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JES JOURNAL OF ENVIRONMENTAL SCIENCES

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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

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ARTICLE INFO

Article history:
Received 24 June 2020
Revised 31 August 2020
Accepted 31 August 2020
Available online 17 September 2020

Keywords:
Carbon nanotubes
Passive sampling
Pharmaceuticals
Sampling rates (R_s)

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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https://doi.org/10.1016/j.jes.2020.08.034
1001-0742/

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. (Brat-

tleboro, 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):

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

which rearranges to

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

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:

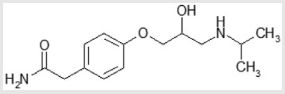
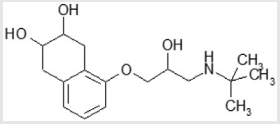
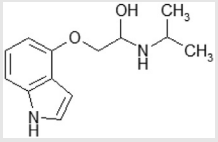
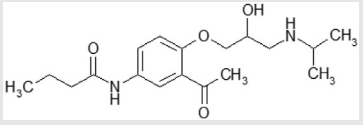
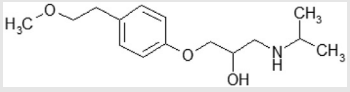
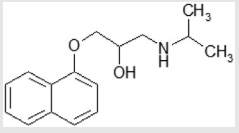
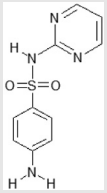
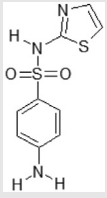
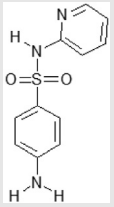
$$R_s = k_U V_T \quad (3)$$

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*

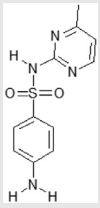
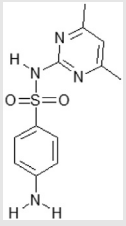
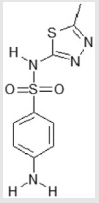
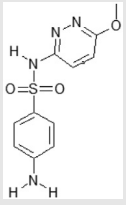
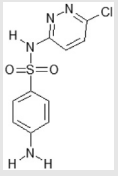
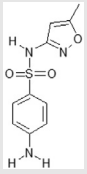
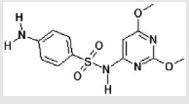
Studies have also been carried out where water donor solutions were characterized by different pH values (3, 5, 7 and 9), concentrations of dissolved humic acids (0, 1, 2.5 and 5 mg/L) and salinity (0, 7, 21 and 35 PSU - 1 practical unit of salinity corresponds to 1 g of salt per kg of solution). Donor 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-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 intermolec-

ular 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):

