościami zasolenia. Zbadano również wpływ mieszania wody na wartości R_s analitów. Uzyskane wyniki wskazują, iż pH wody, obecność rozpuszczonych kwasów humusowych czy zasolenie nie wpływają na szybkości pobierania hormonów, leków cytostatycznych, pochodnych fenolu, niesteroidowych leków przeciwzapalnych, tricyklicznych leków przeciwdepresyjnych przez 8-CNT-PSD. Natomiast w przypadku pobierania sulfonamidów przez COOH8-CNT-PSD wszystkie wyżej wspomniane czynniki środowiskowe miały wpływ na wartości R_s. W przypadku β-blokerów, jedynie zasolenie wody powyżej 7 PSU wpływało na wartości R_s tych analitów, pozostałe czynniki nie powodowały istotnych zmian w tym zakresie. Zaobserwowano, iż wzrost szybkości mieszania matrycy nie wpłynął na szybkości pobierania badanych związków. Zauważono jednak spadek wartości R_s dla wszystkich analitów w warunkach statycznych w porównaniu z warunkami dynamicznymi.

Dokonano również oceny wiarygodności zastosowanego systemu kalibracyjnego. W tym celu wykonano kalibrację zaprojektowanych próbników pasywnych za pomocą metody przepływowej (system otwarty ze stałym dopływem wody zawierającej znane stężenie analitów) oraz metody semi-statycznej (system zamknięty z delikatnym mieszaniem wody zawierającej znane stężenie analitów). Nie wykazano istotnych różnic pomiędzy wyznaczonymi R_s uzyskanymi przy zastosowaniu wyżej wspomnianych metod kalibracji co udowadnia, iż każda z nich jest miarodajna i wiarygodna.

Ostatnim etapem badań przeprowadzonych w ramach niniejszej rozprawy doktorskiej było zastosowanie próbników CNT-PSD w monitorowaniu wybranych mikrozanieczyszczeń w trzech rodzajach wód powierzchniowych, a następnie regeneracja wykorzystanych CNT i ich ponowne użycie w ekstrakcji pasywnej badanych analitów ze ścieków oczyszczonych. Uzyskane wyniki potwierdzają wysoki potencjał stosowania CNT-PSD do pobierania i zatężania szerokiej gamy związków chemicznych różniących się istotnie właściwościami fizykochemicznymi ze środowiska wodnego.

Słowa kluczowe: próbniki pasywne, nanorurki węglowe, mikrozanieczyszczenia, monitoring środowiska wodnego

2. Abstract (w j. angielskim)

This paper presents the research results on the assessment of the possibility of using carbon nanotubes as a sorbent in passive sampling devices (CNTs-PSDs). The attached articles present the conducted experiments, which resulted in the development of a kinetic passive sampler containing carbon nanotubes as the receiving phase.

In the first stage of the research, analytical methods allowing the determination of selected micropollutants in water with the use of high-performance liquid chromatography and high-performance liquid chromatography coupled with mass spectrometry were developed and validated. Then, a semi-static calibration of passive samplers containing multi-walled carbon nanotubes with different outer diameter, length, specific surface, or the type of functional groups was carried out. Based on the obtained results, multi-walled carbon nanotubes modified with –COOH groups with an outer diameter < 8 nm (COOH8-CNTs) were selected as the best for the sampling of β-blockers and sulfonamides. In contrast, unmodified multi-walled carbon nanotubes with an outer diameter < 8 nm (8-CNTs) were selected as the best for the sampling of cytostatic drugs, non-steroidal anti-inflammatory drugs, tricyclic antidepressants, phenol derivatives and hormones. The curves of uptake of target compounds from water using the above-mentioned carbon nanotubes as sorbents were characterized by linearity, hence the developed passive samplers were defined as kinetic.

The next step was to select an appropriate eluent for the desorption of analytes retained on the surface of carbon nanotubes. Several types of solvents and their mixtures were tested to obtain the highest elution efficiency. It was shown that the highest extraction efficiency was obtained for all tested chemical compounds using the ACN:MeOH:CH_3COOH (1:1:1).

The following important stage of the research was to determine the influence of environmental factors on the sampling rate (R_s) of analytes by CNTs-PSDs. For this purpose, experiments were carried out in which the water surrounding the samplers was characterized by different physicochemical parameters, namely: different pH values, concentrations of dissolved humic acids and salinity. The influence of water mixing on the R_s values of analytes was also investigated. The obtained results indicate that the water pH, the presence of dissolved humic acids or salinity do not affect the sampling of hormones, cytostatic drugs, phenol derivatives, non-steroidal anti-inflammatory drugs, and tricyclic antidepressants using 8-CNTs-PSDs. However, in the case of sulfonamides uptake by COOH8-CNTs-PSDs, all the above-mentioned environmental factors influenced the R_s values. In the case of β-blockers, only the salinity of water above 7 PSU influenced the R_s of these analytes, the other factors did not cause significant changes in the sampling rate of these compounds. It was observed that the increase in the speed of mixing the matrix did not affect the R_s of the tested compounds. However, a decrease in the R_s value was noted for all analytes under static conditions compared to dynamic conditions.

The reliability of the applied calibration system was also assessed. For this purpose, the developed passive samplers were calibrated using the flow-through method (open system with a constant inflow of water spiked with analytes) and the semi-static method (closed system with gentle mixing of water spiked with analytes at the beginning of the experiment). There were no significant differences between the determined R_s obtained using the above-mentioned calibration methods, which proves that each of them is reliable and verifiable.

The last stage of the research carried out as part of this doctoral dissertation was the use of CNTs-PSDs in the monitoring of selected micropollutants in three types of surface waters, and then the regeneration of the used CNTs and their reuse in the passive extraction of the target analytes from treated sewage. The obtained results confirm the high potential of using CNTs-PSDs for the sampling and concentration of a wide range of chemical compounds that differ significantly in their physicochemical properties from the aquatic environment.

Keywords: passive samplers, carbon nanotubes, micropollutants, monitoring of the aquatic environment

3. Wstęp

Od ponad dwudziestu lat, spośród wszystkich mikrozanieczyszczeń, które mogą występować w środowisku wodnym i ściekach, szczególną uwagę zwraca się na pozostałości różnych leków i ich metabolitów, jak również związki zaburzające gospodarkę hormonalną (EDC, ang. *endocrine disrupting compounds*). Substancje te, określane mianem zanieczyszczeń „wzbudzających coraz większe obawy” (CEC, ang. *contaminants of emerging concern*), stanowią potencjalne zagrożenie dla organizmów żywych i zdrowia ludzkiego. Dane literaturowe wskazują, iż ponad 3000 środków leczniczych jest stosowanych w celu leczenia lub zapobiegania chorób u ludzi i zwierząt [1–4]. Pod tym pojęciem kryje się szeroka grupa różnorodnych związków organicznych, w tym antybiotyków, leków przeciwzapalnych, leków psychotropowych, przeciwbólowych, regulatorów lipidów krwi, β-blokerów, środków kontrastowych i leków cytostatycznych. Natomiast EDC to grupa substancji chemicznych wpływających na rozwój płciowy, rozmnażanie, układ hormonalny dzikich zwierząt i ludzi, nawet na bardzo niskim poziomie stężeń. Związki te są wydalane przez ludzi i zwierzęta hodowlane (np. hormony estrogenowe) oraz pochodzą z produktów wytworzonych przez człowieka (np. pochodne fenolu). Wspomniane mikrozanieczyszczenia przedostają się do środowiska wodnego na skutek różnych mechanizmów, m.in. nieodpowiedniej utylizacji farmaceutyków i odpadów, nadmiernego zużycia środków leczniczych i ich ponadnormatywnego wydalania przez ludzi i zwierzęta, jak też w wyniku bezpośredniego uwalniania ze strumieni zanieczyszczeń przemysłowych. Wiele substancji leczniczych ulega procesom metabolicznym tylko w niewielkim stopniu, a pozostała część leku jest wydalana z organizmu w postaci natywnej [5,6]. Dodatkowo, farmaceutyki i EDC często charakteryzują się wysokim stopniem polarności, a zatem dobrą rozpuszczalnością w wodzie, przez co są nieefektywnie usuwane w konwencjonalnych oczyszczalniach ścieków, tym samym z łatwością odprowadzane są do wód naturalnych wraz ze strumieniem ścieków oczyszczonych. W rezultacie, coraz większa ilość tych mikrozanieczyszczeń przedostaje się do wód powierzchniowych i podziemnych, a następnie migruje i ulega różnego rodzaju transformacjom chemicznym w środowisku wodnym. Bardziej trwałe substancje mogą być akumulowane w ekosystemach wodnych, stwarzając tym samym zagrożenie dla organizmów. Woda zanieczyszczona pozostałościami leków i EDC może skutecznie zaburzać równowagę ekosystemów, wpływając na bioróżnorodność organizmów wodnych, procesy nitryfikacji i obieg pierwiastków biogennych. Ale przede wszystkim związki te mogą być toksyczne dla organizmów żywych, wpływać na układ hormonalny organizmów (w tym ludzi), powodując feminizację, obniżoną płodność oraz bardzo niebezpieczne zjawisko lekooporności [4,7,8].

Obecność farmaceutyków i EDC w ściekach oczyszczonych i nieoczyszczonych została dobrze udokumentowana na całym świecie. Poziom stężeń tych mikrozanieczyszczeń waha się od kilku do kilku tysięcy ng/l w ściekach oczyszczonych, natomiast w ściekach surowych stężenie tych analitów bardzo często przekracza poziom 100 μg/l [3,9,10]. Dodatkowo, w niektórych badaniach wykryto farmaceutyki na ekstremalnie wysokim poziomie stężeń (> 1000 μg/l) w ściekach pochodzących z przemysłu farmaceutycznego [11,12]. W wodach powierzchniowych najczęściej wykrywane są: niesteroidowe leki przeciwzapalne, takie jak: ketoprofen, naproksen, diklofenak oraz pochodne fenolu i hormony, w tym: 17-β-estradiol, 17-α-etynyloestradiol czy bisfenol A. W rzeczywistości związki te wykryto powyżej granicy oznaczalności w wodzie rzecznej na terenie Europy, Azji, Afryki czy też Ameryki [13–17]. Powszechnie występującym w wodzie powierzchniowej związkiem (w stężeniach od 1 do 2200 ng/l) jest karbamazepina. Lek ten uważany jest za trwałe zanieczyszczenie środowiska ze względu na swoją odporność na degradację, nawet w nowoczesnym wielostopniowym procesie oczyszczania ścieków, stąd zainteresowanie naukowców tym związkiem jako możliwym markerem antropogenicznym w wodzie [18].

Obecnie nie istnieją regulacje prawne dotyczące oceny jakości wody pod względem zawartości farmaceutyków i EDC, pomimo ich potencjalnego zagrożenia dla środowiska i zdrowia publicznego. Jednakże, Parlament Europejski w 2013 roku zatwierdził Dyrektywę 2013/39/UE [19], która wprowadziła obowiązek monitorowania w wodach powierzchniowych substancji chemicznych z tzw. listy obserwacyjnej. Lista ta obejmuje związki, których negatywny wpływ na środowisko wodne jest udowodniony (np. 17-β-estradiol oraz 17-α-etynyloestradiol). Natomiast w 2020 roku w Decyzji 2020/1161/UE [20] opublikowano listę ostrzegawczą zawierającą 18 mikrozanieczyszczeń wzbudzających niepokój (w tym sulfametoksazol), które powinny być monitorowane w celu zebrania informacji do dalszej oceny ich ryzyka środowiskowego. W związku z tym zagrożenia związane z obecnością farmaceutyków i EDC w środowisku wodnym oraz konieczność monitorowania poziomu stężeń tych związków jest bezsprzeczna.

Monitorowanie poziomu stężeń pozostałości substancji leczniczych jest zazwyczaj przeprowadzane za pomocą analiz instrumentalnych punktowo pobranych próbek po ich odpowiednim przygotowaniu. Procedura ta ma niestety szereg wad i ograniczeń. Po pierwsze, analiza jakościowa i ilościowa punktowo pobranych próbek nie dostarcza holistycznego obrazu jakości wody w danym zbiorniku. Podejście to pozwala na określenie stężeń zanieczyszczeń jedynie w danym miejscu i czasie pobrania próbki. Po drugie stężenie związków chemicznych może ulegać znacznym wahaniom lub mogą występować losowe napływy zanieczyszczeń w czasie. Wielokrotne pobieranie próbek w celu uwzględnienia zdarzeń epizodycznych może być trudne do wykonania pod względem fizycznym, organizacyjnym i finansowym, zwłaszcza na obszarach oddalonych od lądu. Konieczność okresowego pobierania próbek wody, a następnie ekstrakcja i zatężanie analitów w laboratorium powoduje, iż podejście to jest dość pracochłonne [21,22].

Z tego względu, coraz większą uwagę przyciągają metody pasywnego (biernego) pobierania próbek, które pozwalają na jednoczesne pobieranie i zatężanie badanych analitów z różnych matryc. Od czasu pojawienia się w 1987 roku pierwszego pasywnego próbnika stosowanego w wodach powierzchniowych, urządzenia do pasywnego pobierania próbek (PSD, ang. *passive sampling devices*) stopniowo stają się atrakcyjną alternatywą do monitorowania jakości wód. Techniki pasywne wykorzystują proces swobodnego przepływu (I prawo dyfuzji Ficka) cząsteczek analitu z badanej matrycy do wnętrza próbnika pasywnego (fazy odbierającej), gdzie ulegają zatrzymaniu. Transport cząsteczek związku chemicznego do fazy odbierającej trwa do momentu ustalenia się stanu równowagi bądź też do momentu zakończenia ekspozycji próbnika w środowisku. Wyróżniamy próbniki działające w trybie równowagowym lub kinetycznym. Próbniki równowagowe są eksponowane w środowisku, aż do osiągnięcia stanu równowagi między stężeniem analitu w fazie odbierającej a stężeniem analitu w matrycy otaczającej próbnik. Próbniki kinetyczne są zaprojektowane w taki sposób, aby akumulacja docelowych związków była liniowa w czasie ekspozycji próbnika [23]. Techniki pasywne posiadają wiele istotnych zalet, w tym prostotę obsługi, niski koszt, brak konieczności korzystania ze skomplikowanego sprzętu, brak konieczności dostarczania energii, bezobsługowość i możliwość uzyskania miarodajnych wyników. Dzięki temu, iż próbniki pasywne umieszczane są w środowisku na okres od kilku dni do kilku miesięcy możliwe jest wykrywanie i analizowanie związków chemicznych w niskich i bardzo niskich stężeniach. Stanowi to ogromną przewagę nad metodami punktowego pobierania próbek, w których stężenia analitów są często poniżej granicy wykrywalności (LOD, ang. *limit of detection*) oraz granicy oznaczalności (LOQ, ang. *limit of quantification*) wybranej metody instrumentalnej, co nie pozwala na oznaczanie śladowych ilości mikrozanieczyszczeń w wodzie [**P1**].

PSD mogą mieć różną konstrukcję, ale wszystkie zawierają fazę odbierającą (sorbent lub ciecz) o wysokim powinowactwie do badanych związków chemicznych. W wyniku długotrwałej ekspozycji PSD w środowisku możliwe jest wyznaczenie średnich ważonych w czasie stężeń (C_{TWA}, ang. *time-weighted average concentration*) analitów, zgodnie ze wzorem przedstawionym poniżej:

$$C_{TWA} = \frac{C_S \times M_S}{R_S \times t} \tag{1}$$

gdzie C_{TWA} [ng/l] to średnie ważone w czasie stężenie analitu w wodzie, C_s [ng/g] to stężenie analitu w próbniku po czasie t [d], M_s [g] to masa sorbentu a R_s [l/d] to współczynnik szybkości pobierania analitu przez próbnik [**P1**].

Jednakże, aby poprawnie wyznaczyć C_{TWA} zatężanych mikrozanieczyszczeń należy uprzednio przeprowadzić kalibracje wykorzystywanych próbników pasywnych w celu wyznaczenia współczynników szybkości pobierania (R_s ang. *sampling rate*) analitów. Zgodnie z danymi literaturowymi, można zastosować trzy metody kalibracji próbników: 1) kalibracja statyczna lub semi-statyczna, 2) kalibracja statyczna odnawialna, 3) kalibracja przepływowa [24]. Kalibrację statyczną przeprowadza się w systemie zamkniętym zawierającym wodny roztwór wzorcowy analitów wprowadzony na początku eksperymentu. Kalibracja semi-statyczna jest przeprowadzana w taki sam sposób przy zastosowaniu delikatnego mieszania wody w celu lepszego odzwierciedlenia warunków środowiskowych. Kalibrację statyczną odnawialną wykonuje się w układzie zamkniętym, do którego wprowadzany jest wodny roztwór wzorcowy analitów w stałych odstępach czasu. Kalibracja przepływowa wykonywana jest w systemie otwartym, do którego doprowadzany jest wodny roztwór wzorcowy o znanym i stałym stężeniu analitów. Kalibracja statyczna, semi-statyczna i odnawialna są powszechnie wykorzystywane ze względu na łatwość wykonania, niską cenę i małą pracochłonność. Natomiast metoda przepływowa jest najbardziej zbliżona do warunków panujących w środowisku i określana jest jako najbardziej wiarygodna. Jak wcześniej wspomniano, na podstawie wartości R_s i zawartości analitów w fazie odbierającej można obliczyć średnie ważone w czasie stężenie (C_{TWA}) analitów w środowisku. Dlatego też prawidłowa kalibracja próbnika ma kluczowe znaczenie dla określenia poziomów stężeń badanych związków [**P2**].

Niestety wartość R_s jest specyficzna dla każdego analitu i może zależeć od wielu różnych czynników (np. rodzaju sorbentu, membrany, warunków środowiskowych, konstrukcji próbnika). W przypadku mikrozanieczyszczeń posiadających grupy funkcyjne, które występują w różnych formach jonowych w roztworze o określonej wartości pH, wyznaczenie wpływu tego parametru jest niezbędne podczas kalibracji próbników. Ponadto pH roztworu może wpływać na właściwości fizykochemiczne związku chemicznego, przede wszystkim rozpuszczalność, a tym samym na proces pobierania analitów. Innym czynnikiem zewnętrznym, który może determinować wartość R_s, jest obecność rozpuszczonej materii organicznej (DOM, ang. *dissolved organic matter*) w wodzie. Miarą całkowitego stężenia DOM jest stężenie rozpuszczonego węgla organicznego, które w środowisku wodnym wynosi zwykle 2–10 mg/l. Większość rozpuszczonego węgla organicznego w wodach naturalnych to frakcja fulwowa i humusowa. Rozpuszczona materia organiczna może oddziaływać ze związkami docelowymi w wodzie, co zmniejsza dostępność tych analitów dla fazy odbierającej. Ponadto, wysokie stężenie DOM może blokować pory membrany, co zmienia kinetykę procesu dyfuzji poprzez tworzenie warstwy sorpcyjnej materii organicznej na membranie. Biorąc pod uwagę fakt, iż wartości zasolenia wód środowiskowych mieszczą się w szerokim zakresie 0-35 PSU, badanie wpływu tego czynnika na proces pobierania analitów z wody wydaje się zasadne. Źródła literaturowe wskazują, iż rozpuszczalność większości zanieczyszczeń organicznych w wodzie zmniejsza się wraz ze wzrostem stężenia soli z powodu tzw. efektu wysalania [25,26]. Efekt ten powinien teoretycznie zwiększyć szybkość pobierania analitów przez próbnik. Jednakże, z drugiej strony kompleksowanie organicznych substancji chemicznych z wielowartościowymi kationami oraz interakcje pomiędzy jonami związków organicznych a jonami soli mogą hamować i opóźniać pobieranie docelowych zanieczyszczeń. Również temperatura jest brana pod uwagę jako czynnik, który może wpływać na wartości R_s ze względu na fakt, iż teoretycznie wzrost temperatury wody powinien zwiększyć ruchliwość analitów i przyspieszyć ich przenoszenie z wody do fazy odbierającej w próbniku. Jako kolejny ważny czynnik środowiskowy, który może potencjalnie wpływać na szybkość pobierania analitów należy wskazać stopniowe zarastanie membrany lub bezpośrednio fazy odbierającej biofilmem (ang. *biofouling*). Jest to proces spowodowany przez mikroorganizmy, zwierzęta, rośliny lub glony.

Rosnący bioflm zmniejsza przepuszczalność membrany zmniejszając tym samym powierzchnię do pasywnej ekstrakcji zanieczyszczeń. Udowodniono, iż membrany polieterosulfonowe (PES) są uważane za mniej podatne na tworzenie się biofilmu (ze względu na ich hydrofilowy charakter) niż membrany z polietylenu o niskiej gęstości stosowane w półprzepuszczalnych urządzeniach membranowych (SPMD, ang. *semi permeable membrane devices*) czy Chemcatchers® [27,28]. Oprócz czynników wymienionych powyżej, ruch wody może mieć również istotne znaczenie, zwłaszcza w przypadku próbnika kinetycznego, gdzie istnieje silna zależność pomiędzy pobieraniem analitów a warstwą graniczną woda/membrana. Przyjmuje się, iż zwiększenie szybkości mieszania czy też przepływu wody powinno zmniejszyć grubość warstwy granicznej, co jest równoważne zwiększeniu szybkości pobierania analitów przez pasywny próbnik kinetyczny. Biorąc powyższe pod uwagę, kluczowe jest, aby podczas kalibracji próbników pasywnych zbadać wpływ warunków środowiskowych na wyznaczone R_s lub też przeprowadzić kalibrację w wodzie o parametrach fizykochemicznych zbliżonych do parametrów wody środowiskowej, w której będzie docelowo umieszczony próbnik. Zasada działania urządzeń do pasywnej ekstrakcji, metody ich kalibracji i czynniki środowiskowe wpływające na ich działanie przedstawiono w pracy przeglądowej [**P2**].

Do pobierania zanieczyszczeń organicznych z wody bardzo często stosowany jest próbnik typu POCIS (POCIS, ang. *polar organic chemical integrative sampler*) oraz jego różnego rodzaju modyfikacje. W POCIS jako fazę odbierającą stosuje się stały sorbent znajdujący się pomiędzy dwiema membranami (najczęściej PES) a całość jest szczelnie zamknięta za pomocą metalowych pierścieni. Najpopularniejszym sorbentem stosowanym w POCIS jest Oasis HLB (Oasis HLB, ang. *hydrophilic-lipophilic balanced copolymer [poly(di-vinylbenzene)-co-N-vinylpyrrolidone]*), który umożliwia pobieranie analitów o charakterze hydrofilowym ($5 \geq \log K_{ow} \geq 0$). Jednakże, coraz częściej prowadzi się modyfikacje komercyjnie dostępnych faz odbierających w celu zwiększenia zakresu ich stosowalności poprzez np. stosowanie innowacyjnych sorbentów w próbnikach typu POCIS. Charakterystykę próbników POCIS oraz szczegółowy opis możliwości zastosowania konwencjonalnych i innowacyjnych sorbentów wykorzystywanych w tego typu próbnikach opisano w pracy przeglądowej [**P2**, **Tabela 1**].

Wielokrotnie udowodniono, iż nanorurki węglowe (CNT, ang. *carbon nanotubes*) charakteryzują się wysokim potencjałem sorpcyjnym zarówno dla pojedynczych analitów jak i dla złożonych mieszanin związków chemicznych różniących się znacząco właściwościami fizykochemicznymi. Wykazano, iż CNT mogą być stosowane jako sorbenty w ekstrakcji związków o log $K_{ow} < 4$ takich jak: większość farmaceutyków, substancji stosowanych w produktach do pielęgnacji ciała, detergentów i hormonów, ale również związków o log $K_{ow} > 4$, w tym większości polichlorowanych bifenyli, wielopierścieniowych węglowodorów aromatycznych czy chlorowanych dioksyn. Co ważniejsze, powierzchnię nanorurek węglowych można w łatwy sposób modyfikować nadając im pożądane właściwości, co zwiększa zakres ich stosowalności jako sorbentów. Wiele badań porównawczych dowiodło, iż CNT były bardziej skuteczne lub tak skuteczne jak inne powszechnie stosowane sorbenty, takie jak: krzemionka modyfikowana grupami C_{18}, węgiel aktywny lub żywice makroporowate [29–31]. Dzięki swoim unikalnym właściwościom sorpcyjnym oraz możliwości regeneracji i ponownego użycia, CNT stanowią obiecujący sorbent w technikach pasywnych nie tylko pod względem analitycznym, ale również ekonomicznym. Istotna wydaje się więc dokładna ocena możliwości zastosowania CNT jako sorbentów w urządzeniach do pasywnego pobierania próbek (CNT-PSD, ang. *passive sampling devices containing carbon nanotubes as a sorbent*). Dlatego też, w ramach niniejszej pracy doktorskiej postanowiono przeprowadzić nowatorskie badania nad możliwością zastosowania nanorurek węglowych jako sorbentów w próbnikach pasywnych w celu pobierania i zatężania szerokiej gamy mikrozanieczyszczeń środowiska wodnego. Na **Rysunku 1** przedstawiono główne etapy badań.

Wyniki eksperymentów przeprowadzonych w ramach niniejszej pracy doktorskiej, zostały w całości opublikowane w recenzowanych czasopismach o zasięgu międzynarodowym.

Rysunek 1 Schemat badań wykonanych w ramach niniejszej pracy doktorskiej [*opracowanie własne*]

4. Cel pracy

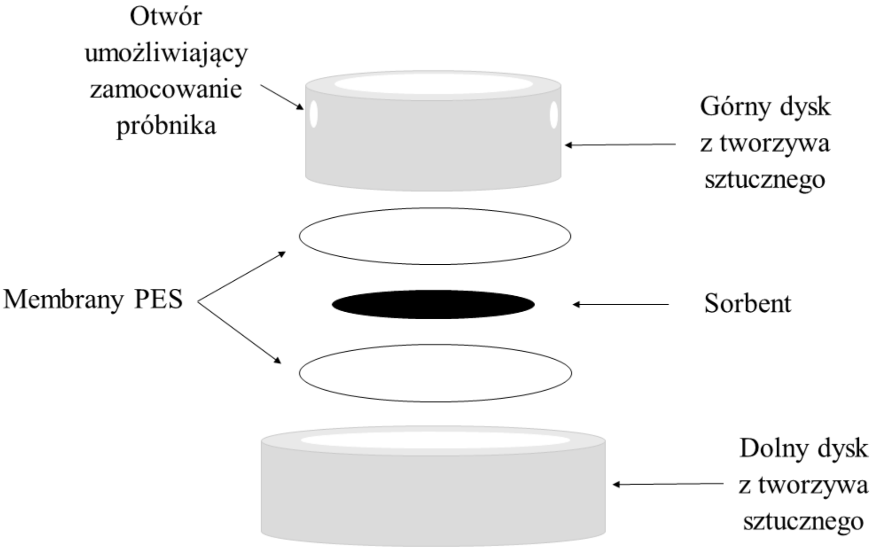
Celem niniejszej rozprawy doktorskiej była ocena możliwości zastosowania nanorurek węglowych jako innowacyjnych sorbentów w urządzeniach do pasywnego pobierania (CNT-PSD) mikrozanieczyszczeń środowiska wodnego. W tym celu przeprowadzono szereg eksperymentów z zastosowaniem różnego rodzaju CNT oraz zróżnicowanych warunków środowiskowych podczas ekspozycji próbników pasywnych w wodzie. Jako związki docelowe wybrano sulfonamidy, β-blokery, niesteroidowe leki przeciwzapalne (NLPZ), tricykliczne leki przeciwdepresyjne (TLPD), leki cytostatyczne, hormony i pochodne fenolu należące do najpowszechniej występujących mikrozanieczyszczeń oznaczanych w środowisku wodnym. Po przeprowadzeniu badań laboratoryjnych, CNT-PSD zostały umieszczone bezpośrednio w warunkach naturalnych wód powierzchniowych (rzeka, jezioro, morze) w celu określenia średnich ważonych w czasie stężeń badanych mikrozanieczyszczeń. Wiarygodność otrzymanych wyników sprawdzano stosując urządzenia do pasywnego pobierania próbek zawierające komercyjnie dostępny sorbent Oasis HLB (Oasis-PSD). Dokonano również oceny możliwości regeneracji CNT oraz ich ponownego zastosowania w ekstrakcji pasywnej.

Cel główny postanowiono zrealizować przez następujące cele szczegółowe:

1. Opracowanie metod analitycznych z wykorzystaniem technik chromatografii cieczowej i chromatografii cieczowej sprzężonej ze spektrometrią mas dla wszystkich oznaczanych analitów.
2. Zbadanie możliwości zastosowania różnego rodzaju nanorurek węglowych jako sorbentów w próbnikach pasywnych.
3. Kalibracja próbników pasywnych metodą semi-statyczną oraz metodą przepływową w celu wyznaczenia współczynników szybkości pobierania analitów oraz oceny wiarygodności zastosowanych systemów kalibracyjnych.
4. Określenie wpływu czynników środowiskowych (pH wody, zasolenie, stężenie rozpuszczonych kwasów humusowych, mieszanie oraz szybkość przepływu fazy wodnej) na szybkości pobierania analitów.
5. Zastosowanie CNT-PSD do monitorowania wybranych mikrozanieczyszczeń w wodach powierzchniowych.
6. Regeneracja i ponowne zastosowanie CNT w próbnikach pasywnych do monitorowania analitów w ściekach oczyszczonych.

5. Wyniki i dyskusja

Próbnik pasywny wykorzystany w badaniach został zaprojektowany i wykonany w zespole naukowym Katedry Analizy Środowiska Wydziału Chemii UG (**Rysunek 2**).



Rysunek 2 Schemat urządzenia do pasywnego pobierania próbek (PSD) wykorzystywanego w niniejszej pracy doktorskiej [*opracowanie własne*]

Wykorzystywany próbnik pasywny zbudowany jest z dwóch dysków wykonanych z polimetakrylanu metylu (plexiglas). Nanorurki węglowe umieszczano pomiędzy dwiema membranami PES (0,22 µm, 47 mm) i całość szczelnie zamykano poprzez skręcenie dysków. Oba dyski posiadają otwory, umożliwiające swobodny kontakt wody z membranami i sorbentem. Całkowita powierzchnia wymiany membrany wynosi ~18 cm^2 na próbnik. Wysokość całego próbnika wynosi 5 cm a średnica 6 cm.

Do badań wybrano związki z grupy sulfonamidów, β-blokerów, niesteroidowych leków przeciwzapalnych, tricyklicznych leków przeciwdepresyjnych, leków cytostatycznych, hormonów oraz pochodne fenolu. Właściwości fizykochemiczne tych związków chemicznych zestawiono w **Tabeli 1.**

Tabela 1 Podstawowe właściwości fizykochemiczne badanych związków chemicznych

Analit	Masa molowa [g/mol]	pK_a	pK_{a2}	log D w pH 3	log D w pH 5	log D w pH 7	log D w pH 9
β-blokery							
Atenolol (ATE)	266,34	9,6	/	-6,44	-4,44	-2,44	-0,53
Nadolol (NAD)	309,40	9,7	/	-5,86	-3,89	-1,86	0,06
Pindolol (PIN)	248,32	9,3	/	-4,55	-2,55	0,28	1,27
Acebutolol (ACE)	336,43	9,6	/	-4,89	-2,89	-0,89	1,01
Metoprolol (MET)	267,36	9,6	/	-4,72	-2,72	-0,72	-1,18
Propranolol (PRO)	259,34	9,4	/	-2,94	-0,92	1,06	2,92
Sulfonamidy							
Sulfadiazyna (SDZ)	250,28	2,0	6,9	-0,09	-0,09	-0,40	-2,11
Sulfatiazol (STZ)	255,31	2,0	7,1	0,05	0,05	-0,20	-1,85
Sulfapirydyna (SPD)	249,29	2,6	8,2	0,35	0,35	0,32	-0,51
Sulfamerazyna (SMZ)	264,31	2,1	6,9	0,14	0,14	-0,21	-1,96
Sulfadimidyna (SDD)	278,33	2,7	7,7	0,14	0,14	0,05	-1,23
Sulfametizol (SMT)	270,30	1,9	5,3	0,54	0,36	-1,18	-3,17
Sulfametoksypirydazyna (SMP)	280,31	2,0	6,8	0,32	0,32	-0,07	-1,84
Sulfachloropirydazyna (SCP)	284,72	1,9	5,5	0,85	0,72	-0,71	-2,70
Sulfametoksazol (SMX)	253,28	1,6	5,7	0,89	0,81	0,37	-2,41
Sulfadimetoksyna (SDX)	310,33	2,1	5,9	1,63	1,58	0,50	-1,47

Tricykliczne leki przeciwdepresyjne							
Imipramina (IMI)	280,40	9,4	/	-1,60	0,40	2,40	4,26
Dezypramina (DEZ)	266,40	10,4	/	-2,50	-0,50	1,50	3,48
Karbamazepina (CBZ)	236,27	13,9	/	-8,45	-6,45	-4,45	-2,45
Niesteroidowe leki przeciwzapalne							
Ketoprofen (KET)	254,28	4,45	/	3,10	2,46	0,57	-1,43
Naproksen (NAP)	230,26	4,15	/	3,15	2,27	0,33	-1,67
Diklofenak (DIC)	296,10	4,15	/	4,48	3,60	1,66	-0,34
Leki cytostatyczne							
Metotreksat (MTX)	454,40	4,70	/	-3,71	-2,18	-2,00	-2,00
Pochodne fenolu							
p-nitrofenol (PNP)	139,11	7,15	/	-2,24	-0,24	1,53	1,91
Bisfenol A (PBA)	228,29	9,6	/	-3,28	-1,28	0,72	2,62
3,5-dichlorofenol (3,5-DCP)	163,00	8,18	/	-1,56	0,44	2,41	3,56
Hormony							
17-β-estradiol (E2)	272,40	10,46	/	-3,45	-1,45	0,55	2,54
17-α-etynyloestradiol (EE2)	296,40	10,33	/	-3,66	-1,66	0,34	2,32

źródło: https://pubchem.ncbi.nlm.nih.gov/

5.1. Opracowanie metod analitycznych w celu oznaczania wybranych mikrozanieczyszczeń

Pierwszym etapem badań przeprowadzonych w ramach niniejszej pracy doktorskiej było opracowanie i walidacja metod analitycznych z wykorzystaniem wysokosprawnej chromatografii cieczowej z detektorem z matrycą fotodiodową (HPLC-DAD, ang. *high performance liquid chromatography with diode array detector*) oraz wysokosprawnej chromatografii cieczowej sprzężonej ze spektrometrią mas (LC-MS/MS, ang. *high performance liquid chromatography coupled with tandem mass spectrometry*). Zestaw do LC-MS/MS wyposażony był w źródło jonów ESI (ESI, ang. *electrospray ionization*) oraz potrójny kwadrupol (QqQ, ang. *triple quadrupole*) jako analizator. Technikę HPLC-DAD wykorzystano w celu monitorowania spadku stężenia analitów w wodzie podczas kalibracji próbników pasywnych metodą semi-statyczną oraz podczas badania wpływu czynników środowiskowych na wartości R_S. Przetestowano kilkanaście różnych metod analitycznych, różniących się: programem elucji, składem faz ruchomych, rodzajem faz stacjonarnych i in. Ostatecznie wybrano cztery metody rozdzielenia jako najlepsze do oznaczeń końcowych analitów, a warunki HPLC-DAD opisano w pracach [**P3**, **P4**]. Oceniono parametry analityczne proponowanych metod, takie jak: liniowość (R^2), powtarzalność, precyzja w ciągu dnia (*intra-day*) oraz precyzja pomiędzy dniami (*inter-day*), LOD, LOQ oraz dokładność (**Tabela 2)**. Technikę LC-MS/MS wykorzystano w celu oznaczania analitów w ekstraktach pochodzących z próbników pasywnych z kalibracji przepływowej oraz ekspozycji w środowisku wodnym. Opracowano dwie metody analityczne do oznaczeń końcowych związków badanych za pomocą LC-MS/MS [**P5**]. Oceniono parametry analityczne proponowanych metod, takie jak: liniowość (R^2), powtarzalność, precyzja w ciągu dnia (*intra-day*) oraz precyzja pomiędzy dniami (*inter-day*), LOD, LOQ oraz dokładność (**Tabela 3**).

Tabela 2 Wybrane parametry walidacji dla metody analitycznej z wykorzystaniem HPLC-DAD

Analit	t_R [min]	Zakres liniowości [mg/l]	R^2	Precyzja [%]		Dokładność [%]	LOD [µg/l]	LOQ [µg/l]
				w ciągu dnia	pomiędzy dniami			
ATE	10,4	0,20-10	1,00	0,14-0,70	0,69-1,4	103,0-104,8	66,7	200
NAD	15,3	0,20-10	0,999	0,21-0,59	0,67-1,5	102,2-105,3	66,7	200
PIN	16,4	0,20-10	0,999	0,090-0,82	0,76-2,0	101,4-105,2	66,7	200
ACE	17,9	0,050-10	0,999	0,22-0,25	0,33-0,97	102,4-104,5	16,7	50,0
MET	18,4	0,050-10	0,999	0,050-0,26	0,60-1,4	102,8-105,3	16,7	50,0
PRO	21,7	0,050-10	0,999	0,86-0,91	0,57-1,1	102,3-104,7	16,7	50,0
SDZ	7,99	0,0050-10	1,00	0,13-0,97	0,13-1,9	100,0-109,5	1,67	5,00
STZ	9,65	0,0050-10	1,00	0,080-0,92	0,080-2,0	101,0-110,5	1,67	5,00
SPD	10,3	0,0050-10	0,999	0,17-0,98	0,17-2,0	99,98-103,5	1,67	5,00
SMZ	11,3	0,0050-10	0,997	0,10-0,97	0,10-2,0	99,95-101,2	1,67	5,00
SDD	13,9	0,0050-10	0,999	0,34-0,99	0,34-2,0	102,0-108,2	1,67	5,00
SMT	14,2	0,0050-10	0,999	0,25-0,35	0,25-1,4	97,51-100,0	1,67	5,00
SMP	14,7	0,0050-10	1,00	0,070-0,31	0,070-1,4	97,95-100,1	1,67	5,00
SCP	18,1	0,0050-10	1,00	0,070-0,91	0,070-2,0	101,2-106,5	1,67	5,00
SMX	20,2	0,0050-10	1,00	0,13-0,94	0,13-2,0	102,2-109,1	1,67	5,00
SDX	25,2	0,0050-10	0,998	0,51-0,99	0,51-2,0	101,1-109,1	1,67	5,00
IMI	10,8	0,050-10	0,999	0,080-2,4	0,13-2,4	95,17-104,9	17,0	50,0
DEZ	11,0	0,050-10	0,999	0,72-2,4	0,25-2,4	95,63-104,5	17,0	50,0
CBZ	12,1	0,050-10	0,999	0,17-2,3	0,94-2,6	95,02-100,6	17,0	50,0
KET	14,6	0,050-10	1,00	0,54-2,6	0,16-2,4	95,33-105,2	17,0	50,0
NAP	15,0	0,050-10	1,00	0,87-2,5	0,19-2,9	95,06-104,9	17,0	50,0
FLU	17,0	0,050-10	1,00	1,1-2,9	0,29-2,3	95,49-104,7	17,0	50,0
DIC	17,6	0,050-10	1,00	0,5-2,6	0,23-2,3	95,21-104,2	17,0	50,0
MTX	5,32	0,050-10	0,999	0,2-2,9	0,96-2,5	95,73-100,6	17,0	50,0
PNP	15,1	0,050-10	0,999	0,19-2,1	0,20-2,4	96,61-104,5	17,0	50,0
PBA	15,3	0,050-10	0,999	0,27-3,0	1,4-2,8	96,81-100,5	17,0	50,0
E2	15,6	0,050-10	0,999	0,060-2,4	0,20-2,7	95,03-103,5	17,0	50,0
EE2	16,2	0,050-10	0,999	0,18-2,9	0,30-2,7	98,14-100,6	17,0	50,0
3,5-DCP	16,8	0,050-10	0,999	0,18-2,9	0,94-2,8	96,42-102,6	17,0	50,0

Tabela 3 Parametry opracowanych metod analitycznych przy użyciu techniki LC-MS/MS

Anality	Jon pseudomolekularny	Jony fragmentacyjne			Jonizacja	Zakres liniowości [ng/ml]	R^2	Precyzja [%]		Dokładność [%]	LOD [ng/ml]	LOQ [ng/ml]
								w ciągu dnia	pomiędzy dniami			
IMI	281,1	86,1	58,0	208,1	Dodatnia	0,20-31	0,999	0,59-2,9	0,75-2,3	97,8-106	0,066	0,20
DEZ	267,0	72,2	208,1	193,1	Dodatnia	0,20-31	0,999	0,95-2,9	0,83-2,3	90,5-106	0,066	0,20
CBZ	237,0	194,0	191,9	179,0	Dodatnia	0,20-63	0,999	0,65-2,6	0,48-2,6	95,5-107	0,066	0,20
KET	254,9	105,1	194,0	209,0	Dodatnia	0,400-125	0,999	0,87-2,9	0,37-2,9	93,1-108	0,13	0,40
NAP	229,0	169,3	170,3	185,3	Ujemna	0,400-125	0,999	0,74-3,0	0,45-2,8	93,8-107	0,13	0,40
DIC	294,0	250,2	214,2	/	Ujemna	0,10-63	0,999	0,76-2,6	0,33-2,1	91,3-105	0,033	0,10
MTX	455,1	308,0	134,2	175,0	Dodatnia	0,20-63	0,999	0,85-1,9	1,1-2,6	85,1-106	0,066	0,20
ATE	267,0	145,1	190,0	225,0	Dodatnia	0,40-31	0,999	0,95-1,5	0,55-2,3	88,5-107	0,13	0,40
NAD	310,0	254,1	201,0	236,0	Dodatnia	0,40-31	0,999	0,23-2,8	2,2-2,8	81,3-106	0,13	0,40
PIN	249,0	116,1	172,1	146,1	Dodatnia	0,40-31	0,999	0,14-1,6	1,4-2,7	82,4-106	0,13	0,40
ACE	337,0	116,1	319,1	260,0	Dodatnia	0,40-31	0,999	0,99-2,8	0,85-2,4	88,3-106	0,13	0,40
MET	268,0	116,1	190,9	159,0	Dodatnia	0,40-31	0,999	1,1-3,0	0,19-2,8	83,4-115	0,13	0,40
PRO	260,3	116,1	183,0	157,0	Dodatnia	0,40-31	0,999	0,45-2,4	1,3-2,5	81,0-107	0,13	0,40
SDZ	250,9	156,0	107,9	92,2	Dodatnia	0,40-31	0,999	0,14-2,2	0,19-1,7	92,2-110	0,13	0,40
STZ	255,9	156,2	108,1	/	Dodatnia	0,20-31	0,999	0,57-1,4	0,87-2,5	85,1-111	0,066	0,20
SPD	249,9	155,9	184,2	108,0	Dodatnia	0,20-31	0,999	0,35-2,6	0,94-2,8	84,5-105	0,066	0,20
SMZ	264,9	156,0	172,0	108,1	Dodatnia	0,20-31	0,999	1,9-2,7	0,66-2,9	86,1-106	0,066	0,20
SDD	278,9	185,9	124,1	/	Dodatnia	0,20-31	0,999	0,67-2,8	0,71-3,0	82,9-110	0,066	0,20
SMT	270,9	156,0	108,0	92,2	Dodatnia	0,20-31	0,999	0,36-1,9	0,76-3,1	91,3-111	0,066	0,20
SMP	280,9	126,2	108,1	156,2	Dodatnia	0,20-31	0,999	1,4-2,6	0,44-2,8	83,7-105	0,066	0,20
SCP	284,9	156,1	92,2	108,1	Dodatnia	0,50-31	0,999	0,87-2,7	0,38-2,6	91,7-119	0,33	0,50
SMX	254,1	156,0	107,9	92,1	Dodatnia	0,20-31	0,999	0,74-2,4	0,71-2,9	96,2-115	0,17	0,20
SDX	310,9	155,9	108,1	92,1	Dodatnia	0,20-31	0,999	0,37-2,6	0,25-1,5	88,6-107	0,17	0,20
PNP	138,2	108,2	46,2	92,2	Ujemna	0,400-125	0,999	0,99-2,5	1,8-2,9	82,6-107	0,13	0,40
PBA	227,1	212,4	133,3	211,4	Ujemna	0,400-250	0,999	0,26-3,0	1,5-2,5	90,5-110	0,13	0,40
3,5-DCP	160,9	125,2	89,2	35,2	Ujemna	0,20-32	0,999	0,58-2,4	0,99-2,9	84,6-105	0,066	0,20
E2	271,1	183,4	/	/	Ujemna	0,200-125	0,999	0,69-1,9	0,84-1,9	80,2-108	0,066	0,20
EE2	295,1	145,3	159,4	227,4	Ujemna	0,200-125	0,999	0,12-2,7	0,95-2,5	81,6-107	0,066	0,20

5.2. Badanie możliwości zastosowania różnego rodzaju nanorurek węglowych jako sorbentów w ekstrakcji pasywnej wybranych mikrozanieczyszczeń

Kolejnym etapem badań była ocena możliwości zastosowania różnego rodzaju wielościennych nanorurek węglowych (MWCNT, ang. *multi-walled carbon nanotubes*) jako sorbentów w próbnikach pasywnych do pobierania związków docelowych. W tym celu do badań wykorzystano sześć rodzajów MWCNT różniących się średnicą zewnętrzną, długością, powierzchnią właściwą czy też obecnością grup funkcyjnych na powierzchni (**Tabela 4**).

