



Insight into selected emerging micropollutant interactions with wastewater colloidal organic carbon: implications for water treatment and analysis

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Received: 27 May 2020 / Accepted: 18 October 2020 / Published online: 4 November 2020
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Abstract

This study reports how adding a membrane filter (0.45- μ m cellulose nitrate filter) between a glass fibre filter and the solid phase extraction (SPE) cartridge affected the GC/MS analysis of 48 emerging organic micropollutants in wastewater. Most of them are widely used as active pharmaceuticals, cosmetic and packaging material ingredients including classes of parabens, benzophenones and bisphenols among other chemicals tested. A high artificial organic carbon (OC) content in wastewater (DOC = 280 \pm 14 mg/L) was investigated to gain insight into micropollutants/colloidal OC filter cake interactions. The results show that even with the use of matrix-matched calibration, the introduction of a second (membrane) filtration step can affect the analysis. Both positive, negative and no effects on the theoretical concentrations calculated from the calibration curves with and without additional filtration were observed. Positive effects on the concentration for the same analyte peak area relative to its surrogate standard were the consequence of a reduced signal for the same concentration, while the negative effects are the consequence of increasing signal for the same concentration. Effect types were dependent on the concentration and the nature of the analytes. Results show that bisphenols and parabens significantly interact with colloidal OC. Statistical analysis of molecular descriptor distribution with effect type showed that micropollutants that have a stronger interaction with colloidal OC have significantly higher ability to act as hydrogen bond donors (HBD) and have larger molar volume (MV). All compounds that experienced either positive or negative effects have a significantly higher median logD. However, further exploration within a single class of compounds (parabens, benzophenones and bisphenols) revealed that selected descriptors are unrelated to an effect type. Pearson's correlations showed that a correlation exists for certain concentration levels and groups of compounds between a negative effect and MV and logD and a positive effect with MV, MW and rotatable bond (RB) count.

Keywords Wastewater analysis · Colloidal organic carbon interactions · Emerging micropollutants · Molecular descriptors · Structure activity relationship

Responsible Editor: Philippe Garrigues

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11356-020-11309-7>.

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Introduction

The presence of emerging organic micropollutants in the aquatic environment has garnered significant attention from researchers and regulators alike. Micropollutants that are not regulated by environmental laws are usually described as contaminants of emerging concern (CEC) including pharmaceuticals and personal care products (PPCP), agricultural products and different kind of chemicals. Since the 1990s, the number of identified CEC in natural and wastewaters has increased, which in turn has raised awareness about the capabilities and limitations of current analytical methodologies. The first legislative action was the Water Framework Directive 2000/60/EC, which has since stimulated research into improving wastewater and drinking water treatments (Rizzo et al. 2019; Ivančev-Tumbas 2014) and in gaining a better understanding of natural remediation processes (Amy et al. 2006).

Wastewater remains the primary source of CEC residues in the aqueous environment, and practitioners in the field have investigated various treatment technologies for their removal (Luo et al. 2014; Rizzo et al. 2019). Dissolved organic carbon (DOC), the principal constituent of municipal wastewaters that needs to be removed, can significantly affect the removal of organic micropollutants during wastewater treatment. Katsoyiannis and Samara (2007) have shown that the presence of DOC means that hydrophobic micropollutants (metals, PCBs and pesticides) remain in the water phase, thereby lowering their removal rate. Mechanisms of DOC interactions are sorption, hydrogen bonding and complex formation (Ivančev-Tumbas 2014). It interacts with process materials, such as activated carbon, but also coagulants and membranes. Recently, Guillosoou et al. (2020a) confirmed that DOC affects micropollutant removal in advanced wastewater treatment. Guillosoou et al. (2020b) also confirmed that interactions between some organic micropollutants and dissolved organic matter could improve the efficiency of activated carbon for their removal. It is common knowledge among experts that the presence of DOC reduces the removal efficiency of activated carbon. However, the micropollutant charge was shown to have a definite impact and can have beneficial effects, but more in-depth knowledge related to the nature of those interactions between dissolved organic matter (e.g. kinetics of the reactions) and micropollutants is needed. Studies on those interactions are still rare in comparison with studies on the occurrence and fate of micropollutants in the environment and different water treatment processes. The literature mostly deals with their removal from wastewater and relates efficiency either with a small (Wick et al. 2011) or, more recently, with a large number of molecular characteristics (Blum et al. 2019). Sorption, where dominant mechanisms are related to hydrophobicity, and biodegradation, were found to be the most important for removal. Dissolved effluent organic matter (dEfOM) is defined as “the fraction that passes