$$D_{base} = \frac{K_{ow}}{1 + 10^{pKa - pH}} \quad (4)$$

$$D_{acid} = \frac{K_{ow}}{1 + 10^{pH - pK_a}} \quad (5)$$

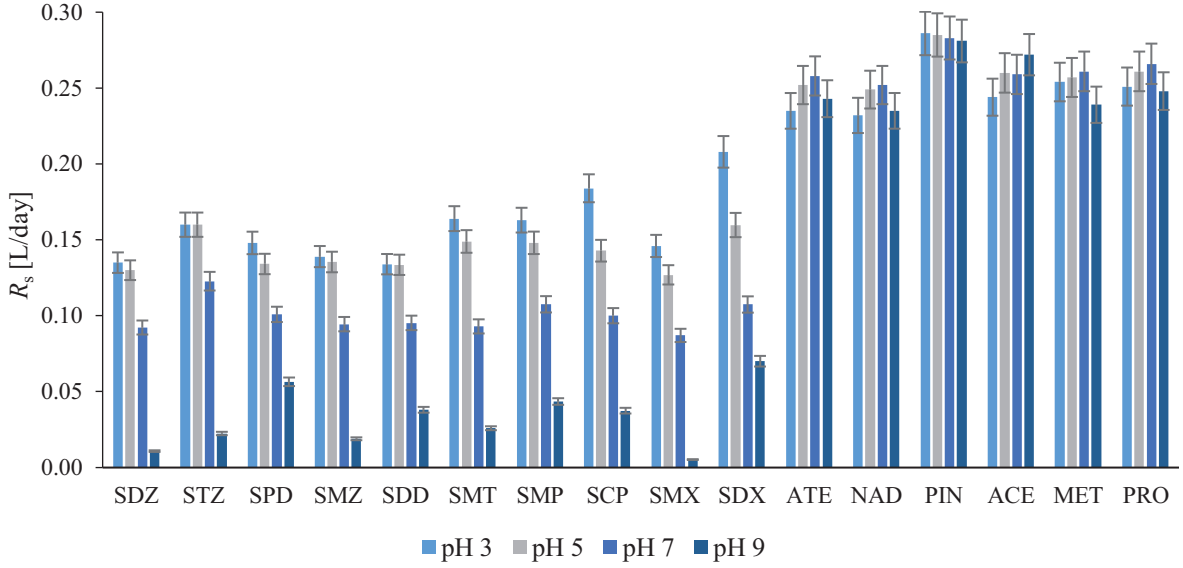


Fig. 1 – The influence of water pH on the sampling rates (R_s) of sulfonamides and β-blockers.

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

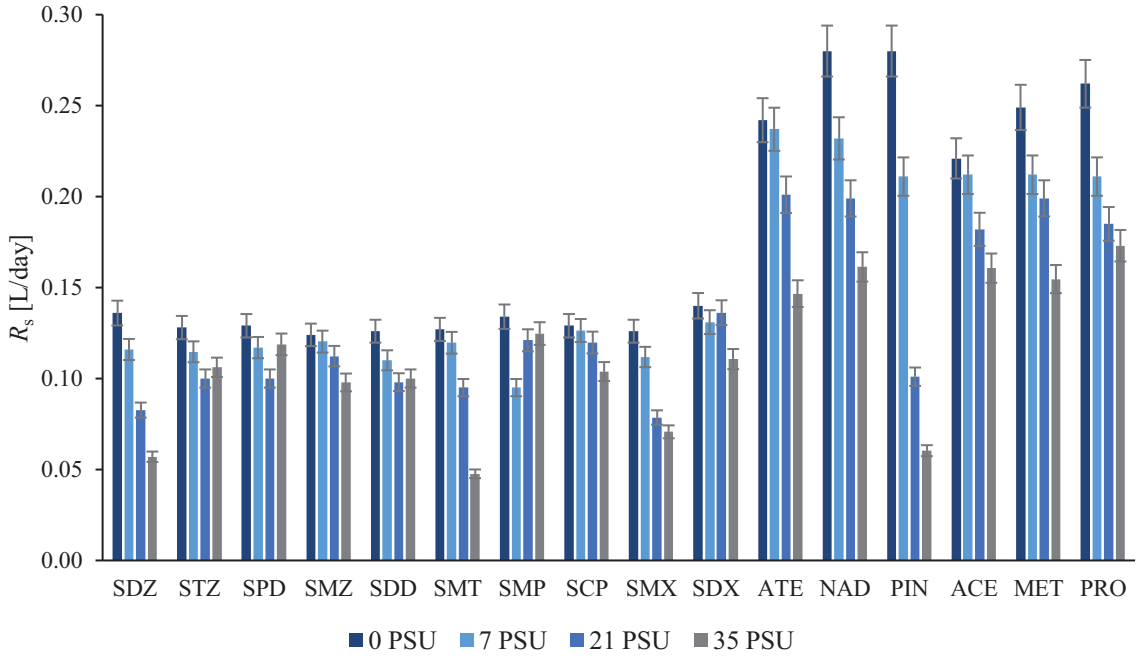


Fig. 2 – The influence of the salinity of the donor phase on the sampling rates (R_s) of sulfonamides and β-blockers.