Tabela 4 Charakterystyka wybranych nanorurek węglowych (CNT) zastosowanych jako sorbent w próbnikach pasywnych

Skrót	Rodzaj	Średnica zewnętrzna	Długość	Powierzchnia właściwa	Czystość
8-CNT	Niemodyfikowane wielościenne nanorurki węglowe	< 8 nm	10-30 μm	500 m^2/g	> 95 %
50-CNT	Niemodyfikowane wielościenne nanorurki węglowe	> 50 nm	10-30 μm	60 m^2/g	> 95 %
s8-CNT	Krótkie niemodyfikowane wielościenne nanorurki węglowe	< 8 nm	0,5-2 μm	500 m^2/g	> 95 %
OH8-CNT	Modyfikowane grupami –OH wielościenne nanorurki węglowe	< 8 nm	10-30 μm	500 m^2/g	> 95 %
COOH8-CNT	Modyfikowane grupami –COOH wielościenne nanorurki węglowe	< 8 nm	10-30 μm	500 m^2/g	> 95 %
hCNT	Helikalne wielościenne nanorurki węglowe	100-200 nm	10-30 μm	> 30 m^2/g	> 90 %

źródło: https://www.cheaptubes.com/

Badania wstępne polegały na przygotowaniu CNT-PSD zawierających po 100 mg każdego rodzaju MWCNT oraz Oasis-PSD zawierającego 100 mg Oasis HLB w celach porównawczych. Następnie próbniki zanurzano w szklanych naczyniach kalibracyjnych wypełnionych wodą dejonizowaną zawierającą badanie związki w stężeniu 2 μg/ml i umieszczano na mieszadłach magnetycznych (kalibracja semi-statyczna z mieszaniem) w termostacie w stałej temperaturze wynoszącej 20°C. Podczas trwania całego eksperymentu (10-14 dni) pobierano próbki wody w określonych odstępach czasu i analizowano za pomocą HPLC-DAD w celu monitorowania spadku stężenia analitów w wodzie w funkcji czasu [**P3, P4**].

Jednocześnie wykonano analogicznie próby kontrolne I (próbniki pasywne bez CNT, które zanurzano w wodnym roztworze analitów) w celu określenia możliwości zatrzymywania związków chemicznych w porach membran PES lub obudowie próbnika oraz próby kontrolne II (wodne roztwory analitów) w celu określenia stabilności związków docelowych w badanej matrycy.

Otrzymane wyniki eksperymentów posłużyły do wykreślenia krzywych spadku stężenia analitów w wodzie ($\ln[Cw_t/Cw_0]$) w funkcji czasu ekspozycji próbników [**P3**, **Rysunek A2**] [**P4**, **Rysunki S2-S5**]. Współczynniki szybkości pobierania wyznaczono zgodnie z równaniem:

$$Cw_t = Cw_0 \exp[-(k_U + k_D)t] = Cw_0 \exp[-kt] \tag{2}$$

które można przekształcić otrzymując:

$$\ln \frac{Cw_t}{Cw_0} = -kt \tag{3}$$

gdzie k_U [l/d] to stała szybkości pobierania a k_D [l/d] to stała szybkości rozpraszania, Cw_0 [µg/ml] to stężenie analitów w wodzie na początku eksperymentu a Cw_t [µg/ml] to stężenie analitów w wodzie po czasie t [doba]. Szybkość pobierania R_s [l/d] wynosi zatem:

$$R_s = k_U V_t \tag{4}$$

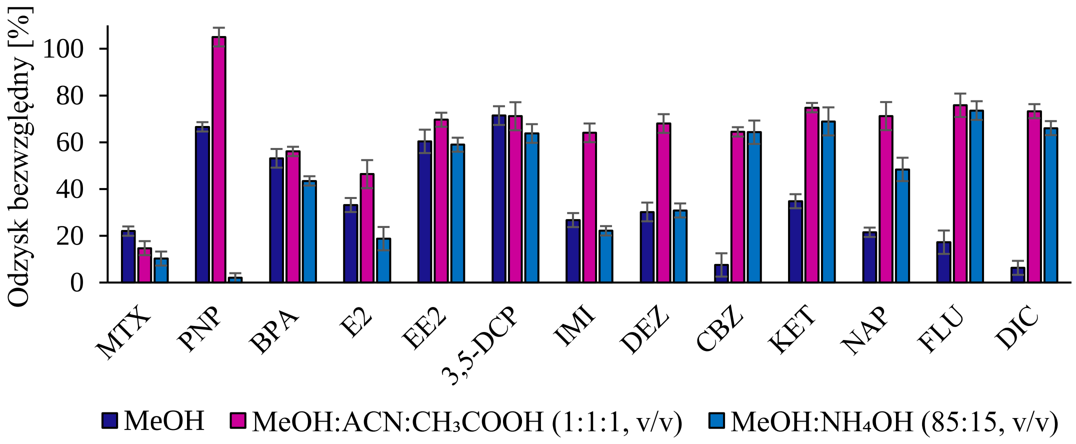
gdzie V_t [l] to objętość wody w komorze kalibracyjnej. Stałą szybkości pobierania k_U, przyjęto jako równą k, ponieważ rozpraszanie analitów nie było obserwowane w próbach kontrolnych.

Pobieranie NLPZ, TLPD, leków cytostatycznych, hormonów i pochodnych fenolu przez próbniki zawierające hCNT i 50-CNT odbywało się w trybie równowagowym lub kinetycznym w zależności od analitu. Natomiast krzywe ubytku analitów z wody dla próbników zawierających 8-CNT, s8-CNT, COOH8-CNT i OH8-CNT charakteryzowały się liniowością co potwierdza kinetyczny charakter tych PSD. Na podstawie zebranych danych wybrano 8-CNT jako najbardziej efektywny sorbent do pobierania NLPZ, TLPD, leków cytostatycznych, hormonów i pochodnych fenolu z wody ze względów analitycznych i ekonomicznych [**P4**]. Natomiast COOH8-CNT wybrano do pobierania sulfonamidów i β-blokerów z wody, ponieważ wartości R_s były najwyższe przy zastosowaniu tego rodzaju CNT co ma kluczowe znaczenie zwłaszcza w analityce zanieczyszczeń śladowych [**P3**].

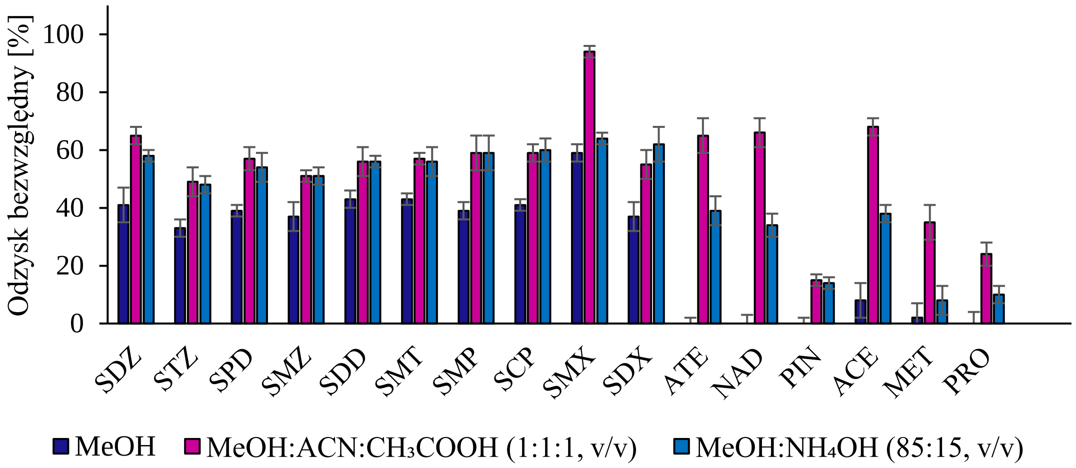
W celu potwierdzenia braku wpływu objętości wody oraz stężenia analitów podczas kalibracji CNT-PSD wykonano również identyczne eksperymenty przy wykorzystaniu 1000 ml wody zwierającej 2 µg/ml związków docelowych oraz 100 ml wody zawierającej 50 ng/ml związków docelowych. Wykazano, iż niezależnie od użytej objętości wody oraz stężenia analitów wartości R_s nie różniły się znacząco (ANOVA; $p > 0,05$) [**P4**, **Rysunek S1**].

Po ekspozycji próbników w wodzie zawierającej badanie związki, PSD były wyjmowane z wody i osuszane na powietrzu przez 24 h. Po tym czasie, próbniki rozmontowywano a sorbent wraz z membranami zanurzono w 30 ml eluentu na czas 30 min. Przetestowano kilka rodzajów rozpuszczalników oraz ich mieszaniny w celu uzyskania jak najwyższych efektywności ekstrakcji [**P4**].

Następnie eluat filtrowano i zatężano za pomocą wyparki próżniowej. Określono, iż przy zastosowaniu mieszaniny ACN:MeOH:CH_3COOH (1:1:1) uzyskano najwyższy odzysk bezwzględny badanych analitów zarówno z powierzchni 8-CNT jak i COOH8-CNT (**Rysunek 3** i **4**).



Rysunek 3 Odzysk bezwzględny analitów z powierzchni niemodyfikowanych wielościennych nanorurek węglowych o średnicy zewnętrznej < 8 nm w zależności od rodzaju eluentu



Rysunek 4 Odzysk bezwzględny analitów z powierzchni wielościennych nanorurek węglowych modyfikowanych grupami -COOH o średnicy zewnętrznej < 8 nm w zależności od rodzaju eluentu

5.3. Badanie wpływu czynników środowiskowych na szybkości pobierania analitów przez CNT-PSD

5.3.1. pH wody

Biorąc pod uwagę fakt, iż kluczowym parametrem mogącym wpłynąć na proces ekstrakcji związków występujących w postaci jonowej jest pH próbki, przeprowadzono szereg eksperymentów kalibracyjnych przy zastosowaniu matrycy wodnej o pH 3, pH 5, pH 7 oraz pH 9. Aby ocenić wpływ pH wody na szybkość pobierania badanych analitów przez CNT-PSD przeprowadzono kalibrację semi-statyczną analogicznie jak opisano w Rozdziale 5.2. Na podstawie badań próbek kontrolnych wykazano, iż pH fazy wodnej było stałe a związki docelowe stabilne podczas trwania eksperymentów.

Uzyskane wyniki wskazują, iż wraz ze wzrostem pH wody zmniejszają się wartości R_s sulfonamidów przy zastosowaniu COOH8-CNT-PSD [**P3**, **Rysunek 1**]. Jednakże różnice pomiędzy szybkościami pobierania sulfonamidów z wody o pH 3 i pH 5 były nieistotne statystycznie (ANOVA, p > 0,05). Badane anality występują w postaci obojętnych cząsteczek w rozworach wodnych o pH 3 i pH 5, natomiast w roztworach wodnych o pH 7 i pH 9 sulfonamidy występują w formie ujemnie naładowanych cząsteczek. Co ważne, punkt zerowego ładunku (ang. *point of zero charge*) COOH8-CNT wynosi 5,8, a więc powierzchnia tych nanorurek będzie naładowana ujemnie w roztworach o pH > 5,8. Prawdopodobnie spadek szybkości pobierania sulfonamidów wraz ze wzrostem pH w zakresie 5-9 związany jest ze zjawiskiem odpychania ujemnie naładowanych cząsteczek analitu z ujemnie naładowaną powierzchnią CNT [**P3**].

W przypadku pobierania β-blokerów przez COOH8-CNT-PSD nie wykazano wpływu pH wody w badanym zakresie na wartości R_s [**P3**, **Rysunek 1]**. Związki te występują w formie dodatnio naładowanych cząsteczek w roztworach o pH ≤ 9, stąd możliwe przyciąganie protonowanych form β-blokerów z ujemnie naładowaną powierzchnią COOH8-CNT w wodzie o pH 7 i pH 9. Jednakże wydaje się, iż w przypadku β-blokerów oddziaływania elektrostatyczne nie mają kluczowego znaczenia w procesie sorpcji. Związane jest to z faktem, iż w roztworach o pH 3 i pH 5 zarówno powierzchnia COOH8-CNT jak i cząsteczki analitów naładowane są dodatnio. Stąd teoretycznie powinno się obserwować spadek szybkości pobierania β-blokerów z roztworów o takich pH ze względu na odpychanie się jednoimiennie naładowanych struktur. Co ciekawe, efektu takiego nie zaobserwowano, co pozwala przypuszczać, iż oddziaływania π-π między powierzchnią COOH8-CNT a cząsteczkami β-blokerów mają większe znaczenie w procesie zatrzymywania tych związków [**P3**].

Na podstawie wyników kalibracji dla próbnika zawierającego 8-CNT-PSD w wodzie o różnym pH wykazano, iż wartości R_s dla NLPZ, TLPD, leków cytostatycznych, pochodnych fenolu oraz hormonów (ANOVA, $p > 0,05$) są niezależne od pH wody w badanym zakresie [**P4**, **Rysunek 3**]. Można zatem wnioskować, iż prawdopodobnie oddziaływania π-π pomiędzy cząsteczkami tych analitów a powierzchnią 8-CNT mają istotne znaczenie w procesie zatrzymywania tych związków przez opracowany próbnik pasywny [**P4**].

5.3.2. Zasolenie

Kolejnym czynnikiem środowiskowym, którego wpływ na szybkości pobierania wybranych mikrozanieczyszczeń postanowiono zbadać było zasolenie wody. Wykonano kalibrację semi-statyczną przy użyciu syntetycznej wody morskiej o zasoleniu 7 PSU, 21 PSU oraz 35 PSU. Na podstawie badań próbek kontrolnych wykazano, iż zasolenie fazy wodnej było stałe a związki docelowe stabilne podczas trwania eksperymentów.

Uzyskane wyniki wskazują, iż wzrost stężenia soli w fazie wodnej powoduje zmniejszenie szybkości pobierania sulfonamidów i β-blokerów przez COOH8-CNT-PSD [**P3**, **Rysunek 2**]. Niemniej jednak analizy statystyczne wykazały, że różnice pomiędzy wartościami R_s wyżej wymienionych analitów uzyskane po kalibracji próbników w wodzie bez dodatku soli oraz w wodzie o zasoleniu 7 PSU nie były znaczące (ANOVA, $p > 0,05$). Dopiero kolejny wzrost zasolenia matrycy wodnej do 21 PSU oraz 35 PSU spowodował znaczący spadek wartości R_s sulfonamidów i β-blokerów (ANOVA,

$p < 0,05$; post hoc Tukey). Zgodnie z danymi literaturowymi, rozpuszczalność większości związków organicznych w wodzie maleje wraz ze wzrostem ilości soli z powodu tzw. efektu wysalania, co teoretycznie powinno zwiększyć efektywność sorpcji związków docelowych [25]. Jednakże w przypadku sulfonamidów i β-blokerów zaobserwowano efekt odwrotny – szybkość pobierania tych analitów przez COOH8-PSD malała wraz ze wzrostem zasolenia matrycy. Aby wytłumaczyć to zjawisko wzięto pod uwagę formy jonowe analitów w syntetycznej wodzie morskiej. β-blokery występują w postaci dodatnio naładowanych cząsteczek, natomiast sulfonamidy przeważnie w postaci ujemnie naładowanych cząsteczek w pH syntetycznej wody morskiej. Bazując na tych informacjach, założono, iż jony różnych soli obecne w matrycy o zasoleniu 21 PSU oraz 35 PSU konkurują z jonami związków badanych o miejsca aktywne sorbentu lub też bezpośrednio oddziałują z jonami analitów, zmniejszając ich powinowactwo do fazy odbierającej próbnika [**P3**].

Wyniki kalibracji 8-CNT-PSD w wodzie o różnym zasoleniu wykazały, iż wartości R_s dla NLPZ, TLPD, leków cytostatycznych, pochodnych fenolu oraz hormonów (ANOVA, $p > 0,05$) są niezależne od stężenia jonów soli w matrycy [**P4**, **Rysunek 4**].

5.3.3. Stężenie rozpuszczonych kwasów humusowych

W kolejnym etapie badań, określono również wpływ rozpuszczonych kwasów humusowych na wartości R_s badanych analitów, poprzez wykonanie kalibracji semi-statycznej w wodzie o stężeniu 1 mg/l, 2,5 mg/l oraz 5 mg/l rozpuszczonych kwasów humusowych. Na podstawie badań próbek kontrolnych wykazano, iż stężenie rozpuszczonych kwasów humusowych w fazie wodnej było stałe a związki docelowe stabilne podczas trwania eksperymentów.

Otrzymane wyniki wskazują, iż obecność rozpuszczonych kwasów humusowych w matrycy wodnej wpływa na zmniejszenie wartości R_s sulfonamidów przez COOH8-CNT-PSD w porównaniu z R_s uzyskanymi dla wody dejonizowanej (ANOVA, $p < 0,05$; post hoc Tukey) [**P3**, **Rysunek 3**]. Prawdopodobnie, w wyniku oddziaływania rozpuszczonych kwasów humusowych z badanymi związkami zmniejsza się dostępność tych analitów dla fazy odbierającej. Co więcej, kwasy humusowe rozpuszczone w wodzie mogą blokować pory membrany, wpływając tym samym na kinetykę procesu dyfuzji poprzez utworzenie warstwy sorpcyjnej na powierzchni membrany PES. Co ciekawe, zwiększanie stężenia kwasów humusowych w wodzie (od 1 mg/l do 5 mg/l) nie powodowało dalszych zmian wartości R_s sulfonamidów. Biorąc pod uwagę wyniki dla β-blokerów nie odnotowano zmiany szybkości pobierania tych związków przez COOH8-CNT-PSD z wody zawierającej rozpuszczone kwasy humusowe w porównaniu z pobieraniem z wody dejonizowanej [**P3**, **Rysunek 3**].

Odnosząc się do wyników kalibracji uzyskanych dla 8-CNT-PSD w wodzie o różnym stężeniu rozpuszczonych kwasów humusowych stwierdzono, iż wartości R_s dla NLPZ, TLPD, leków cytostatycznych, pochodnych fenolu oraz hormonów (ANOVA, $p > 0,05$) są zbliżone zarówno podczas kalibracji w wodzie dejonizowanej jak i w wodzie zawierającej rozpuszczone kwasy humusowe [**P4**, **Rysunek 5**].

5.3.4. Mieszanie fazy wodnej

Kolejnym etapem badań wpływu czynników środowiskowych na wartości R_s analitów była ocena znaczenia mieszania fazy wodnej. Wykonano kalibrację semi-statyczną w szklanych komorach umieszczonych na mieszadłach magnetycznych z prędkością obrotów 0 rpm, 350 rpm i 700 rpm. Zaobserwowano, iż wzrost szybkości mieszania próbki wody z 350 rpm na 700 rpm nie wpłynął znacząco na szybkości pobierania związków docelowych. Niemniej jednak, wykazano znaczący spadek wartości R_s wszystkich badanych analitów w warunkach statycznych (0 rpm) w porównaniu z warunkami dynamicznymi (350 rpm, 700 rpm) [dane nieopublikowane].

5.3.5. Rzeczywista matryca środowiskowa

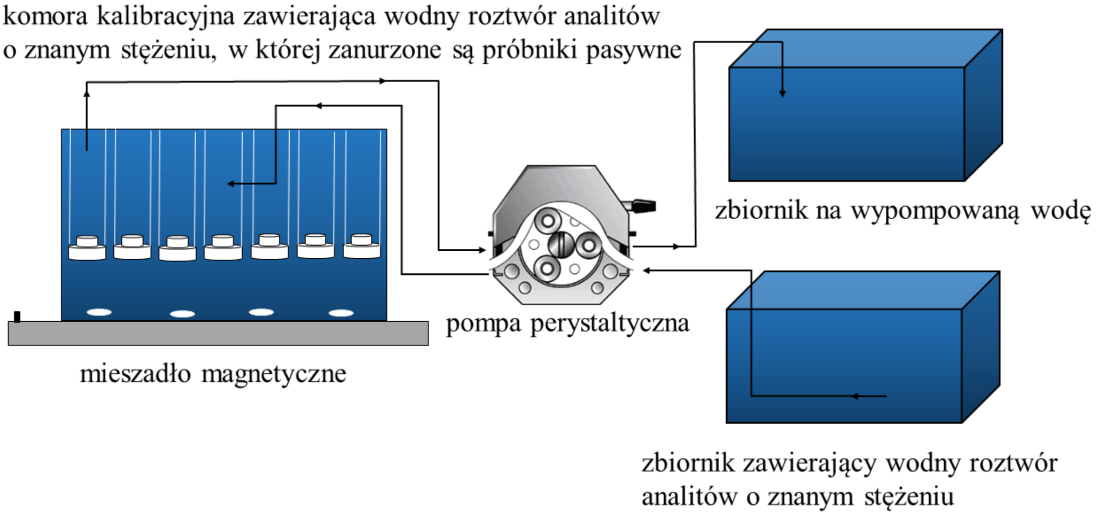
Wykonano również kalibrację semi-statyczną opracowanych próbników pasywnych w rzeczywistej wodzie pobranej z Wisły oraz Oczyszczalni Ścieków „Wschód” w Gdańsku [**P3**, **Tabela 2**] [**P4**, **Tabela 2**]. Na podstawie badań próbek kontrolnych wykazano, iż związki docelowe były stabilne zarówno w wodzie z Wisły, jak i ściekach oczyszczonych i nieoczyszczonych podczas trwania eksperymentów.

Wykazano zmniejszenie wartości R_s sulfonamidów i β-blokerów przez COOH8-CNT-PSD podczas kalibracji w matrycy rzeczywistej w porównaniu z wartościami R_s uzyskanymi z kalibracji w wodzie dejonizowanej [**P3**, **Rysunek 4**]. Jest to zgodne z wcześniej uzyskanymi wynikami, które udowodniły wpływ zasolenia, pH wody oraz obecności kwasów humusowych w matrycy na szybkości pobierania sulfonamidów oraz wpływ zasolenia matrycy na szybkości pobierania β-blokerów. Stąd wniosek, iż kalibrację COOOH8-CNT-PSD powinno się wykonywać w wodzie o parametrach fizykochemicznych zbliżonych do parametrów wody, w której docelowo będą umieszczone próbniki pasywne [**P3**].

Natomiast wartości R_S dla NLPZ, TLPD, leków cytostatycznych, pochodnych fenolu oraz hormonów (ANOVA, $p > 0,05$) są zbliżone zarówno podczas kalibracji w wodzie dejonizowanej jak i w ściekach oczyszczonych i nieoczyszczonych [**P4**, **Rysunek 6**]. Jest to zgodne z wcześniej uzyskanymi wynikami, które udowodniły brak wpływu czynników środowiskowych takich jak: zasolenie, pH wody czy obecność rozpuszczonych kwasów humusowych na szybkości pobierania wyżej wymienionych związków [**P4**].

5.4. Kalibracja próbników CNT-PSD oraz Oasis-PSD za pomocą metody przepływowej i porównanie dokładności dwóch systemów kalibracyjnych

W celu przeprowadzenia kalibracji przepływowej próbników pasywnych, skonstruowano system przepływowy (**Rysunek 5**), tak aby zapewnić stałe stężenie badanych mikrozanieczyszczeń w wodzie podczas trwania eksperymentu.



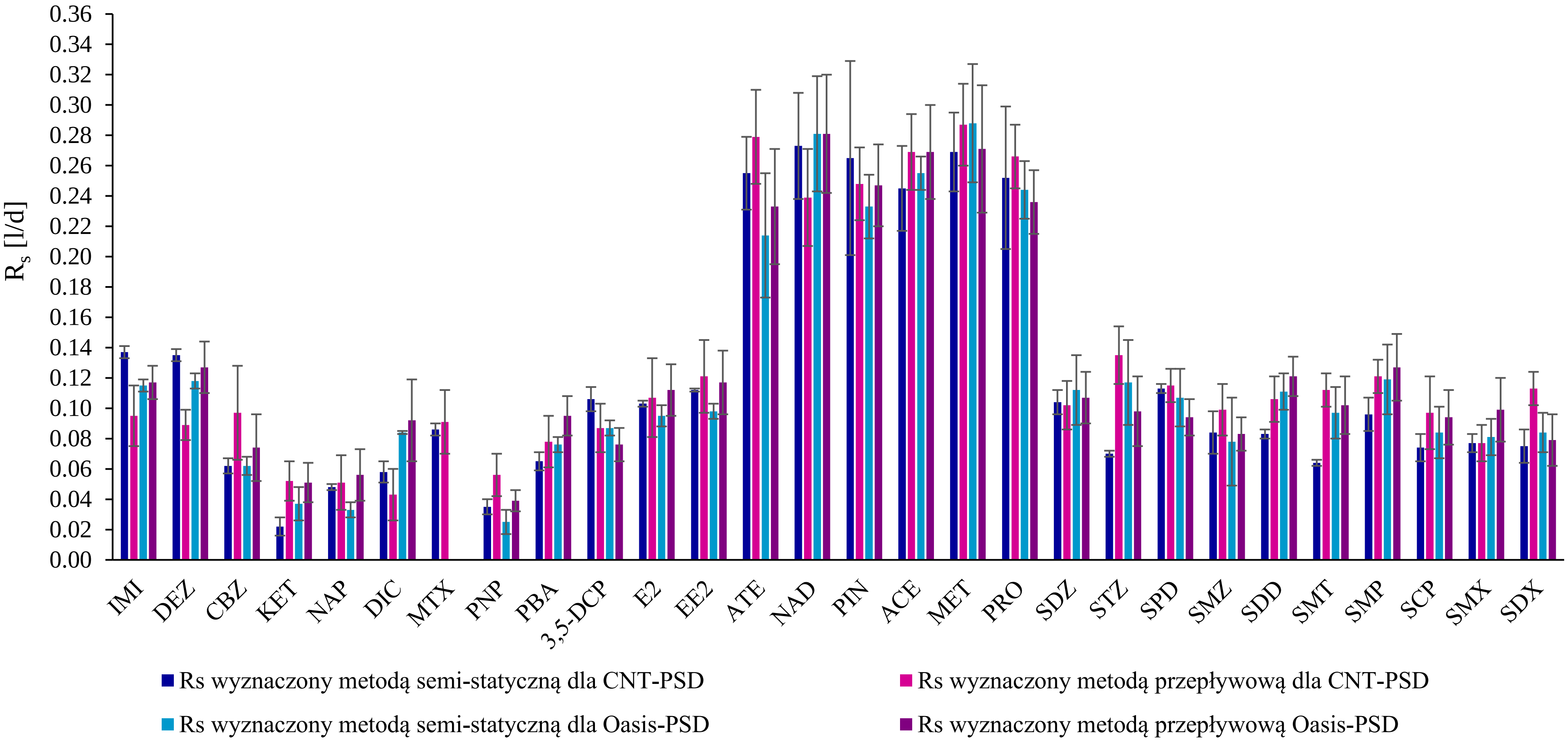
Rysunek 5 Schemat systemu do kalibracji przepływowej [opracowanie własne]

Do komory kalibracyjnej wprowadzono wodę (o parametrach fizykochemicznych zbliżonych do parametrów badanej wody środowiskowej) zawierającą związki docelowe, w której zanurzano siedem próbników pasywnych. Z komory kalibracyjnej była jednocześnie odprowadzana woda i doprowadzana świeża porcja wody zawierającej znane i stałe stężenie analitów. Co 2 dni wyjmowano jeden próbnik pasywny, osuszano na powietrzu i rozmontowywano. Następnie wprowadzano sorbent do 30 ml ACN:MeOH:CH_3COOH (1:1:1, v/v/v, pH 2,1) w celu desorpcji zatrzymanych na powierzchni sorbentu analitów. Otrzymane ekstrakty filtrowano, zatężano i analizowano za pomocą LC-MS/MS. Uzyskane wyniki posłużyły do wykreślenia krzywych pobierania analitów przez badane próbniki i obliczenia wartości R_s zgodnie ze wzorem:

$$R_s = \frac{C_S \times M_S}{C_{TWA} \times t} \tag{5}$$

gdzie C_s [ng/g] to stężenie związku chemicznego w fazie odbierającej próbnika, C_{TWA} [ng/l] to średnie ważone w czasie t [d] stężenie analitu w wodzie, M_s to masa sorbentu [g] [**P5**].

Krzywe pobierania wszystkich związków docelowych charakteryzowały się liniowością podczas 14 dni ekspozycji zarówno CNT-PSD jak i Oasis-PSD w wodzie [**Rysunek 2**, **P5**]. W związku z tym, opracowane próbniki pasywne scharakteryzowano jako kinetyczne i wykorzystano wzór (5) do obliczenia wartości R_s. Wyznaczone wartości R_s dla badanych analitów za pomocą metody semi-statycznej oraz metody przepływowej przedstawiono na **Rysunku 6**.



Rysunek 6 Szybkości pobierania (R_s) badanych mikrozanieczyszczeń przez urządzenia pasywne zawierające nanorurki węglowe (CNT-PSD) lub Oasis HLB (Oasis-PSD) jako sorbent wyznaczone za pomocą metody kalibracji semi-statycznej oraz przepływowej

Do określenia różnic między obliczonymi wartościami R_s uzyskanymi dwiema metodami kalibracji zastosowano jednokierunkową analizę ANOVA. Nie wykazano istotnych statystycznie różnic między wartościami R_s (ANOVA; $p > 0,05$) co udowadnia skuteczność i miarodajność zarówno semi-statycznej kalibracji jak i kalibracji przepływowej [**P5**].

Ponadto wykazano, iż niezależnie od natężenia przepływu wody i stężenia analitów, szybkości pobierania badanych związków chemicznych nie różniły się istotnie (ANOVA; $p > 0,05$) [**P5**, **Tabela S2**].

5.5. Zastosowanie próbników CNT-PSD do monitorowania wybranych mikrozanieczyszczeń w środowisku wodnym

Opracowane próbniki pasywne zawierające modyfikowane (COOH8-CNT-PSD) i niemodyfikowane (8-CNT-PSD) CNT zastosowano do monitorowania poziomu stężeń badanych związków w wodach powierzchniowych. W tym celu kanistry ze stali nierdzewnej zawierające 3 próbniki COOH8-CNT-PSD, 3 próbniki 8-CNT-PSD oraz 3 próbniki Oasis-PSD umieszczono w Morzu Bałtyckim, rzece Nogat oraz jeziorze w Sztumskim Polu [**P5**, **Tabela 2**, **Rysunek 3**] na 10 oraz 20 dni. Po 10 dniach wyjmowano jeden z kanistrów z wody, przewożono do laboratorium, gdzie próbniki pasywne osuszano i rozmontowywano. Zatrzymane na powierzchni sorbentów związki chemiczne ekstrahowano zgodnie z procedurą opisaną w Rozdziale 5.2. i analizowano za pomocą LC-MS/MS. Analogicznie postąpiono z próbnikami wyjętymi z wody po 20 dniach ekspozycji w wodach powierzchniowych [**P5**].

Za pomocą CNT-PSD zidentyfikowano oraz określono średnie ważone w czasie stężenia karbamazepiny (1,71 ± 0,24 ng/l) oraz bisfenolu A (1,28 ± 0,23 ng/l) w Morzu Bałtyckim. W jeziorze w Sztumskim Polu zidentyfikowano i określono C_{TWA} diklofenaku (3,23 ± 0,17 ng/l), p-nitrofenolu (13,3 ± 2,1 ng/l), bisfenolu A (31,1 ± 2,7 ng/l), 3,5-dichlorofenolu (23,0 ± 2,7 ng/l), 17-β-estradiolu (2,45 ± 0,76 ng/l) i 17-α-etynyloestradiolu (4,89 ± 0,70 ng/l). W rzece Nogat zidentyfikowano i określono C_{TWA} karbamazepiny (2,34 ± 0,66 ng/l), diklofenaku (3,61 ± 0,23 ng/l), p-nitrofenolu (8,86 ± 0,23 ng/l), 3,5-dichlorofenolu (3,51 ± 0,11 ng/l), 17-β-estradiolu (7,39 ± 0,15 ng/l) i metoprololu (0,22 ± 0,12 ng/l) (**Tabela 5**) [**P5**].

Tabela 5 Średnie ważone w czasie stężenie (C_{TWA}) wybranych mikrozanieczyszczeń w wodach powierzchniowych uzyskane z punktowego pobierania próbek oraz pasywnego pobierania próbek za pomocą CNT-PSD i Oasis-PSD. C_{TWA} z próbników pasywnych są wyrażone jako średnia ± SD (n = 3). C_{TWA} z punktowego pobierania próbek wyrażone są jako średnia ± SD (średnie stężenie analitów w wodzie pobranej w dniach 0, 10 i 20 ekspozycji próbników w wodzie)

	C_{TWA} otrzymane z CNT-PSD [ng/l]			**C_{TWA} otrzymane z Oasis-PSD [ng/l]**			**C_{TWA} otrzymane z punktowego pobierania próbek [ng/l]**		
Analit	Morze Bałtyckie	Jezioro w Sztumskim Polu	Rzeka Nogat	Morze Bałtyckie	Jezioro w Sztumskim Polu	Rzeka Nogat	Morze Bałtyckie	Jezioro w Sztumskim Polu	Rzeka Nogat
IMI	< LQp	< LQp	< LQp	< LQp	< LQp	NW	< LQg	< LQg	NW
DEZ	< LQp	< LQp	NW	< LQp	< LQp	NW	< LQg	< LQg	NW
CBZ	1,71 ± 0,24	< LQp	2,34 ± 0,66	1,45 ± 0,58	< LQp	2,57 ± 0,58	1,41 ± 0,36	< LQg	1,13 ± 0,11
KET	NW	NW	NW	NW	NW	NW	NW	NW	NW
NAP	NW	NW	NW	NW	NW	NW	NW	NW	NW
DIC	NW	3,23 ± 0,17	3,61 ± 0,23	NW	2,71 ± 1,9	3,19 ± 0,94	NW	3,78 ± 0,24	3,01 ± 0,93
MTX	NW	NW	NW	NW	NW	NW	NW	NW	NW
PNP	< LQp	13,3 ± 2,1	8,86 ± 0,23	< LQp	14,3 ± 1,2	8,40 ± 0,38	< LQg	12,8 ± 1,6	< LQg
PBA	1,28 ± 0,23	31,1 ± 2,7	NW	1,630 ± 0,020	32,1 ± 2,4	NW	< LQg	29,7 ± 2,9	NW
3,5-DCP	< LQp	23,0 ± 2,7	3,51 ± 0,11	< LQp	21,4 ± 2,3	3,46 ± 0,57	NW	20,7 ± 3,5	< LQg
E2	NW	2,45 ± 0,76	7,39 ± 0,15	NW	2,32 ± 0,52	7,37 ± 0,34	NW	< LQg	< LQg
EE2	NW	4,89 ± 0,70	NW	NW	4,37 ± 0,62	NW	NW	< LQg	NW
ATE	NW	NW	NW	NW	NW	NW	NW	NW	NW
NAD	NW	NW	NW	NW	NW	NW	NW	NW	NW
PIN	NW	NW	NW	NW	NW	NW	NW	NW	NW
ACE	< LQp	NW	< LQp	< LQp	NW	< LQp	NW	NW	NW
MET	< LQp	< LQp	0,22 ± 0,12	< LQp	< LQp	0,32 ± 0,12	NW	NW	< LQg
PRO	NW	< LQp	< LQp	NW	< LQp	< LQp	NW	NW	NW
SDZ	NW	NW	NW	NW	NW	NW	NW	NW	NW
STZ	NW	NW	NW	NW	NW	NW	NW	NW	NW
SPD	NW	NW	NW	NW	NW	NW	NW	NW	NW

SMZ	NW	NW	NW	NW	NW	NW	NW	NW	NW
SDD	NW	NW	NW	NW	NW	NW	NW	NW	NW
SMT	NW	NW	NW	NW	NW	NW	NW	NW	NW
SMP	NW	NW	NW	NW	NW	NW	NW	NW	NW
SCP	NW	NW	NW	NW	NW	NW	NW	NW	NW
SMX	NW	NW	NW	NW	NW	NW	NW	NW	NW
SDX	NW	NW	NW	NW	NW	NW	NW	NW	NW

NW - nie wykryto, LQp – granica oznaczalności próbnika pasywnego (ang. *limit of quantification of passive sampler),*
LQg - granica oznaczalności punktowego pobierania próbek (ang. *limit of quantification of grab sampling)*

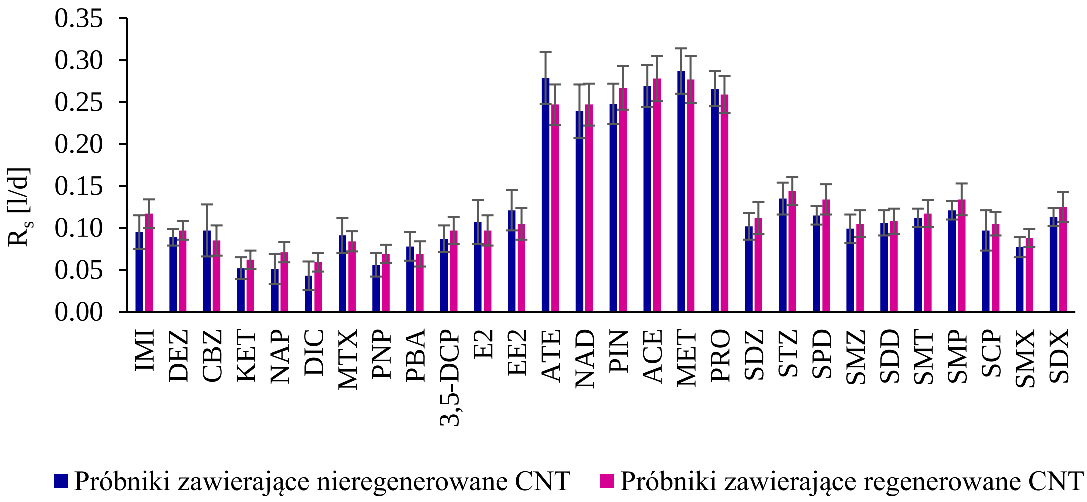
Nie stwierdzono istotnych różnic pomiędzy C_{TWA} analitów uzyskanych z próbników wyjętych z wody po 10 dniach i po 20 dniach (ANOVA; $p > 0,05$) [**P5**, **Rysunek S4**].

Za pomocą punktowego pobierania próbek oraz ekstrakcji do fazy stałej oznaczono karbamazepinę (1,41 ± 0,36 ng/l) w Morzu Bałtyckim. W jeziorze w Sztumskim Polu oznaczono diklofenak (3,78 ± 0,24 ng/l), p-nitrofenol (12,8 ± 1,6 ng/l), bisfenol A (29,7 ± 2,9 ng/l) i 3,5-dichlorofenol (20,7 ± 3,5 ng/l). W rzece Nogat oznaczono karbamazepinę (1,13 ± 0,11 ng/l) i diklofenak (3,01 ± 0,93 ng/l) (**Tabela 5**). Nie stwierdzono statystycznie istotnych różnic między C_{TWA} mikrozanieczyszczeń wyznaczonych przy użyciu metody punktowego pobierania próbek a C_{TWA} mikrozanieczyszczeń wyznaczonych przy użyciu pasywnej metody pobierania próbek (ANOVA; $p > 0,05$).

Co jednak najważniejsze, przy użyciu próbników pasywnych określono średnie ważone w czasie stężenia większej liczby mikrozanieczyszczeń niż przy użyciu metody punktowego pobierania próbek (bisfenol A w Morzu Bałtyckim, 17-β-estradiol i 17-α-etynyloestradiol w jeziorze w Sztumskim Polu oraz p-nitrofenol, metoprolol, 3,5-dichlorofenol i 17-β-estradiol w rzece Nogat były poniżej granicy oznaczalności metody punktowego pobierania próbek) [**P5**].

5.6. Ocena możliwości zastosowania próbników pasywnych zawierających regenerowane nanorurki węglowe jako sorbent (dane niepublikowane)

Niewątpliwą zaletą CNT, wskazywaną przez wielu Autorów, jest możliwość ich regeneracji [32–37]. Dlatego też, w ramach niniejszej pracy doktorskiej postanowiono wykonać regenerację CNT użytych wcześniej jako faza odbierająca w próbnikach pasywnych. Po etapie elucji analitów z sorbentu, CNT pozostałe na filtrze polietylenowym poddano regeneracji chemicznej za pomocą metanolu [34], a następnie regeneracji termicznej w 300°C przez 2 h [32]. Przygotowano próbniki pasywne zawierające zregenerowane COOH8-CNT oraz 8-CNT i wykonano kalibrację metodą przepływową w celu oceny wpływu regeneracji sorbentu na szybkości pobierania badanych mikrozanieczyszczeń. Nie wykazano istotnych statystycznie różnic między wartościami R_s (ANOVA; $p > 0,05$) uzyskanymi dla próbników zawierających nieregenerowane CNT oraz dla próbników zawierających ponownie użyte CNT (**Rysunek 7**).



Rysunek 7 Wpływ ponownego zastosowania zregenerowanych nanorurek węglowych jako sorbentów w próbnikach pasywnych na szybkości pobierania analitów (R_s)

W następnym etapie nanorurki węglowe użyte jako sorbenty w próbnikach pasywnych do pobierania i zatężania badanych związków chemicznych z wód powierzchniowych zostały zregenerowane zgodnie z procedurą opisaną powyżej i ponownie użyte. W tym celu w kanistrach ze stali nierdzewnej umieszczono 3 próbniki zawierające nieregenerowane COOH8-CNT, 3 próbniki zawierające regenerowane COOH8-CNT, 3 próbniki zawierające nieregenerowane 8-CNT oraz 3 próbniki zawierające regenerowane 8-CNT. Tak przygotowane kanistry umieszczono w odpływie ścieków oczyszczonych w oczyszczalni ścieków w Sztumie na 10 dni.