through a 0.45 μm membrane filter” and constitutes the main fraction of EfOM (Michael-Kordatou et al. 2015). It consists of dissolved natural organic matter, soluble microbial products and traces of organic micropollutants such as PPCPs, disinfection by-products and endocrine-disrupting chemicals (Michael-Kordatou et al. 2015). Current treatments do not entirely remove this fraction from the wastewater, and micropollutants can end up in receiving waters (Luo et al. 2014; Rizzo et al. 2019). Due to the complexity of EfOM, which derives from its numerous constituents each with their own physicochemical properties and biodegradability, it remains a challenge to predict how wastewater treatment affects these different organic micropollutants without testing under real conditions.

Understanding the interactions of micropollutants with colloidal organic carbon is also vital for wastewater analysis. Before chromatographic separation, water samples can be analysed or extracted whole or after being filtered, depending on the goal of the analysis. In addition to traditionally used liquid-liquid extraction (LLE), solid-phase extraction (SPE) and increasingly solid-phase microextraction (SPME) are popular sample preparation techniques for gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) (Comerton et al. 2009; Lindholm et al. 2014; Richardson and Ternes 2018). Wastewater organic carbon can interfere with the extraction process, i.e. with the SPE sorbent, or, in the case that some dissolved molecules are retained in the extracts, with the chromatographic process itself. In GC-MS, such compounds may interfere with the glass surface of the injector liner and with the stationary phase, resulting in poor peak shape, lower resolution, reduced sensitivity and greater uncertainty of the results.

The goal of this study was to gain insight into the interaction between colloidal organic carbon in artificial wastewater (model OC) and 48 selected emerging micropollutants. The groups of substances studied include the same set of micropollutants as in Česen et al. (2018b). These compounds include active pharmaceutical ingredients and their transformation products, natural hormones, constituents of personal care products like UV filters and parabens, representatives of industrial compounds (e.g. bisphenols and phenols etc.), the herbicide mecoprop (MEC) and 4,4'-dihydroxydiphenyl ether (DHDPE) which is a transformation product of the pesticide fenoxycarb (Kiefer et al. 2019). Bisphenols are synthetic organic chemicals mostly used in the manufacture of polycarbonate type plastics and epoxy resins and used in a multitude of applications, including food contact materials (e.g. sports bottles and food and drink cans). Their global occurrence has been confirmed in recent studies (Česen et al. 2018a). Parabens are used as preservatives in cosmetics, pharmaceutical and food products and are detected in nature despite their biodegradability in wastewater treatment plants and the

environment (Haman et al. 2015). Similarly, UV filters, which are added to many types of product to protect against UV rays, may also pose a risk to the environment and are removed to varying degrees during wastewater treatment processes (Karthikraj and Kannan 2017; Tsui et al. 2014; Česen et al. 2018b).

To date, information regarding the interactions of these substances with colloidal and dissolved organic carbon is limited at best. Wick et al. (2011), showed that sorption on sludge improves the removal of benzophenone-3 in WWTP to a small extent. They also found that the sorption of benzophenone-1 and benzophenone-2 was higher than estimated according to their logD values. Concerning the sorptive behaviour of bisphenols, Wang et al. (2019) observed the importance of π - π interactions in sorption of bisphenol A (BPA) and tetrabromobisphenol A (TBBPA) on river biofilm where hydrophobic partitioning into the organic matter was confirmed, and polysaccharides represent the main fraction responsible for sorption. Park et al. (2015) reported that interactions between BPA and natural organic matter (NOM) are beneficial for BPA removal by activated carbon, both in its raw state and impregnated with iron-oxide nanoparticles. Schäfer et al. (2006) also revealed how organic foulants such as humic acid and other compounds affect the retention of BPA during the ultrafiltration of grey water. Similarly, the sorptive behaviour of parabens depends on their interaction with organic matter which was shown in column tests where the hydrophobic interactions of a series of parabens with the organic matter present in different aquifer materials' were studied (López-Ortiz et al. 2018).