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-

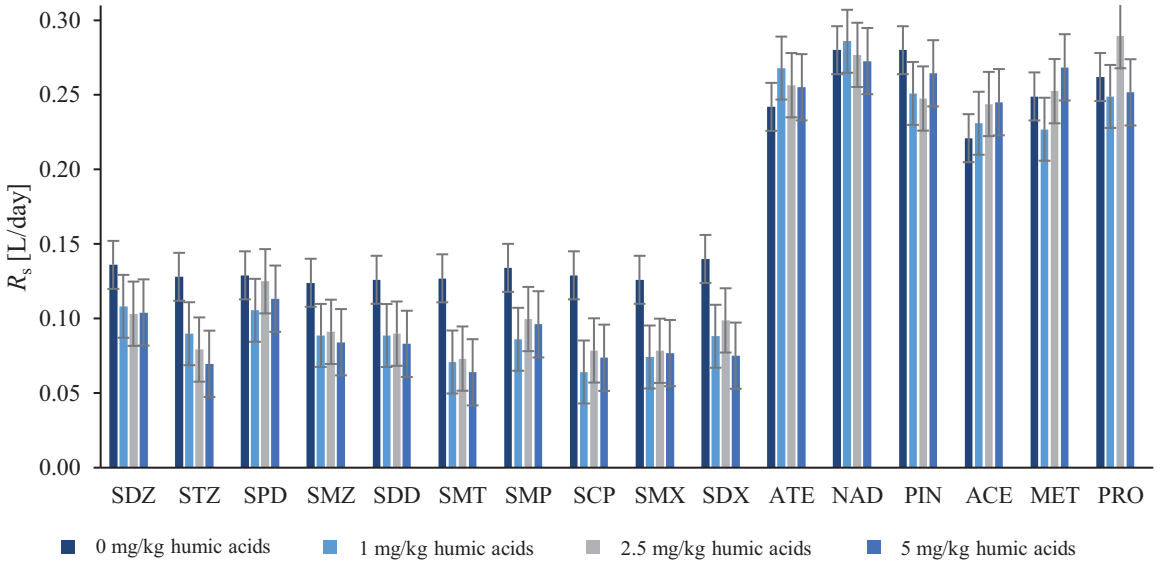


Fig. 3 – The influence of the dissolved humic acids concentration in donor phase on the sampling rates (R_s) of sulfonamides and β-blockers.

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

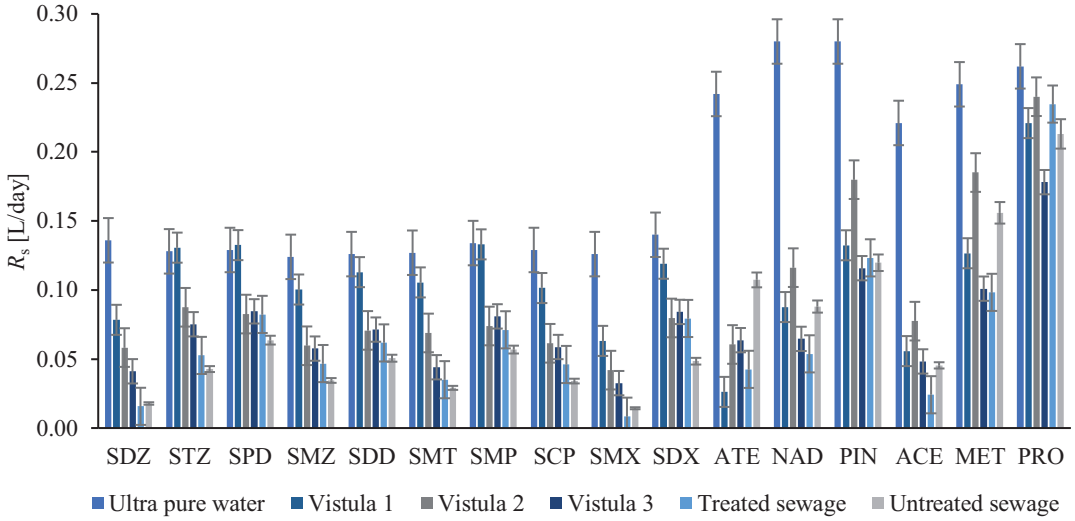


Fig. 4 – The influence of donor phase type on the sampling rates (R_s) of sulfonamides and β-blockers.

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.

Acknowledgments

Financial support was provided by the National Science center (Poland) under the grant UMO-2019/33/N/ST4/01376.

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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