Nie stwierdzono istotnych różnic pomiędzy C_{TWA} związków docelowych uzyskanych z próbników zawierających jako sorbent nieregenerowane CNT a z próbników zawierających jako sorbent regenerowane CNT (ANOVA; $p > 0,05$) (**Tabela 6**).

Tabela 6 Średnie ważone w czasie stężenia (C_{TWA}) badanych mikrozanieczyszczeń w ściekach oczyszczonych uzyskane na skutek ekspozycji próbników pasywnych zawierających nieregenerowane i regenerowane nanorurki węglowe (CNT). C_{TWA} z próbników pasywnych są wyrażone jako średnia ± SD (n = 3)

Związek chemiczny	**Średnie ważone w czasie stężenie [ng/l]**	
	Próbnik zawierający nieregenerowane CNT	**Próbnik zawierający regenerowane CNT**
Imipramina	< LQp	< LQp
Dezypramina	< LQp	< LQp
Karbamazepina	1659 ± 34	1613 ± 34
Ketoprofen	219 ± 29	163 ± 25
Naproksen	70,2 ± 8,7	58 ± 18
Diklofenak	361 ± 17	362 ± 25
Metotreksat	NW	NW
p-nitrofenol	12,0 ± 2,5	12,1 ± 1,4
Bisfenol A	5,7 ± 1,3	8,3 ± 2,4
3,5-dichlorofenol	< LQp	< LQp
17-β-estradiol	NW	NW
17-α-etynyloestradiol	NW	NW
Atenolol	0,77 ± 0,22	1,5 ± 1,8
Nadolol	NW	NW
Pindolol	NW	NW
Acebutolol	0,529 ± 0,057	0,755 ± 0,021
Metoprolol	8,4 ± 2,8	3,95 ± 0,90
Propranolol	NW	NW
Sulfadiazyna	NW	NW
Sulfatiazol	NW	NW
Sulfapirydyna	41,6 ± 5,7	49 ± 18
Sulfamerazyna	4,59 ± 0,65	5,4 ± 1,9
Sulfadimidyna	NW	NW
Sulfametizol	NW	NW
Sulfametoksypirydazyna	NW	NW
Sulfachloropirydazyna	NW	NW
Sulfametoksazol	27,0 ± 4,9	25,5 ± 1,1

NW - nie wykryto, LQp - granica oznaczalności próbnika pasywnego

6. Podsumowanie

Głównym celem niniejszej pracy doktorskiej była ocena możliwości zastosowania wielościennych nanorurek węglowych w ekstrakcji pasywnej jako innowacyjnego podejścia do pobierania i monitorowania budzących niepokój mikrozanieczyszczeń środowiska wodnego. Wszystkie zadania badawcze i cele szczegółowe określone w ramach niniejszej pracy doktorskiej zostały z powodzeniem zrealizowane. Po raz pierwszy wykonano szereg eksperymentów z zastosowaniem różnego rodzaju wielościennych nanorurek węglowych oraz zróżnicowanych warunków zewnętrznych podczas kalibracji opracowanych próbników pasywnych.

Udowodniono możliwość stosowania wielościennych nanorurek węglowych jako sorbentów w próbnikach pasywnych do pobierania i zatężania szerokiej gamy związków chemicznych z wody. Przeprowadzono efektywną ekstrakcję związków docelowych zatrzymanych na powierzchni nanorurek węglowych za pomocą mieszaniny ACN:MeOH:CH_3COOH (1:1:1). Dzięki zastosowaniu kalibracji semi-statycznej i kalibracji przepływowej uzyskano wartości R_s dwiema metodami i potwierdzono, iż każda z nich jest wiarygodna i dokładna. Wykazano również, iż pH wody, obecność rozpuszczonych kwasów humusowych czy zasolenie nie wpływają na szybkości pobierania leków cytostatycznych, NLPZ, TLPD, hormonów i pochodnych fenolu przez 8-CNT-PSD. Natomiast w przypadku pobierania sulfonamidów przez COOH8-CNT-PSD wszystkie wymienione powyżej czynniki środowiskowe wpływały na wartości R_s. W przypadku pobierania β-blokerów przez COOH8-CNT-PSD jedynie zasolenie wody powyżej 7 PSU wpływało na wartości R_s tych analitów, pozostałe czynniki nie powodowały istotnych zmian w szybkości pobierania tych związków. Co ciekawe, zaobserwowano, iż wzrost szybkości mieszania wody nie wpłynął na szybkości pobierania związków docelowych. Zauważono jednak spadek wartości R_s dla wszystkich badanych analitów w warunkach statycznych w porównaniu z warunkami dynamicznymi.

Po raz pierwszy z powodzeniem zastosowano opracowany próbnik w wodach powierzchniowych oraz w ściekach oczyszczonych Nie stwierdzono statystycznie istotnych różnic w wyznaczonych średnich ważonych w czasie stężeniach związków badanych przy zastosowaniu CNT-PSD i Oasis-PSD (ANOVA; $p > 0,05$). Uzyskane wyniki potwierdzają przydatność zastosowania CNT-PSD do pobierania próbek i zatężania szerokiej gamy związków chemicznych różniących się istotnie właściwościami fizykochemicznymi. Co więcej, nanorurki węglowe użyte w próbnikach pasywnych mogą być w prosty sposób zregenerowane i z powodzeniem ponownie wykorzystane do monitorowania badanych mikrozanieczyszczeń w ściekach oczyszczonych.

Podsumowując, opracowany próbnik CNT-PSD może być stosowany do monitorowania poziomu stężeń szerokiej gamy mikrozanieczyszczeń w wodzie środowiskowej i ściekach a dostarczone dane stanowią istotny wkład w rozwój technik pasywnych stosowanych do pobierania i zatężania zanieczyszczeń środowiska wodnego. Obecnie zwraca się uwagę na stosowanie przyjaznych dla środowiska i odnawialnych metod w celu zrównoważonego rozwoju. Dlatego też, należy wyraźnie podkreślić, iż zastosowanie nanorurek węglowych jako sorbentów w technikach ekstrakcji znacznie lepiej wpisuje się w ten trend niż Oasis HLB. Przede wszystkim nanorurki węglowe można łatwo i szybko zregenerować, a następnie ponownie wykorzystać jako sorbenty przy zachowaniu wysokiej efektywności ekstrakcji. Ponadto, nadal prowadzone są badania nad doskonaleniem metod syntezy nanorurek węglowych w celu otrzymywania tych materiałów z zastosowaniem mniej kosztochłonnych i bardziej ekologicznych metod. Biorąc powyższe pod uwagę, CNT-PSD mają ogromny potencjał do zastosowania w rutynowych procedurach monitorowania środowiska wodnego.

W ramach niniejszej pracy doktorskiej opublikowano 3 prace eksperymentalne i 2 prace przeglądowe w czasopismach o zasięgu międzynarodowym.

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8. Oświadczenia autorów

Uniwersytet
Gdański

dr hab. Monika Paszkiewicz, prof. UG
Katedra Analizy Środowiska
Wydział Chemii

4.05.2022r., Gdańsk

Oświadczenie

Oświadczam, iż w poniżej wymienionych pracach:

P1 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Application of the polar organic chemical integrative sampler for isolation of environmental micropollutants - a review, *Critical Reviews in Analytical Chemistry* (2020), 50 (1), 1-28, DOI:10.1080/10408347.2019.1565983, IF$_{2020}$ 6,54

P2 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Pollutant analysis using passive samplers: principles, sorbents, calibration and applications. A review, *Environmental Chemistry Letters* (2021), 19 (1), 465-520, DOI:10.1007/s10311-020-01079-6, IF$_{2020}$ 9,03

P3 K. Godlewska, A. Jakubus, P. Stepnowski, M. Paszkiewicz, Impact of environmental factors on the sampling rate of β-blockers and sulfonamides from water by a carbon nanotube-passive sampler, *Journal of Environmental Sciences* (2021), 101, 413-427, DOI:10.1016/j.jes.2020.08.034, IF$_{2030}$ 5,57

P4 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Carbon nanotubes, activated carbon and Oasis HLB as sorbents of passive samplers for extraction of selected micropollutants - comparison of sampling rates and extraction efficiency, *Microchemical Journal* (2022), 172, 1-12, DOI:10.1016/j.microc.2021.106975, IF$_{2020}$ 4,82

P5 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Carbon nanotube-passive samplers as novel tools for sampling and determining micropollutants in the aquatic environment, *Science of the Total Environment* (2022), 836, 155551, DOI: 10.1016/j.scitotenv.2022.155551, IF$_{2020}$ 7,96

mój udział polegał na konceptualizacji, opiece merytorycznej, nadzorowaniu badań oraz współuczestniczeniu w pisaniu manuskryptów.

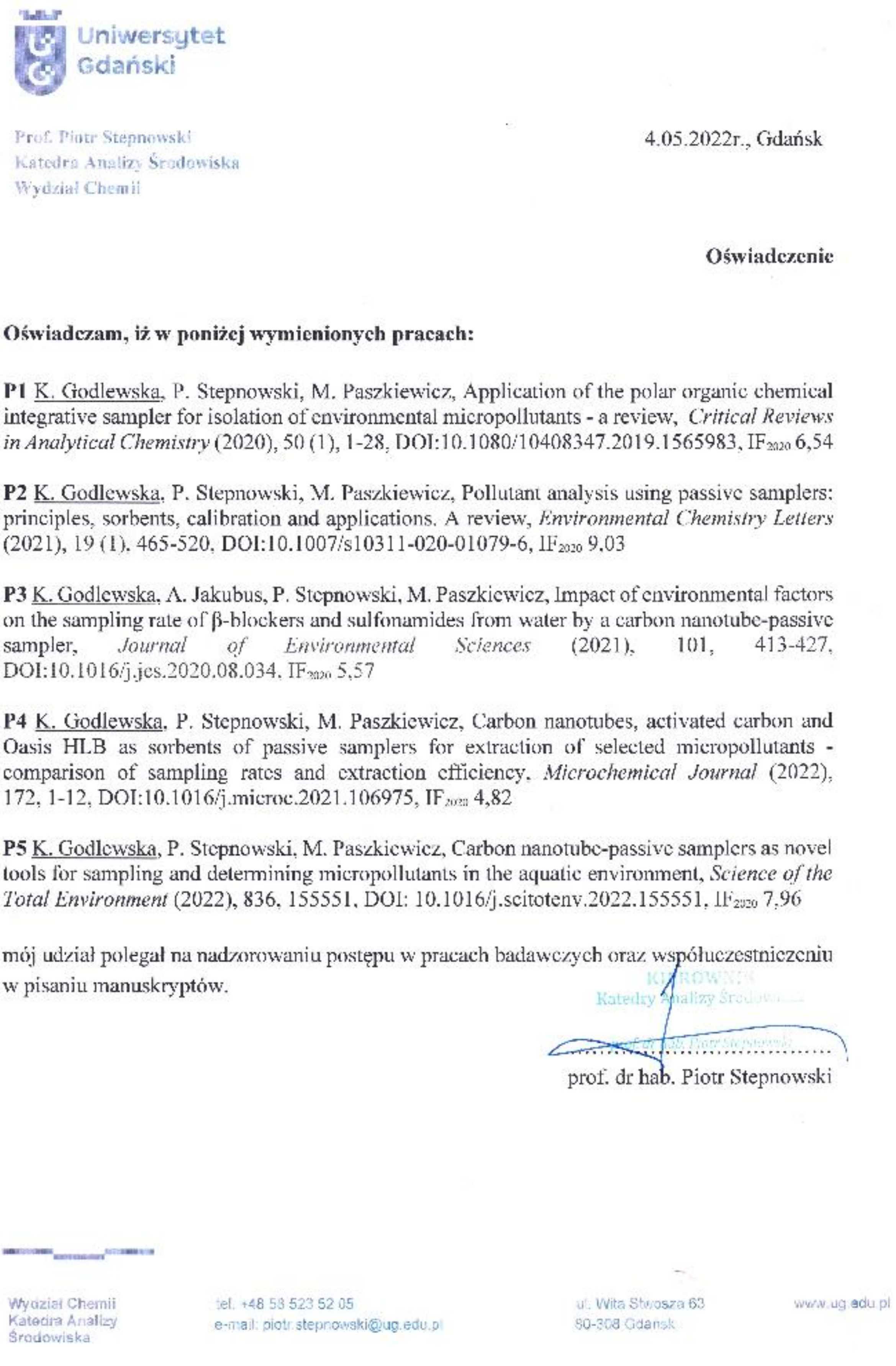
Paszkiewicz Monika
....
dr hab. Monika Paszkiewicz, prof. UG

Wydział Chemii
Katedra Analizy
Środowiska

tel. +48 58 523 52 09
e-mail: monika.paszkiewicz@ug.edu.pl

ul. Wita Stwosza 63
80-308 Gdańsk

www.ug.edu.pl



Uniwersytet
Gdański

Prof. Piotr Stepnowski
Katedra Analizy Środowiska
Wydział Chemii

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Oświadczenie

Oświadczam, iż w poniżej wymienionych pracach:

P1 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Application of the polar organic chemical integrative sampler for isolation of environmental micropollutants - a review, *Critical Reviews in Analytical Chemistry* (2020), 50 (1), 1-28, DOI:10.1080/10408347.2019.1565983, IF_{2020} 6,54

P2 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Pollutant analysis using passive samplers: principles, sorbents, calibration and applications. A review, *Environmental Chemistry Letters* (2021), 19 (1), 465-520, DOI:10.1007/s10311-020-01079-6, IF_{2020} 9,03

P3 K. Godlewska, A. Jakubus, P. Stepnowski, M. Paszkiewicz, Impact of environmental factors on the sampling rate of β-blockers and sulfonamides from water by a carbon nanotube-passive sampler, *Journal of Environmental Sciences* (2021), 101, 413-427, DOI:10.1016/j.jes.2020.08.034, IF_{2020} 5,57

P4 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Carbon nanotubes, activated carbon and Oasis HLB as sorbents of passive samplers for extraction of selected micropollutants - comparison of sampling rates and extraction efficiency, *Microchemical Journal* (2022), 172, 1-12, DOI:10.1016/j.microc.2021.106975, IF_{2020} 4,82

P5 K. Godlewska, P. Stepnowski, M. Paszkiewicz, Carbon nanotube-passive samplers as novel tools for sampling and determining micropollutants in the aquatic environment, *Science of the Total Environment* (2022), 836, 155551, DOI: 10.1016/j.scitotenv.2022.155551, IF_{2020} 7,96

mój udział polegał na nadzorowaniu postępu w pracach badawczych oraz współuczestniczeniu w pisaniu manuskryptów.

KIEROWNIK
Katedry Analizy Środowiska
prof. dr hab. Piotr Stepnowski

....
prof. dr hab. Piotr Stepnowski

Wydział Chemii
Katedra Analizy
Środowiska

tel. +48 58 523 52 05
e-mail: piotr.stepnowski@ug.edu.pl

ul. Wita Stwosza 63
80-308 Gdańsk

www.ug.edu.pl

Uniwersytet
Gdański

mgr Aleksandra Jakubus

4.05.2022r., Gdańsk

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mój udział polegał na przygotowaniu próbników pasywnych i wykonaniu wstępnych badań w celu określenia współczynników szybkości pobierania β-blokerów.

Jakubus... Aleksandra
mgr Aleksandra Jakubus

tel. +48 58 523 31 54
e-mail: aleksandra.jakubus@ug.edu.pl

ul. Wita Stwosza 63
80-308 Gdańsk

www.ug.edu.pl

9. Prace opublikowane wchodzące w skład rozprawy doktorskiej P1-P5

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Application of the Polar Organic Chemical Integrative Sampler for Isolation of Environmental Micropollutants – A Review

Klaudia Godlewska, Piotr Stepnowski, and Monika Paszkiewicz

Department of Environmental Analytics, Faculty of Chemistry, University of Gdansk, Gdansk, Poland

ABSTRACT

Aquatic passive samplers have been extensively tested and deployed in the field over the past two decades. Among these devices is relatively recently developed the Polar Organic Chemical Integrative Sampler (POCIS) for isolation of hydrophilic organic micropollutants in aquatic environment. The use of POCIS allows the measurement of low and fluctuating trace concentrations of such micropollutants, which is often troublesome using classical sampling. In this review, POCIS applications based on numerous articles to assess the suitability of these devices for use in environmental analytics information were summarized. Additionally, the possibilities of using POCIS for the isolation of complex chemical mixtures in order to highlight the high potential of this devices were presented. The types of sorbents used in POCIS, exposure duration and sampling media are juxtapose in this review. Based on the existing literature, attention was paid to both promising opportunities but also to limitations of passive methods.

KEYWORDS

Aquatic environment; bioassay; monitoring of micropollutants; passive techniques; performance and reference compounds; polar organic chemical integrative samplers (POCIS); sampling rates (R_s)

1. Introduction

Contamination of ecosystems by organic compounds, especially from the group of Persistent Organic Pollutants (POPs) and newly emerging micropollutants creates a threat to both the environment and human health. In addition, these pollutants are persistent substances that are difficult to prone to biochemical degradation and disrupt the biological balance of the environment. Very low, although already harmful levels of these chemical compounds in various environmental matrices force us to constantly search for simple and cheap devices and methods of isolation and enrichment of organic compounds in environmental samples.[1–4] For this reason, the development of passive techniques is a very important in the field of analytics and monitoring of pollutants in various environmental components, for example in air and water.

1.1. Development of passive techniques

Since 1973, many monographic and review have been published, many design solutions have been proposed that enable isolation and/or enrichment of a wide range of both organic and inorganic analytes.[5] The passive dosimeters can be classified due to the construction, the type of sorbent used or the phenomenon used at the stage of isolation and enrichment. The best known and most frequently used dosimeter is the SPMD (Semi-Permeable Membrane Device),[6–9] but polar organic chemical integrative samplers (POCIS),[1,10] Chemcatcher,[11,12] PISCES (Passive in Situ Concentration-Extraction Sampler)[13] or MESCO (Membrane Enclosed Sorptive Coating)[14] types of passive samplers are also practical. Most passive sampling devices (PSDs) are built in a similar way. They have a receiving phase (e.g. solvent, solid sorbent) in which the analytes are retained and the limiting phase (membrane) which is largely responsible for the rate of chemical uptake and allows the selective transport of analytes.[15] The principle of PSDs operation is based on the free-flowing transport of the mass of analytes through the membrane to the receiving medium, which is caused by the difference concentration of analyte between the external environment and the solid or liquid medium.[16] However, SPMD, MESCO, and PISCES passive dosimeters are most often used for the collection of hydrophobic analytes. Whereas, POCIS dosimeter is designed to polar analytes monitoring.[17–22] Passive techniques have many important advantages, including simplicity, low cost, no need to use expensive and complicated equipment, no power demand, and no maintenance. The ability of the passive dosimeters to accumulate the target compounds, and thus to measure time average concentrations is more important from the toxicological point of view. The current generation of passive dosimeters enables detecting and analyzing bioavailable contaminants at low and very low concentrations, and examining the environmental concentration of organic and inorganic contaminants not only on a local scale, but also on a continental and global scale.[17,22–32]

CONTACT Monika Paszkiewicz monikapasz@wp.pl; monika.paszkiewicz@ug.edu.pl Department of Environmental Analytics, Faculty of Chemistry, University of Gdansk, ul. Wita Stwosza 63, Gdansk, 80-308, Poland

1.2. Polar organic chemical integrative sampler

POCIS consists of two hydrophilic microporous flat-disk shaped membranes (usually polyethersulphone (PES) with $0.1\,\mu m$ pore size) between which the adsorbent phase is closed. Considering that the PES membranes can not be welded, rings made of stainless steel or other rigid inert material are used to prevent loss of sorbent from the probes.[33] The conventional POCIS device (Figure 1) has an exposed membrane diameter of 5.4 cm, which gives a surface area of $45.8\,cm^2$ and contains 200 mg receiving phase.[34] Two phase configurations are commercially available: one is a pesticide-POCIS containing a triphasic admixture of a hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) and a carbonaceous adsorbent (Ambersorb 1500) dispersed on a styrene divinylbenzene copolymer (S-X3 Bio Beads), while the other is a pharmaceutical-POCIS consisting of a hydrophilic-lipophilic balanced copolymer [poly(divinylbenzene)-co-*N*-vinylpyrrolidone] (Oasis HLB). Using commercially available sorbents, POCIS can be applied to isolate compounds with $0 \le \log K_{ow} \le 5$.[35,36] When using Isolute ENV+, Ambersorb 1500, S-X3 BioBeads sorbents, the POCIS can be applied to enrich pesticides, natural and synthetic hormones and other hydrophilic compounds.[31,36,37] On the other hand, when using an Oasis HLB sorbent, most classes of pharmaceuticals can be isolated in POCIS dosimeters.[38,39] It is worth mentioning that, recent literature reports show the possibility of using other receiving phases in POCIS to increase range of polarity of the isolated compounds, namely: carbon nanotubes,[15] ionic liquids,[40] molecularly imprinted polymers (MIP),[41,42] or Strata WAX (Weak Anion Exchange) sorbent,[43] which are described in more detail in the following text.

1.3. The principle of POCIS operation

The accumulation of the compound from water in the adsorbent phase can be described by the first Fick diffusion law by adopting linear concentration gradients between the bulk water phase and the receiving medium.[44] POCIS exhibited *in situ* demonstrate three phases of accumulation (Figure 2). During phase I (time-integrative), the kinetics of compound uptake follow a pseudo-linear curve (when the concentration in the aqueous phase is kept constant). In phase II (indirect), the kinetics of accumulation is curvilinear. Whereas, phase III (stationary) corresponds to the equilibrium separation of the relationship between the receiving phase (in the sampler) and the water ambient the dosimeter. It should be remembered that the time of each of these phases depends on the tested compounds and exposure conditions.

To estimate the time-weighted average (TWA) concentration of micropollutants ambient the sampler, the POCIS should be exposed during the linear phase (phase I), after which the calculation is made on the basis of Equation (1) below:

$$Cw = \frac{Cs \times Ms}{Rs \times t} \qquad (1)$$

where Cw is the mean contaminant concentration in the ambient water during the deployment period (µg l^{-1}); Cs is the concentration of analytes in the adsorbent phase (µg g^{-1}), Ms is the mass of the adsorbent in the POCIS (g); R_s is the sampling rate (l d^{-1}), which corresponds to the volume of water purified per unit-of-time; and t is the total exposure time (d).

Thanks to this method, more than 300 different organic and inorganic substances can be detected or quantified in laboratory and *in situ*.[45] Literature data indicate that POCIS samplers are most often used in monitoring of surface waters, including river waters[19] and sewage treatment plants,[46] while less often in the case of seas, coastal waters,[17] lakes, tropical waters,[47,48], and water treatment stations.[49] Regular use of POCIS also allows the analysis of changes occurring in the water environment depending on the season and changing weather conditions.[50]

1.4. Sampling rates (R_s)

As previously mentioned, R_s specifies the volume of purified water per unit time and is specific for each chemical compound. Taking this into account, the determination of R_s is crucial in the calculation of the concentration of analytes ambient the sampler. To determine R_s of the tested compounds, calibration of dosimeters in a laboratory (lab-derived R_s), in controlled temperature and turbulence conditions should be performed. The available literature lists various calibration procedures, among others: static renewal, static depletion, flow-through system, *in situ* calibration.[1] Determining the exposure times of the probes, during which the accumulation of compounds in the adsorption phase

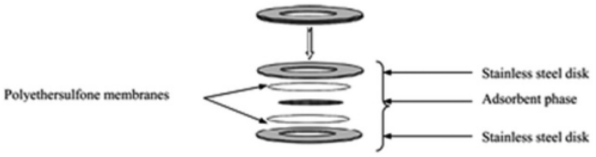

Figure 1. Schematic illustration of a POCIS device. Reprinted from [33] with the permission of Elsevier B.V. All rights reserved.

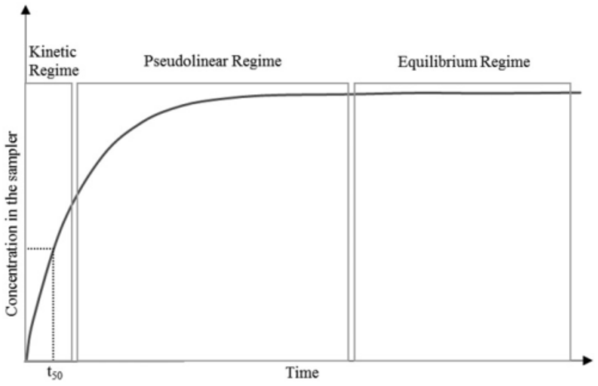

Figure 2. The three POCIS accumulation phases - integrative (Phase I), curvilinear (Phase II), and equilibrium (Phase III) – are governed by exposure time.

increases linearly or when the accumulation of analytes is independent of the concentration, is also possible during calibration procedure. It should be noted, that the sampling rate depends on the physicochemical properties of the tested pollutants and may vary depending on environmental conditions (temperature, water flow rate, pH, salinity, or dissolved organic matter).[51] Thus, in most cases, which there are some differences in environmental conditions between laboratory and field, lab-derived values of R_s may not be directly used to calculate the concentration of target compounds in the field, but must first be adjusted. For this purpose, one or more performance reference compounds (PRCs) are used, which are introduced into the passive sampler, before its exposure in the field. PRCs are compounds that do not occur in the tested environmental matrices (e.g. deuterated compounds) and desorption of PRCs during the exposure period can be used to correct *in situ* R_s. Unfortunately, the main problem in this approach is to find compounds that can significantly desorb during the exposure of samplers, which is a difficult task when using a solid receiving phase, the operation of which is based on adsorption processes.[33] For this reason, the practicality of the PRCs concept is constantly being tested experimentally, which will be presented later in the text.

The main purpose of this review was to present promising possibilities of using POCIS passive dosimeters for isolation and monitoring of a wide range of chemical compounds, differing in both structures and physicochemical properties. These aspects were studied throughout the detailed examination of data collected from 197 references covering the period 2004–2018. The merits and limitations of POCIS are presented in detail. On the basis of many scientific peer reviewed articles, the advantage of passive sampling over classical methods has been proven. Methods of calibration of passive dosimeters and environmental factors influencing the value of R_s were also indicated in this review.

2. The use of POCIS for pesticides monitoring

The widest group of chemical compounds that has been repeatedly isolated from water samples using POCIS dosimeters are pesticides. Due to the fact that more and more studies confirm scientists' assumptions about the negative impact of pesticides on living organisms, it is important to develop new, cheap, and sensitive methods for monitoring these chemicals in various components of the environment. Research shows a significant statistical relationship between the use of plant protection products and an increase in the risk of developmental disorders, neurological diseases and some cancers. So far, the residues of these substances have been identified in all type of water, that is, both in surface and underground waters, using a passive dosimetry.[19,27,52] Table 1 reports that, POCIS can be used for the screening of pesticide residues in the aquatic environment.[19,27,52] However, much more often in the literature there are reports on the use of POCIS for quantitative analysis,[26,28,41,42,53–69] a combination of both quantitative analysis and screening or monitoring of pesticides in waters such as: rivers, lakes, cave streams, lagoons, coastal waters, or WWTP influent and effluent.[17,23,29,70–80] The use of the POCIS for screening and for evaluation of TWA concentrations estimate the chemical quality of aquatic environments spatially and temporally (Table 1). As literature shows, the most frequently used sorbent in POCIS, enclosed between PES diffusion-limiting membranes, was HLB Oasis with a mass of 200 mg.

For the first time, POCIS was used to isolate pesticides from real samples using triphasic sorbent admixture in 2004 by Petty et al.[75] The exposure time of all probes was 28 days. The samplers were in stainless steel canisters (4 dosimeters per canister) that were suspended and immersed directly in water. After a specific exposure time, each dosimeter was removed from the water and stored at −15 °C, in the dark. Then, in the laboratory, the samplers were opened and the sorbent was transferred to chromatographic columns for subsequent elution of the analytes with a suitable solvent. The obtained extracts were concentrated and analyzed by GC-MS and LC-MS. They were able to determine qualitatively atrazine, propoxur, desethyl-desisopropyl atrazine, hydroxyatrazine in the Missouri river and wastewater influent and effluent.

However, the development of passive techniques is still progressing and it is not surprising that in 2016 POCIS was used to monitor 45 pesticides in Lebanese surface waters. Aisha et al.[17] used passive dosimeters containing 200 mg of Oasis HLB sorbent for this purpose. The POCIS were introduced for 14 days in three representative locations, selected in the main agricultural provinces in Lebanon, one on the Ibrahim River (Mount Lebanon), Qaraoun Lake (Bekaa Valley) and Hasbani River (southern Lebanon). After completion of the exposure, POCIS and water samples were preserved at −4 °C up to the extraction stage. The studies provided for the first time preliminary data on the occurrence of a wide range of pesticides in Lebanese surface waters using a POCIS as an alternative to the spot sampling technique. POCIS guarantee more realistic data on environmental pollution by integrating the contamination during a determinate period of time, while spot sampling only gives a snapshot of contamination at the exact time of sampling. This feature of POCIS is of key importance when monitoring compounds in environments in which micropollutants migrate, as is the case, for example, in rivers. Additionally, passive sampling allows to reduce detection limits since in field pre-concentration rates are much higher than those commonly used in the laboratory for a spot sample. It is worth mentioning, Ahrens et al.[27] performed a comparison of five passive sampling devices including silicone rubber (SR), POCIS-A (220 mg Oasis HLB), POCIS-B (220 mg sorbent mixture of 80% Isolute ENV + and 20% dispersion of Ambersorb 1500 and S-X3 bio-beads), Chemcatcher® SDB-RPS (styrene-divinyl benzene reversed phase polymer), and Chemcatcher® C_{18} for monitoring pesticides in water samples. The authors optimized and validated an analytical method for 124 individual pesticides using five different types of passive samplers. Subsequently, laboratory uptake

Table 1. Different applications of the POCIS for pesticides.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
Screening TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Assessment of the bioavailable fractions of organic chemical contaminants • Hydrological monitoring • Contaminants identification and quantitation	228 mg Oasis HLB	32	Cave streams	[74]
Screening TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Screening of micropollutants	200 mg Oasis HLB	14–28	Lagoons Coastal waters	[23]
Screening	• Screening of micropollutants • Evaluation of a contamination source • Environmental risk assessment	200 mg Oasis HLB	14	Headwater streams	[19]
Screening TWA concentrations	• Comparison of the POCIS and spot sampling strategies for pesticide monitoring • Comparison of spot and passive sampling for risk assessment • Comparison of POCIS concentrations with grab sampling concentrations	/Triphasic sorbent admixture*	28	River waters Wastewaters	[75]
Screening	• Optimization and validation an analytical method • Assessment the R_s and K_{PW} in a laboratory • Comparison of POCIS concentrations with active sampling concentrations • Comparison of the five types of passive samplers	220 mg Oasis HLB 220 mg Triphasic sorbent admixture*	26	River waters	[27]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	200 mg Triphasic sorbent admixture*	28	Lake	[26]
Screening TWA concentrations	• R_s determination in laboratory • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	14	River waters	[29]
Screening TWA concentrations	• Screening of micropollutants • R_s estimation (from other author) • TWA concentrations • Environmental risk assessment • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	More than 60	River water	[76]
TWA concentrations	• R_s determination *in situ* • TWA concentrations thanks to a PRC	200 mg Oasis HLB	22	Stream waters River waters	[64]
Screening TWA concentrations	• R_s estimation (from other authors) • TWA concentrations • Screening of micropollutants • Comparison of POCIS quantities with spot sampling concentration • Environmental risk assessment	200 mg Oasis HLB	14	River waters Lakes	[17]
Screening	• Screening of micropollutants • Evaluation of a contamination source	200 mg Oasis HLB 200 mg Triphasic sorbent admixture*	21	River waters WWTP influent WWTP effluent	[52]
TWA estimations	• R_s determination *in situ* • TWA estimation • Comparison POCIS with classical water analysis in terms of quantitative limits, sample treatment and processing • Environmental risk assessment	200 mg Oasis HLB	14	River waters	[28]
Screening TWA concentrations	• R_s determination in laboratory • PRC determination • Screening of micropollutants	200 mg Oasis HLB	21	River waters	[77]
TWA concentrations	• R_s estimation (from previous reference from them) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	9	Spiked river water (in laboratory)	[65]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Triphasic sorbent admixture*	21	River waters	[66]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	/	10	River waters	[67]

(*continued*)

Table 1. Continued.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
TWA concentrations Coupling with bioassay	• Comparison of POCIS concentrations with grab sampling concentrations • R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with photosynthesis bioassay	200 mg Oasis HLB	14	Upstream river water Middle river water Downstream river water	[81]
TWA concentrations Coupling with bioassay	• Comparison of POCIS concentrations with grab sampling concentrations • R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with photosynthesis bioassay	/	More than 60	River waters	[82]
TWA concentrations	• Comparison of POCIS concentrations with grab sampling concentrations • R_s determination in laboratory • Evaluation of the effect of DOM (dissolved organic matter) on the R_s magnitude • Assessment of the effect of hydrodynamics on the R_s	/ Oasis HLB	21	River waters	[69]
TWA concentrations	• R_s determination in laboratory • Assessment of the effect of hydrodynamics on the R_s • TWA concentrations thanks to a PRCs	200 mg Oasis HLB	40	Coastal waters	[68]
TWA concentrations	• TWA concentrations • Comparison of passive stir bar sorptive extraction (SBSE) and POCIS	200 mg Oasis HLB	30	River waters	[53]
TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs • Determination of the influence of the sorbent amount on the uptake curves	200/400/600 mg Oasis HLB	35	Laboratory water	[54]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with short-term photosynthetic bioassay	/	14	River waters	[83]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with short-term photosynthetic bioassay	/	14	River waters	[84]
Screening TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Screening of micropollutants	450 mg Oasis HLB	21	Groundwater	[78]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	200 mg Oasis HLB	21	Tap water	[55]
TWA concentrations	• R_s determination *in situ* • TWA concentrations • Comparison of POCIS concentrations with spot sampling concentrations	230 mg Oasis HLB	20	River waters	[56]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with short-term photosynthetic bioassay	/ Oasis HLB	28	River waters	[85]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations • Coupling of POCIS extracts with animals bioassay	/	14	River waters	[140]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs	/	14	Sewage lagoon River water	[57]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with embryo-larval bioassay	200 mg Oasis HLB	7	Coastal waters	[86]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Assessment of the impact of environmental variables on R_s	200 mg Oasis HLB	56	River waters	[58]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Comparison of Pharm-POCIS concentrations with Pest-POCIS concentrations	200 mg Oasis HLB 200 mg Triphasic sorbent admixture*	21	Tap water	[59]
Screening TWA concentrations	• R_s estimation (from previous reference from them)	200 mg Oasis HLB	14	River waters	[79]

(*continued*)

Table 1. Continued.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
	• Assessment of the impact of biofouling and water rate on R_s • TWA concentrations thanks to a PRCs • Comparison of passive sampling with active sampling				
Environmental monitoring TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Environmental monitoring • Comparison of POCIS concentrations with spot sampling concentrations	200 mg Oasis HLB	14	River waters	[80]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Coupling of POCIS extracts with short-term photosynthetic bioassay • Toxicological assessment	/ Oasis HLB	14	River waters	[87]
Environmental monitoring TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations • Environmental monitoring • Coupling of POCIS extracts with bioassay • Risk assessment	/	60	River waters	[70]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs	200 mg Oasis HLB	14	River waters	[60]
TWA concentrations	• R_s determination in laboratory • Assessment of the impact of temperature on R_s	220 mg Oasis HLB	28	River waters	[61]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Determination of the influence of membrane porosity (nylon membrane and PES membrane) on accumulation	200 mg MIP	35	Mineral water	[41,42]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Comparison of POCIS concentrations with spot sampling concentrations	/ Oasis HLB	35	River waters	[62]
Environmental monitoring TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to a PRCs • Environmental monitoring • Comparison of POCIS concentrations with spot sampling concentrations • Risk assessment	200 mg Oasis HLB	21	River waters	[71]
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs • Environmental monitoring • Comparison of POCIS concentrations with active sampling concentrations • Risk assessment	220 mg Oasis HLB	42	Surface waters	[72]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Risk assessment	230 mg Oasis HLB	20	River waters	[141]
TWA concentrations	• R_s estimation (from previous reference from them) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	220 mg Oasis HLB	14	River waters	[63]
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs • Environmental monitoring • Comparison of POCIS concentrations with grab sampling concentrations	220 mg Oasis HLB	13–15	Drinking water treatment plants	[73]

*Hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+)/carbonaceous sorbent (Ambersorb 572), 80:20 (w/w), dispersed on styrene-divinylbenzene copolymer (S-X3 Bio Beads).

experiments were carried out to quantify the uptake kinetics for target compounds for the tested passive devices under controlled conditions. On the basis of the obtained data, R_s and K_{pw} (passive sampler-water partition coefficient) for individual pesticides were calculated. The last stage of the research was a comparison the pesticide concentrations derived by the passive samplers to time-integrated active sampling in the field. The results indicate that the uptake of selected analytes depended on their physicochemical properties, that is, SR showed better uptake of hydrophobic compounds with log $K_{ow} > 5.3$ and POCIS-A, POCIS-B and Chemcatcher® showed better uptake of hydrophilic compounds with log $K_{ow} < 0.7$. In addition, the results points to that POCIS-B and POCIS-A have the highest sorption capacity compared to the other passive probes. In conclusion, the comparison between the PSDs and the time-integrated active sampler concentration showed good agreement, and the tested passive samplers (including POCIS) are the ideal tool for screening of pesticides and can be used to study temporal-spatial trends.

Conventional POCIS are only useful for organic compounds with log $K_{ow} \geq 0$, which is related to their weakness in capturing highly polar analytes such as acidic and highly polar herbicides. For this reason, in 2017 Berho et al.[41] proposed the use of molecularly imprinted polymer (MIP) as the receiving phase in the POCIS-like passive sampler for the capture of glyphosate (log $K_{ow} = -3.2$) and its main degradation product aminomethylphosphonic acid (log $K_{ow} = -2.17$). Innovative POCIS were home-made by trapping 200 mg humidified MIP phase between two membranes. MIP-POCIS (MIP receiving phase, PES $0.2\,\mu$m membrane) was calibrated in stable laboratory conditions to obtain the R_s for both glyphosate and AMPA (aminomethylphosphonic acid). The effect of the membrane type on accumulation of target compounds using a nylon membrane and PES membrane was also investigated. The results showed that the average accumulation of glyphosate and AMPA in nylon membrane was greater with the PES membrane. POCIS with PES membranes have a longer period of linear uptake than POCIS with nylon membranes and therefore appear more suitable for most hydrophilic compounds. The usefulness of MIP as the receiving phase in POCIS for the isolation of highly polar compounds has been proved and the need for further research into the development of MIP-POCIS was emphasized.

Given the fact that environmental conditions can affect the performance of POCIS, some Authors use PRCs to determine the *in situ* sampling rates of target compounds.[54,57–60,64,68,71–73,77,79–87] Belles et al.[68] tested 21 substances to select compounds with sufficient sorption dispersion rates that are suitable as PRCs for POCIS. Satisfactory results were obtained for *desisopropyl-atrazine-d*$_5$ (DIA), *cyanazine*, *desethyl-atrazine*, *pymetrozine*, *nicosulfuron*, and *chlorsulfuron* for use as PRCs. In the next stage, DIA and *cyanazine* were used as PRCs to calibrate passive devices under various hydrodynamic conditions in the laboratory to determine R_s of tested pesticides. After that, the POCIS enriched PRCs were deployed in the Arcachon Bay to determine the TWA concentration of the pesticides in this environment. The obtained results show that both in laboratory and field conditions DIA was approximately 3.5 times faster dispersed than *cyanazine*. In addition, POCIS analyzes without PRCs have shown that the field water does not contain DIA and *cyanazine* and will not interfere with the dispersal of PRCs with POCIS. According to the Authors, the two PRCs dispersed at significantly different rates enable the use of the PRCs approach for use in very different environmental conditions and different periods of exposure. Moreover, water concentrations obtained from POCIS using DIA as PRCs are shown to be closer to the grab sampling concentration than the concentrations obtained with POCIS using only laboratory sampling rates (without PRC correction). The PRCs technique seems to be an interesting opportunity to improve the quantitative aspect of polar passive samplers and should be constantly developed.

Moreover, as shown in Table 1, some researchers combine the use of passive techniques with biological tests. Pesce et al.[81] used POCIS to determine the TWA concentration of diuron and N-(3,4-dichlorophenyl)-N-methylurea (DCPMU) in the river during biofilm colonization. Diuron and DCPMU were quantified using calibrated kinetic constants reported by other authors. Next, the effects of selected analytes on photosynthetic activity in natural periphyton communities were investigated. To increase the significance of the studies performed, the authors used the concept of pollution-induced community tolerance (PICT) to assess single and joint acute toxicity of target compounds on natural phototrophic biofilm communities. PICT is an ecotoxicological tool used to measure reactions caused by the pollution of selective pressure on the community. The research results indicated that the sensitivity of biological environments to diuron and DCPMU decreased from upstream to downstream, revealing the induction of tolerance in contaminated river sections, which is in line with the expectations of the PICT concept. In conclusion, POCIS combined with bioassays can be a powerful tool for the chemical and toxicological risk assessment of pesticides in the aquatic environment.

3. The use of POCIS for pharmaceuticals and endocrine disrupting substances monitoring

In recent years, there has been an increase in interest in the ecotoxicity of pharmaceuticals, their determination in the aquatic environment and effective elimination from various components of the environment.[88–90] The presence of drug residues in wastewater, groundwater, and surface water is a significant problem that can cause various environmental and health effects among animals and humans. The majority of research concerns the content of nonsteroidal anti-inflammatory drugs, hypolipemic agents, and regulating blood pressure, hormonal substances, and antibiotics. The greatest difficulty in removing and determining pharmaceuticals is related to their high dilution and biological activity as well as the lack of biodegradability. Due to the unknown toxicity of chronic exposure to pharmaceuticals present in water and treated wastewater discharged to water and soil, there is a need to develop new efficient techniques for monitoring these chemicals in the environment.[39,91,92] Table 2 presents the different purposes of POCIS-based research and their applications. The main goals of using POCIS for pharmaceuticals are: (1) R_s determination (in laboratory or/and *in situ*); (2) Estimation TWA concentrations; (3) Screening or/and monitoring pharmaceuticals; (4) Comparison of POCIS concentrations with grab sampling concentrations; (5) Coupling of POCIS extracts with bioassays. As Table 2 indicates, several scientists use passive techniques both to determine TWA concentration and to screen/monitor pharmaceuticals in the aquatic environment.[39,92–99] Furthermore, the most frequently used sorbent as the

Table 2. Different applications of the POCIS for pharmaceuticals.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
TWA concentrations	• R_s determination in laboratory and *in situ* • Comparison of R_s for POCIS using PES and PS membranes • Sampler size optimization • Estimation of the impact of environmental factors on R_s • Comparison between spot and passive sampling	100 mg Oasis HLB	10	Sewage effluent River waters	[122]
Screening TWA concentrations	• R_s determination in laboratory • TWA concentrations • Screening of micropollutants	200 mg Oasis HLB	7	Mediterranean coastal waters	[39]
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentrations • Environmental monitoring • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	54	Stream waters	[100]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	37	Estuarine waters	[123]
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentrations • Environmental monitoring • Comparison of POCIS concentrations with grab sampling concentrations	/ Oasis HLB	28	Drinking water treatment plants	[94]
Screening Coupling with bioassay	• Coupling of POCIS extracts with photosynthesis bioassay • Screening of micropollutants • Environmental risk assessment	/ Oasis HLB	30	River waters downstream	[142]
TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs • Estimation of effects of DOM and pH on R_s	200 mg Oasis HLB	8	Laboratory water	[51]
Screening TWA concentrations	• R_s determination *in situ* • TWA concentrations • Estimation of the effects of exposure conditions on R_s • Screening of micropollutants	200 mg Oasis HLB	31	Wastewaters	[92]
TWA concentrations	• R_s determination in laboratory • Impact of water temperature and flow on R_s • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	29	Lake	[48]
TWA concentrations	• R_s determination *in situ* • TWA concentrations • Assessment the bioavailable concentrations of micropollutants • Estimation of effects of environmental conditions on R_s	200 mg Triphasic sorbent admixture*	21	River waters Wastewaters	[143]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	200 mg Oasis HLB	28	Coastal waters	[144]
Screening	• Screening of micropollutants • Comparison of POCIS quantities with fish concentrations	100 mg Oasis HLB	21	Sewage treatment works (STW)	[145]
Screening	• Screening of micropollutants • Determination of POCIS quantities • Evaluation of a contamination source • Comparison of POCIS quantities with the response of fish concentrations	200 mg Oasis HLB	21	Downstream WWTP River waters	[146]
Screening	• Screening of micropollutants • Evaluation of a contamination source • Determination of a gradient of concentration • Comparison of POCIS quantities with fish responses	/	7	Upstream WWTP Downstream WWTP	[147]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations • Impact of water temperature and flow on R_s • Screening of micropollutants • Environmental risk assessment	200 mg Oasis HLB	31	Estuarine waters	[91]
TWA concentrations	• R_s estimation (calculated or from other author) • TWA concentrations	200 mg Oasis HLB	7	Upstream WWTPs Downstream WWTPs WWTP effluent	[148]

(*continued*)

Table 2. Continued.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations • Comparison of POCIS concentrations with mussel concentrations	/ Oasis HLB	14 to 21	Upstream WWTPs Downstream WWTPs WWTP effluent	[149]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Triphasic sorbent admixture*	28	WWTP effluents Upstream WWTPs Downstream WWTPs	[20]
TWA concentrations	• R_s determination *in situ* • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	24	WWTP effluents Upstream WWTPs Downstream WWTPs River water	[150]
Environmental monitoring TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Environmental monitoring	200 mg Oasis HLB	27	Sewage water	[95]
TWA concentrations	• R_s estimation (from previous reference from them) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	14	WWTP influents WWTP effluents	[151]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Triphasic sorbent admixture*	28	Stream water River water	[152]
Coupling with bioassay	• Coupling of POCIS extracts with YES test	200 mg Triphasic sorbent admixture*	30	Upstream WWTPs Downstream WWTPs WWTP effluent	[153]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	/	28	Drinking water treatment plant	[154]
TWA concentrations	• R_s determination in laboratory and *in situ* • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	100 mg Triphasic sorbent admixture*	14	Laboratory water	[134]
Coupling with bioassay	• Coupling of POCIS extracts with *in vitro* bioassay	200 mg Oasis HLB	21	Water river	[155]
TWA concentrations Coupling with bioassay	• R_s determination in laboratory • TWA concentrations • Coupling of POCIS extracts with YES test	100 mg Oasis HLB	39	Upstream WWTPs Downstream WWTPs	[156]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations • Coupling of POCIS extracts with in vitro bioassay	/	23	WWTP influents WWTP effluents	[157]
Coupling with bioassay	• Coupling of POCIS extracts with YES test • Comparison of passive sampling and biomonitoring	/	14	Wastewater	[158]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Risk assessment	/	28	Upstream WWTPs Downstream WWTPs	[159]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	200 mg Oasis HLB	30	Coastal waters	[160]
TWA concentrations	• R_s determination in laboratory • Influence of temperature and flow velocity on R_s value • TWA concentrations	200 mg Oasis HLB	4	Hospital sewage	[129]
Coupling with bioassay	• Coupling of POCIS extracts with YES test	300 mg Strata X	/	River waters	[161]
Environmental monitoring Coupling with bioassay	• Coupling of POCIS extracts with ELISA (enzyme-linked immunosorbent assay) • Environmental monitoring	/ Oasis HLB / Triphasic sorbent admixture*	21–28	Upstream WWTPs Downstream WWTPs	[93]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	/ Oasis HLB	21	River waters	[162]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations • Coupling of POCIS extracts with YES test	200 mg Oasis HLB	44	Headwater	[163]
TWA concentrations	• R_s determination in laboratory • TWA concentration • Comparison of POCIS concentrations with grab sampling concentrations	/	14	Wastewaters	[164]
TWA concentrations	• R_s determination in laboratory • TWA concentration thanks to PRCs	200 mg Oasis HLB	15	River waters	[165]

(continued)

Table 2. Continued.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	200 mg Oasis HLB	22–52	River waters	[166]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations thanks to PRCs	200 mg Oasis HLB	/	River waters	[167]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Risk assessment	/	15–19	Bay	[168]
Environmental monitoring TWA concentrations	• R_s determination *in situ* • TWA concentrations • Environmental monitoring	/	14	Upstream WWTPs Downstream WWTPs	[96]
Environmental monitoring TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Environmental monitoring	200 mg Oasis HLB	14	Headwater	[97]
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentration • Comparison of POCIS concentrations with grab sampling concentrations • Environmental monitoring	/ Oasis HLB	/	River waters	[98]
Environmental monitoring TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Environmental monitoring	200 mg Oasis HLB	14	Wastewaters	[99]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	/ Oasis HLB	14	River waters	[169]
TWA concentrations	• R_s determination in laboratory and *in situ* • TWA concentration thanks to PRCs • Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB	14	Upstream WWTPs Downstream WWTPs	[101]

*Hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+)/carbonaceous sorbent (Ambersorb 572), 80:20 (w/w), dispersed on styrene-divinylbenzene copolymer (S-X3 Bio Beads).

receiving phase in POCIS is Oasis HLB with a mass of 200 mg.

To assess the suitability of POCIS for the capture of target compounds, scientists often compare the analyte concentrations estimated from POCIS extracts with concentrations obtained by spot sampling in their studies. Such a comparison is difficult because of the difference in duration of the sampling period between the two sampling methods. As previously mentioned, the biggest disadvantage of spot sampling is that it only provides an assessment of environmental pollution concentrations only at the time of sampling, omitting episodic events. Therefore, the results obtained with passive sampling often differ from those obtained using spot sampling. Many authors emphasize that the data from the direct comparison of these two sampling methods should be interpreted with caution.

Alvarez et al.[100] in 2004 used POCIS to integratively concentrate the trace levels of pharmaceuticals and determine TWA water concentrations. The Authors compared the passive method using POCIS with standard sampling methodologies. For this purpose, previously prepared probes were put in the New Jersey stream for 54 days. Water samples were collected four times during the exposure of the dosimeters. Analysis of POCIS extracts and water samples revealed 33 pharmaceuticals in POCIS extracts compared to 29 in water samples. The data had shown the usefulness of POCIS for the determination of chemicals that dissipate quickly or get into the water through an episodic event. In addition, Alvarez et al.[100] saw the opportunity to use POCIS as an innovative method of estimating the potential exposure of aquatic organisms to these complex mixtures of waterborne contaminants. In 2010, Li et al.[48] set of uptake rates for 30 chemical compounds, including: pharmaceuticals, personal care products (PCPs), and endocrine-disrupting substances (EDSs), focusing on determining the effect of water temperature and flow on the collection of polar chemicals to POCIS. The R_s increased with water temperature and flow, but these environmental parameters had a relatively minor influence on uptake. The designated R_s were used for POCIS field deployment at stations in Lake Ontario. The calculations made it possible to estimate the concentrations of these analytes in water that were consistent with the concentrations of these compounds measured in grab samples of surface water.

Shi et al.[91] focused on optimization, validation, and application of POCIS for major antibiotic compounds including seven sulfonamides, two macrolides, three chloramphenicols, and five EDSs in estuarine waters. They set down a R_s values in both laboratory and *in situ* conditions. The influence of sample salinity (0‰, 14‰, 35‰) on the R_s of the target analytes was investigated. It was shown that the increase in salinity of water caused an increase in the R_s of all tested compounds with the exclusion of estriol, with a further increase in salinity up to 35‰ caused a decrease in the sampling rate for all compounds except bisphenol A, erythromycin, and roxithromycin. The highest R_s values were observed with salinity 14‰. On the other hand, water flow and turbulence in the area can reduce the thickness of the boundary layer, therefore the impact of this parameter has also been studied. It was observed that a 2–4-fold increase in R_s was obtained when the flow rate was doubled. In the case of estrone, 17-β-estradiol, 17-α-ethylestradiol, macrolide, and chloramphenicol their R_s was increased three to four times when the flow rate was doubled. The authors suggest that such a complex relationship indicates that POCIS should be thoroughly tested for various environmental conditions before deployment. The validated device was subsequently used to sample and determine the target pollutants in the Yangtze Estuary. The results of the test proved that passive sampling effectively provides data of TWA concentrations of target compounds in estuarine waters, which are crucial for risk assessment after thorough validation.

However, it often happens that external factors significantly affect the uptake of analytes by POCIS. The biggest challenge before using POCIS is the lack of a correction method for ambient conditions (e.g. water flow, temperature and pH) that affect the uptake process. To solve this problem during the capture of pharmaceuticals, Li et al.[101] in 2018 proposed the use of antipyrine-d_3 (ATP-d_3) as a performance reference compound in POCIS. It was shown that lab-derived R_s (without using PRCs) differed from field-derived R_s (using PRCs) by a factor of 1.5-4.75. Additionally, the concentrations of tested analytes with ATP-d_3 in passive sampling were consistent with the spot sampling concentrations.

It is worth to noting that differences between the R_s values obtained during the calibration of dosimeters in the laboratory and the R_s values obtained during calibration *in situ* are very common. Therefore, it is necessary to validate PSDs both in the laboratory and *in situ* in order to determine the correct values of R_s before beginning dosimeters exposure and determining the TWA concentration of the target chemical compounds. A promising approach to solving this problem is also the use of PRCs, which is applied by several authors. Based on numerous literature reports, it can be concluded that POCIS passive samplers can be successfully used to isolate and monitor such a wide variety of chemical compounds as pharmaceuticals.

4. The use of POCIS for perfluorinated compounds monitoring

Perfluorinated compounds (PFCs) are applied in materials, products, and equipment exerted for industrial and everyday use for about 60 years. It has been determined that among the previously synthesized PFCs up to 50 are substances that may be a problem as pollution of the environment and food.[43] The fact that certain PFCs pollute the environment, as well as their occurrence in foodstuffs, body fluids, human and animal tissues, and toxicity, led to the ban on the production, marketing, and use of perfluorooctane acid (PFOS) and perfluorooctane sulfonate (PFOA) and their derivatives. Despite the large progress in the analysis of perfluorinated compounds, the development of ever-better methods of extraction and analysis of these compounds, our knowledge of their sources and quantitative and qualitative composition in various environmental materials and organisms is still quite limited.[102] One of the innovative and modern methods of isolation and monitoring of these chemicals have recently been POCIS. The data included in Table 3 show that there are currently few scientific reports regarding the applicability of POCIS to perfluorinated compounds. Literature reports indicate that the main application of POCIS is in coupling with chemical analysis to assess TWA concentration of PFCs in water (river waters, lakes, bays, and WWTP effluents).[40,43,102–108] Moreover, researchers are constantly developing the use of passive techniques for monitoring and screening of PFCs (Table 3).

Relatively recently in 2012, Kaserzon et al.[43] used POCIS for the isolation and determination of perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), and perfluorododecanoate (PFDoDA). They used 200 mg Oasis HLB as a sorbent in POCIS, which is most often used for a wide range of chemical compounds. In addition, the authors introduced a modification of the sorbent used a specific configuration different from the commercially available POCIS. This modified POCIS contained 600 mg (600 compared to 200 mg) of Strata WAX (Weak Anion Exchange) as the receiving phase, enclosed between PES diffusion-limiting membranes. This approach was to ensure an increase the sorption capacity of the sampler. Based on the obtained results, no significant differences were observed in the amount of retained analytes in the modified POCIS and in the standard POCIS. However, during the desorption of the analytes from the Oasis HLB sorbent surface, recoveries of only 30% for perfluorohexanoate (PFHxA) and even less for homologs with a smaller chain length were obtained. This suggests that the HLB Oasis sorbent is useful as a receiving phase only for the longer PFCs considered in these studies, which desorption is effective. This suggests a standard POCIS may have application, but with a more limited range of analytes than a modified one containing a sorbent with a mixed mode of action. In fact, thanks to the application of Strata WAX sorbent, PFHxA, perfluorobutanesulfonate (PFBS), and perfluoropentanoate (PFPeA) could be quantified in the Sydney Harbor field study with levels of the first two in good agreement with those from grab samples. The consequence of the results obtained by Kaserzon et al.[43] was the use of WAX sorbent as the receiving phase in POCIS for perfluorinated compounds in subsequent studies by other scientists, which is consistent with the data presented in Table 3. In results of that, Li et al.[102] used 200 mg Oasis WAX as a sorbent in POCIS devices to determine the R_s value for selected PFCs including PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, and PFDoDA. Then they performed a field study to test the qualitative and quantitative use of the modified POCIS device. The R_s values of selected compounds were used to determine analyte concentrations in POCIS extracts distributed at several places in Meiliang Bay, the calculated concentrations of analytes were in consistent with the corresponding value by grab sampling.

Kaserzon et al.[103] also examined the effect of flow rate (0.02 m s^{-1}, 0.06 m s^{-1}, 0.16 m s^{-1}, 0.34 m s^{-1}) on the uptake of perfluorinated compounds by POCIS under laboratory conditions. A slight increase in the R_s value of smaller PFCs with a molecular mass $\leq$464 was observed along with an increase in the flow rate, while for larger PFCs (MW $\geq$ 500) the flow rate did not affect the efficiency

Table 3. Different applications of the POCIS for perfluorinated compounds.

Application(s)	Aim(s)	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
Screening	- Screening of micropollutants - Comparison of POCIS concentrations with fish muscle and liver tissue concentrations	/	30	River waters	[106]
TWA concentrations	- R_s determination in laboratory - Impact of environmental factors on R_s - TWA concentrations	200 mg Oasis WAX	10	Bay waters	[102]
TWA concentrations	- R_s determination in laboratory - TWA concentrations - Comparison of Oasis HLB concentrations with Strata WAX concentrations in POCIS - Comparison of POCIS concentrations with grab sampling concentrations	200 mg Oasis HLB 600 mg Strata WAX	7	Estuarine waters	[43]
TWA concentrations	- R_s determination in laboratory - Impact of water flow rate on R_s - TWA concentrations	600 mg Strata WAX	15	River waters	[103]
TWA concentrations	- R_s determination *in situ* - TWA concentrations thanks to a PRCs - Assessment of use of PRCs as well as PFMs (passive flow monitors) as *in situ* correction methods - Impact of water flow on R_s	600 mg Strata WAX	21	WWTP effluents	[104]
TWA concentrations	- R_s determination *in situ* - TWA concentrations - Impact of environmental factors on R_s - Comparison of Pharm-POCIS capacity with Pest-POCIS capacity	200 mg Oasis HLB 200 mg Triphasic sorbent admixture*	21	WWTP effluents	[105]
TWA concentrations	- R_s determination in laboratory - TWA concentrations - The impact of DOM, pH, water flow and temperature on R_s - Comparison of uptake on the IIL-sampler and the HLB-sampler	30 mg immobilized ionic liquid 30 mg Oasis HLB	7	WWTP effluents WWTP influents	[40]
Environmental monitoring TWA concentrations	- R_s determination *in situ* - TWA concentrations thanks to a PRCs - Environmental monitoring	/	30	Upstream WWTPs Downstream WWTPs	[106]
TWA concentrations	- R_s estimation (from other author) - TWA concentrations	/ Triphasic sorbent admixture*	21	River waters	[107]
TWA concentrations	- R_s estimation (from other author) - TWA concentrations - Comparison of data obtained from analysis of different fish tissues and from POCIS	/ Triphasic sorbent admixture*	21	River waters	[108]

*Hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+)/carbonaceous sorbent (Ambersorb 572), 80:20 (w/w), dispersed on styrene-divinylbenzene copolymer (S-X3 Bio Beads).

of the uptake. Finally, it was found that the R_s values slightly depend on the flow rate.

As an innovative approach in passive techniques Wang et al.[40] proposed the use of immobilized ionic liquids (IIL) as the receiving phase in POCIS-like devices for the capture of perfluorinated compounds. 30 mg of imidazole ionic liquid, immobilized on silica gel, were closed between two PES membranes and sealed with silica plates and synthetic glass ring flanges to assemble the IIL-sampler. The surface area per mass of sorbent ratio of the sampler was twice as large (358 $cm^2\ g^{-1}$) than the value in the traditional POCIS (180 $cm^2\ g^{-1}$). As a control, sampler containing 30 mg of Oasis HLB as the receiving phase was also used. Calibration of the developed passive probes (with IIL as the receiving phase) were performed and the uptake for the five perfluorinated compounds were compared to those obtained for classical POCIS (with Oasis HLB as the receiving phase). In laboratory studies, the IIL-sampler showed greater ability to capture short-chain PFASs (perfluoroalkyl substances) compared to the HLB-sampler and provided integrative accumulation within 21 days of the experiment. Additionally, the influence of environmental factors (flow rate, pH, temperature, DOM) on the efficiency of accumulation was examined. The results showed that the flow rate had a significant impact on the passive sampling capacity. When using both low (8.7 cm s^{-1}) and high speed (17.7 cm s^{-1}), the uptake efficiency was higher than in static conditions. During the study of the effect of temperature (10 °C, 25 °C, and 35 °C), a gentle increase in R_s was observed with increasing temperature for the target compounds. Only for the long-chain homolog (perfluorododecanoic acid) a significant increase in R_s was observed with increasing temperature. The influence of pH on passive sampling of the tested analytes proved to be significant. The concentration of PFHxA, PFOA, and PFHxS (perfluorohexane sulfonic acid) in the IIL-sampler was increased along with the increase in pH (from pH 5 to 9). However, in the case of PFOS and PFDoDA, an increase in the uptake efficiency was found at pH 5 compared to their uptake at pH 7 and 9. The results of the DOM impact study show that it is negligible for the target analytes. The authors emphasize that in the studied hydrological and hydrochemical conditions the kinetics of perfluorinated compounds uptake was linear. After conducting such thorough laboratory tests, the dosimeter was applied in the waters of the sewage treatment plant for a period of 7 days. The concentrations of the majority of PFASs obtained after using the IIL-sampler in the field were essentially consistent with those obtained from spot sampling. For this reason, it can be concluded that IIL is a promising alternative of receiving phases in passive sampling.

5. The use of POCIS for mixtures of chemical compounds monitoring

Almost all currently used analytical and biomonitoring sampling techniques are inherently limited in their ability to completely assess exposure because: they do not have the possibility of integrally sampling over time, analytical sensitivity and selectivity are insufficient to detect and quantify trace amounts of complex mixtures of pollutants in water, on-site conditions (e.g. water quality) affect the survival of indicator organisms (e.g. fish in cages or clams) and causal relationships between observed biological effects and mixtures of environmental pollutants are rarely determined.[36,109–114] Therefore, scientists are trying to develop analytical methods that will be useful for a wide range of chemicals that differ in both chemical and physical properties, combating the disadvantages of classical sampling methods. One of the techniques that can be used both for the isolation of analytes with similar properties as well as for a mixture of analytes significantly differing in structure and properties is passive technique. Table 4 shows the main applications of POCIS for mixtures of chemical compounds. The number of tests carried out and the diversity of analytes and aqueous environmental matrices prove that POCIS is a promising tool for monitoring micropollutants. As a result of comparing the possibilities of passive sampling with spot sampling, many advantages of using POCIS have been underlined.[34,50,115,116]

As indicated in Table 4, POCIS type dosimeters are used for screening, monitoring and determination of TWA concentrations of chemical compounds with a wide range of hydrophilicity. The presented POCIS applications pertain to various environmental media (rivers, marine waters, lakes, lagoons, bays, estuarine waters, produced water discharges, and WTTP influents and effluents) with an exposure time from 7 to 68 days, however, most often it is a period of ~3–4 weeks.[109,110,115,117–121] Moreover, Table 4 shows that TWA concentrations were obtained for numerous organic molecules (fragrances, flame retardants, plasticizers, pharmaceuticals, pesticides, hormones, phenols, surfactants, polychlorinated biphenyls, terpenes, and detergents) in different media. It should be emphasized, that the POCIS was designed to trap polar organic contaminants with $0 \leq \log K_{ow} \leq 5$. This parameter is not fixed, since analytes with higher K_{ow} coefficients can also be accumulated, however, strongly hydrophobic substances have low affinity for the sorbents currently used in POCIS.[36] Much more often another type of dosimeters, such as semi-permeable membrane device (SPMD) or polyethylene devices (PEDs), are used for the isolation of hydrophobic impurities.

Alvarez et al.[36], as one of the first scientists, has developed a POCIS-type dosimeter capable of isolating analytes belonging to different chemical groups. They performed calibrations in the laboratory of developed PSDs to determine the R_s value. By combining theoretical models and laboratory data on the sampling rate, they were able to estimate the concentration of residual polar organic compounds (POCs) in water, more specifically in the river Ravensbourne, after 30 days of probe exposures. They prepared two types of POCIS, the first contained 100 mg Oasis HLB as a sorbent, which they used to isolate pharmaceuticals (azithromycin, fluoxetine, levothyroxine, omeprazole) while the other contained 100 mg triphasic admixture as a sorbent which they used to isolate atrazine, diazinon, diuron, 17-α-ethynylestradiol, and isoproturon. The development, calibration, and subsequent use of POCIS type dosimeters in the water environment allowed to determine the TWA concentration of target analytes belonging to the group of pharmaceuticals, hormones, and pesticides. This shows that POCIS can be used to isolate and monitor mixtures of hydrophilic organic pollutants. This method is a promising alternative to classical methods of sampling, the use of which for determining TWA concentrations as part of regular monitoring of contaminants is unprofitable logistic and financial.

Simultaneously, Alvarez et al.[36] emphasized that an important aspect of the calibration is to determine the impact of external conditions (e.g. water flow rate) on the R_s values, which will allow for accurate estimation of analyte concentrations in water. In the publication of the same Authors, it was proved that the combination of results obtained thanks to both the POCIS and PEDs is useful for monitoring the concentration of chemical substances with a wide range of $\log K_{ow}$. Data were obtained suggesting that one monitoring technique should not be used but different types of PSDs should be considered as complementary techniques, each providing a unique picture of chemical occurrence in the environment.[36] Miège et al.[115] in their studies on the use of passive techniques to monitor eight metals, 16 polycyclic aromatic hydrocarbons (PAHs), and nine pesticides in surface water have proven that the use of PSDs (including POCIS) allows the reduction of the limit of quantification (LOQ) compared with spot sampling. Obviously, the decrease in LOQ depends mainly on the type of passive dosimeter, the type of contamination and environmental conditions during exposure. A significant reduction in LOQ using POCIS was demonstrated than for spot sampling for pesticides. Also, the results of studies by Alvalez et al.[50] indicate that the use of POCIS enables isolation and detection of chemical compounds that occur in concentrations below the LOQ of spot sampling. They managed to isolate 8 additional analytes (diazinon, indole, 5-methyl-1*H*-benzotriazole, pentachlorophenol, diethylhexyl phthalate, *N*,*N*-diethyltoluamide (DEET), 4-tert-octylphenol,

Table 4. Different applications of the POCIS for mixtures of chemical compounds.

Application(s)	Aim(s)	Family of molecules	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentrations • Environmental monitoring	Pharmaceuticals, hormones, pesticides	100 mg Oasis HLB 100 mg Triphasic sorbent admixture*	30	River waters	[36]
Environmental monitoring	• Comparison of POCIS method with standard water-column sampling method • Environmental monitoring	Pesticides, pharmaceuticals, personal care products, fragrances, fire retardants, plasticizers	/ Oasis HLB Triphasic sorbent admixture*	54	River waters WWTP effluents	[50]
R_s determination	• R_s determination in laboratory	Polycyclic aromatic hydrocarbons, alkylphenols, carbazoles	/ Oasis HLB	28	Filtered seawater	[109]
Environmental monitoring TWA concentrations	• R_s determination in laboratory • TWA concentrations • Environmental monitoring	Antibiotics, fungicides, herbicides and biocides	100 mg Oasis HLB 100 mg Triphasic sorbent admixture*	14–15	Marine waters	[170]
TWA concentrations	• R_s estimation (from previous references from them) • TWA concentrations	Polycyclic aromatic hydrocarbons, alkylphenols	100 mg Oasis HLB	42	Waters in the vicinity of the oil production platform	[171]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	Detergents, hormones, plasticizer	200 mg Oasis HLB 100 mg Triphasic sorbent admixture*	7	WWTP Effluents Estuarine waters Seawaters	[37]
Coupling with bioassay	• Coupling of POCIS extracts with Fathead Minnow bioassays	Polycyclic aromatic hydrocarbons, caffeine, terpenes, chlorinated organophosphate chemicals, sterols, phenols, indole and its derivatives	/	28–35	Cave streams	[172]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	Synthetic organic chemicals	/ Oasis HLB Triphasic sorbent admixture*	29–30	Upstream of WWTPs Downstream WWTPs	[173]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Impact of water flow on R_s • Comparison of the uptake efficiency of pharmaceutical and pesticide POCIS under environmental conditions	Pharmaceuticals, personal care products, endocrine disrupting substances	200 mg Oasis HLB 200 mg Triphasic sorbent admixture*	21	Treated sewage effluent	[110]
TWA concentrations Coupling with bioassay	• R_s determination in laboratory • TWA concentrations • Impact of water flow on R_s • Combination of POCIS extracts with algal test and	Pharmaceuticals, pesticides	/	35	Treated sewage effluent	[174]

(continued)

Table 4. Continued.

Application(s)	Aim(s)	Family of molecules	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
	bioluminescence assay					
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Comparison of POCIS concentrations with biological methods concentrations	Polycyclic aromatic hydrocarbons, alkylphenols	240 mg Oasis HLB	30	Produced water discharges	[175]
Screening TWA concentrations	• R_s determination in laboratory and *in situ* • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations • Screening of micropollutants	Alkylphenols, phenolated polimer, estrogenic hormones, pharmaceuticals, hypolipidemic agent	200 mg Oasis HLB	28	River waters	[34]
TWA concentrations	• R_s estimation (from other author) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	Polycyclic aromatic hydrocarbons, pesticides	/ Oasis HLB	7–21	Marine waters River waters	[115]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Evaluation the impacts of small towns and their WWTP discharges on concentrations of micropollutants in rivers	Hormones, pharmaceuticals, pesticides, perfluorinated organics	/ Oasis HLB Triphasic sorbent admixture*	28	Headwater streams	[117]
TWA concentrations Coupling with bioassay	• R_s estimation (from other author) • TWA concentrations • Coupling of POCIS extracts with the Yeast Estrogen Screen (YES) test • Comparison of POCIS concentrations with YES tests performed on POCIS extracts	Polycyclic aromatic hydrocarbons, pesticides, plasticizers, terpenes, pharmaceuticals	200 mg Oasis HLB	28	Seawaters	[118]
Coupling with bioassay	• Coupling of POCIS extracts with the Pulse Amplitude Modulation (PAM) assay • Comparison of PAM assay performed on POCIS extracts and grab sampling concentrations	Polychlorinated biphenyls, polycyclic aromatic hydrocarbons, pesticides	300 mg Oasis HLB	56–68	Estuarine waters	[116]
TWA concentrations	• R_s estimation (from other author)	Detergent, hormones, plasticizer	200 mg Triphasic sorbent admixture*	14–28	WWTP influent WWTP effluent	[119]

(continued)

Table 4. Continued.

Application(s)	Aim(s)	Family of molecules	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
	• TWA concentrations					
TWA concentrations	• R_s estimation (from other author) • TWA concentrations	Fragrances, flame retardants, plasticizers, pharmaceuticals	200 mg Oasis HLB	28–30	River waters Lagoons Bay waters Estuarine waters	[120]
Screening TWA concentrations Coupling with bioassay	• Screening of micropollutants • TWA concentrations • Seasonal influence on POCIS concentrations • Coupling of POCIS extracts with bioluminescent yeast estrogen screen (BLYES) • Comparison of POCIS concentration with response of BLYES test performed on POCIS extracts	Pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, hormones, flame retardants, cosmetic, fragrances	/ Triphasic sorbent admixture*	31/49	Upstream WWTPs Downstream WWTPs	[176]
Screening TWA concentrations Coupling with bioassay	• R_s estimation (from other authors) • TWA concentrations thanks to a PRCs • Screening of micropollutants • Coupling of POCIS extracts with YES test • Estimation of spatial and temporal trends in occurrence of micropollutants	Pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, fragrances, plasticizers, surfactants	200 mg Oasis HLB	16–36	River waters	[121]
TWA concentrations	• R_s determination in laboratory • Evaluation of the use of carbon nanotubes as a sorbent	Pharmaceuticals, hormone, phenols	100 mg Carbon nanotubes	14	Laboratory water	[15]
Screening Coupling with bioassay	• Coupling of POCIS extracts with *in vitro* bioassays • Screening of micropollutants	Alkylphenols, hormones, pharmaceuticals, pesticides, polychlorinated biphenyls, bisphenol A	200 mg Oasis HLB	31	River water	[177]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	Pesticides, steroid hormones, pharmaceuticals	200 mg Oasis HLB	28	WWTP effluent River waters	[178]
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations	Herbicides, pharmaceuticals, personal care products, flame retardants	/ Oasis HLB / Triphasic sorbent admixture*	62	Estuarine waters Groundwater	[179]
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations	Sweeteners, pharmaceuticals, flame retardants, insecticides	/	14	WWTP influent WWTP effluent	[180]
TWA concentrations Coupling with bioassay	• R_s determination in laboratory • TWA concentrations	Pharmaceuticals, alkylphenols, PAHs, hormones, pesticides	200 mg Oasis HLB	31	River waters	[181]

(*continued*)

Table 4. Continued.

Application(s)	Aim(s)	Family of molecules	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
Environmental monitoring TWA concentrations	• Coupling of POCIS extracts with *in vitro* bioassays • R_s estimation (from other authors) • TWA concentrations • Environmental monitoring	Hormones, caffeine	/	7	Upstream WWTPs Downstream WWTPs	[182]
TWA concentrations	• R_s determination in laboratory and *in situ* • TWA concentrations thanks to a PRCs	Polycyclic aromatic hydrocarbons, terpenes, phenols, polychlorinated biphenyls	/ Oasis HLB	28	Freshwater	[183]
Coupling with bioassay	• Coupling of POCIS extracts with *in vitro* bioassays	phthalates, phenols, pharmaceuticals, indoles, chlorinated organophosphate chemicals	200 mg Oasis HLB	/	WWTP effluent	[184]
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations • Comparison of POCIS concentrations with grab sampling concentrations	Urobilin, pharmaceuticals, illicit drugs	/	30	River water	[185]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Effects of fouling on uptake by POCIS	Alkylphenols, halogenated organic compounds,	/ Triphasic sorbent admixture*	28	Seawater	[136]
TWA concentrations	• R_s determination in laboratory • TWA concentrations • Determination of the influence of flow rate on R_s	Pesticides, pharmaceuticals, perfluorinated compounds	200 mg Oasis HLB	14	Tap water River water	[186]
TWA concentrations	• TWA concentrations	Pesticides, pharmaceuticals	200 mg Oasis HLB	21	River water	[187]
TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs • Determination of the influence of membrane porosity (nylon membrane and PES membrane) on accumulation	Pesticides, pharmaceuticals	200 mg Oasis HLB	30	/	[139]
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations	Pharmaceuticals, indoles, chlorinated organophosphate chemicals, terpenes, phenols, sterols	/ Oasis HLB	29	River water	[188]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	Pesticides, pharmaceuticals and personal care products	600 mg StrataWAX 200 mg Oasis HLB	26	Wastewater	[189]
TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs	Pharmaceuticals, personal care products	220 mg Oasis HLB	14	untreated and treated wastewater streams	[190]

(continued)

Table 4. Continued.

Application(s)	Aim(s)	Family of molecules	Amount/type(s) of sorbent	Exposure duration (days)	Type(s) of water	Ref.
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations	Pesticides, pharmaceuticals	200 mg Oasis HLB	30	River waters	[191]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	Pharmaceuticals, polyfluoroalkyl substances, pesticides	200 mg Oasis HLB	14	River waters	[192]
Environmental monitoring TWA concentrations Coupling with bioassay	• R_s estimation (from other authors) • TWA concentrations • Environmental monitoring • Coupling of POCIS extracts with *in vitro* bioassays	Polycyclic aromatic hydrocarbons, alkylphenols	/ Oasis HLB	/	Seawater	[193]
TWA concentrations	• R_s determination in laboratory • TWA concentrations	Pharmaceuticals, perfluorinated compounds, caffeine	200 mg Oasis HLB	3	Drinking water	[194]
Screening	• Screening of micropollutants	Industrial compounds, pesticides, pharmaceuticals, personal care products	/ Oasis HLB	15	Groundwater	[195]
TWA concentrations	• R_s determination in laboratory • TWA concentrations thanks to a PRCs • -Determination of the influence of membrane porosity (nylon membrane and PES membrane) on accumulation	Pesticides, pharmaceuticals, perfluorinated compounds, caffeine	100 mg Strata WAX and 100 mg of polymeric HLB	14–28	Estuarine water	[138]
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations	Pesticides, hormones	/	7	River waters	[196]
TWA concentrations	• R_s estimation (from other authors) • TWA concentrations	Pharmaceuticals, pesticides, caffeine, sucralose	200 mg Oasis HLB	14	River water	[197]

*Hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+)/carbonaceous sorbent (Ambersorb 572), 80:20 (w/w), dispersed on styrene-divinylbenzene copolymer (S-X3 Bio Beads).

and 4-cumylphenol) using POCIS, which were not determined using traditional water-column sampling methodologies. This is probably related to the sequestration of TWA concentrations of trace levels of these pollutants from water during the exposure period. It was also proved that POCIS has the ability to accumulate chemical compounds appearing in the environment by episodic events. Such substances often have a short residence time in the aquatic environment so that they can be missed by spot sampling.

It is worth to noting that recently carbon nanotubes (CNTs) have been used for the first time as a sorbent in passive dosimetry. Jakubus et al.[15] performed a preliminary assessment of the application of CNTs as an alternative to conventionally used sorbents in POCIS for the purpose of isolation and determination of analytes belonging to different groups of chemical compounds. Studies have shown that the use of CNTs as a sorption material significantly increases the R_s values for the target compounds as compared to the R_s values obtained for these analytes using commonly used sorbents. This is mainly due to the large sorption surface and short diffusion rout of CNTs which causes a higher sorption ability than Oasis HLB. However, the authors bring out that the use of CNTs in PSDs is an innovative approach and further research should be carried out to analyze and assess the usefulness of this sorbent for monitoring micropollutants in water.

6. Possibilities and limitations in the use of POCIS

As presented in this review, more and more scientific papers report on the value and suitability of passive POCIS type samplers as an alternative to point sampling. The articles have proven many advantages of passive techniques[1] such as:

- The ability to detect ultra-trace pollutants.
- The possibility of long-term sampling of analytes.
- The ability to easily determine the TWA concentrations of analytes in water.
- The possibility of risk assessment thanks to the obtained TWA concentrations.
- Simplicity of use.
- Elimination of portable pumps and power sources.

Due to the above-mentioned features, POCIS passive dosimeters have an advantage over traditional methods of sampling, as described in this review earlier. However, these tools have some drawbacks. First, there is a need to calibrate passive probes before applying them in field conditions. Calibration is performed to determine R_s for target compounds since R_s values are characteristic of individual chemical compounds. The calibration method of passive dosimeters becomes the main problem at this stage. Several calibration techniques used for POCIS can be found in the literature. One of the most frequently used methods is flow-through systems, in which the PSDs are placed in the exposure chamber, into which a stream of fresh water is continuously supplied and the used water is discharged. A stream of standard solution is also fed into the chamber at a constant flow rate, in which the analyte concentration is known and stable. In this way, a constant concentration of the target compounds should always be maintained in the display chamber. After the exposure time, the samplers are removed from the exposure tank and the sorbent is analyzed to assess the analytical uptake of compounds by POCIS. In addition, calibration methods are distinguished, such as: static renewal, static depletion and *in situ* calibration.[2]

Unfortunately, the selection of the calibration method has a large impact on the R_s values. It was proved by the results obtained by Zhang et al.[122], who compared the R_s values of the tested compounds obtained during laboratory calibration and *in situ* calibration. It has been shown that the field-derived sampling rates for some analytes are significantly greater than those from laboratory experiments. It was found that this phenomenon is related to differences in the conditions during calibration. More specifically, significantly higher water flow and associated water turbulence under field conditions have resulted in an increase in the mass transfer of analytes to POCIS. In the studies of Charlestra et al.[69] it has been proved that both water flow and mixing significantly increase the sampling rate of the target analytes (increase in R_s), which is closely related to the reduction of the diffusion boundary layer. Similar results were also recorded in other reports.[1,38,91,103,110,123] These results indicate another problem which is the impact of environmental factors on the efficiency of pollutant accumulation by POCIS.

Yabuki et al.[61] carried out studies on the influence of sample temperature on the sampling rate of selected pesticides. R_s of 43 pesticides increased with increasing water temperature, while R_s of 5 pesticides decreased with increasing temperature from 18 °C to 30 °C. Djomte et al.[124] also proved that the uptake efficiency of target compounds increases with increasing temperature which may be related to the increase of the rate of diffusion of analytes by PES membranes. The effect of temperature on R_s was generally greater for exposures performed under flow conditions than for similar experiments using static conditions. The water temperature is one of the most commonly studied environmental factors affecting the R_s of micropollutants.[1,7,40,47,48,58,125–129]

Many environmental micropollutants, including some pharmaceuticals and hormones, have functional groups that are ionizable at various pH. In addition, the pH may influence the physicochemical properties of the chemical compound as hydrophobicity and solubility. Avdeef et al.[130] proved that the hydrophobicity of certain drugs varies depending on the pH of the solution. For this reason, Li et al.[51] conducted studies on the effect of DOM concentration and pH of the solution on R_s values for POCIS (Oasis HLB as a sorbent). It has been demonstrated that the sampling rate for acidic pharmaceuticals decreased with increasing pH from 3 to 9, while the sampling rate for basic chemicals (e.g. β-blockers) increased with increasing pH from 3 to 9. What is more important, uptake efficiency for inert drugs and phenolic compounds with high pKa values (e.g. bisphenol A) were unchanged in the pH range 3–9. Zhang et al.[122] in their studies also proved that the R_s for target compounds with a pKa greater than 10 remain relatively similar at pH 4–10 with an RSD of less than 5% using POCIS.

Another important factor that can affect the uptake of analytes by POCIS is the DOM concentration in the water matrix.[33,40,102,131] The measure of total DOM concentration is the concentration of dissolved organic carbon (DOC), which in an aqueous environment is usually 2-10 mg L^{-1}. Most DOC in natural waters are fulvic and humic acid. Li et al.[51] examined the dependence of R_s values of selected pharmaceuticals and hormones on the DOC concentration (3.33, 3.86, and 4.92 mg L^{-1}) in the sample. It was shown that there was a tendency to increase the sampling rate for POCIS for acidic, neutral and basic analytes as the DOM concentration in water increased, but these differences were not statistically significant. Simultaneously, the authors emphasize the need to conduct further studies using higher DOM concentrations to completely exclude the effect of dissolved organic matter on R_s.

Bayen et al.[47] compared the efficiency of accumulation of target compounds from water samples with 0‰ and 30‰ salinity. It has been shown that the R_s of analytes decrease with high salinity of the sample, with the exception of caffeine, risperidone, and sulfamethazine. Togola et al.[123] observed that the influence of salinity on the uptake of compounds depends on their properties. The salinity did not affect the R_s of acidic pollutants, however, it affect on R_s of alkaline analytes, which means that the effect of salinity on POCIS sampling rates is compound-specific.[1,91,122,132]

The above-set examples prove that the sampling rate of micropollutants can vary depending on the conditions ambient the sampler. For this reason, during calibration in the laboratory, the influence of these environmental factors on R_s should be taken into account so that the obtained results are reliable and useful. Performing *in situ* calibration or applying PRCs are the main solutions proposed by researchers in the literature, allowing to obtain accurate TWA values.[30,60,72,77,79,101,133–136] PRCs have been successfully used in the case of hydrophobic passive sampler. However, in the case of POCIS, only a few studies showed positive results.[68,101,109,137] This is mainly due to the fact that isotropic exchange is not always ensured for PRCs and analytes. Keeping in mind that, the uptake process in POCIS is driven by adsorption, not partitioning. For this reason, the PRCs approach to use in polar passive sampler is constantly being developed.

Second, there is a lack of homogeneous POCIS type dosimeters in the trade. Most dosimeters are hand-made in scientific laboratories. However, these samplers that can be purchased differ in the amount of sorbent, the material they are made of and the type of membranes. All this means that the obtained R_s results cannot be compared with each other when dosimeters come from other manufacturers.[122] The POCIS limitations identified above should be considered and resolved to facilitate the implementation of this technique for field use.

7. Conclusion

This review, focused on POCIS, describes the various applications for this sampler and indicates both advantages and limitations of the use of this device. The number of publications in this area indicates that interest in POCIS is constantly increasing. This is mainly due to the fact that passive techniques are a promising alternative to traditionally used sampling methods. Spot sampling has many shortcomings, including:

- The volume of water drawn in may be insufficient to ensure that the concentration of pollutants is above the LOQ of commonly used analytical methods.
- The determined concentration of analytes applies only to the moment of sampling.
- Frequent skipping of the influence of episodic events (leaks, precipitation) on the value of concentrations of target compounds.
- It is not possible to determine TWA concentrations without sufficient sampling repeatability.

To sum up the data collected in this review, POCIS is mainly used for monitoring, screening, and determination of TWA concentrations of water pollutants. The possibility of combining passive techniques with bioassay has also been proven. The most frequently used sorbent in POCIS is Oasis HLB (pharm-POCIS). Nevertheless, this device is not only used to isolate pharmaceuticals from water but also other chemical compounds or complex mixtures of impurities. Pest-POCIS has found application for a wide range of chemicals too, but it is not used as often as pharm-POCIS. Weak anion-exchange (WAX) sorbents have been applied item as a receiving phase in modified POCIS for the isolation of perfluorinated compounds. As previously mentioned, the use of POCIS is limited to compounds with $0 \leq \log K_{ow} \leq 5$. To overcome this, it has been proposed to use molecularly imprinted polymers,[41,42] immobilized ionic liquids,[40] or Strata WAX and polymeric HLB mixtures[138] as receiving phases in POCIS. Interestingly, even carbon nanotubes have found application as a sorbent in POCIS as an innovative approach in passive dosimetry for the isolation of chemicals that differ in their physicochemical properties.[15] The possibility of using nylon membranes instead of PES membranes has also been proven.[41,42,138,139] The ability of applying different receiving phases and membranes is a strong advantage of POCIS over other passive samplers.

However, it should be remembered that the search for new solutions of passive samplers, including POCIS, is underway. This is due to the imperfections of currently used dosimeters, mainly related to the environmental conditions impacting the operation of the device. Although, both standard POCIS construction solutions and prototype solutions have a large potential application in water monitoring, there is still a gap between determining the sampling rate in the laboratory and its applicability in the field. Therefore, it is important to continue researching and developing of POCIS in order to solve problems with the utility of this tool in the environmental field.

ORCID

Monika Paszkiewicz https://orcid.org/0000-0002-3163-145X

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REVIEW

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

Klaudia Godlewska[1] · Piotr Stepnowski[1] · Monika Paszkiewicz[1]

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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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✉ Klaudia Godlewska
klaudia.godlewska@phdstud.ug.edu.pl

[1] Department of Environmental Analytics, Faculty of Chemistry, University of Gdansk, ul. Wita Stwosza 63, 80-308 Gdansk, Poland

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 Voutsa 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 $0 \leq \log Kow \leq 5$. 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), Sepra 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 [Å]	Surface area [$m^2 g^{-1}$]	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 [Å]	Surface area [m^2 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[1]	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 [Å]	Surface area [$m^2 g^{-1}$]	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 [Å]	Surface area [$m^2 g^{-1}$]	Advantages	Disadvantages	References
Carbon nanotubes	Non-modified multiwalled 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)

[1] Information from https://www.phenomenex.com/

[2] Information from https://www.waters.com/

[3] Information 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 mm) 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 Ambersorb 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 Voutsa (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 the uptake efficiency of the pharm-POCIS (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) Coupling of POCIS extracts with short-term photosynthesis bioassays	Pesce et al. (2010)
Pharmaceuticals	200	PES	MeOH, 40 mL	Surface water, groundwater	–	Monitoring of pharmaceuticals	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 Estimation of Time-weighted average concentrations	Vercraene-Eairmal et al. (2010)
Pesticides, polycyclic aromatic hydrocarbons	200	PES	MeOH, 40 mL	Groundwater	–	R_s estimation using performance reference compounds (from other authors) Estimation of Time-weighted average concentrations using POCIS and SPMDs	Fox et al. (2010)
Endocrine disrupting substances	200	PES	MeOH	Lake	–	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 pharm-POCIS 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	Bartelt-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 $R_{s(lab)}$ with $R_{s(in\ situ)}$	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	Kaserzon 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 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 $R_{s(lab)}$ and $R_{s(in\ situ)}$ 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 $R_{s(lab)}$ 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	Bailly 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	Berho 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	Metcalfe 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 $R_{s(lab)}$ with $R_{s(cor)}$	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 Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Bayen et al. (2014)
Contaminants of emerging concern	200	PES	DCM/methyl-tert-butyl ether (8:2, v:v), 25 mL	Coastal water	–	R_s estimation (from other authors) Time-weighted average concentrations Monitoring of micropollutants	Alvarez et al. (2014)
Pesticides	200	PES	MeOH, 3 mL then MeOH/ethyl acetate, 75:25 (v/v), 3 mL	River water	–	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)./	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	Poulier 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 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	–	–	–	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	Martínez 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 Voutsa (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	Metcalfe 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 × MeOH, 5 mL	River water	–	Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Zha et al. (2017)
Pesticides	200	PES	MeOH	Surface water	–	R_s estimation (from other authors) Time-weighted average concentrations Comparison of POCIS with the spot sampling method Ecological risk assessment	Aisha et al. (2017)
Pharmaceuticals	200	PES	MeOH, 100 mL	Surface water	–	R_s estimation (from other authors) Time-weighted average concentrations	Vystavna et al. (2017)
Pharmaceuticals	200	PES	MeOH, 5 mL, then MeOH/DCM (1:1, v/v), 5 mL, then MeOH, 5 mL	–	–	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 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	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	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 $R_{s(lab)}$ with $R_{s(cor)}$ and $R_{s(in\ situ)}$	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 Monitoring of pesticides	Metcalfe et al. (2019)
Insecticides	200	PES	ACN, 10 mL	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)
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 micropollutants	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 Ecological risk assessment	Jaša et al. (2019)
Pharmaceuticals	200	PES	MeOH, 3 mL, then MeOH/ethyl acetate, 75:25 v/v, 3 mL	Ultrapure water	–	R_s estimation (from other authors) Time-weighted average concentrations Performance reference compounds validation Comparison of POCIS and DGT	Buzier et al. (2019)
Pharmaceuticals, pesticides, hormones	200	PES	MeOH, 20 mL	River water	–	R_s estimation (from other authors) Screening for micropollutants Time-weighted average concentrations Comparison of POCIS with the spot sampling method	Rico et al. (2019)
Pharmaceuticals, pesticides, hormones	–	PES	–	River water	–	Monitoring of micropollutants Ecological risk assessment	Arenas-Sánchez et al. (2019)
Contaminants	220	PES	3 × Acetone, 3 mL	Surface water	–	R_s estimation (from other authors) using performance reference compounds Time-weighted average concentrations Coupling of POCIS extracts with in vitro bioassay	De Baat et al. (2019)
Explosive substances	200	PES	2 × MeOH, 3 mL	Lake	Flow-through	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 Comparison of POCIS with the spot sampling method	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) (Paszkiewicz 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 Voutsa, (2008)
Herbicides	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v), 50 mL	Surface water, groundwater	–	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	Černoch et al. (2011)
Pharmaceuticals	200	PES	DCM/MeOH/Toluene (8:1:1, v:v:v)/	River water	–	Monitoring of pharmaceuticals	Černoch 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	Cerveny 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 Voutsa, (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	Cerveny 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):

$$C_s = C_w K_{SW} \tag{1}$$

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 Voutsa 2008; Harman et al. 2011b; Thomatou et al. 2011; Tanwar et al. 2015):

$$C_{W=\frac{C_s M_s}{R_s t}} \tag{2}$$

where R_s [L 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 kg^{-1}] and C_w [g 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, alkyphenols, hormones, musk compounds	Wastewater	Flow-through, In-situ	R_s calculation using performance reference compounds Performance reference compounds validation Time-weighted average concentrations Comparison $R_{s(lab)}$ with $R_{s(cor)}$ and $R_{s(in\ situ)}$	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

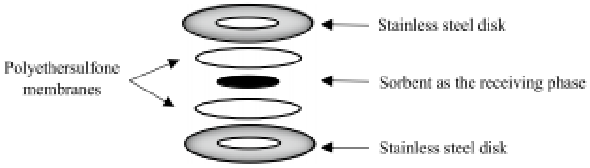

Fig. 1 Polar organic chemical integrative sampler (POCIS) consisting solid sorbent, polyethersulfone membranes and two stainless steel rings—schematic illustration

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

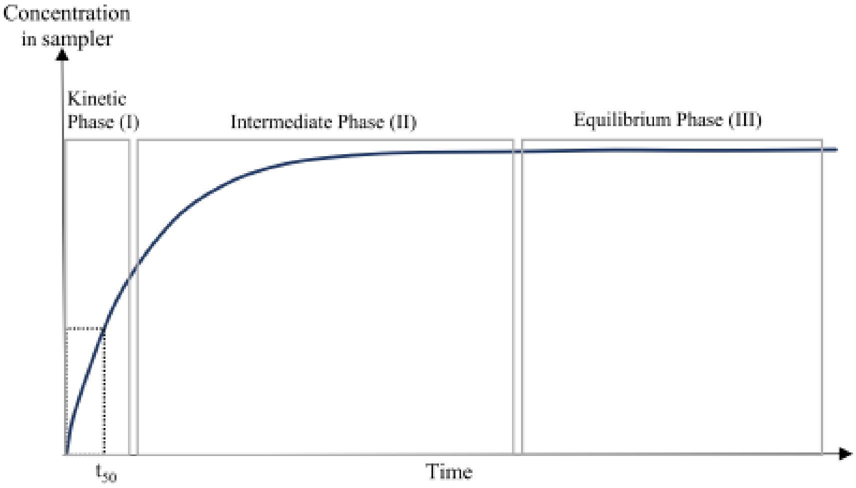

Fig. 2 Kinetic and equilibrium uptake phases as a function of time—kinetic (phase I), intermediate (phase II) and equilibrium (phase III)

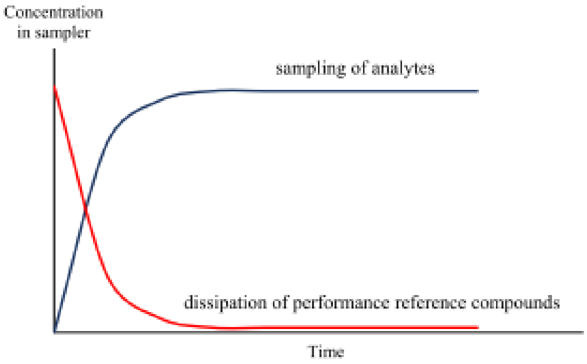

Fig. 3 Simultaneous sampling of analytes by a passive sampler and dissipation of performance reference compounds (PRCs) from the receiving phase during its exposure in the environment

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):

$$\ln \frac{C_t}{C_0} = k_e t \tag{3}$$

where C_t and C_0 are the concentrations in the receiving phase [μg 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 ($R_{s(cor)}$). Therefore, $R_{s(cor)}$ can be determined by the following equation (Morin et al. 2012a):

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

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 (^{2}H-, ^{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_{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 – 800 $m^2\ g^{-1}$) 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 mg $(cm^2)^{-1}$), 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, clofibric acid-d4, bezafibrate-d6, ibuprofen-d3 and naproxen-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 (Metcalfe et al. 2014). For the sampling of chemicals that differ significantly in hydrophilicity, 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 Voutsa 2016), perfluorinated compounds (Cerveny 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, Arditsoglou and Voutsa (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 polyethersulfone 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][$(2O)_2PO_2$]). 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 C_{18}-silica sorbent. The mixture of the ionic liquid ([P666-14][$N(CN)_2$]) and C_{18} 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

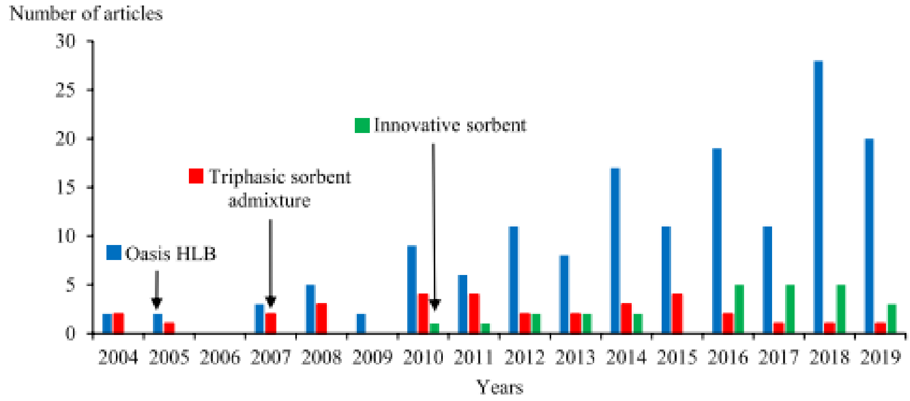

Fig. 4 Summary of the number of studies in 2004–2019 years on the POCIS-like sampler depending on the type of sorbents used

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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Impact of environmental factors on the sampling rate of β-blockers and sulfonamides from water by a carbon nanotube-passive sampler

Klaudia Godlewska, Aleksandra Jakubus, Piotr Stepnowski, Monika Paszkiewicz*

Department of Environmental Analysis, Faculty of Chemistry, University of Gdansk, ul. Wita Stwosza 63, Gdansk 80-308, Poland

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ABSTRACT

Passive techniques are a constantly evolving approach to the long-term monitoring of micropollutants, including pharmaceuticals, in the aquatic environment. This paper presents, for the first time, the calibration results of a new CNTs-PSDs (carbon nanotubes used as a sorbent in passive sampling devices) with an examination of the effect of donor phase salinity, water pH and the concentration of dissolved humic acids (DHAs), using both ultrapure and environmental waters. Sampling rates (R_s) were determined for the developed kinetic samplers. It has been observed that the impact of the examined environmental factors on the R_s values strictly depends on the type of the analytes. In the case of β-blockers, the only environmental parameter affecting their uptake rate was the salinity of water. A certain relationship was noted, namely the higher the salt concentration in water, the lower the R_s values of β-blockers. In the case of sulfonamides, water salinity, water pH 7–9 and DHAs concentration decreased the uptake rate of these compounds by CNTs-PSDs. The determined R_s values differed in particular when the values obtained from the experiments carried out using ultrapure water and environmental waters were compared. The general conclusion is that the calibration of novel CNTs-PSDs should be carried out under physicochemical conditions of the aquatic phase that are similar to the environmental matrix.

Introduction

Pharmaceuticals are a group of micropollutants repeatedly detected in natural water reservoirs (Bayen et al., 2016; Bringolf et al., 2010; Golet et al., 2001; Hilton and Thomas, 2003; Kim and Carlson, 2007; Madikizela and Chimuka, 2016), whose harmful impact on environmental life has been proven (Di Lorenzo et al., 2019; Heye et al., 2019; Kurwadkar et al., 2011; Lyu et al., 2019; Nantaba et al., 2019; Neves and Mol, 2019; Palli et al., 2019; Straub et al., 2019; Tang et al., 2019; Yang et al., 2019; Zhu et al., 2019). Particular attention is paid to the antibiotics, due to the development of resistance among pathogenic bacteria to them (Chee-Sanford et al., 2009; Malik and Bhattacharyya, 2019). One of the most frequently detected antibiotics in the environment are sulfonamides (SAs), which were one of the first drugs widely used as chemotherapeutic and preventive agents in various diseases (Hansch et al., 1990). Currently, SAs are determined in the environment at low levels (2–165 ng/L (Madureira et al., 2010; Tamtam et al., 2008;

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* Corresponding author at: University of Gdansk, Faculty of Chemistry, Wita Stwosza 63, 80-308 Gdansk, Poland
E-mail: klaudia.godlewska@phdstud.ug.edu.pl (K. Godlewska).

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Zheng et al., 2012)). However, continuous introduction of these chemicals into the environment may contribute to the development of bacterial strains resistant to antibiotics that can have a harmful effect on the environment and human health (Nur et al., 2019).

β-blockers are another group of pharmaceuticals commonly detected in the environment. Many sewage treatment plants are not adapted to remove such micropollutants, which contributes to their occurrence in surface waters at concentrations from 3 to 6167 ng/L (Kasprzyk-Hordern et al., 2009; Madureira et al., 2010; Valcárcel et al., 2011). Such concentrations are already sufficient to cause neurotoxic and reproductive disorders in living organisms (Franzellitti et al., 2011). It should be emphasized that pharmaceuticals that affect behavior and reproduction are a huge threat to aquatic organisms and can lead to the breakdown of the entire fish population (Kidd et al., 2007).

The examples given above underline the necessity to improve the monitoring of drugs in the environment. Relatively recently, a new approach to the method of monitoring these micropollutants in water reservoirs has been proposed, namely the use of passive techniques (Alvarez et al., 2005). The first report of a passive sampler appeared in 1987 and since then passive sampling devices (PSDs) have raised increasing interest among scientists. PSDs have many important advantages, including ease of use, low cost, they do not require complicated equipment or an energy supply, they are maintenance-free and they provide the possibility of reliable results (Booij and Chen, 2018; Rakotonimaro et al., 2017; Sodergren, 1987). As a result of long-term exposure, PSDs provide time-weighted average (TWA) concentrations of the analytes. The best known and most frequently used dosimeter is the SPMD (Semi-Permeable Membrane Device). However, POCIS (Polar Organic Chemical Integrative Sampler), Chemcatcher, PISCES-type samplers (Passive in Situ Concentration-Extraction Sampler), or MESCO (Membrane Enclosed Sorptive Coating) popularity increases. Nevertheless, passive techniques are constantly evolving, and scientists are still looking for innovative solutions for passive samplers, like using unconventional sorption materials (Berho et al., 2017; Claude et al., 2017; Fauvelle et al., 2012; Męczykowska et al., 2017; Wang et al., 2019). Recently, there have been reports on the use of such innovative sorbents as: ionic liquids, molecularly imprinted polymers (MIP), Strata WAX (Weak Anion Exchange) sorbent or carbon nanotubes (CNTs) (Godlewska et al., 2019). CNTs, due to their unique properties and applicability in many fields, arouse interest among scientists. The described nanostructures have been found as stationary phases in analytical chemistry and sorbent-based extraction techniques such as: solid-phase extraction (SPE) (Ravelo-Pérez et al., 2010), solid-phase microextraction (SPME) (Wang et al., 2006), matrix solid-phase dispersion (MSPD) (Socas-Rodríguez et al., 2014), stir-bar sorptive extraction (SBSE) (Liang et al., 2014). It is possible to control the CNTs surface, which allows for appropriate functionalization, aggregation or combination with other molecules, increasing their potential application as sorbents (Dai, 2002; Iijima, 2002; Nowicki et al., 2015; Ravelo-Pérez et al., 2010; Reilly, 2007; Socas-Rodríguez et al., 2014). Available literature proves that CNTs have high sorption potential for both single analytes and complex mixtures of chemicals that differ in their physicochemical properties. There have been many comparative studies that have shown that CNTs are more effective or as effective as other commonly used sorption materials in active extraction methods, such as C18 bound silica, activated carbon or microporous resins (Bele, 2010). CNTs can be used as a sorbent in dynamic methods of isolating compounds with a log K_{ow} <4, such as most drugs, personal care products, detergents and hormones (Herrera-Herrera et al., 2013; Hu et al., 2017; Valc et al., 2007; Xu et al., 2015), but also compounds with a log K_{ow} >4, like most polychlorinated biphenyls, polycyclic aromatic hydrocarbons or chlorinated dioxins (Carrillo-Carrión et al., 2009; Jia et al., 2018; Li et al., 2013; Ndunda and Mizaikoff, 2015; Wang et al., 2016; Zhang et al., 2015). Our team was the first and only one to propose the application of CNTs as a sorbent in PSDs (Jakubus et al., 2017). Therefore, in this study, the usefulness of multi-walled carbon nanotubes (MWCNTs) as an alternative sorbent for the passive extraction of selected β-blockers and sulfonamides using passive sampling devices was assessed. It is necessary to calibrate newly developed dosimeters before using them in the field. During calibration, the values of sampling rates (R_s) are determined, which is required for the correct determination of TWA concentrations of micropollutants. The sampling rates are specific for each compound and determine the amount of water purified by the sampler per unit of time. It is also worth noting that the R_s values are determined in the laboratory using the appropriate measurement system (Harman et al., 2012) and depends on the physicochemical properties of analytes (molecular mass, hydrophobicity, solubility) and environmental conditions such as temperature, salinity, the pH of the sample and the DOM (Dissolved Organic Matter) concentration (Djomte et al., 2020, 2018; Godlewska et al., 2019; Harman et al., 2012; Męczykowska et al., 2018). Taking into account that many research results prove that environmental factors significantly affect the sampling rates of the analytes by commercially available POCIS (**Appendix A Table S1**) (Djomte et al., 2020; Godlewska et al., 2019; Gong et al., 2018; Li et al., 2011, 2016; Yabuki et al., 2016; Yang et al., 2017), we decided to investigate whether environmental factors such as: water salinity, the sample pH, the concentration of DHAs (dissolved humic acids) and different matrixes also affect the sampling rates of selected analytes by the developed passive sampler using semi-static calibration (static calibration with gentle mixing of water). This precursor study is aimed to increase knowledge about passive sampling of pharmaceuticals from water, which is necessary to increase the reliability of monitoring data. The data collected in the described article constitute the initial basis for further research and the possibility of subsequent use of CNTs-PSDs (carbon nanotubes used as a sorbent in passive sampling devices) in the field.

1. Material and methods

1.1. *Chemicals*

Commercially available multi-walled carbon nanotubes modified with carboxyl groups with an outer diameter <8 nm (MWCNTs-COOH) were supplieded by Cheap Tubes Inc. (Brattleboro, USA). Acetonitrile (ACN) and methanol (HPLC-grade) were supplied by POCH S.A. (Gliwice, Poland). Trifluoroacetic acid (TFA) and humic acids (HAs) were purchased from Sigma-Aldrich (Steinheim, Germany). Ultrapure water was produced by the Hydrolab System (Gdansk, Poland). β-blocker standards (Table 1, propranolol sodium salt, pindolol, nadolol, acebutolol sodium salt, atenolol), were obtained from Sigma-Aldrich (Steinheim, Germany), except for metoprolol tartrate, which was purchased from Santa Cruz Biotechnology, Inc. (Heidelberg, Germany). Standards of SAs (Table 1, sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfadimidine, sulfamethizole, sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole and sulfadimethoxine) were purchased from Sigma-Aldrich (Steinheim, Germany). β-blockers and SAs stock solutions were made by dissolving each compound in methanol to obtain a concentration of 1000 µg/mL. All solutions were stored in the dark at −20 °C.

1.2. *HPLC-DAD analysis*

For quantitative and qualitative analyses, a High Performance Liquid Chromatography system with an SPD-M20A diode array detector (HPLC-DAD) and a SIL-20AHT autosampler was used (Shimadzu, Germany). The separation of the β-blockers mixture was carried out at 30 °C in a Phenomenex Gemini® C6-Phenyl chromatographic column (4.6 × 150 mm, 3.5 µm). Mobile phase A was deionized water with 0.025% TFA and phase B was ACN containing 0.05% TFA. The initial conditions were 5% phase B, and a linear gradient was performed to increase phase B from 5% to 60% within 20 min, then it returned to initial conditions in 5 min. The flow rate, injection volume and wavelength were: 1 mL/min, 10 µL and 230 nm, respectively. The analytical parameters of the proposed method, such as: linearity (R^2), repeatability, intermediate precision, limits of detection and quantification, and accuracy were evaluated (**Appendix A Table S2**).

The separation of the sulfonamides mixture was carried out with a Gemini C18 column (150 × 4.6 mm, 5 μm, Phenomenex) at 27 °C. Mobile phase A was ACN and phase B was a mixture of 0.005 mol/L CH_3COONH_4/CH_3COOH:ACN (95:5, v/v, pH 4). The initial conditions were 6% phase A, and a linear gradient was performed to increase phase A from 6% to 25% within 17 min, then it was isocratic for 3 min and returned to the initial conditions in 3 min. The flow rate, injection volume and wavelength were: 0.8 mL/min, 10 µL and 272 nm, respectively. The validation parameters were evaluated and presented in **Appendix A Table S3**. The HPLC-DAD technique was used to monitor the decrease in the analyte concentration in water as a function of time, which is necessary for the correct determination of the analyte R_s values.

1.3. *Determination of the R_s values*

CNTs-PSDs are POCIS-like samplers and consist of two plastic rings with two polyethersulfone (PES) filtration membranes (0.22 µm, 47 mm) placed inside (**Appendix A Figure S1**). Between the membranes, 100 mg of the MWCNTs-COOH for the isolation of sulfonamides and 200 mg of the MWCNTs-COOH for the isolation of β-blockers were placed. Preliminary experiments were also carried out using samplers containing 100 mg MWCNTs-COOH for sampling β-blockers, however, the uptake of these analytes was neither linear nor equilibrium, while when using 200 mg of MWCNTs-COOH it operated in kinetic mode. The total exchanging surface area of the membrane is ≅ 18 cm^2 per sampler and the surface area per mass of sorbent ratio is ≅ 180 cm^2/g for sulfonamides and ≅ 90 cm^2/g for β-blockers. The donor phase was 100 mL of an aqueous solution of sulfonamides or β-blockers with an initial concentration of 2 μg/mL. Prepared CNTs-PSDs were placed in glass calibration chambers containing 100 mL of the respective donor phase. During each experiment, a blank sample (donor phase without analytes) and control sample (donor phase spiked with the target compounds without PSDs) were prepared. The experimental system (semi-static calibration) was kept for 14 days in a thermostat on a magnetic stirrer with gentle mixing, protected from light radiation and at a constant temperature of 20 °C. All of the experiments were conducted separately in triplicate. On the first day of the exposure of CNTs-PSDs in the appropriate donor phase, water samples were taken every 30 min for 7 hr and then every 24 hr to monitor the dropping concentration of the analytes in water over time. The collected samples were analyzed by HPLC-DAD. R_s values were calculated by measuring the decrease in water concentration over time according to the equations as describes in many papers (Amdany et al., 2014; Bartelt-Hunt et al., 2011; Li et al., 2011, 2010; Macleod et al., 2007; Metcalfe et al., 2014):

$$C_{w(t)} = C_{w(0)} \exp\left[-(k_U + k_D)t\right] = C_{w(0)} \exp[-kt] \tag{1}$$

which rearranges to

$$\mathrm{Ln}\left(\frac{C_{w(t)}}{C_{w(0)}}\right) = -kt \tag{2}$$

where $C_{w(0)}$ (g/L) is initial concentration of the analytes in water, $C_{w(t)}$ (g/L) is water concentration at time t (day), k (1/day) is the sum of k_U (the uptake rate constants) and k_D (the dissipation rate constant). The sampling rate (R_s) is calculated as:

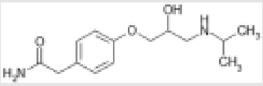
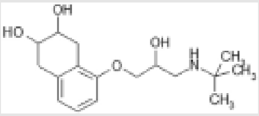
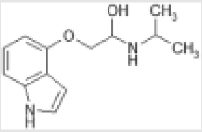
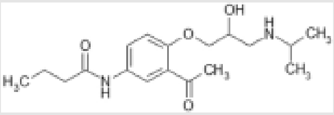
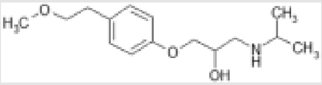
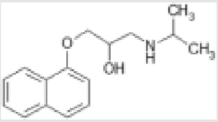
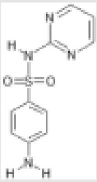
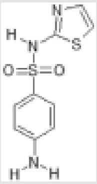
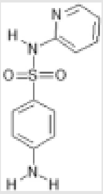
$$R_s = k_U V_T \tag{3}$$

where V_T is initial water volume in calibration chamber (L). The k_U was taken to equal k, as dissipation of the target compounds was not observed in the control samples.

1.4. *Impact of pH, salinity, the concentration of dissolved humic acids and different matrixes*

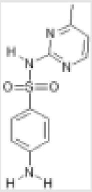
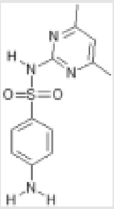
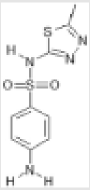
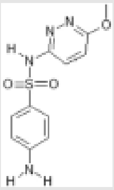
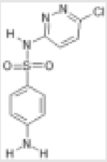
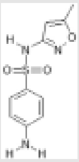
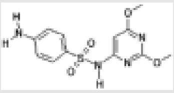
Studies have also been carried out where water donor solutions were characterized by different pH values (3, 5, 7 and 9), concentrations of dissolved humic acids (0, 1, 2.5 and 5 mg/L) and salinity (0, 7, 21 and 35 PSU - 1 practical unit of salinity corresponds to 1 g of salt per kg of solution). Donor solutions at pH 3, pH 5 and pH 7 were prepared by adding 0.1 mol/L HCl or 0.1 mol/L NaOH to ultrapure water. However, to obtain a solution at pH 9, a borate buffer was prepared by mixing 21.3 mL of 0.1 mol/L NaOH with 50 mL of 0.1 mol/L boric acid and supplementing with water up to 100 mL. For the preparation of fortified sea water (35 PSU), the recipe of Lyman and Fleming (1940) was used. 7 PSU and 21 PSU solutions were obtained by the appropriate dilution of 35 PSU

Table 1 – Chemical structures, selected properties and calibration data of the analyzed target compounds from the group of β-blockers and sulfonamides.

Analyte	Chemical structure	Molar mass (g/mol)	pK_a, pK_{a2} [a]	log K_{ow} [a]	log D at pH 3, 5, 7, 9 [b]	Mass balance (%)
Atenolol (ATE)		266.34	9.6	0.16	−6.44, −4.44, −2.44, −0.53	95 ± 1
Nadolol (NAD)		309.40	9.7	0.81	−5.86, −3.89, −1.86, 0.06	97 ± 2
Pindolol (PIN)		248.32	9.3	1.75	−4.55, −2.55, 0.28, 1.27	94 ± 2
Acebutolol (ACE)		336.43	9.6	1.71	−4.89, −2.89, −0.89, 1.01	96 ± 1
Metoprolol (MET)		267.36	9.6	1.88	−4.72, −2.72, −0.72, −1.18	92 ± 1
Propranolol (PRO)		259.34	9.4	3.48	−2.94, −0.92, 1.06, 2.92	97 ± 2
Sulfadiazine (SDZ)		250.28	2.0, 6.9	−0.09	−0.09, −0.09, −0.4, −2.11	91 ± 3
Sulfathiazole (STZ)		255.31	2.0, 7.1	0.05	0.05, 0.05, −0.2, −1.85	96 ± 1
Sulfapyridine (SPD)		249.29	2.6, 8.2	0.35	0.35, 0.35, 0.32, −0.51	94 ± 2

(continued on next page)

Table 1 (*continued*)

Analyte	Chemical structure	Molar mass (g/mol)	pK$_a$, pK$_{a2}$ [a]	log K_{ow} [a]	log D at pH 3, 5, 7, 9 [b]	Mass balance (%)
Sulfamerazine (SMZ)		264.31	2.1, 6.9	0.14	0.14, 0.14, −0.21, −1.96	95 ± 1
Sulfadimidine (SDD)		278.33	2.7, 7.7	0.14	0.14, 0.14, 0.05, −1.23	99 ± 1
Sulfamethizole (SMT)		270.30	1.9, 5.3	0.54	0.54, 0.36, −1.18, −3.17	90 ± 3
Sulfamethoxypyridazine (SMP)		280.31	2.0, 6.8	0.32	0.32, 0.32, −0.07, −1.84	99 ± 2
Sulfachloropyridazine (SCP)		284.72	1.9, 5.5	0.85	0.85, 0.72, −0.71, −2.7	94 ± 1
Sulfamethoxazole (SMX)		253.28	1.6, 5.7	0.89	0.89, 0.81, 0.37, −2.41	89 ± 3
Sulfadimethoxine (SDX)		310.33	2.1, 5.9	1.63	1.63, 1.58, 0.5, −1.47	92 ± 2

[a] log K_{ow} and pK$_a$ values from https://pubchem.ncbi.nlm.nih.gov/ and (Kurwadkar et al., 2011).

[b] log D values calculated from Eqs. (4) and (5).

Table 2 – Characteristics of environmental waters used in the described experiments.

	pH	Conductivity (µS/cm)	COD (mgO_2/L)	TOC (mg/L)	TN (mg/L)	$N\text{-}NH_4$ (mg/L)	TSS (mg/L)	DO (mg/L)
Untreated sewage	7.6	1648	1170	no data	no data	71.25	no data	no data
Treated sewage	7.8	1188	36.00	14.0	no data	0	no data	no data
Vistula water I 52°18′18.7″N 20°57′01.7″E	7.5	1077	15.10	8.67	1.42	<0.078	31.0	6.2
Vistula water II 52°18′27.1″N 20°56′52.6″E	7.8	994.0	42.90	17.5	6.44	3.630	45.0	5.9
Vistula water III 52°32′37.4″N 19°39′15.4″E	7.9	903.0	29.00	8.94	1.29	<0.078	16.0	9.4

synthetic seawater. These salinity levels were selected considering that the maximum salinity in the environment is usually 35 PSU. To obtain water solutions containing dissolved humic acids, 5 mg of these organic compounds were weighed and dissolved in 1 L of deionized water to obtain a stock solution of 5 mg/L. Humic acid donor solutions of 2.5 and 1 mg/L were obtained by the appropriate dilution of the stock solution. In addition, a control experiment and a blank test using ultrapure waters were carried out. Each experiment lasted 2 weeks, and samples (100 µL) were collected every 30 min for 7 hr on the first day and every 24 hr for 2 weeks and analyzed by HPLC-DAD. The R_s values were calculated using the Eq. (3).

For the experiments with environmental waters, untreated and treated sewage from the wastewater treatment plant "Wschód" (Gdańsk, Poland) were collected and water from the Vistula river was taken at three different sampling points (Vistula I, Vistula II, Vistula III). The characteristics of the surface and wastewater samples are shown in Table 2. Before the experiments, the collected samples were filtered by vacuum filtration, placed on 0.45 μm membranes to eliminate insoluble impurities or organisms and stored in glass bottles at 4 °C, away from light radiation. The passive sampling of sulfonamides and β-blockers from environmental waters was carried out in 100 mL of water enriched with analytes to obtain an initial concentration of 2 μg/mL, analogous to experiments carried out in ultrapure water. The impact of environmental factors (e.g. pH, salinity, dissolved organic matter) on the R_s values of tested pharmaceuticals from wastewater and river water was investigated. In addition, a control experiment and a blank test using environmental waters were carried out. Each experiment lasted 2 weeks, and samples (100 µL) were collected every 30 min for 7 hr on the first day and every 24 hr for 2 weeks and analyzed by HPLC-DAD. The R_s values were calculated using the Eq. (3).

One-way analysis of variance (ANOVA) was used to investigate differences in sampling rates from water of different pH. ANOVA was also carried out to investigate the potential effect of DHAs concentration, water salinity and type of water on the sampling rates of CNTs-PSDs. Tukey's post hoc test with significance criterion $p < 0.05$ was used to par-wise comparison. The homogeneity of variance was checked prior statistical analysis.

2. Results and discussion

2.1. *Sampling rates of the analytes in ultrapure water*

The most important parameter determined during the calibration of passive samplers in the laboratory is the R_s value. For this reason, calibration chambers were prepared (as well as control and blank samples) in which CNTs-PSDs were placed in order to define the R_s values for sulfonamides and β-blockers and semi-static calibration was performed (Table 1). Results indicate that all analytes show the stability in tested conditions. Uptake by the CNTs-PSDs was followed by analyzing the decrease in the water concentrations. The plotted elimination curves of the analytes are linear in the first seven hr for all selected β-blockers, after 24 hr the presence of these analytes in the water was not detected, which proves that the water was purified of β-blockers (**Appendix A Figure S2**). In the case of sulfonamides, the elimination curves of analytes from water are linear over 24 hr, after 48 hr no sulfonamides were detected in water (**Appendix A Figure S3**). The obtained results confirm that the developed CNTs-PSDs uptake target compounds in the kinetic mode, which is consistent with the basic principles of passive techniques and confirms the usefulness of carbon nanotubes as innovative sorbents in passive samplers. The sampling rates of sulfonamides and β-blockers ranged from 0.126 to 0.140 L/day and from 0.221 to 0.280 L/day (**Appendix A Table S5**), respectively. The obtained R_s values for sulfonamides exceeded 0.100 L/day, with the highest uptake rates achieved for SDX (0.140 ± 0.018 L/day) and the lowest for SMZ (0.124 ± 0.012 L/day) (**Appendix A Table S5**). In contrast, the R_s values for β-blockers exceeded 0.200 L/day, with the highest collection rates achieved for NAD and PIN (0.280 ± 0.021 L/day and 0.280 ± 0.026 L/day, respectively) and the lowest for ACE (0.221 ± 0.011 L/day) (**Appendix A Table S5**). However, it should be considered that in the samplers for the passive uptake of β-blockers, twice as much sorbent mass was used as in the samplers for the uptake of sulfonamides. Moreover, the increased sampling rates of β-blockers may also be due to stronger ionic interactions between the surface of the MWCNTs-COOH and these analytes Section 2.2.

Nevertheless, it should be considered that the sorption process is a complex mechanism in which many intermolecular interactions are involved. In the case of sulfonamides, π-π interactions are probably more important for the sorption on the surface of MWCNTs-COOH than ionic interactions, which may be the reason for obtaining higher R_s values than when using classic POCIS sorbents. Macleod et al. (2007) performed a laboratory semi-static calibration of POCIS containing 200 mg Oasis HLB ((hydrophilic-lipophilic balanced copolymer [poly(divinylbenzene)-co-*N*-vinylpyrrolidone]) sorbent. It should be noted that the 100 mg CNTs samplers proposed in this work accumulated selected sulfonamides faster compared to the 200 mg Oasis HLB samplers. As an example, the R_s values obtained for sulfapyridine via POCIS and CNTs-PSDs were 0.051 L/day and 0.145 L/day, respectively. In the case of β-blockers, larger R_s values have also been obtained using CNTs-PSDs. For instance, the R_s values of atenolol by POCIS and CNTs-PSDs were 0.040 L/day and 0.181 L/day, respectively. Taking the above into account, carbon nanotubes are promising sorption material and have high potential for the application in passive samplers to extract pharmaceuticals from the aquatic environment. The possibility of using a smaller sorbent mass and a shorter exposure time of CNTs-PSDs are valuable factors in environmental analytics.

2.2. *Influence of pH*

One of the most important parameters, often affecting both the passive and active extraction processes, is the pH of the sample. Therefore, it is important to study the effect of the matrix pH on the sampling rates of analytes, especially in the case of ionic compounds (such as selected pharmaceuticals) that may exist in various forms of ionization. The results show that the concentration of pharmaceuticals in control samples was constant during the experiments (2 weeks) regardless of the pH of water, which means no analyte degradation and no sorption of target compounds in the sorbent-free samplers occurred.

The point of zero charge for MWCNTs-COOH was determined in the laboratory according to the procedure presented by Paszkiewicz et al. (2017). The research results indicate that the point of zero charge for CNTs used in this study is 5.8, which means that in solutions with a pH below that value the surface of this sorbent is charged positively, while the surface charge of MWCNTs-COOH is negative at pH values higher than 5.8. The pKa of all selected β-blockers is >9 (Table 1), which allows us to conclude that these compounds exist in the form of positively charged molecules in an aqueous solution with a pH <9. Also, all selected SAs have a pKa_2 <8.2 (Table 1), which means that these analytes will occur in the form of negatively charged particles in an aqueous solution at pH >8.2.

Considering the results in Fig. 1, it can be seen that the pH of the donor phase reduces the sampling rate of sulfonamides from water. For example, for SMZ R_s are 0.139 ± 0.005 L/day, 0.135 ± 0.004 L/day, 0.094 ± 0.004 L/day and 0.019 ± 0.001 L/day for water pH 3, 5, 7 and 9, respectively. However, the differences in the extraction rates are not statistically significant at pH 3 and pH 5 (ANOVA and post hoc Tukey test, p >0.05). This is due to the fact that SAs are in the neutral form in the above-mentioned pH range of water. Therefore, it can be concluded that the main sorption mechanism of these analytes is based on π-π interactions between pharmaceutical aromatic rings and the surface of CNTs. However, at pH 7 and pH 9, the tested compounds are in anionic form, which may affect the uptake efficiency. Changes in the SAs uptake rate within pH 5–9 are already statistically significant (ANOVA and post hoc Tukey test, p <0.05). As mentioned, the surface of MWCNTs-COOH will be negatively charged at pH >5.8. Probably the decrease of sampling rates of SAs with the increase of the donor phase pH, is closely associated with the phenomenon of increasingly stronger repulsion of negatively charged analyte molecules with negatively charged surface of the CNTs. Interestingly, the results obtained are consistent with the literature, which indicates that the R_s of acidic compounds (sulfonamides are weakly acidic compounds (Cairns, 2012)) decreases with increasing water pH when using Oasis HLB as a sorbent in passive samplers (Li et al., 2011).

On the other hand, positively charged β-blockers interact more strongly with the negatively charged surface of the sorbent, which may be the reason for the faster sampling of β-blockers than sulfonamides by CNTs-PSDs. Considering β-blockers, a slight increase in the R_s value can be noticed with an increase in the water pH in the range of 3–7, followed by a slight decrease in the R_s value at pH 9 (excluding PIN), however, the differences are not statistically significant (ANOVA; p = 0.468), thus it can be assumed that the uptake of these compounds was independent of the donor phase pH in the range of 3–9. Due to the high pKa (above 9) of β-adrenergic blocking agents, their the cationic forms will dominate in the studied pH range, because protonation occurs below their pKa. The explanation of the obtained results may be the fact that at a pH above 5 the surface of MWCNTs-COOH is negatively charged, which leads to electrostatic interactions and promotes cation sorption. However, at pH 3 and 5, MWCNTs-COOH have a positive charge, which allows us to presume that, in addition to the electrostatic attraction mentioned earlier, the π-π interaction between MWCNTs-COOH and chemical molecules containing both the aromatic ring and double bonds is crucial in the process of analyte retention. Interestingly, Li et al. (2011), found that the sampling rate of β-blockers increases with increasing pH from 3 to 9 with using Oasis HLB as a sorbent in passive samplers. This allows us to conclude that R_s values depend not only on the type of chemical compound and environmental conditions, but also on the type of sorbent used. Such complex relationship indicates that the passive sampling device should be thoroughly tested before application in the field.

It is known that the hydrophobicity and solubility of chemicals can vary at different pH of the solution (Magnér et al., 2009). Changes in the hydrophobicity of some chemical compounds as a function of water pH can be represented by determining the effective logarithmic octanol-water distribution coefficient (log *D*), which takes into account the pH of the solution and the pKa of the chemical. In order to determine the *(D)* value for basic and acidic compounds, the following equations were used (Li et al., 2011):

$$D_{\text{base}} = \frac{K_{ow}}{1 + 10^{pK_a - pH}} \tag{4}$$

$$D_{\text{acid}} = \frac{K_{ow}}{1 + 10^{pH - pK_a}} \tag{5}$$

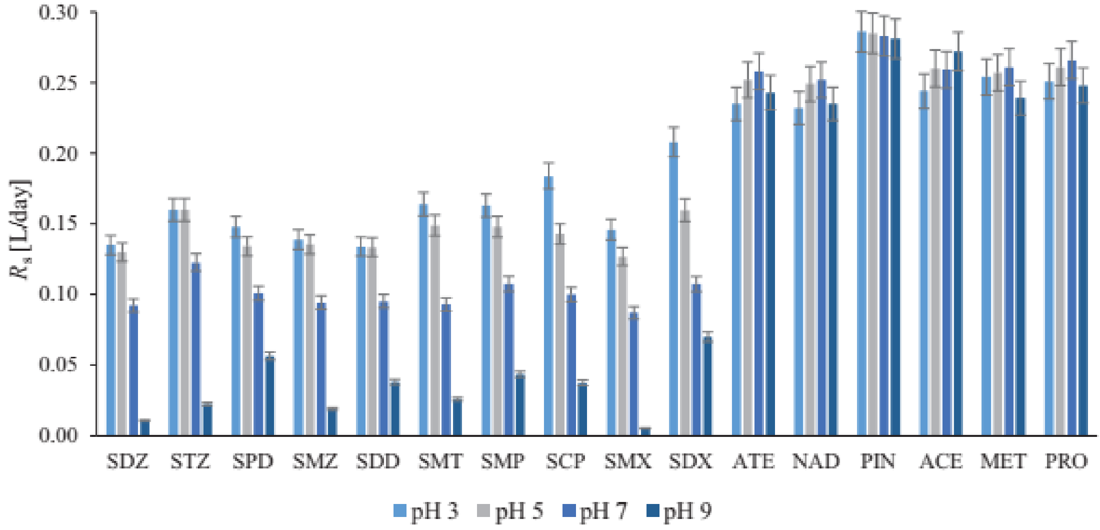


Fig. 1 – The influence of water pH on the sampling rates (R_s) of sulfonamides and β-blockers.

The calculated log *D* values are summarized in Table 1 for β-blockers and sulfonamides. In the pH range 3–9, the log *D* values of sulfonamides decrease with increasing water pH, while the log *D* values of β-blockers increase with water pH. It should be noted that the log *D* for SAs at pH 3 and pH 5 are identical (or slightly different), which may also affect the lack of significant differences in the rate of uptake of these compounds from water with the aforementioned pH. In addition, the dependence of the sampling rates and log *D* for sulfonamides and β-blockers was investigated (**Appendix A Figure S4**). Pearson's correlation coefficients (r_p) were determined in order to discover possible relationships between those parameters (**Appendix A Figure S4**). Statistical significance was set at $p < 0.05$. A strong positive correlation was noted between R_s and log D in water at pH 3 ($r_p = 0.82$) for SAs while there was no correlation for β-blockers. In other cases, no linear relationship was found between R_s and log *D* values at pH 5–9. Based on log *D* values, it can be seen that an increase in pH from 3 to 9 causes a significant change in the hydrophobicity of β-blockers. In water at pH 9 selected drugs should be less soluble compared to water at pH 3. However, the change in lipophilicity did not affect the accumulation of these compounds in CNTs-PSDs. Based on the obtained data, it can be stated that in the environmental pH range, R_s values for selected β-blockers will not be changed.

2.3. *Influence of salinity*

The salinity values of environmental waters are in a wide range of 0–35 PSU, depending on the type of water reservoir, temperature, precipitation and melting glaciers, etc. Therefore, determining the impact of the aquatic phase salinity on the uptake rate of micropollutants by passive samplers seems to be an important element during the calibration of CNTs-PSDs.

Our results show that as the matrix salinity increases, the uptake rate of both sulfonamides and β-blockers decreases (Fig. 2). Nevertheless, statistical tests showed that salinity of water significantly affects the R_s values only when CNTs-PSDs were exposed in water with a salinity of 21 PSU and higher (ANOVA and post hoc Tukey test, $p < 0.05$). The differences in the sampling rates from salt-free water and 7 PSU-water were not significant (ANOVA and post hoc Tukey test, $p > 0.05$) (**Appendix A Table S4**). Many literature data indicate that the solubility of most organic impurities in water decreases with increasing salt concentration due to the so-called salting out effect (Delle, 2000; Harman et al., 2012; Lis et al., 2019; Togola and Budzinski, 2007). This effect should theoretically increase their sampling rates, however, in the case of β-blockers and SAs, the extraction rate decreases with increasing salt concentration in water. To explain this phenomenon, the ionic form of the studied analytes was taken into account in the pH of artificial seawater, which was in the range of 7.5–8.5. As mentioned earlier, β-blockers are in the form of positively charged species in an aqueous solution with a pH <9, while SAs are mostly in the form of negatively charged species in an aqueous solution with a pH >7.6. Based on the collected data, it was assumed that the ions of various salts present in artificial seawater compete with analyte ions, so that the number of analyte ions that can be adsorbed by the sorbent is much lower.

Interestingly, some similarities were observed between traditionally used POCIS and CNTs-PSDs regarding the effect of salinity. Similar results were obtained by Shi et al. (2014), who studied the effect of matrix salinity on the uptake of selected pharmaceuticals by POCIS containing 200 mg Oasis HLB sorbent. The R_s values for SDZ and SMX were significantly lower for saltwater (35 PSU) than for fresh water. Bayen et al. (2014) also compared the accumulation efficiency of micropollutants from water samples with salinity 0‰ and 35‰. It was shown that the sampling rates of most analytes (including ATE, PRO, SMX) decreased during the exposure of the sampler in the high salinity donor phase. By contrast, Zhang et al. (2008), using POCIS, showed that the R_s values of

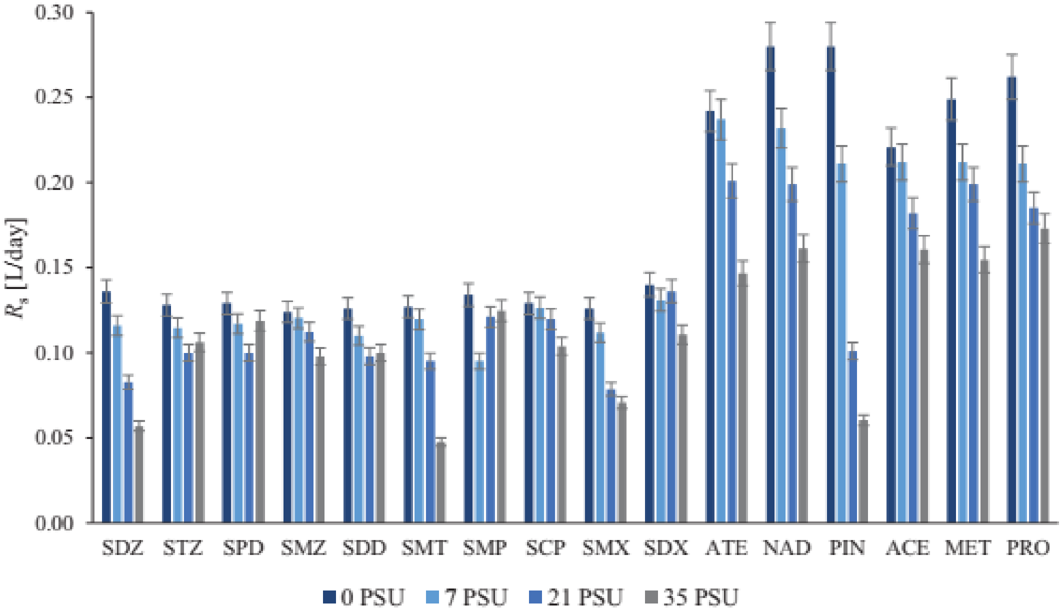


Fig. 2 – The influence of the salinity of the donor phase on the sampling rates (R_s) of sulfonamides and β-blockers.

the target analytes (including PRO, SMX) did not vary significantly with the changing salinity in water. The observed differences emphasize the need for further research to be able to predict sampling rates depending on the salinity of the aquatic environment during the exposure of the samplers. The current results confirm the information available in the literature, that the effect of salinity on the sampling frequency is compound-specific, thus confirming the need to determine R_s values in salinity conditions.

2.4. *Influence of dissolved humic acid concentration*

Based on the literature, one of the environmental factors that can affect the sampling rate of micropollutants by a passive sampler is the presence of dissolved organic matter, especially humic acids. Humic acids present in water can bind to target molecules, which reduces the availability of these compounds for the receiving phase. Additionally, dissolved humic acids in water can block membrane pores which changes the kinetics of the diffusion process by creating a sorption layer of humic acids on the membrane (Gong et al., 2018). The sorption of chemicals to DOM depends on their hydrophobicity, which is determined by the octanol-water partition coefficient (K_{ow}). Organic pollutants penetrate into the hydrophobic organic matter center through induced dipole interactions. Many studies define hydrophobic compounds as a log $K_{ow} > 4$, others classify compounds with a log K_{ow} between 2.5 and 4.3 as slightly hydrophilic with a lower sorption affinity to DOM (Delle, 2000). However, a study by Togola and Budzinski (2007), and other studies, have shown the sorption of analytes to DOM was not determined only by the K_{ow} compound, but also by the combined effect of DOM, pH and complex chemical properties on the sorption process.

Considering the above, it was expected that the presence of DHAs would not affect the β-blockers and sulfonamides (log $K_{ow} < 4$) accumulation by CNTs-PSDs. Referring to the results for β-blockers, it was noted that regardless of the concentration of DHAs in the donor phase, the R_s values were not significantly affected (ANOVA; $p = 0.931$) (**Appendix A Table S4 and Table S5**). Li et al. (2011) also noticed no effect of DOM concentrations in ultrapure water on the sampling rate of selected analytes (including metoprolol, nadolol, propranolol). Yang et al. (2017) showed that an increase in DOM concentration (in the range of 5 to 15 mg/L) had a slight effect on the R_s values of the tested analytes, which was also suggested by Charlestra et al. (2012a). In the research of Morin et al. (2013), the R_s values of analytes (including β-blockers) from water containing 10 mg/L of dissolved organic carbon (DOC) were not significantly affected. Harman et al. (2012) collected literature data that also demonstrated no effect of DOM concentration on the R_s values of pharmaceuticals from water using POCIS. It should be emphasized that all the aforementioned studies concerned the use of POCIS containing Oasis HLB as a sorbent. Despite this, the literature data are consistent with the results obtained in our research (Charlestra et al., 2012b; Harman et al., 2012; Li et al., 2011; Morin et al., 2013; Yang et al., 2017).

In the view of the obtained results, it can be seen that the presence of DHAs in the matrix significantly reduces the uptake rate of SAs by CNTs-PSDs (ANOVA, $p < 0.05$) (Fig. 3). It may be due to the complexation of analytes with dissolved humic acid, which decreases the number of available molecules of target compounds, and the complexes formed are more difficult to diffuse through the sampler. Interestingly, the concentration of DHAs does not have an influence on the sampling rates of SAs (ANOVA and post hoc Tukey test, $p > 0.05$) (**Appendix A Table S4**). In contrast, the R_s values are signif-

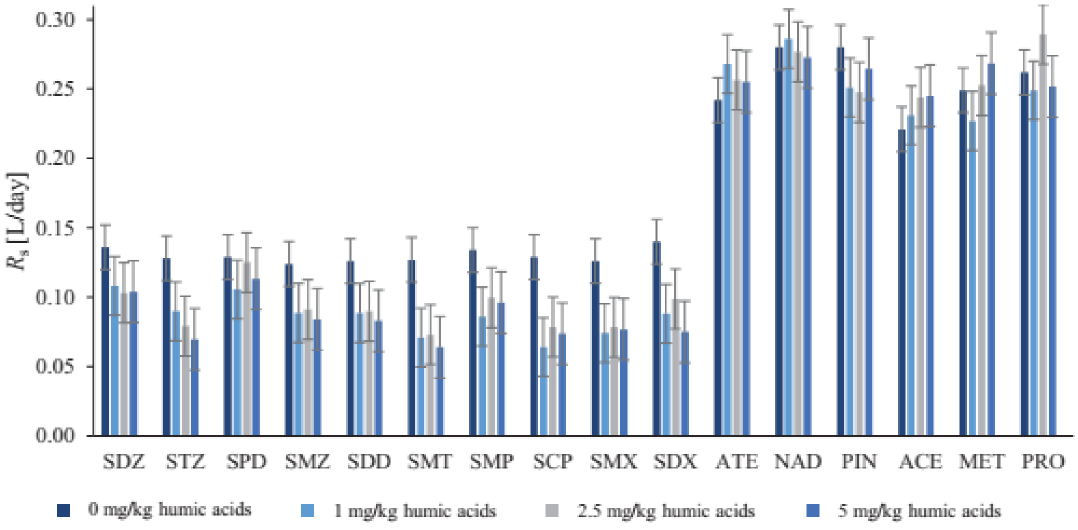


Fig. 3 – The influence of the dissolved humic acids concentration in donor phase on the sampling rates (R_s) of sulfonamides and β-blockers.

icantly higher for SAs when the solution does not contain any DHAs (for SMZ, 0.139 ± 0.012 L/day (**Appendix A Table S4 and Table S5**)). However, it was not possible to clearly determine the dependence of the R_s values on the log K_{ow} of sulfonamides with the CNTs-PSDs used in this study, because despite of the high hydrophilicity of SAs, they interact with dissolved humic acids in water, which reduces the rate of uptake of these analytes. In addition, the literature indicates a wide variety of interaction mechanisms between humic acids and other chemical compounds, including: electrostatic (Coulomb) attraction, water molecule binding, complexation/chelation, ion exchange processes, surface sorption and coagulation processes (Boguta et al., 2019; Boguta and Sokołowska, 2016; Charlestra et al., 2012b). For this reason, it becomes extremely difficult to clearly explain the results obtained.

2.5. *Passive sampling from environmental waters*

Bearing in mind that CNTs-PSDs are intended for the analysis of environmental samples, it was also decided to carry out passive extraction from real samples (Table 2). The results indicate that the uptake rate of SAs and β-blockers significantly decreased when using environmental waters as the donor phase (ANOVA and post hoc Tukey test, $p < 0.05$). For instance, the R_s values of sulfonamides were in the range of 0.063–0.133 L/day, 0.042–0.087 L/day¸ 0.033–0.085 L/day, 0.009–0.082 L/day and 0.014–0.064 L/day for Vistula I, Vistula II, Vistula III, treated wastewater and untreated wastewater (**Appendix A Table S5**), respectively (Fig. 4). The R_s values determined for deionized water were higher and ranged from 0.124–0.140 L/day. As previously stated, the R_s values of sulfonamides are affected by dissolved organic matter and salinity (at pH 7–8). The determined R_s values from the Vistula I were significantly higher than other environmental waters (ANOVA and post hoc Tukey test, $p < 0.05$), while the lowest values were observed in treated and untreated wastewater (**Appendix A Table S5**). The conductivity and pH values of the Vistula I water are close to the values for other surface waters. However, this matrix has the lowest COD and TOC values, which means that it contains the least dissolved organic matter in comparison with other environmental waters. The lowest R_s values of sulfonamides were obtained at the exposure of samplers in untreated sewage water. Interestingly, the sampling rate from untreated wastewater was only slightly lower than the sampling rate of analytes from treated sewage and the differences were not significant (ANOVA; $p = 0.271$), though the physicochemical parameters of these two types of environmental waters differ (Table 2). Therefore, it can be concluded that the salinity of wastewater could have contributed to a reduction in the sampling rate of SAs by CNTs-PSDs. In addition, there is a high concentration of dissolved organic matter/suspended matter in the wastewater, which also contributed to a reduction in the efficiency of passive extraction. It should also be mentioned that during the exposure of CNTs-PSDs in wastewaters, a biofilm was formed on the PES membrane, which may also be the reason for obtaining lower R_s values, especially in untreated wastewater.

The determined R_s values of β-blockers were in the range of 0.048–0.178 L/day, 0.061–0.240 L/day, 0.026–0.221 L/day, 0.024–0.235 L/day and 0.045–0.213 L/day for Vistula III, Vistula II, Vistula I, treated wastewater and untreated wastewater (**Appendix A Table S5**), respectively (Fig. 4). During the exposure of samplers in untreated sewage water, the lowest R_s values of β-blockers were obtained, while during exposure in surface water (Vistula III) the highest R_s values were obtained. Untreated wastewater was characterized by the highest conductivity (1648 μS/cm), thus the highest salinity, while the Vistula III water samples had the lowest conductivity (903 μS/cm), i.e. the lowest salinity among the tested environmental waters. During experimental studies with the ultrapure water, it was shown that the DOM concentration and the water pH do not

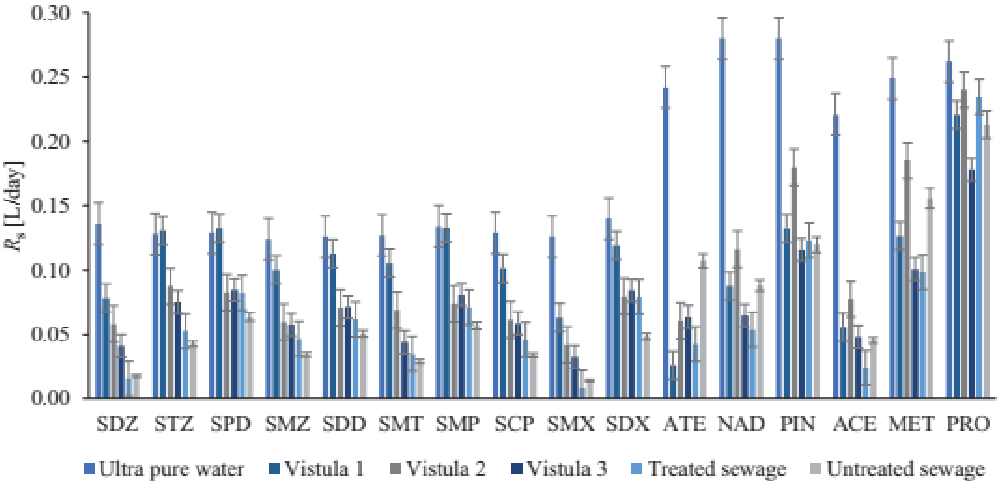


Fig. 4 – The influence of donor phase type on the sampling rates (R_s) of sulfonamides and β-blockers.

affect the sampling rates of β-blockers, while salinity does. The obtained R_s values of these chemical compounds from environmental waters confirm that the greater the salinity of the donor phase, the lower the β-blocker uptake efficiency by CNTs-PSDs.

It should be explicitly emphasized that there are factors other than the pH of the water, salinity or DOM concentration which should be tested before introducing CNTs-PSDs into the field. Li et al. (2011) studied the effect of dissolved organic matter on the uptake of pharmaceuticals (including sulfonamides and β-blockers) by POCIS containing Oasis HLB as a sorbent. They also received lower R_s values for all tested analytes when using environmental waters (Plastic Lake water, Tap water) compared to deionized water. Męczykowska et al. (2018) determined the sampling rates of therapeutic agents (including sulfonamides and β-blockers) from ultrapure water, surface water and seawater using an innovative passive sampler containing ionic liquids as the receiving phase. The obtained R_s values were significantly lower for environmental waters, which is consistent with our results. Although the literature includes research based on passive samplers containing sorbents other than carbon nanotubes, the sampling rates by PSDs were strictly dependent on the type of donor phase (composition, physicochemical parameters), which is consistent with the results obtained in our research.

3. Conclusions

The paper presents data on the impact of water pH, donor phase salinity and the presence and concentration of humic acids on the laboratory calibration of CNTs-PSDs in the passive uptake of sulfonamides and β-blockers from water. It has been found that the most important factor among all those presented in this paper is the salinity of the donor phase, which directly affects the R_s values of both SAs and β-blockers obtained from CNTs-PSDs. Considering the fact, that initially passive samplers were used in freshwater reservoirs (lakes, rivers), yet nowadays, they are increasingly used in marine waters which are characterized by significant salinity, the obtained data is very valuable. The presence of DHAs in the solution causes a decrease in the uptake rate of SAs but not of β-blockers. Nevertheless, the pH of the donor phase in the studied range did not affect the R_s values of β-blockers. However, the sampling rate of all SAs decreases significantly at pH 9. This is due to the fact that at pH 9 all sulfonamides occur in the form of negatively charged particles, which are strongly repelled by the negatively charged surface of MWCNTs-COOH. The collected results also confirm the high potential of MWCNTs as a sorbent in passive sampling devices. The obtained R_s values of the tested analytes are higher than the R_s values (available in the literature) obtained using conventional sorbents. In addition, the mass of sorbent in passive samplers is generally 200 mg. However, we managed to reduce this mass to 100 mg (for sulfonamides), while maintaining high sampling rate. Furthermore, the effect of various types of donor phases (ultrapure water, treated and untreated sewage, surface waters) on the R_s values of 10 sulfonamides and 6 β-blockers has been studied. The experiments show that many environmental factors may influence the sampling rates. Studies on the impact of physicochemical conditions on the calibration of passive samplers containing carbon nanotubes are the starting point for the practical use of CNTs-PSDs in the aquatic environment. In summary, the determination of the R_s values of the tested micropollutants using CNTs-PSDs should be carried out under physicochemical conditions of the aquatic phase which are similar or the same as the environmental matrix. Nonetheless, the presented results are only a preliminary stage for further research on the application of CNTs-PSDs in the field.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.08.034.

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Carbon nanotubes, activated carbon and Oasis HLB as sorbents of passive samplers for extraction of selected micropollutants — Comparison of sampling rates and extraction efficiency

Klaudia Godlewska [*], Piotr Stepnowski, Monika Paszkiewicz

Department of Environmental Analysis, Faculty of Chemistry, University of Gdansk, ul. Wita Stwosza 63, 80-308 Gdansk, Poland

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ABSTRACT

Currently, the POCIS (passive organic chemical integrative samplers) are promising tools for future regular monitoring of the aquatic environment. As the commercially available POCIS has its limitations, innovative solutions, and modifications of conventionally used samplers are sought. For this reason, this study compares the sampling rates (R_s) and extraction efficiencies (EE) of ketoprofen, naproxen, flurbiprofen, diclofenac, imipramine, desipramine, carbamazepine, methotrexate, bisphenol A, 17-β-estradiol, 17-α-ethinylestradiol, *p*-nitrophenol and 3,5-dichlorophenol by kinetic passive samplers containing various types of sorbents. Five types of multi-walled carbon nanotubes, activated carbon and Oasis HLB were used as receiving phases. Additionally, the influence of environmental factors such as: water salinity, water pH, dissolved humic acids and the real water matrix (treated and untreated sewage) on the R_s and EE values was investigated. The advantage of using unmodified multi-walled carbon nanotubes with an outer diameter < 8 nm in passive sampling devices (8-CNTs-PSD) compared to other used sorbents was demonstrated. Using 8-CNTs, sampling rates in the range of 0.037–0.132 L d^{-1} and extraction efficiencies in the range of 46–105% (excluding methotrexate) were obtained, which were independent of environmental factors. The collected results show that 8-CNTs-PSDs are the best choice for the future monitoring of the target analytes in the aquatic environment compared to the other tested samplers.

1. Introduction

Nowadays, the typical monitoring approach is to take small amounts (~1 L) of spot water samples in specified time intervals. Unfortunately, this procedure has several shortcomings, as it is often the case that the concentration of a substance can fluctuate significantly, or there are random contamination flows over time. Additionally, the necessity of periodic water sampling and then the extraction and pre-concentration of organic analytes in the laboratory makes this approach quite labour-intensive. In order to overcome these difficulties, unconventional monitoring strategies such as the use of passive sampling devices (PSDs) have been proposed [1]. These devices can be constructed in various ways, but they all consist of a receiving phase with high affinity for the tested chemicals. PSDs enable simultaneous sampling and extraction of analytes, and due to the fact that they are introduced into the environment for a period of several days to several months, it is possible to determine the time-weighted average (TWA) concentrations of target compounds [2,3]. However, to determine the TWA concentration of the pollutants, the passive samplers must first be calibrated to establish the sampling rate (R_s) of the analytes [4]. The R_s value describes the volume of water purified from a target chemical compound in a day. Unfortunately, R_s values are specific to each analyte and may depend on many different factors (e.g., type of sorbent, membrane, environmental conditions, sampler design). The literature has proved the influence on R_s values of such factors as: water salinity [5–7], water pH [8,9], presence of dissolved organic matter [10,11], temperature [12,13], biofouling [14–16]. For this reason, it is important to examine the influence of environmental conditions on the determined R_s during the calibration of passive samplers or to calibrate the samplers in water with physical–chemical parameters similar to those of the environmental water in which the sampler will be placed [17]. One of the most frequently used samplers for sampling organic pollutants from water is the Polar Organic Chemical Integrative Sampler (POCIS) and its various modifications [18]. In this case, the receiving phase is a sorbent located between two

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[*] Corresponding author.
E-mail address: klaudia.godlewska@ug.edu.pl (K. Godlewska).

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membranes (most often polyethersulfone [PES] membranes) and the whole is enclosed with rings. POCIS was designed for the sampling of polar organic analytes (~log K_{ow} 0.1–3.0) [19] and originally contained the copolymer poly(divinylbenzene)–co-*N*-vinylpyrrolidone (Oasis HLB) as a sorbent [20]. In order to increase the applicability of POCIS-type passive samplers, other types of sorption materials were started to be tested, e.g., molecularly imprinted polymers [21], Strata-X [22], Strata XAW [23], Strata XCW [24] or carbon nanotubes (CNTs) [10].

The high sorption potential of CNTs has delighted many scientists, thanks to which carbon nanotubes have found several applications in analytical chemistry and separation techniques. Until now, CNTs have been successfully used as a sorbent in solid phase extraction [25], solid phase microextraction [26], dispersive solid phase extraction [27], and magnetic dispersive solid phase extraction [28]. It has also been proved that with the use of CNTs it is possible to obtain a higher extraction efficiency (EE) while reducing the amount of solvents than when using conventional C_{18} silica [29]. The sorption potential of another carbon material, which is activated carbon (AC), is also widely researched and used in the techniques of preparing samples for analysis [30–32].

For this reason, in the presented paper, comparative studies of the sampling rate and the extraction efficiency of organic analytes were carried out using various types of sorbents in kinetic POCIS-like samplers: six types of multi-walled carbon nanotubes and activated carbon as unconventional sorbents in passive techniques and Oasis HLB as a commonly used receiving phase in POCIS. Organic chemical compounds were selected for the study: phenol derivatives, which due to their biological activity should be carefully monitored (especially bisphenol A), highly consumed drugs which concentration in the aquatic environment is constantly increasing, and hormones strongly affecting the endocrine system of aquatic organisms, which may result, inter alia, in the feminization of fish. All passive samplers were calibrated using the semi-static method to determine the sampling rate of the tested chemical compounds belonging to non-steroidal anti-inflammatory drugs (NSAIDs) (ketoprofen, naproxen, flurbiprofen, diclofenac), tricyclic antidepressants (TCADs) (imipramine, desipramine, carbamazepine), hormones (17-β-estradiol, 17-α-ethinylestradiol), cytostatic drugs (methotrexate), and phenol derivatives (bisphenol A, p-nitrophenol, 3,5-dichlorophenol) (Table 1). Then, the extraction efficiencies of target compounds from the developed passive samplers with the use of three types of eluents were determined. In addition, the effect of water salinity (7 PSU, 21 PSU, 35 PSU), water pH (pH 3, pH 5, pH 7, pH 9), dissolved humic acids concentration in water (1 mg L^{-1}, 2.5 mg L^{-1} and 5 mg L^{-1}) as well as real water matrices (treated and untreated sewage) on the sampling rate and extraction efficiency of target chemicals by tested samplers were determined. The research was carried out to state which type of carbon nanotubes used as a sorbent will provide the highest R_s and EE values and whether the values obtained with the use of CNTs are comparable or higher than those obtained with the use of activated carbon or Oasis HLB. Our research carried out earlier confirmed the possibility of using multi-walled carbon nanotubes modified with carboxyl groups (COOH8-CNTs) as a sorbent in kinetic passive samplers for the sampling of β-blockers and sulfonamides from water [10]. However, the comparison of the sampling rate and the extraction efficiency of chemical compounds with such significantly different structure and physicochemical properties (e.g., log K_{ow} ranging from −1.82 to 4.90) using eight different sorbents in passive samplers was presented for the first time.

2. Materials and methods

2.1. Reagents and standards

Unmodified multi-walled carbon nanotubes with an outer diameter of < 8 nm (8-CNTs), unmodified multi-walled carbon nanotubes with an outer diameter of > 50 nm (50-CNTs), short unmodified multi-walled carbon nanotubes with an outer diameter of < 8 nm (s8-CNTs), multi-walled carbon nanotubes modified with –OH group with an outer diameter of < 8 nm (OH8-CNTs), multi-walled carbon nanotubes modified with –COOH group with an outer diameter of < 8 nm (COOH8-CNTs), and helical multi-walled carbon nanotubes with an outer diameter of 100–200 nm (hCNTs) (Table S1) were purchased from Cheap Tubes Inc. (Brattleboro, USA). The activated charcoal was obtained from PerkinElmer, Inc. (Shelton, USA) and Oasis HLB was supplied by Waters™ (Milford, USA) (Table S1). Acetonitrile (ACN), methanol (MeOH) and acetic acid were provided by POCH S.A. (Gliwice, Poland). Ammonium acetate was obtained from Chempur (Piekary Śląskie, Poland), and ammonia hydroxide from EUROCHEM (Wejherowo, Poland). Humic acids (HAs), ketoprofen (KET), naproxen (NAP), flurbiprofen (FLU), diclofenac (DIC), imipramine (IMI), desipramine (DEZ), carbamazepine (CBZ), 17-β-estradiol (E2), 17-α-ethinylestradiol (EE2), methotrexate (MTX), bisphenol A (BPA), p-nitrophenol (PNP), and 3,5-dichlorophenol (3,5-DCP) were purchased from Sigma-Aldrich (Steinheim, Germany).

The concentrations of target compounds were determined by high performance liquid chromatography with a diode array detector (HPLC-DAD) and liquid chromatography coupled with mass spectrometry (LC-MS/MS). A detailed description is included in the appendix materials in Section 1.

2.2. Semi-static exposure system

100 mg of each type of carbon nanotubes, activated carbon and Oasis HLB were weighed and then placed between two PES membranes (0.22 μm, 47 mm) and sealed in a home-made passive device. In the developed passive samplers, the total surface of the membrane exchange is ≅ 18 cm^2 per sampler, and the surface of the membrane to mass ratio of the sorbent is ≅ 180 cm^2 g^{-1}. 1 L of deionised water spiked with a standard analytes solution was placed in the calibration chambers to achieve a concentration of 2 μg mL^{-1}, and then the chambers were placed on a magnetic stirrer (gentle stirring) in a thermostat in the dark at a constant temperature of 20 °C for 24 h. The next day, passive samplers were introduced into the exposure water for a period of 10 days. Water samples were taken every 24 h during the experiment and analysed by HPLC-DAD to monitor the decrease in the concentration of the target compounds in the water as a function of time. At the same time, membrane control samples (sorbent-free passive samplers placed in an aqueous solution of analytes) were prepared to determine the sorption capacity of compounds on PES membranes and/or on the sampler. In addition, analytical control samples (aqueous solutions of analytes without samplers) were made to determine the stability of the target compounds in the tested matrix. To confirm the lack of influence of the volume of water used and the concentration of tested compounds in the calibration process of passive samplers, identical experiments were also carried out with the use of 100 mL water spiked with 2 μg mL^{-1} analytes and 100 mL water spiked with 50 ng mL^{-1} analytes. It was shown that regardless of the water volume used and the concentration of analytes, the sampling rates of chemical compounds did not differ significantly for each sorbent tested (ANOVA; $p > 0.05$) (Fig. S1).

2.3. Determination of sampling rates

The sampling rates were determined by measuring the decrease in the concentration of the analytes in water by HPLC-DAD and LC-MS/MS according to the equation [9,10,33]:

$$Cw_t = Cw_0\exp[-(k_U + k_D)t] = Cw_0\exp[-kt] \tag{1}$$

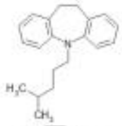
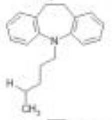
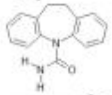
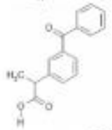
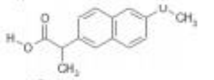
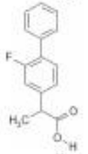
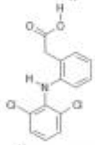
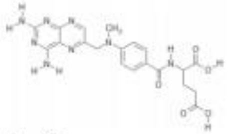
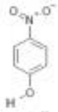
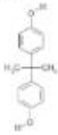
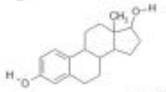
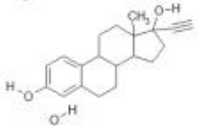
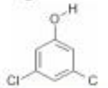
Which transforms to:

$$\ln\frac{Cw_t}{Cw_0} = -kt \tag{2}$$

where k_U [1 d^{-1}] and k_D [1 d^{-1}] are the uptake rate constant and the

Table 1

Characteristics of selected chemical compounds.

Analyte	Chemical structure	Molar mass [g mol^{-1}]	pK_a, pK_{a2}[a]	log K_{ow}[a]	log D in pH 3, 5, 7, 9[b]
Imipramine (IMI)		280.40	9.4	4.80	−1.60, 0.40, 2.40, 4.26
Desipramine (DEZ)		266.40	10.4	4.90	−2,50, −0,50, 1.50, 3.48
Carbamazepine (CBZ)		236.27	13.9	2.45	−8.45, −6.45, −4.45, −2,45
Ketoprofen (KET)		254.28	4.45	3.12	3.10, 2.46, 0.57, −1.43
Naproxen (NAP)		230.26	4.15	3.18	3.15, 2.27, 0.33, −1.67
Flurbiprofen (FLU)		244.26	4.42	3.94	3.93, 3.23, 1.36, −0.64
Diclofenac (DIC)		296.10	4.15	4.51	4.48, 3.60, 1.66, −0.34
Methotrexate (MTX)		454.40	4.70	−1.85	−3.71, −2.18, −2.00, −2.00
p-nitrophenol (PNP)		139.11	7.15	1.91	−2.24, −0.24, 1.53, 1.91
Bisphenol A (PBA)		228.29	9.6	3.32	−3.28, −1.28, 0.72, 2.62
17-*β*-estradiol (E2)		272.40	10.46	4.01	−3.45, −1.45, 0.55, 2.54
17-*α*-ethinylestradiol (EE2)		296.40	10.33	3.67	−3.66, −1.66, 0.34, 2.32
3,5-dichlorophenol (3,5-DCP)		163.00	8.18	3.62	−1.56, 0.44, 2.41, 3.56

[a] log K_{OW} and pK_a values from https://pubchem.ncbi.nlm.nih.gov/ and Pyka et al. [44], [b] log *D* values calculated from Eqs. in Section 3 in appendix materials.

dissipation rate constant, respectively, and Cw_0 [μg mL^{-1}] and Cw_t [μg mL^{-1}] are the concentrations of the analytes in water at the beginning of the experiment and after time t [d]. The R_s is therefore:

$$R_s = k_U V_t \tag{3}$$

where V_t is the volume of water in the calibration chamber. The absorption rate constant k_U, was set equal to k because the dissipation of the analytes was not observed in the control samples.

2.4. Determination of extraction efficiency

Passive samplers, after exposure to water, were removed, air dried for 24 h, and disassembled. The sorbent with the analytes retained on its surface was immersed in the appropriate eluent (30 mL) for 30 min. After this time, the eluate was filtered through polyethylene filters placed in empty solid phase extraction (SPE) columns and evaporated to dryness using a vacuum evaporator. The analytes were then dissolved in methanol to obtain an approximate concentration of 2 μg mL^{-1}, and the received samples were analysed by HPLC-DAD. The obtained results were used to determine the extraction efficiency (EE) according to the formula:

$$EE = \frac{m_e}{m_0 - m_t} \times 100\% \tag{4}$$

where, m_e [μg] is the analyte mass in the extract, and m_0 [μg] and m_t [μg] are the initial mass of the analyte in the water and the mass of the analyte in the water after removal of the sampler, respectively.

In order to obtain the highest extraction efficiency, three types of eluents for desorbing analytes from all studied sorbents were tested: MeOH (pH 9.3), MeOH:NH_4OH (85:15, v/v, pH 12.3), ACN:MeOH:CH_3OOH (1:1:1, v/v/v, pH 2.1).

2.5. Impact of environmental factors on sampling rates and extraction efficiency

The effect of environmental factors on R_s was examined, including the effect of sample salinity ranging from 0 to 35 PSU (0 PSU, 7 PSU, 21 PSU and 35 PSU; 1 PSU — 1 practical unit of salinity corresponds to 1 g of salt per kg of solution), sample pH (pH 3, pH 5, pH 7 and pH 9), humic acid content (0 mg L^{-1}, 1 mg L^{-1}, 2.5 mg L^{-1} and 5 mg L^{-1}) and other matrix constituents (treated and untreated sewage from the 'Wschód' sewage treatment plant; Gdańsk, Poland, Table 2) in the sample. A detailed description of the preparation of the above-mentioned waters is included in the appendix materials in Section 2. The calibration experiments were the same as those in Section 2.2.

2.6. Statistical analysis

One-way ANOVA was used to determine the differences between the calculated sampling rates and the extraction efficiencies obtained for passive samplers with different sorbents. Additionally, ANOVA was also used to determine the potential influence of the studied environmental factors on Rs and EE. Tukey's post hoc test with significance criterion $p < 0.05$ was used for pair-wise comparison. The homogeneity of variance was checked prior to statistical analysis.

Table 2
Characteristics of untreated sewage and treated sewage used in the described experiments.

	pH	Conductivity [μS cm^{-1}]	COD[1] [mgO_2 L^{-1}]	BOD[2] [mgO_2 L^{-1}]	TOC[3] [mg L^{-1}]	N-NH_4 [mg L^{-1}]
Untreated sewage	7.8	1630	1270	440	>50	66.6
Treated sewage	8.0	1130	32.70	1.90	12.5	0

[1] Chemical Oxygen Demand, [2]Biochemical Oxygen Demand, [3] Total Organic Carbon.

3. Results and discussion

3.1. Sampling rates (R_s)

Considering the fact that it is necessary to determine the R_s value before application of passive samplers *in situ*, a semi-static (with gentle mixing) calibration of the developed passive samplers was performed; the obtained R_s values are presented in Fig. 1 and in Table S4. All the tested chemical compounds were stable in water throughout the experiments and no loss of analytes was observed on calibration chamber walls. There are reports in the literature that PES membranes can affect the sampling of analytes [34], especially hydrophobic ones, through their accumulation in the pores of the membrane. Therefore, a membrane control was performed, and the ratio of the mass of the target compound in the membrane (m_m) and the mass of the target compound retained on the sorbent surface (m_s) was determined after 10 days of exposure of the samplers in water spiked with analytes. The m_m/m_s ratio for all tested compounds was lower than 0.1, which means that the target compounds did not accumulate in the PES membrane and could quickly transfer to the sorbent. Since the target compounds in the used deionised water with a neutral pH have strongly hydrophilic or moderately hydrophilic properties (log D < 3, Table 1). Studies by Li et al. [35] also prove that compounds with log $K_{ow} < 4$ do not accumulate in the pores of the PES membrane. Only those analytes with log $K_{ow} > 4.5$ showed a tendency to retain in the pores of the PES membrane.

The R_s were determined by plotting the $\ln Cw_t/Cw_0$ dependence on time t, which were linear for most of the tested compounds (Fig. S2, Fig. S4, Fig. S5), which made it possible to use formulas (1)-(3) to calculate R_s. Interestingly, in the case of samplers containing hCNTs, the curve was linear in the first days of sampling for most of the analytes, and then the equilibrium state was established between the concentration of the analytes in the water and the concentration of the analytes in the sampler (Fig. S3). Only the loss of MTX, 3,5-DCP, E2 and EE2 was linear in the case of using hCNTs-PSDs. The tendency to work in the equilibrium mode of hCNTs-PSDs may be related to the small specific surface area (i.e., the part of the total surface area that is available for adsorption) of this sorbent (> 30 m^2 g^{-1}) compared to the other sorbents used (Table S1), because after a few days, the places available for sorption are saturated (loss of analytes in water at the level of 4–40 %). Also, the spatial arrangement of hCNTs may affect the process of sampling analytes from water. Since most of the tested samplers "operate" in kinetic mode, while hCNTs-PSDs "operate" in kinetic or equilibrium mode depending on the compounds sampled, it was decided to reject this type of sampler in further stages of the research.

The Oasis-PSDs "operated" in an equilibrium mode during methotrexate sampling. The loss of methotrexate in water was 5 % ± 3 %, which proves a very low sorption potential of Oasis HLB for this chemical compound. This may result directly from the properties of a given sorbent, which shows the highest extraction efficiency for low molecular weight compounds. The predisposition of Oasis HLB to more effective sorption of low molecular weight compounds is related, among others, to the porous structure of this sorbent. High molecular weight compounds can block the pores of the sorbent, resulting in low extraction efficiency [36]. In the case of the target analytes, methotrexate is characterised by the highest molecular weight (454.4 g mol^{-1}) and the most spatially extensive structure.

On the other hand, the sampler containing 50-CNTs "operated" in an equilibrium mode during the sampling of p-nitrophenol and bisphenol A. Apart from the above-mentioned cases, the remaining samplers "operated" in the kinetic mode. To standardise the results and to make a

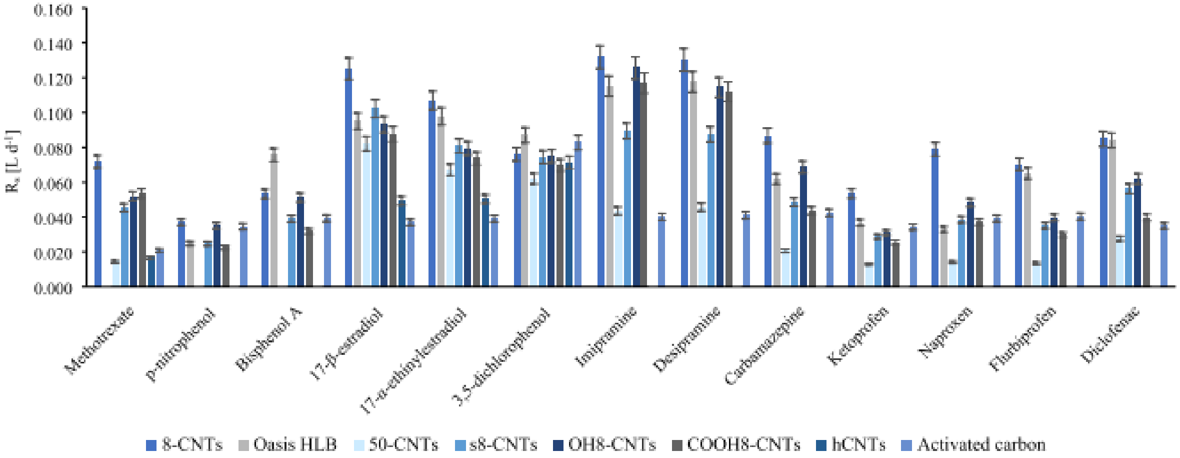


Fig. 1. Comparison of the sampling rates (R_s) of the tested analytes by passive samplers containing 8-CNTs (unmodified multi-walled carbon nanotubes with outer diameter < 8 nm), Oasis HLB (Hydrophilic-Lipophilic Balanced Copolymer), 50-CNTs (unmodified multi-walled carbon nanotubes with outer diameter > 50 nm), s8-CNTs (short unmodified multi-walled carbon nanotubes with outer diameter < 8 nm), OH8-CNTs (multi-walled carbon nanotubes modified with –OH groups), COOH8-CNTs (multi-walled carbon nanotubes modified with –COOH groups), hCNTs (helical multi-walled carbon nanotubes) and activated carbon as sorbents.

reliable comparison of the sampling rate of analytes by samplers containing various types of sorbents, the R_s were determined only for analytes sampling by PSDs "operating" in the kinetic mode (Table S4).

The obtained results prove that the work of the passive sampler depends strictly on the type of the sampling chemicals from the water and the sorbent used. However, at this stage of the research it is impossible to say exactly why for some compounds the samplers "operate" in the kinetic mode and for others in the equilibrium mode. Certainly, the process of sampling analytes by passive samplers is quite complex and the interactions between the analyte and the sorbent surface are of great importance. Focussing on CNTs, the use of modified CNTs did not significantly increase or decrease the R_s of analytes compared to the R_s values obtained for unmodified CNTs (ANOVA and post hoc Tukey test, $p < 0.05$) (Fig. 1, Table S4). It can therefore be concluded that the –OH and –COOH groups present on the surface of CNTs, which favour the formation of hydrogen bonds and Lewis's acid-base interactions, do not play too much of a role in the process of sampling selected compounds from water. Probably the dispersive interactions and the weak electrostatic interactions of the π-π type play a key role in the process of sampling analytes by passive samplers containing CNTs as a sorbent. Also, no significant differences were noticed in the R_s of analyte by samplers containing 10–30 μm long CNTs (8-CNTs) and samplers containing 0.5–2 μm long CNTs (s8-CNTs) (ANOVA and post hoc Tukey test, $p < 0.05$) (Fig. 1, Table S4).

The highest R_s values were obtained for 8-CNTs-PSDs (0.037–0.132 L d^{-1}), while the lowest R_s were obtained for 50-CNTs-PSDs (0.013–0.082 L d^{-1}) and the AC-PSDs (0.021–0.083 L d^{-1}). The R_s values obtained for AC-PSDs and 50-CNTs-PSDs were significantly lower compared to the R_s obtained for the other samplers (ANOVA and post hoc Tukey test, $p < 0.05$). It is assumed that lower R_s values are related to the small specific surface area of 50-CNTs (60 m^2 g^{-1}) compared to other sorbents (500 m^2 g^{-1} for 8-CNTs, s8-CNTs, OH8-CNTs, COOH8-CNTs and 800 m^2 g^{-1} for Oasis HLB). In contrast, the low R_s values obtained by AC-PSDs may be due to the porous structure of the activated carbon. The AC sorption process is mainly based on the diffusion of analytes in the pores, which extends the sorption time and promotes clogging of the pores. In the case of CNTs, sorption takes place mainly on the sorbent surface, therefore the time of sampling the analytes is much shorter [37]. There were no significant differences between the R_s of analytes by samplers containing carbon nanotubes such as: 8-CNTs-PSDs, s8-CNTs-PSDs, OH8-CNTs-PSDs, COOH8-CNTs-PSDs, and the Oasis HLB, which is commonly used in POCIS-like samplers (ANOVA; $p = 0.318$).

3.2. *Extraction efficiency (EE)*

The extraction efficiencies depending on the sorption material used in PSDs and the elution mixture are presented in Fig. S6. In the case of 8-CNTs-PSDs, the highest EE values were obtained for all tested compounds using the ACN:MeOH:CH_3COOH – 46–105 % excluding methotrexate. The highest efficiency of MTX extraction was achieved by using MeOH as the eluent — 22 %, when using ACN:MeOH:CH_3COOH it was 15 %, when using MeOH:NH_4OH it was 10 %. The extraction efficiencies of MTX were in the range of 0–22 % for all the sorbents and eluents used. The low extraction efficiency may be related to the spatially expanded MTX molecule, the presence of three aromatic rings and several functional groups, so that the interactions of MTX with the sorbent are too strong to be able to effectively elute this analyte. Attempts were made to increase the extraction efficiency (especially MTX) using ultrasound, longer extraction time, and higher eluent volume, but no significant changes in the EE of the analytes were noticed (ANOVA; $p = 0.428$). Extraction efficiencies for the target analytes from 8-CNTs ranged from 6 to 67 % with MeOH and 2–74 % with MeOH:NH_4OH. Statistical studies showed that EE obtained with MeOH was significantly lower than EE obtained with ACN:MeOH:CH_3COOH and MeOH:NH_4OH (ANOVA and post hoc Tukey test, $p < 0.05$).

Whereas for AC-CNTs-PSDs, the highest EE values were obtained for the tested compounds using the ACN:MeOH:CH_3COOH — 19–55 % except for 17-β-estradiol and methotrexate. E2 extraction efficiency was 0 %, 4 % and 6 % eluting with ACN:MeOH:CH_3COOH, MeOH:NH_4OH and MeOH, respectively. The efficiency of MTX extraction was 0 %, 0 % and 7 % eluting with MeOH, ACN:MeOH:CH_3COOH and MeOH:NH_4OH, respectively. The EE for the tested analytes from AC ranged from 0 to 31 % with the use of MeOH and 0–21 % with the use of MeOH:NH_4OH. Statistical studies have shown that EE obtained with MeOH and MeOH:NH_4OH are significantly lower than EE obtained with ACN:MeOH:CH_3COOH (ANOVA and post hoc Tukey test, $p < 0.05$). It is worth noting that both the R_s and EE obtained using AC-PSDs were significantly lower than the R_s and EE obtained using the remaining POCIS-like samplers (ANOVA and post hoc Tukey test, $p < 0.05$).

In the case of Oasis HLB samplers, the highest EE values were obtained for the tested compounds using the ACN:MeOH:CH_3COOH — 40–105 %, excluding MTX. It was not possible to extract MTX from the

Oasis HLB surface regardless of the eluent used. The EE for the tested analytes from Oasis HLB ranged from 4 to 69 % with the use of MeOH and 3–59 % with the use of MeOH:NH_4OH. Statistical studies have shown that EE obtained with MeOH and MeOH:NH_4OH are significantly lower than EE obtained with ACN:MeOH:CH_3COOH (ANOVA and post hoc Tukey test, $p < 0.05$).

A detailed description of the extraction efficiency for the remaining carbon nanotubes is described in Section 4 in appendix materials.

As the application of the ACN:MeOH:CH_3COOH gave the highest EE for most analytes, regardless of the sorption material used, it was selected as the most optimal eluent in further stages of the research. In addition, in the case of passive samplers containing carbon nanotubes, it was decided that 8-CNTs would be used as representatives of carbon nanotubes in further stages of the research (examination on influence of environmental conditions on R_s and EE) from an economical and analytical point of view. It was possible to obtain high R_s (Fig. 1) and EE (Fig. 2) for the tested chemical compounds using 8-CNTs-PSDs, and 8-CNTs are less expensive than the other used CNTs.

3.3. *Impact of environmental factors on sampling rates and extraction efficiency*

3.3.1. *Impact of water pH*

A very important factor that may affect the process of uptake and extraction of chemical compounds by passive samplers is the water pH. The pH value of the solution determines the charge on the sorbent surface and the form of analytes ionisation. All tested chemical compounds were stable in the tested range of water pH during the experiment. The results of the calibration of passive samplers in water with different pH showed that the sampling rates and extraction efficiencies of target compounds using 8-CNTs-PSDs (ANOVA; $p = 0.225$) and Oasis HLB-PSDs (ANOVA; $p = 0.315$) are independent of the water pH in the range pH 3–9 (Fig. 3 and Fig. S7, Table S5). Therefore, it can be concluded that probably the ionic interactions play a negligible role in the process of sampling analytes by 8-CNTs and Oasis HLB. The results discussed in Section 3.1. also suggest that the dispersive interactions and weak electrostatic interactions of the π-π type play a key role in the process of sampling target compounds by passive samplers containing CNTs. Lis et al. [38] also noted that in the case of NSAIDs, beta-blockers and antiparasitic agents, the change in both pH and salinity had a negligible effect on the extraction efficiency and sampling rates by samplers containing Oasis HLB as a sorbent.

In the case of AC-PSDs, a statistically significant difference was found in the sampling rates of analytes from water with pH 7 (ANOVA and post hoc Tukey test, $p < 0.05$). The R_s values of all analytes increased at pH 7 compared to sampling from waters with other pH. On the other hand, no statistically significant differences were found between the R_s values of the analytes when using AC-PSDs in water at pH 3, pH 5 and pH 9. Unfortunately, considering the log D and pKa of the target compounds, no relationships between sampling rates and these parameters were established. The extraction efficiencies were independent of the pH of the exposure water (ANOVA; $p = 0.308$).

3.3.2. *Impact of salinity*

Considering that the salinity of environmental waters is in a wide range (0–35 PSU), it was decided to investigate the effect of water salinity on the sampling rates and extraction efficiencies of the tested compounds. All chemicals were stable in the tested range of water salinity during the experiment. Calibration results of passive samplers in water of different salinity showed that the R_s and EE of target compounds using 8-CNTs-PSDs (ANOVA; $p = 0.752$) and Oasis HLB-PSDs (ANOVA; $p = 0.874$) are independent of the water salinity in the range 0–35 PSU (Fig. 4 and Fig. S8, Table S6). In the case of AC-PSDs, it was shown that the presence of salt in water significantly reduces the sampling rates of all analytes. It is presumed that the salt ions diffuse into the pores of the activated carbon, thus reducing the access of these pores for organic compounds, hence the reduction of the R_s values of analytes from the salt solution. In the work Cevallos Toledo [39] it has also been shown that activated carbon loses its efficiency due to the progressive deposition of calcium salts in the pores of the sorbent. Moreover, the formation of complexes of analytes with multivalent salt cations is possible, which can also inhibit their diffusion into the pores of activated carbon. Interestingly, increasing the salinity concentration in water above 7 PSU did not significantly affect the R_s of analytes by AC-PSDs (Fig. 4). The extraction efficiencies of analytes significantly increased in the case of samplers after exposure to saline water compared to the extraction efficiencies of analytes from the sampler after exposure to deionised water (Fig. S8) (ANOVA and post hoc Tukey

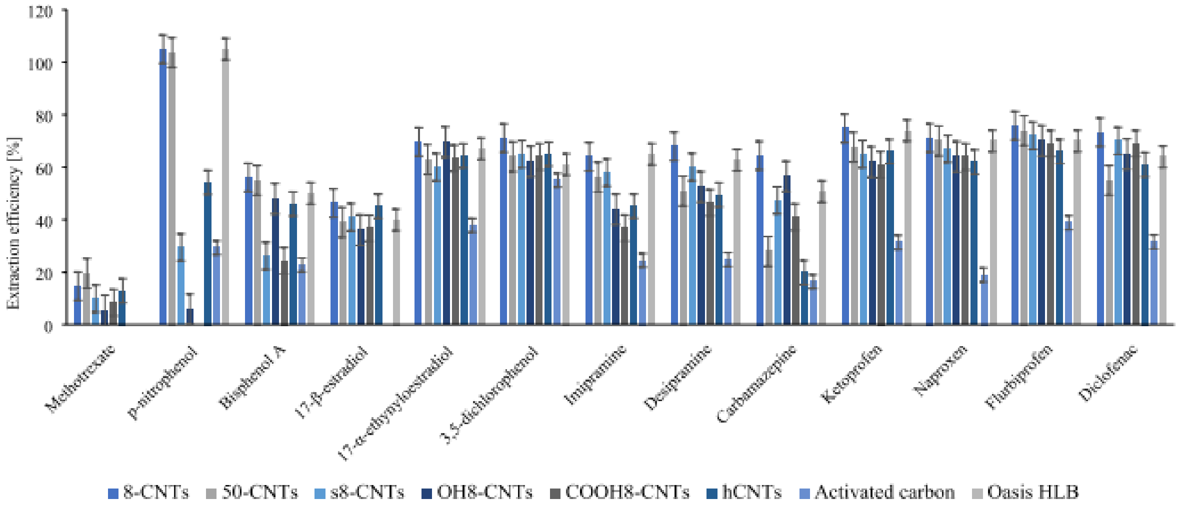


Fig. 2. Extraction efficiency using ACN:MeOH:CH_3COOH to elute analytes from sorbents. 8-CNTs (unmodified multi-walled carbon nanotubes with outer diameter < 8 nm), Oasis HLB (Hydrophilic-Lipophilic Balanced Copolymer), 50-CNTs (unmodified multi-walled carbon nanotubes with outer diameter > 50 nm), s8-CNTs (short unmodified multi-walled carbon nanotubes), OH8-CNTs (multi-walled carbon nanotubes modified with –OH groups), COOH8-CNTs (multi-walled carbon nanotubes modified with –COOH groups), hCNTs (helical multi-walled carbon nanotubes) and activated carbon.

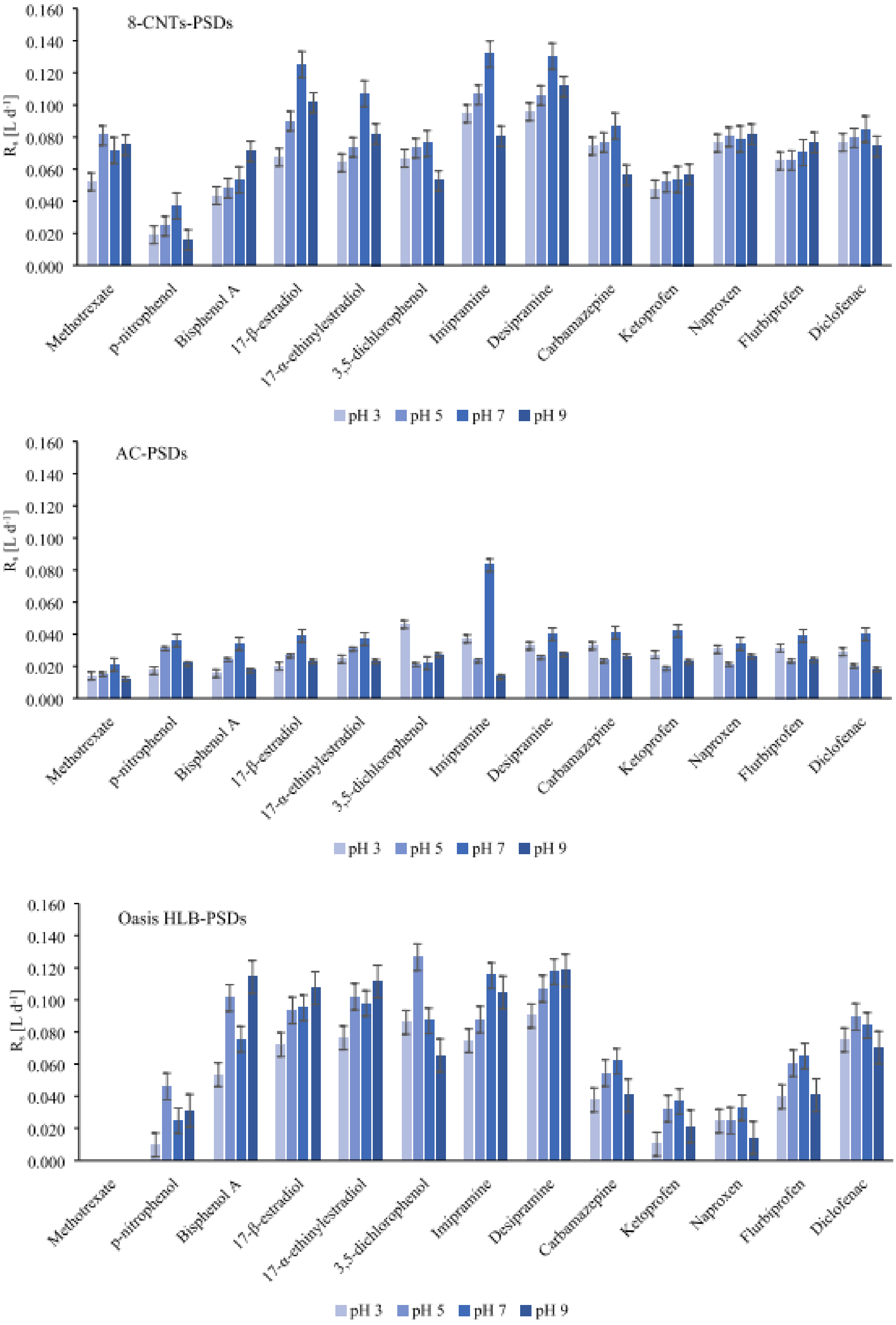


Fig. 3. Impact of water pH on the sampling rates (R_s) of the tested analytes by 8-CNTs-PSDs – passive sampling devices containing unmodified multi-walled carbon nanotubes with outer diameter < 8 nm, AC-PSDs - passive sampling devices containing activated carbon, Oasis HLB-PSDs - passive sampling devices containing Oasis HLB.

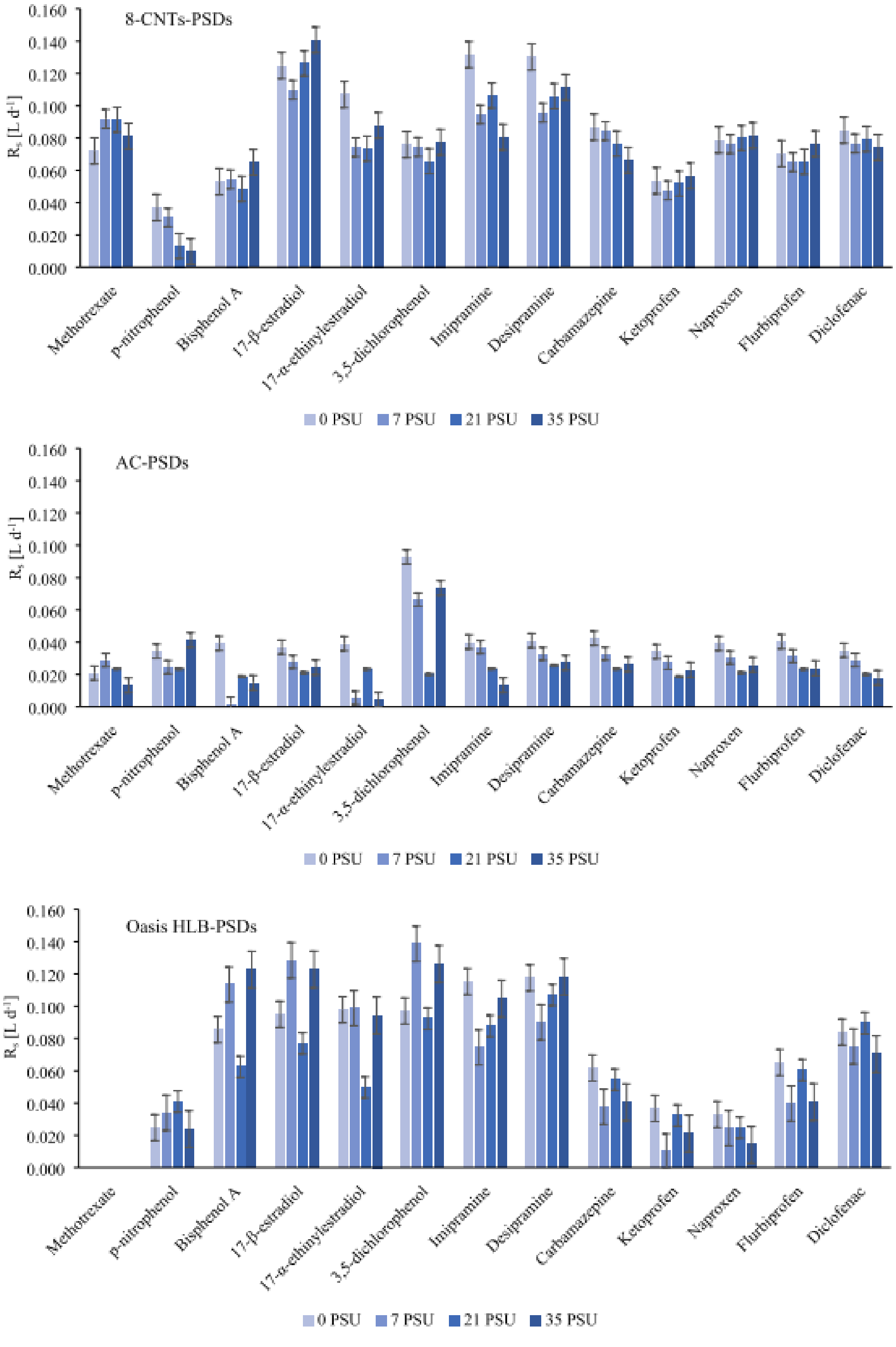


Fig. 4. Impact of water salinity on the sampling rates (R_s) of the tested analytes by 8-CNTs-PSDs – passive sampling devices containing unmodified multi-walled carbon nanotubes with outer diameter < 8 nm, AC-PSDs - passive sampling devices containing activated carbon, Oasis HLB-PSDs - passive sampling devices containing Oasis HLB.

test, $p < 0.05$). It is possible that the presence of salts and/or complexes in the pores of the activated carbon facilitates the desorption of organic compounds from the sorbent.

3.3.3. Impact of dissolved humic acid concentration

The concentrations of humic substances in the water environment are quite variable depending on the water source. In the case of colourless waters (e.g., an oligotrophic lake), humic substances may constitute 25 % of the total carbon, while highly cloudy waters (e.g., from wetlands) may constitute up to 90 % of the humus. Linnik et al. [40] showed that the concentrations of humic substances in lakes, rivers and other water bodies in Ukraine vary in a wide range of concentrations from 1.2 (river Seret) to 126.5 mg L^{-1} (wetlands), due to different sources of their formation. However, in surface waters, where passive samplers are most often used to sampling and monitoring chemicals, dissolved humic acids are frequently determined in the range 0.1–5.4

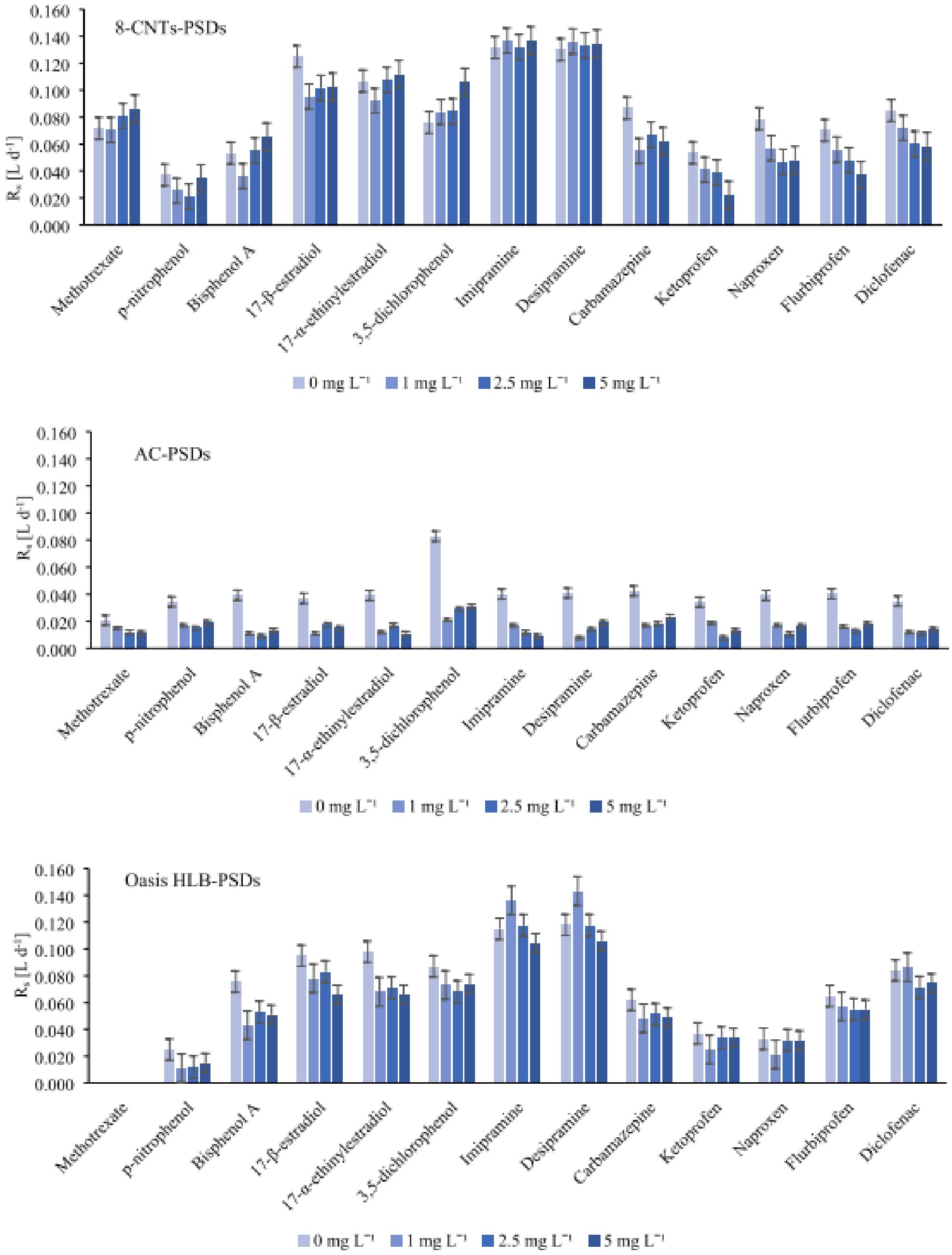


Fig. 5. Impact of the concentration of dissolved humic acids on the sampling rates (R_s) of the tested analytes by 8-CNTs-PSDs – passive sampling devices containing unmodified multi-walled carbon nanotubes with outer diameter < 8 nm, AC-PSDs - passive sampling devices containing activated carbon, Oasis HLB-PSDs - passive sampling devices containing Oasis HLB.

mg L^{-1} [41,42]. For this reason, the influence of dissolved humic acids in concentrations: 1 mg L^{-1}, 2.5 mg L^{-1} and 5 mg L^{-1} on the sampling rates and the extraction efficiency of analytes by the tested passive samplers was also investigated. All chemical compounds were stable in the tested range of dissolved humic acids concentration in water during the experiment. The results showed that the sampling rates and extraction efficiencies of target compounds using 8-CNTs-PSDs (ANOVA; $p = 0.876$) and Oasis HLB-PSDs (ANOVA; $p = 0.816$) are independent of the concentration of dissolved humic acids in water in the range of 0–5 mg L^{-1} (Fig. 5 and Fig. S9, Table S7). Li et al. [9] also showed that dissolved organic matter did not affect the R$_s$ values of selected pharmaceuticals, hormones and phenolic compounds by a

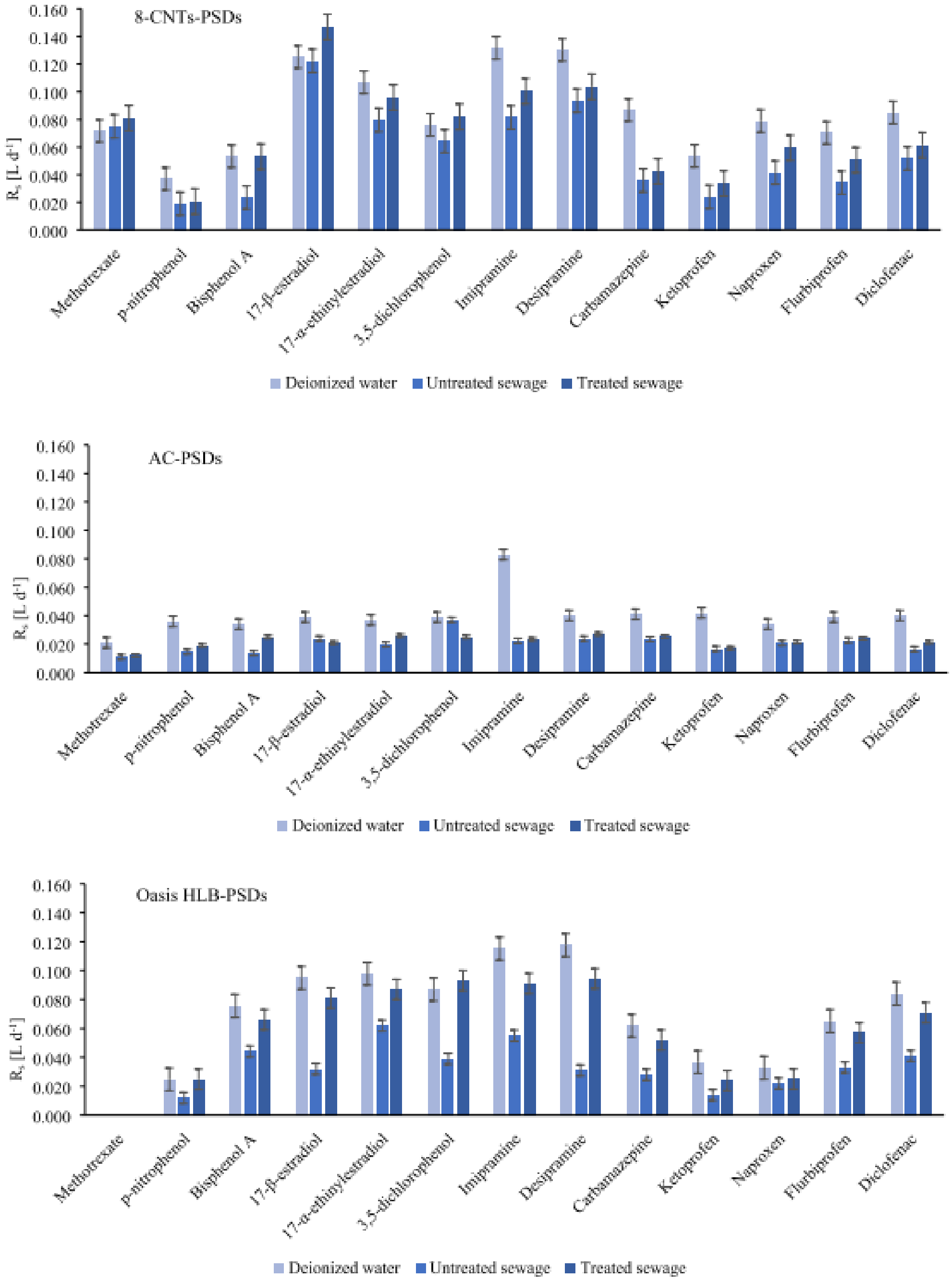


Fig. 6. Impact of real water matrix on the sampling rates (R$_s$) of the tested analytes by 8-CNTs-PSDs – passive sampling devices containing unmodified multi-walled carbon nanotubes with outer diameter < 8 nm, AC-PSDs - passive sampling devices containing activated carbon, Oasis HLB - passive sampling devices containing Oasis HLB.

passive sampler containing Oasis HLB as a sorbent.

In the case of AC-PSDs, it was shown that the presence of dissolved humic acids in water significantly reduces the sampling rates of all analytes (ANOVA and post hoc Tukey test, $p < 0.05$). It is assumed that dissolved humic acids, penetrating the passive sampler, could block the pores of activated carbon, which changes the kinetics of the diffusion process. Humic acids can also bind to compounds present in water, which can slow down the diffusion of these compounds into the receiving phase. However, increasing the concentration of dissolved humic acids in water did not have a significant effect on the R_s of analytes by AC-PSDs (Fig. 5). The extraction efficiencies of analytes significantly increased in the case of samplers after exposure to water containing dissolved humic acids compared to the extraction efficiencies of analytes from the sampler after exposure to deionised water (Fig. S9) (ANOVA and post hoc Tukey test, $p < 0.05$). It is possible that, as in the case of the presence of salt in the pores of the activated carbon, also in the case of the presence of humic acids, it facilitates the desorption of organic compounds from the activated carbon.

3.3.4. *Impact of real water matrix*

The influence of the real water matrix on the sampling rates and the extraction efficiencies of passive samplers was also checked. All chemical compounds were stable in treated and untreated sewage during the experiment. The results of the calibration of passive samplers in wastewater and deionised water showed that the sampling rates and extraction efficiencies of target compounds using 8-CNTs-PSDs (ANOVA; $p = 0.104$) are independent of the matrix used (Fig. 6 and Fig. S10, Table S8).

For Oasis HLB-PSDs, a decrease in the sampling rates of all analytes from untreated sewage was demonstrated (ANOVA and post hoc Tukey test, $p < 0.05$) (Fig. 6, Table S8). The R_s values were not significantly different for the exposure Oasis HLB-PSDs to treated sewage and deionised water (ANOVA; $p = 0.119$). This is important information because it indicates that the sampling process of analytes from water by Oasis-HLB-PSDs is also influenced by parameters other than those tested in this study. Untreated sewage is a very complex matrix containing both numerous inorganic and organic compounds and various microorganisms such as bacteria. On the other hand, the extraction efficiencies from Oasis HLB were similar, regardless of the sampler's exposure environment (ANOVA; $p = 0.352$).

In the case of the AC-PSDs sampler, a decrease in the sampling rate of all analytes was noted, both in treated and untreated sewage (ANOVA and post hoc Tukey test, $p < 0.05$). This confirms the assumption that the physicochemical parameters of the water in which AC-PSDs are placed have a significant impact on the process of sampling the tested compounds. On the other hand, the extraction efficiencies from activated carbon were similar regardless of the sampler's exposure environment (ANOVA; $p = 0.151$).

In the aquatic environment, contaminants often occur in mixtures with other chemicals over a wide concentration range, and competition between these compounds can also affect sampling rates and extraction efficiency. Calibration of the samplers in such complex matrices as treated and untreated sewage allows us to assume that the presence of other compounds does not affect the R_s and EE values obtained using 8-CNTs-PSDs. However, it is very possible that the presence of various chemical compounds in the untreated sewage reduces the sampling rate of the tested analytes by the sampler containing Oasis HLB.

No biofilm formation was observed on the sampler membranes during their exposure to both untreated and treated sewage. Biofouling is also considered to be one of the important environmental factors that can potentially affect the sampling rate and extraction efficiency of the tested organic compounds. Its impact essentially depends on the type of membrane, i.e. PES membranes are considered less biofouling sensitive (because of their hydrophilic nature) than Low Density Polyethylene (LDPE) membranes used in Semi Permeable Membrane Devices (SPMD) or Chemcatchers® [43]. The biofilm effect may also be compound dependent, as previously noted for POCIS by Harman et al. [4] who suggested that the biofilm layer effect may be more significant for less polar chemicals.

4. Conclusion

Summing up, the obtained results prove the high potential of carbon nanotubes as innovative sorbents in passive samplers for sampling compounds belonging to the groups of non-steroidal anti-inflammatory drugs, tricyclic antidepressants, hormones, cytostatic drugs, and phenol derivatives. The effect of water salinity, water pH, concentration of dissolved humic acids in water, as well as treated and untreated sewage on the sampling rates and extraction efficiency of target organic chemicals by the tested samplers was investigated. Thanks to the use of many sorbents, it was possible to demonstrate that the determined sampling rates and extraction efficiency for target compounds using unmodified carbon nanotubes with outer diameter < 8 nm in passive samplers are independent of environmental conditions. The obtained results are very interesting and important because the development of a passive device that samples analytes regardless of external factors significantly facilitates the work and allows the sampler to be introduced into various aquatic environments without the need to repeat the calibration of the samplers in water with physicochemical parameters similar to the target environmental water. Hence, the conclusion is that 8-CNTs-PSDs is a better choice than AC-PSDs and Oasis HLB-PSDs for later use *in situ* to monitor non-steroidal anti-inflammatory drugs, tricyclic antidepressants, hormones, cytostatic drugs, and phenol derivatives in the aquatic environment. These are preliminary studies, and the obtained results constitute a promising basis for the continuation of research on the use of CNTs in passive samplers and the possibility of their subsequent use in the aquatic monitoring.

CRediT authorship contribution statement

Klaudia Godlewska: Methodology, Conceptualization, Formal analysis, Investigation, Writing – original draft, Validation, Visualization, Project administration, Funding acquisition. **Piotr Stepnowski:** Writing – review & editing. **Monika Paszkiewicz:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2021.106975.

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Carbon nanotube-passive samplers as novel tools for sampling and determining micropollutants in the aquatic environment

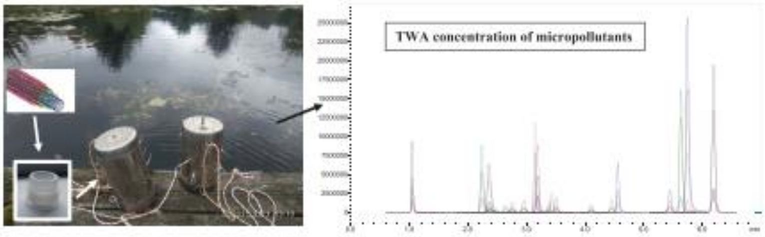
Klaudia Godlewska *, Piotr Stepnowski, Monika Paszkiewicz

Department of Environmental Analysis, Faculty of Chemistry, University of Gdansk, ul. Wita Stwosza 63, 80-308 Gdansk, Poland

HIGHLIGHTS

- The R_s obtained by flow-through and semi-static calibration methods were compared.
- Three types of surface water were sampled using grab and passive sampling.
- Eight contaminants of concern in surface waters were determined using CNTs-PSDs.
- The effectiveness of using carbon nanotubes in passive samplers has been shown.
- The advantage of passive sampling over grab sampling has been demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

Passive sampling is an interesting and cost-effective strategy for the quantification of micropollutants in the aquatic environment. When combined especially with a sensitive analytical method such as liquid chromatography coupled with triple quadrupole mass spectrometry (LC-MS/MS), the use of passive sampling devices (PSDs) enables long-term and reliable determination of a wide range of chemicals. In this study, carbon nanotubes (CNTs) were used as an innovative sorbent in POCIS-like samplers (Polar Organic Chemical Integrative Sampler). The developed CNTs-PSDs were calibrated by the flow-through method and the obtained sampling rates (R_s) of analytes were compared with the previously obtained R_s values using the semi-static method. Subsequently, passive samplers were placed in the Baltic Sea, the Nogat River, and the Sztumskie Pole Lake in order to sample and concentrate 28 chemical compounds belonging to the group of contaminants of emerging concern (CECs). For the first time, the effectiveness of the use of CNTs-PSDs in the field was proven by the quantification of carbamazepine, diclofenac, *p*-nitrophenol, bisphenol A, 3,5-dichlorophenol, 17-β-estradiol, 17-α-ethinylestradiol and metoprolol in the tested surface waters. The obtained time-weighted average (TWA) concentrations of analytes ranged from 0.22 ± 0.12 ng/L (for metoprolol in the Nogat River) to 32.1 ± 2.4 ng/L (for bisphenol A in the Sztumskie Pole Lake). More importantly, CNTs-PSDs determined a greater amount of micropollutants than grab sampling and solid-phase extraction (SPE), which proves the advantage of passive sampling over grab sampling, especially when monitoring contaminants in the aquatic environment at low concentration levels.

1. Introduction

Pharmaceuticals and endocrine disrupting chemicals (EDCs) find their way into the aquatic environment through a variety of mechanisms, including inappropriate drug disposal, the expulsion of human and animal waste, and direct release from manufacturing, veterinary and agricultural practices. Moreover, due to their high polarity and solubility, they are inefficiently removed in conventional wastewater treatment plants and consequently discharged into environmental waters as treated wastewater. Pharmaceuticals and EDCs are among the most persistent micropollutants in the environment and therefore they are considered to be contaminants of emerging concern (CECs) that can pose a real threat to humans and

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* Corresponding author.
E-mail address: klaudia.godlewska@ug.edu.pl (K. Godlewska).

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biota (Birošová et al., 2014; Khan et al., 2020; Mhuka et al., 2020; Waleng and Nomngongo, 2021).

Currently, there are no legal regulations regarding water quality for these compounds, despite their potential threat to the environment and public health (Ncibi et al., 2017; Thomaidis et al., 2012). However, the European Parliament, in 2013, approved Directive 2013/39/EU, which introduced the obligation to monitor chemical substances in surface waters from a so-called watch list. This list includes chemical compounds for which it is confirmed that they may pose a risk to the aquatic environment (e.g., 17-β-estradiol and 17-α-ethinylestradiol). Whereas, in 2020, in Decision 2020/1161/EU a watch list was published of 18 CECs (including sulfamethoxazole) that should be monitored to gather information for further evaluation. This confirms that increasing attention is being paid to the risks associated with the presence of CECs in the aquatic environment (Fernandes et al., 2021). Therefore, the monitoring of these chemical compounds is a hot topic and is constantly being developed and improved.

At present, the common practice in aquatic environment monitoring procedures is grab sampling, transporting the samples to the laboratory, filtration, solid-phase extraction (SPE) and instrumental analysis using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). The whole procedure is quite laborious and allows the concentration of pollutants to be determined only at each place and time of sampling. For this reason, more and more attention is paid to passive sampling methods that allow the simultaneous sampling and accumulation of tested analytes from water (Godlewska et al., 2020; Harman et al., 2012). Passive samplers are placed in the tested environment, most often for a period of 14 to 28 days (Godlewska et al., 2019). During this time, the chemicals in the water are passively extracted into the receiving phase. The receiving phase, depending on the type of sampler, is either liquid or solid. Commonly used passive samplers in the research of the aquatic environment are Polar Organic Chemical Integrative Samplers (POCIS) containing a solid sorbent as the receiving phase, inter alia, Oasis HLB (hydrophilic-lipophilic balanced copolymer [poly(di-vinylbenzene)-co-*N*-vinylpyrrolidone]) (Morin et al., 2012). However, modifications of commercially available samplers are more and more often carried out to increase the scope of their applicability, e.g., by using innovative sorbents in POCIS-like samplers. Carbon nanotubes have recently been shown to be an alternative receiving phase in passive sampling devices (CNTs-PSDs) (Godlewska et al., 2022; Godlewska et al., 2021). Due to their unique sorption properties and the possibility of regeneration and reuse (Cui et al., 2015; Hou et al., 2019; Karimifard et al., 2016; Toński et al., 2021; Xu et al., 2015; Zhan et al., 2010), they are a promising sorbent in passive techniques.

Importantly, passive samplers should be calibrated prior to their placement in the environment, usually in a laboratory, to ensure full control of the experimental conditions. According to the literature, three sampler calibration methods can be used: I) static calibration (closed system, spiked with analytes at the beginning of the experiment), II) renewable static calibration (closed system, spiked with analytes at constant time intervals), III) flow calibration (open system, with continuous enrichment of analytes) (Harman et al., 2012). Calibration methods I and II are most often performed due to the ease of implementation, low price, and low labour consumption. On the other hand, method III is the closest to the environmental specificity and is described as the most reliable. Based on the R_s values and the content of analytes in the receiving phase, the time-weighted average (TWA) concentration of the chemicals in the environment can be calculated (Męczykowska et al., 2017). Therefore, proper sampler calibration is critical for determining the concentration levels of the tested compounds. In our previous studies, kinetic CNTs-PSDs and passive sampling devices containing Oasis HLB as a sorbent (Oasis-PSDs) were calibrated using the semi-static method (Godlewska et al., 2022; Godlewska et al., 2021).

Therefore, in this study, the samplers were calibrated with the flow-through system in order to compare the two calibration systems. In addition, CNTs-PSDs were used in the aquatic environment for the first time (Sztumskie Pole Lake, River Nogat, Baltic Sea) to determine the TWA concentrations of a wide group of 28 chemical compounds belonging to: non-steroidal anti-inflammatory drugs (NSAIDs), tricyclic antidepressants (TCADs), β-blockers, sulfonamides (SAs), hormones, cytostatic drugs, and phenol derivatives. The Baltic Sea was chosen as the sampling site because it is one of the most polluted seas in the world. Anthropogenic pollutants are introduced into the Baltic Sea mainly by river discharge and atmospheric deposition. Contaminants of emerging concern, as well as many others, have been repeatedly determined in the Baltic Sea at various concentration levels (Kanwischer et al., 2021). The next site for the exposition of passive samplers was the Nogat River, which is the eastern estuary arm of the Vistula River, which in turn is the longest river flowing into the Baltic Sea. Near the site where the passive samplers were exposed, is the location of a mechanical and biological sewage treatment plant (Przedsiębiorstwo "Nogat" Sp. Z o.o.), from which the sewage is discharged into the Nogat River. Passive samplers were also placed in the lake in Sztumskie Pole to assess the usefulness of the developed PSDs for the sampling and monitoring of the target compounds in stagnant waters. There are many households, livestock farms and agricultural fields within the lake that can be potential sources of pollution. Solid-phase extraction was used as a reference method to compare the obtained concentration values of the tested micropollutants in surface waters.

2. Materials and methods

2.1. Reagents and standards

Unmodified multi-walled carbon nanotubes with an outer diameter of <8 nm (8-CNTs) and multi-walled carbon nanotubes modified with the -COOH group with an outer diameter of <8 nm (COOH8-CNTs) were purchased from Cheap Tubes Inc. (Brattleboro, USA). Oasis HLB was supplied by Waters™ (Milford, USA). Acetonitrile (ACN), methanol (MeOH) and acetic acid were provided by POCH S.A. (Gliwice, Poland). Ammonium acetate was obtained from Chempur (Piekary Śląskie, Poland). All standards of target compounds were obtained from Sigma-Aldrich (Steinheim, Germany): ketoprofen (KET), naproxen (NAP), diclofenac (DIC), imipramine (IMI), desipramine (DEZ), carbamazepine (CBZ), atenolol (ATE), nadolol (NAD), pindolol (PIN), acebutolol (ACE), metoprolol (MET), propranolol (PRO), sulfadiazine (SDZ), sulfathiazole (STZ), sulfapyridine (SPD), sulfamerazine (SMZ), sulfadimidine (SDD), sulfamethizole (SMT), sulfamethoxypyridazine (SMP), sulfachloropyridazine (SCP), sulfamethoxazole (SMX), sulfadimethoxine (SDX), 17-β-estradiol (E2), 17-α-ethinylestradiol (EE2), methotrexate (MTX), bisphenol A (BPA), *p*-nitrophenol (PNP), 3,5-dichlorophenol (3,5-DCP). Humic acids were also purchased from Sigma-Aldrich (Steinheim, Germany). Polyethersulfone (PES) membranes (0.22 μm, 47 mm) were purchased from Anchem Plus (Warsaw, Poland). A four-channel integrated dosing system equipped with YZ1515x heads (peristaltic pump) was purchased from Envisense (Lublin, Poland).

2.2. Instrumental analysis

The concentrations of analytes were measured for laboratory calibration samples and for environmental samples using liquid chromatography coupled with triple quadrupole mass spectrometry (LCMS-8050, Shimadzu Corporation, Japan) with a Heated ESI Probe. More information regarding the instrumental analysis is provided in Table S1 and Section 1 in the Supplementary Material.

Knowing the limits of quantification (LOQ, Table S1) and the extract volumes (1 mL), the limits of quantification of passive sampling (LQp) and grab sampling (LQg) were calculated using Eqs. (1) and (2), respectively (Xiong et al., 2019):

$$LQ_p = LOQ \times \frac{V_{inj}}{R_s \times t} \tag{1}$$

$$LQ_g = LOQ \times \frac{V_{inj}}{V_w} \tag{2}$$

where V_{inj} is the final volume of the extract (1 mL) and V_w is the volume of grab water samples used for extraction (200 mL). R_s is the sampling rate and t is the exposure time of the samplers in the water (20 d). The LQ_p and LQ_g for the analytes are shown in Table 1.

2.3. Preparation of passive samplers

Homemade passive samplers were made in the same way as in previous studies (Godlewska et al., 2022; Godlewska et al., 2021). Passive sampling devices containing multi-walled carbon nanotubes modified with the COOH group (COOH8-CNTs-PSDs) as a sorbent, with an outer diameter of <8 nm, were used to monitor sulfonamides and β-blockers in surface waters (Godlewska et al., 2021). On the other hand, passive sampling devices containing unmodified multi-walled carbon nanotubes (8-CNTs-PSDs) as a sorbent, with an outer diameter of <8 nm, were used to monitor hormones, cytostatic drugs, NSAIDs, TCADs and phenol derivatives in surface waters (Godlewska et al., 2022). Additionally, passive sampling devices containing the commercially and commonly used Oasis HLB (Oasis-PSDs) were prepared in order to compare the obtained TWA concentrations of the tested analytes. In the developed passive samplers, the total PES membrane exchange area was 18 cm² per sampler.

2.4. Laboratory calibration of passive samplers in a flow-through system

A flow-through system was constructed to keep the analyte concentrations in the water constant during the calibration of the passive samplers (Fig. 1). During the control experiments (details in Section 2 in the Supplementary Material), the concentration of analytes showed no significant decrease, indicating that the flow-through system was designed to be suitable for the study of the sampling rate (R_s).

To calibrate the PSDs, 20 L of water (with physicochemical parameters akin to the tested environmental waters, Table 2) spiked with analytes (100 ng/L) were poured into a glass calibration chamber and placed on a magnetic stirrer, and a peristaltic pump was started. The peristaltic pump simultaneously introduced a fresh portion of the aqueous analyte solution and discharged the "purified" water from the calibration chamber to the outside at a flow rate of 828 mL/h (left in such a system for 24 h at 20 °C) (Fig. 1). The chamber was constantly filled with water (20 L). Then, seven passive samplers were immersed in the exposure tank. All glass vessels were covered with aluminium foil to reduce light exposure and minimize evaporation. One passive sampler was removed every 2 days, air dried and disassembled. Subsequently, the analytes retained on the sorbent surface were desorbed with 30 mL of ACN:MeOH:CH_3COOH (1:1:1, v/v/v, pH 2.1) according to previous studies (Godlewska et al., 2022). The obtained extracts were sequentially concentrated to 1 mL and analyzed by LC-MS/MS. The obtained results were used to plot the uptake curves of analytes by the tested samplers (Fig. 2 and Fig. S1) and to calculate the R_s values according to the formula (Di Carro et al., 2014; Xiong et al., 2019):

$$R_s = \frac{C_s \times M_s}{C_w \times t} \tag{3}$$

where C_s and C_w are the pollutant concentrations in the sampler (ng/g) and the TWA concentrations of the analytes in the water (ng/L), respectively. M_s is the mass of the sorbent (g), and t is the exposure time (d). Moreover, the concentrations of the analytes in water were measured on 1, 7, 14 and

Table 1

Log octanol-water distribution coefficient (log D), pK_a, sampling rate (R_s) of the analytes obtained using semi-static calibration method and flow-through calibration method, limits of quantification (LQp) of COOH-CNTs-PSDs - passive sampling devices containing multi-walled carbon nanotubes modified with COOH group with an outer diameter of <8 nm as a sorbent and uCNTs-PSDs - passive sampling devices containing unmodified multi-walled carbon nanotubes with an outer diameter of <8 nm as a sorbent, limits of quantification of grab sampling (LQg) for target compounds. The R_s is expressed as mean ± SD.

Class	Analyte	pK_a, pK_{a2}[a]	log D at pH 7[a]	uCNTs-PSDs		COOH-CNTs-PSDs		LQ_p [ng/L]	LQ_g [ng/L]
				Semi-static-R_s [L/d][b]	Flow-through-R_s [L/d]	Semi-static-R_s [L/d][c]	Flow-through-R_s [L/d]		
Tricyclic antidepressants (TCADs)	Imipramine (IMI)	9.4	2.40	0.137 ± 0.004	0.095 ± 0.020	ND	ND	0.11	1.0
	Desipramine (DEZ)	10.4	1.50	0.135 ± 0.004	0.046 ± 0.010	ND	ND	0.22	1.0
	Carbamazepine (CBZ)	13.9	−4.45	0.062 ± 0.005	0.097 ± 0.031	ND	ND	0.10	1.0
Non-steroidal anti-inflammatory drugs (NSAIDs)	Ketoprofen (KET)	4.5	0.57	0.022 ± 0.006	0.111 ± 0.013	ND	ND	0.18	2.0
	Naproxen (NAP)	4.2	0.33	0.048 ± 0.002	0.051 ± 0.018	ND	ND	0.39	2.0
	Diclofenac (DIC)	4.2	1.66	0.058 ± 0.007	0.043 ± 0.017	ND	ND	0.12	0.5
Cytostatic drugs	Methotrexate (MTX)	4.7	−2.00	0.086 ± 0.004	0.091 ± 0.021	ND	ND	0.11	1.0
Phenol derivatives	*p*-nitrophenol (PNP)	7.2	1.53	0.035 ± 0.005	0.056 ± 0.014	ND	ND	0.36	2.0
	Bisphenol A (PBA)	9.6	0.72	0.065 ± 0.006	0.078 ± 0.017	ND	ND	0.26	2.0
	3,5-dichlorophenol (3,5-DCP)	8.2	2.41	0.106 ± 0.008	0.087 ± 0.016	ND	ND	0.12	1.0
Hormones	17-β-estradiol (E2)	10.5	0.55	0.103 ± 0.002	0.107 ± 0.026	ND	ND	0.093	1.0
	17-α-ethinylestradiol (EE2)	10.3	0.34	0.112 ± 0.001	0.121 ± 0.024	ND	ND	0.083	1.0
B-blockers	Atenolol (ATE)	9.6	−2.44	ND	ND	0.255 ± 0.024	0.279 ± 0.031	0.072	2.0
	Nadolol (NAD)	9.7	−1.86	ND	ND	0.273 ± 0.035	0.239 ± 0.032	0.084	2.0
	Pindolol (PIN)	9.3	0.28	ND	ND	0.265 ± 0.064	0.248 ± 0.024	0.081	2.0
	Acebutolol (ACE)	9.6	−0.89	ND	ND	0.245 ± 0.028	0.269 ± 0.025	0.074	2.0
	Metoprolol (MET)	9.6	−0.72	ND	ND	0.269 ± 0.026	0.287 ± 0.027	0.070	2.0
	Propranolol (PRO)	9.4	1.06	ND	ND	0.252 ± 0.047	0.266 ± 0.021	0.075	2.0
Sulfonamides (SAs)	Sulfadiazine (SDZ)	2.0, 6.9	−0.40	ND	ND	0.104 ± 0.008	0.102 ± 0.016	0.20	2.0
	Sulfathiazole (STZ)	2.0, 7.1	−0.20	ND	ND	0.070 ± 0.002	0.135 ± 0.019	0.074	1.0
	Sulfapyridine (SPD)	2.6, 8.2	0.32	ND	ND	0.113 ± 0.003	0.115 ± 0.011	0.087	1.0
	Sulfamerazine (SMZ)	2.1, 6.9	−0.21	ND	ND	0.084 ± 0.014	0.099 ± 0.017	0.10	1.0
	Sulfadimidine (SDD)	2.7, 7.7	0.05	ND	ND	0.083 ± 0.003	0.106 ± 0.015	0.094	1.0
	Sulfamethizole (SMT)	1.9, 5.3	−1.18	ND	ND	0.064 ± 0.002	0.112 ± 0.011	0.089	1.0
	Sulfamethoxypyridazine (SMP)	2.0, 6.8	−0.07	ND	ND	0.096 ± 0.011	0.121 ± 0.011	0.083	1.0
	Sulfachloropyridazine (SCP)	1.9, 5.5	−0.71	ND	ND	0.074 ± 0.009	0.097 ± 0.024	0.26	2.5
	Sulfamethoxazole (SMX)	1.6, 5.7	0.37	ND	ND	0.077 ± 0.006	0.077 ± 0.012	0.13	1.0
	Sulfadimethoxine (SDX)	2.1, 5.9	0.50	ND	ND	0.075 ± 0.011	0.113 ± 0.011	0.088	1.0

ND: not determined.

[a] log *D* values calculated from Eqs. in Section 3 in Supplementary Material.

[b] R_s determined in water with pH 7 and the content of dissolved humic acids 5 mg/L (Godlewska et al., 2022).

[c] R_s determined in water with pH 7 and the content of dissolved humic acids 5 mg/L (Godlewska et al., 2021).

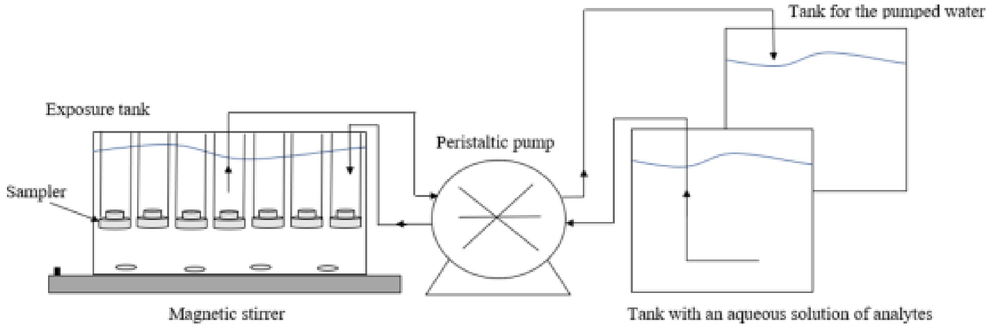

Fig. 1. Schematic of homemade flow-through system for calibrating developed passive samplers.

20 days in triplicate and the relative standard deviations (RSD) of the measurements were 9.1%–14.3%.

In order to examine the possible impact of the analyte concentrations in water and the water flow rate on the R_s values, various calibration experiments (in triplicate) were performed using the flow-through system: I) analyte concentration 100 ± 11 ng/L, flow rate 828 mL/h, II) analyte concentration 500 ± 21.3 ng/L, flow rate 828 mL/h, III) analyte concentration 100 ± 14 ng/L, flow rate 1242 mL/h. It was shown that regardless of the water flow rate and the concentration of analytes, the sampling rates of chemical compounds did not differ significantly (ANOVA; $p > 0.05$) (Table S2).

2.5. Site description and passive sampling

Stainless steel canisters (E&H services, Inc., Czech Republic) were placed in three types of surface water (Table 2, Fig. 3) for a period of 10 days and 20 days to determine the TWA concentrations of the tested micropollutants. Each canister contained three 8-CNTs-PSDs (for sampling hormones, cytostatic drugs, NSAIDs, TCADs and phenol derivatives), three COOH8-CNTs-PSDs (for sampling sulfonamides and β-blockers) and three Oasis-PSDs (for sampling all target compounds). After 10 days, one of the canisters was removed from the water and transported to the laboratory, where the passive samplers were dried and dismantled. The analytes retained on the surface of the sorbents were extracted with 30 mL of ACN:MeOH:CH_3COOH (1:1:1, v/v/v, pH 2.1). The obtained extracts were sequentially concentrated to 1 mL and analyzed by LC-MS/MS. The obtained results were used to calculate the TWA concentrations of the tested analytes. The same was done with canisters removed from the water after 20 days. The Baltic Sea (N 54°26′52.9″, E 18°34′33.4″), the Nogat River (N 54°02′52.5″, E 19°02′16.9″) and the Sztumskie Pole Lake (N 53°56′ 17.9″, E 19°01′27.9″) were selected as the sampling sites.

2.6. Water sample extraction

During the exposure of the samplers to the environment, grab samples of water (1 L) were taken: I) on the day of immersion of the PSDs in water (day 0); II) on the day of removal of the first canister (after 10 days); III) on the day of removal of the second canister (after 20 days). The water samples were transported to the laboratory, where they were filtered through 0.2 μm paper filters. Solid-phase extractions were performed using Oasis HLB cartridges (200 mg/6 cm^3) in triplicate for each sample separately according to the procedure outlined in Fig. S2. Then, the average concentration of the tested micropollutants in water during the 20 days of exposure of the samplers was calculated as the average of the concentrations of the analytes determined on the day of immersion of the PSDs (day 0), after 10 days and after 20 days of exposure of the PSDs.

The matrix effect (ME), extraction efficiency (EE) and absolute recovery (AR) of the method used were also determined for the tested environmental waters at four levels of analyte concentration: 20 ng/L, 50 ng/L, 80 ng/L and 110 ng/L, according to the diagram shown in Fig. S3 (Borecka et al., 2014; Caban et al., 2012).

2.7. Measurement of the dissolved humic acids concentration in water

A stock solution of humic acids in water (1000 mg/L) was prepared. Then, using appropriate dilutions, standard solutions were made with the following nominal concentrations: 100 mg/L, 50 mg/L, 25 mg/L, 12.5 mg/L, 6.25 mg/L, 3.13 mg/L, 1.56 mg/L, 0.78 mg/L. Initially, absorbance measurements were performed in the entire UV–Vis range (Spectroquant® Prove 300 UV/VIS Spectrophotometer). The maximum absorption at 300 nm was read from the absorption spectrum. Then, the absorbance of standard solutions was measured (λ 300 nm). The method was linear in the range of 0.78–100 mg/L, with accuracy 92.3–101.5%, intra-day precision 0.65–2.3%, inter-day precision 1.7–2.9%, LOD = 0.26 mg/L, LOQ = 0.78 mg/L.

3. Results and discussion

3.1. Comparison of flow-through calibration and semi-static calibration

According to the literature (Charlestra et al., 2012; Godlewska et al., 2022; Godlewska et al., 2021; Li et al., 2011; Męczykowska et al., 2018; Wang et al., 2017; Zhang et al., 2008), R_s values are specific to each chemical and may depend on many different factors (e.g., environmental

Table 2
Physicochemical parameters of surface waters in which passive samplers were placed.

Sampling site	Geographic location	pH	Salinity [PSU]	Conductivity [mS/cm]	Concentration of dissolved humic acids [mg/L]
Lake in Sztumskie Pole	N 53°56′17.9″ E 19°01′27.9″	7.7	0.12	0.245	9.04
River Nogat	N 54°02′52.5″ E 19°02′16.9″	7.8	0.85	1.67	5.55
Baltic Sea	N 54°26′52.9″ E 18°34′33.4″	6.5	5.6	11.4	<0.39

Salinity, conductivity, and pH were measured with the CPC-401 pH/Conductivity set (Elmetron®, Poland), measurement details of dissolved humic acids concentration are described in Section 2.7.

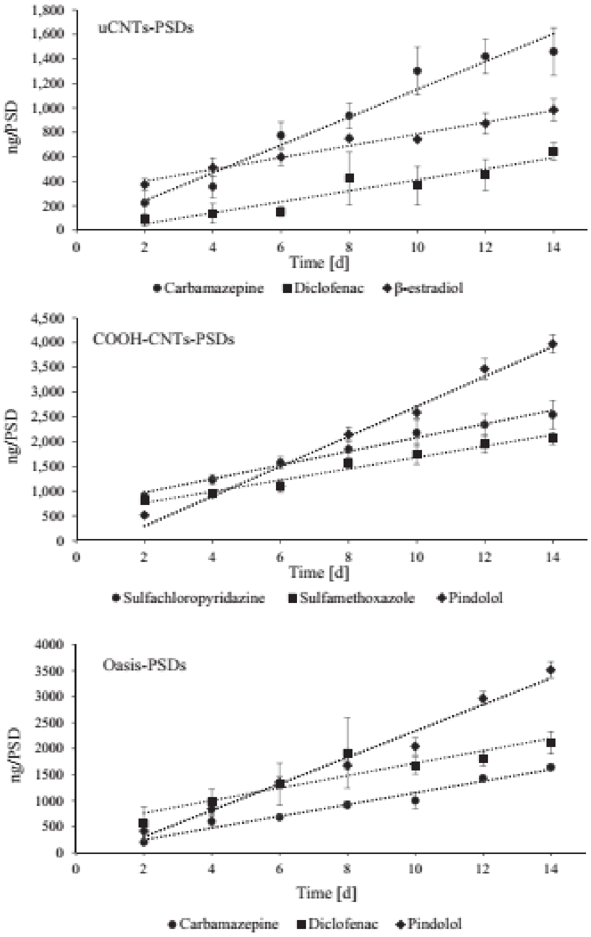

Fig. 2. Exemplary passive sampling devices (PSDs) uptake curves of the target compounds in a laboratory by 14 days. Data represent flow-through exposure at 20 °C with a constant flow rate of 828 mL/h and an analyte concentration in water of 100 ng/L.

conditions). The influence on R_s values was shown by, among others, such factors as: water salinity, water pH or the dissolved humic acids. Our previous studies (Godlewska et al., 2022; Godlewska et al., 2021) have shown that the salinity of the water surrounding the 8-CNTs-PSDs and COOH8-CNTs-PSDs below 7 PSU does not affect the sampling rate of the target compounds. In the case of water pH, only R_s values of the sulfonamides decreased with increasing water pH. The R_s of the remaining chemical compounds were independent of the water pH. On the other hand, the presence of dissolved humic acids in water (regardless of the concentration) caused a reduction in the R_s of sulfonamides compared to the R_s obtained from deionized water. The sampling rates of the remaining chemical compounds were independent of the concentration of dissolved humic acids (Godlewska et al., 2022; Godlewska et al., 2021). Therefore, the mean pH parameters (~7) and concentration of dissolved humic acids (~5 mg/L) were determined from the physicochemical parameters of the environmental waters (Table 2) in which the passive samplers were placed. The salinity of the investigated environmental waters was below 7 PSU, hence this parameter was omitted. The passive samplers were subsequently calibrated with the flow-through method in water with physicochemical parameters akin to the average parameters of environmental waters.

The uptake curves of all target compounds were linear (R^2 in the range of 0.86–0.99) during 14 days of exposure of the passive samplers in water (Fig. 2, Fig. S1). Therefore, the developed passive samplers were characterized as kinetic. The calculated R_s values of the analytes obtained by the flow-through method are summarized in Table 1 and Table S3. The R_s values of the analytes obtained by the semi-static method were taken from previous studies (Godlewska et al., 2022; Godlewska et al., 2021) and are also presented in Table 1. There were no statistically significant differences between the R_s values obtained by the flow-through method and the semi-static method (ANOVA; $p > 0.05$). The collected results prove the effectiveness and reliability of both the semi-static calibration method and the flow-through calibration method. Moreover, Charlestra et al. (2012) proved that the determined sampling rates of pesticides by POCIS using semi-static calibration (renewable) and flow-through calibration do not show statistical differences. However, they demonstrated that the use of static calibration (without mixing) results in obtaining lower R_s values. This is because by mixing water, the mass transfer of chemical compounds increases, reducing the thickness of the diffusive boundary layer.

3.2. TWA concentrations

The TWA concentrations of the tested chemical compounds in the Baltic Sea, the Nogat River and the Sztumskie Pole Lake are presented in Table 3 and mass of the analytes sampled by PSDs is presented in Table S4. In the Baltic Sea, only two analytes were determined, namely: carbamazepine (1.71 ± 0.24 ng/L) and bisphenol A (1.28 ± 0.23 ng/L), one of the most common water pollutants (Batucan et al., 2021; Corrales et al., 2015). Carbamazepine is a persistent environmental pollutant due to its resistance to degradation, even in a modern multi-stage wastewater treatment process, hence the interest of scientists in this compound as a possible anthropogenic marker in water (Hai et al., 2018). According to research by Björlenius et al. (2018), carbamazepine was the most frequently detected pharmaceutical at various sampling sites in the Baltic Sea (1.1–81 ng/L). Other drugs that were frequently present in the Baltic Sea samples were orphenadrine (0.01–26 ng/L), flecainide (0.02–7.5 ng/L), bisoprolol (0.04–14 ng/L), fluconazole (0.5–4.2 ng/L), diclofenac (1.4–28 ng/L), and diphenhydramine (0.08–0.5 ng/L). In the work of Borecka et al. (2015), samples from 17 sampling sites in the Baltic Sea were tested for antibacterial and anti-inflammatory agents. The most frequently quantified drug was trimethoprim (present in 16 out of 17 sampling sites in the concentration range of 1.1–14.2 ng/L). Other pharmaceuticals such as: sulfamerazine (5.5–17.9 ng/L), sulfapyridine (10.9–167.1 ng/L), sulfathiazole (6.3 ng/L), sulfadimethoxine (0.5–1 ng/L), sulfamethoxazole (5.4–70.1 ng/L), ketoprofen (42.4–135.0 ng/L), diclofenac (92.6 ng/L) and ibuprofen (34.9 ng/L) were also present in some samples from the Baltic Sea. On the other hand, bisphenol A has been repeatedly determined in the Baltic Sea in the concentration range of a few ng/L to even a few μg/L (Kanwischer et al., 2021; Staniszewska et al., 2015), which raises widespread concern due to its demonstrated toxicity (Mikołajewska et al., 2015). Beck et al. (2005) looked for five naturally occurring estrogens, one synthetic hormone and three xenoestrogens in the Baltic Sea. Estrone (0.10–0.53 ng/L), bisphenol A (0.22–5.4 ng/L), 4-nonylphenol (2.5–18.8 ng/L) and 4-*tert*-octylphenol (0.12–0.45 ng/L) were quantified in all samples, and 17-α-ethinylestradiol in 9 out of 10 samples (1.7–17.2 ng/L). However, the mere fact that only 2 out of 28 examined micropollutants were determined gives a positive impression and allows us to assume that multi-annual programs and cooperation on the purification of the Baltic Sea are beginning to take effect.

In the case of the lake in Sztumskie Pole, diclofenac (3.23 ± 0.17 ng/L), *p*-nitrophenol (13.3 ± 2.1 ng/L), bisphenol A (31.1 ± 2.7 ng/L), 3,5-dichlorophenol (23.0 ± 2.7 ng/L), 17-β-estradiol (2.45 ± 0.76 ng/L) and 17-α-ethinylestradiol (4.89 ± 0.70 ng/L) were determined.

In the Nogat River, carbamazepine (2.34 ± 0.66 ng/L), diclofenac (3.61 ± 0.23 ng/L), *p*-nitrophenol (8.86 ± 0.23 ng/L), 3,5-dichlorophenol (3.51 ± 0.11 ng/L), 17-β-estradiol (7.39 ± 0.15 ng/L) and metoprolol (0.22 ± 0.12 ng/L) were determined. It is possible that the discharge of sewage into the Nogat River contributes to the presence of characteristic pollutants (carbamazepine, diclofenac, 17-β-estradiol, metoprolol). No

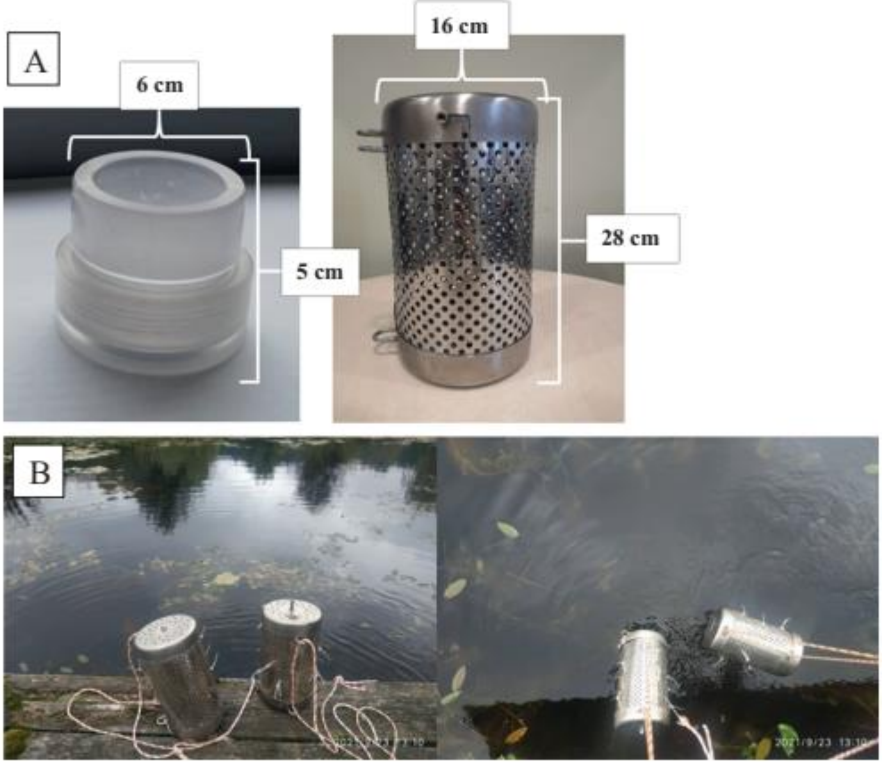

Fig. 3. A - Pictures and dimensions of home-made passive sampler and stainless steel canister. B - Pictures from deployment of passive samplers immersed to a depth of ~2 m in Lake in Sztumskie Pole.

data of pollution in the Nogat River have been found; however, several papers show the contamination of the Vistula River (River Nogat is the eastern estuary arm of the Vistula River). Giebułtowicz and Nałecz-Jawecki (2014) investigated the presence of antidepressants (including imipramine and desipramine) at several sampling points on the Vistula River. They quantified 11 drugs out of 21 sought, moclobemid being present in all tested samples in the concentration range of 0.3–45 ng/L. Moreover, Giebułtowicz et al. (2018) investigated the presence of antimicrobial agents (including sulfadiazine, sulfadimethoxine, sulfamethazine, sulfamethoxazole, sulfanilamide, sulfathiazole) in the Vistula River. They quantified all 32 tested pharmaceuticals, 22 drugs of which were present at all sampling points.

3.2.1. Impact of the exposure time of the samplers

The canisters with passive samplers were placed in surface waters for a period of 10 and 20 days in order to assess the effect of the exposure time of PSDs on the obtained TWA concentrations. No statistically significant differences were found between the TWA concentrations obtained from the samplers removed from the water after 10 days and from the samplers removed after 20 days (Fig. S4) (ANOVA; $p > 0.05$). Longer exposure of passive samplers in water is also associated with the risk of biofouling, which contributes to blocking the pores of the membranes and slowing or stopping the sampling of analytes by the receiving phase of the sampler. Based on the obtained results, it can be concluded that exposure of PSDs in the environment both for 10 days and 20 days makes it possible to obtain reliable TWA concentrations of the tested micropollutants.

3.2.2. Comparison between CNTs-PSDs and Oasis-PSDs

Passive samplers containing Oasis HLB as a sorbent were used to confirm the accuracy of the obtained TWA concentrations from passive samplers with carbon nanotubes as a sorbent, which were used in the environmental water for the first time. There were no statistically significant differences in the obtained TWA concentrations of analytes from CNTs-PSDs and Oasis-PSDs (ANOVA; $p > 0.05$). The obtained results confirm the usefulness of the application of CNTs-PSDs for the sampling and concentration of a wide range of chemical compounds that differ significantly in their physicochemical properties (Table 1). CNTs-PSDs have been successfully used in various water environments: in flowing water with high salinity (5.6 PSU) and low content of dissolved humic acids (<0.39 mg/L), in flowing water with low salinity (0.85 PSU) and higher content of dissolved humic acids (5.55 mg/L) as well as in still water with negligible salinity (0.12 PSU) but a significant content of dissolved humic acids (9.04 mg/L). The use of environmentally friendly and renewable methods is crucial for sustainable development. The application of carbon nanotubes as sorbents in extraction techniques fits better with this trend than Oasis HLB. First of all, carbon nanotubes can be easily and quickly regenerated and then reused as sorbents while maintaining high extraction efficiency (Arroyo-Manzanares et al., 2020; Asensio-Ramos et al., 2011; Liu et al., 2015; Salam and Burk, 2009; Toński et al., 2021; Xu et al., 2015). Toński et al. (2021) proved that the application of thermal regeneration at 300 °C for 2 h allows for the reuse of carbon nanotubes as a sorbent for the extraction of anti-cancer drugs from water. Five cycles of regeneration-resorption were performed and it was shown that the thermal regeneration did not affect the EE of analytes. Asensio-Ramos et al. (2011) showed that regeneration by washing with small volumes of solvents, followed by vacuum drying, also allows the reuse of CNTs 5 times while maintaining high extraction efficiency of pesticide from water. Moreover, research is still being conducted to improve the methods of synthesizing carbon nanotubes in order to produce these materials using ever cheaper and greener methods. Makgabutlane et al. (2021) in their review based on green

Table 3

Time weighed (20 days) average (TWA) concentrations [ng/L and μM] of selected micropollutants in surface waters obtained from grab sampling and CNTs-PSDs and Oasis-PSDs sampling. TWA concentrations from passive samplers are expressed as mean ± SD (n = 3). TWA concentrations from grab sampling are expressed as mean ± SD (mean concentration of analytes in the water sampled on days 0, 10 and 20 of exposure of the samplers in the water).

Analyte	TWA concentrations from CNTs-PSDs			TWA concentrations from Oasis-PSDs			TWA concentrations from grab sampling		
	Baltic Sea	Lake in Sztumskie Pole	River Nogat	Baltic Sea	Lake in Sztumskie Pole	River Nogat	Baltic Sea	Lake in Sztumskie Pole	River Nogat
IMI	<LQp	<LQp	<LQp	<LQp	<LQp	ND	<LQg	<LQg	ND
DEZ	<LQp	<LQp	ND	<LQp	<LQp	ND	<LQg	<LQg	ND
CBZ	1.71 ± 0.24 ng/L ($7.2 \ast 10^{-6} \pm 1.0 \ast 10^{-6}$ μM)	<LQp	2.34 ± 0.66 ng/L ($9.9 \ast 10^{-6} \pm 2.8 \ast 10^{-6}$ μM)	1.45 ± 0.58 ng/L ($6.1 \ast 10^{-6} \pm 2.5 \ast 10^{-6}$ μM)	<LQp	2.57 ± 0.58 ng/L ($10.9 \ast 10^{-6} \pm 2.5 \ast 10^{-6}$ μM)	1.41 ± 0.36 ng/L ($6.0 \ast 10^{-6} \pm 1.5 \ast 10^{-6}$ μM)	<LQg	1.13 ± 0.11 ng/L ($47.8 \ast 10^{-7} \pm 4.7 \ast 10^{-7}$ μM)
KET	ND	ND	ND	ND	ND	ND	ND	ND	ND
NAP	ND	ND	ND	ND	ND	ND	ND	ND	ND
DIC	ND	3.23 ± 0.17 ng/L ($109.1 \ast 10^{-7} \pm 5.7 \ast 10^{-7}$ μM)	3.61 ± 0.23 ng/L ($121.9 \ast 10^{-7} \pm 7.8 \ast 10^{-7}$ μM)	ND	2.71 ± 1.9 ng/L ($9.2 \ast 10^{-6} \pm 6.4 \ast 10^{-6}$ μM)	3.19 ± 0.94 ng/L ($10.8 \ast 10^{-6} \pm 3.2 \ast 10^{-6}$ μM)	ND	3.78 ± 0.24 ng/L ($127.6 \ast 10^{-7} \pm 8.1 \ast 10^{-7}$ μM)	3.01 ± 0.93 ng/L ($10.2 \ast 10^{-7} \pm 3.1 \ast 10^{-7}$ μM)
MTX	ND	ND	ND	ND	ND	ND	ND	ND	ND
PNP	<LQp	13.3 ± 2.1 ng/L ($9.6 \ast 10^{-5} \pm 1.5 \ast 10^{-5}$ μM)	8.86 ± 0.23 ng/L ($63.7 \ast 10^{-6} \pm 1.7 \ast 10^{-6}$ μM)	<LQp	14.3 ± 1.2 ng/L ($102.8 \ast 10^{-6} \pm 8.6 \ast 10^{-6}$ μM)	8.40 ± 0.38 ng/L ($60.4 \ast 10^{-6} \pm 2.7 \ast 10^{-6}$ μM)	<LQg	12.8 ± 1.6 ng/L ($9.2 \ast 10^{-5} \pm 1.2 \ast 10^{-5}$ μM)	<LQg
PBA	1.28 ± 0.23 ng/L ($5.6 \ast 10^{-6} \pm 4.4 \ast 10^{-6}$ μM)	31.1 ± 2.7 ng/L ($13.6 \ast 10^{-5} \pm 1.2 \ast 10^{-5}$ μM)	ND	1.630 ± 0.020 ng/L ($714.0 \ast 10^{-8} \pm 8.8 \ast 10^{-8}$ μM)	32.1 ± 2.4 ng/L ($14.1 \ast 10^{-5} \pm 1.1 \ast 10^{-5}$ μM)	ND	<LQg	29.7 ± 2.9 ng/L ($13.0 \ast 10^{-5} \pm 1.3 \ast 10^{-5}$ μM)	ND
3,5-DCP	<LQp	23.0 ± 2.7 ng/L ($14.3 \ast 10^{-5} \pm 1.4 \ast 10^{-5}$ μM)	3.51 ± 0.11 ng/L ($215.3 \ast 10^{-7} \pm 6.7 \ast 10^{-7}$ μM)	<LQp	21.4 ± 2.3 ng/L ($13.1 \ast 10^{-5} \pm 1.4 \ast 10^{-5}$ μM)	3.46 ± 0.57 ng/L ($21.2 \ast 10^{-6} \pm 3.5 \ast 10^{-6}$ μM)	ND	20.7 ± 3.5 ng/L ($12.7 \ast 10^{-5} \pm 2.1 \ast 10^{-5}$ μM)	<LQg
E2	ND	2.45 ± 0.76 ng/L ($9.0 \ast 10^{-6} \pm 4.4 \ast 10^{-6}$ μM)	7.39 ± 0.15 ng/L ($271.3 \ast 10^{-7} \pm 5.5 \ast 10^{-7}$ μM)	ND	2.32 ± 0.52 ng/L ($8.5 \ast 10^{-6} \pm 1.9 \ast 10^{-6}$ μM)	7.37 ± 0.34 ng/L ($27.1 \ast 10^{-6} \pm 1.2 \ast 10^{-6}$ μM)	ND	<LQg	<LQg
EE2	ND	4.89 ± 0.70 ng/L ($16.5 \ast 10^{-6} \pm 2.4 \ast 10^{-6}$ μM)	ND	ND	4.37 ± 0.62 ng/L ($14.7 \ast 10^{-6} \pm 2.1 \ast 10^{-6}$ μM)	ND	ND	<LQg	ND
ATE	ND	ND	ND	ND	ND	ND	ND	ND	ND
NAD	ND	ND	ND	ND	ND	ND	ND	ND	ND
PIN	ND	ND	ND	ND	ND	ND	ND	ND	ND
ACE	<LQp	ND	<LQp	<LQp	ND	<LQp	ND	ND	ND
MET	<LQp	<LQp	0.22 ± 0.12 ng/L ($8.2 \ast 10^{-7} \pm 4.5 \ast 10^{-7}$ μM)	<LQp	<LQp	0.32 ± 0.12 ng/L ($12.0 \ast 10^{-7} \pm 4.5 \ast 10^{-7}$ μM)	ND	ND	<LQg
PRO	ND	<LQp	<LQp	ND	<LQp	<LQp	ND	ND	ND
SDZ	ND	ND	ND	ND	ND	ND	ND	ND	ND
STZ	ND	ND	ND	ND	ND	ND	ND	ND	ND
SPD	ND	ND	ND	ND	ND	ND	ND	ND	ND
SMZ	ND	ND	ND	ND	ND	ND	ND	ND	ND
SDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
SMT	ND	ND	ND	ND	ND	ND	ND	ND	ND
SMP	ND	ND	ND	ND	ND	ND	ND	ND	ND
SCP	ND	ND	ND	ND	ND	ND	ND	ND	ND
SMX	ND	ND	ND	ND	ND	ND	ND	ND	ND
SDX	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND - not detected, LQp - limits of quantification of passive sampler, LQg - limits of quantification of grab sampling.

synthesis of carbon nanotubes, showed that greener processes can be competent and even better than conventional CNTs production methods. Taking the above into account, CNTs-PSDs have great potential for use in routine procedures in water environment monitoring.

3.3. Comparison between passive sampling and grab sampling

The solid-phase extraction method was used to isolate and concentrate the tested chemical compounds from environmental water samples. The extraction efficiency, absolute recovery (Table S5) and matrix effect (Fig. S5) were determined for each matrix. For the Baltic Sea, the EE was in the range of 82.5–102.5%, and the AR in the range of 71.5–101.4%. For the Sztumskie Pole Lake, the EE was in the range of 81.6–95.6%, while the AR in the range of 72.3–99.5%. For the Nogat River, the EE was in the range of 83.2–98.7%, and the AR in the range of 73.5–101.3%. For β-blockers, ion enhancement was observed in each environmental matrix, while for the remaining compounds, ion suppression was observed in each environmental matrix. The matrix had the greatest effect on the suppression of ketoprofen ions (maximum ME: −49%) and methotrexate (maximum ME: −39%). For the remaining compounds, the ME ranged from −19 to 22.5%.

It was possible to determine carbamazepine (1.41 ± 0.36 ng/L) in the Baltic Sea; diclofenac (3.78 ± 0.24 ng/L), *p*-nitrophenol (12.8 ± 1.6 ng/L), bisphenol A (29.7 ± 2.9 ng/L) and 3,5-dichlorophenol (20.7 ± 3.5 ng/L) in the Sztumskie Pole Lake; carbamazepine (1.13 ± 0.11 ng/L) and diclofenac (3.01 ± 0.93 ng/L) in the Nogat River, using grab sampling and the SPE method (Fig. S6). No statistically significant differences were found between the average concentrations of the detected micropollutants by means of grab sampling and the TWA concentrations of the detected micropollutants by passive sampling (ANOVA; $p > 0.05$).

However, most importantly, CNTs-PSDs were able to detect and quantify a greater number of chemical compounds than by grab sampling and SPE (Table 3). Using CNTs-PSDs, it was possible to quantify p-nitrophenol in the Baltic Sea, while using grab sampling, its concentration was below LQg. Using CNTs-PSDs, it was possible to quantify 17-β-estradiol and 17-*α*-ethinylestradiol in the lake in Sztumskie Pole, while using grab sampling, their concentration was below LQg. Using CNTs-PSDs, it was possible to quantify p-nitrophenol, 3,5-dichlorophenol, 17-*β*-estradiol and metoprolol in the Nogat River, while using grab sampling, their concentration was below LQg. The obtained results confirm the advantage of passive sampling over grab sampling, especially when monitoring pollutants occurring in the aquatic environment at low concentration levels.

4. Conclusion

Considering that the literature proposes several methods of calibrating passive samplers and there are no data on the repeatability of the obtained R_s values, regardless of the method used, it was decided to compare the R_s values obtained by the flow-through method and the semi-static method. It is said that the flow-through method best reflects environmental conditions; however, at the same time, it is the most labour-consuming and costly method. In contrast, the semi-static method (with gentle mixing) is easier to implement and less costly. The data collected in this work prove similar R_s values of the target compounds are obtained using the flow-through calibration method and the semi-static method.

CNTs-PSDs were used successfully in the aquatic environment for the first time. There were no statistically significant differences between the TWA concentrations of analytes obtained from CNTs-PSDs and Oasis-PSDs. This encourages further work on the use of carbon nanotubes in passive techniques, especially due to the possibility of their regeneration and reuse, which is an advantage over conventional Oasis HLB. The following step should be research on the regeneration of used carbon nanotubes and test the utility and effectiveness of using regenerated CNTs in passive samplers.

A common approach to monitoring pollution of the aquatic environment is grab sampling followed by solid-phase extraction in the laboratory. CNTs-PSDs were able to detect and quantify a greater number of chemicals than grab sampling and SPE, confirming the advantage of passive sampling over grab sampling, especially when monitoring low-concentration aquatic pollutants.

CRediT authorship contribution statement

Klaudia Godlewska: Methodology, Conceptualization, Formal analysis, Investigation, Validation, Writing - Original Draft, Visualization, Project administration, Funding acquisition.

Monika Paszkiewicz: Conceptualization, Supervision.

Piotr Stepnowski: Writing - Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.155551.

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10. Wykaz tabel i rysunków

Tabele:

Rysunki:

Rysunek 7 Wpływ ponownego zastosowania zregenerowanych nanorurek węglowych jako sorbentów w próbnikach pasywnych na szybkości pobierania analitów (R_s)

11. Dorobek naukowy

DANE LICZBOWE

Sumaryczny IF[1] wszystkich publikacji	**37,51**
Sumaryczna liczba cytowań[2] wszystkich publikacji	**37**
Sumaryczna punktacja MEiN	**670**
Indeks Hirscha[3]	**3**

[1] Wartości IF zgodnie z rokiem opublikowania oprócz publikacji z lat 2021-2022 (brak wskaźnika)
[2] Liczba cytowań publikacji (bez autocytowań) według bazy Web of Science (WoS)
[3] Indeks Hirscha według bazy Web of Science (WoS)

2022

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2021

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Poster

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