In the present study, a more extensive set of compound classes were tested under identical conditions. In order to elucidate the interactions between the selected compounds and colloidal organic carbon, two GC/MS calibrations were prepared using the same artificial wastewater. The first involved SPE with a single filtration step (glass fibre filter) to remove suspended solids and part of the colloidal OC ($> 0.7 \mu\text{m}$). The second involved SPE with a two-step filtration process incorporating a glass fibre filter ($0.7 \mu\text{m}$) and a membrane filter ($0.45 \mu\text{m}$) to remove both suspended solids and colloidal OC ($> 0.45 \mu\text{m}$). It was assumed that a two-step filtration would favour the formation of a colloidal OC filter cake on the filter membrane (retaining the sizes of 0.45 – $0.7 \mu\text{m}$) and, due to compound-colloidal OC interactions, will measurably affect the results of the analysis. The ratios of the estimated (i.e., theoretical) concentrations obtained from the two-step filtration calibration curve and the concentrations measured from the one-step filtration calibration curve for the same analyte peak area relative to the surrogate standard were grouped according to the observed effect (positive, negative and no effect). This grouping was done to relate the effects to the concentration and physicochemical properties of the selected compounds. In addition to the interactions of pollutants with

the colloidal OC filter cake, additional matrix effects in the GC/MS system (Pinho et al. 2012) could occur from the presence of colloidal organic matter not removed by GF/F filters. However, it should be noted that subsequent SPE procedure with hydrophilic/lipophilic phase (Oasis HLB Prime) contributes to the elimination of differences between the two types of samples regarding possible matrix effects due to OC reaching the GC/MS instrument. Also, trimethylsilyl derivatives (TMS) and (tert-butyl)dimethylsilyl derivatives (TBDMS) can prevent analyte/colloidal OC interactions in the injector liner or the column. However, the possibility that in the case when two-step filtration is used, less OC reaches GC/MS system than in the case when one-step filtration cannot be excluded. This effect can enhance the analytical signal due to lower sorptive losses of analytes on OC. However, if the analyte interacts with an active liner surface instead of with OC, a decrease in the signal can happen since there is less OC present to prevent this interaction. Since derivatization with silylation reagents was performed, this effect was likely prevented by not only forming stable volatile derivatives but also by the deactivation of active sites on the surface of the liner when adding an excess of the derivatizing agent.

Materials and methods

All reagents and solvents used were of analytical grade. Stock solutions of the standards ($\approx 0.1 \text{ mg/mL}$) were prepared in MeOH (J. T. Baker (Deventer, Netherlands)). Calibration standards were prepared by appropriate serial dilutions of the stock solutions with MeOH. The standards contained bisphenol A (BPA, $> 97\%$), 2-ethylhexyl 4-methoxycinnamate (CNM, Eusolex 2292®) and 2-hydroxy-4-methoxybenzophenone (HM-BP, $> 97\%$) that were purchased from Merck, Darmstadt, Germany, and 2,2'-methylenediphenol (BIS2, 98%), 4,4'-biphenol (BP4,4, 98%), 4,4'-dihydroxydiphenyl ether (DHDPE, 98%), bisphenol AF (BPAF, $> 99\%$), bisphenol AP (BPAP, $> 99\%$), bisphenol C (BPC, $> 99\%$), bisphenol E (BPE, $> 98\%$), bisphenol F (BPF, $> 98\%$), bisphenol FL (BPFL, $> 98\%$), bisphenol M (BPM, 99%), bisphenol BP (BPBP, $> 98\%$), bisphenol P (BPP, $> 99\%$), bisphenol S (BPS, $> 98\%$), bisphenol Z (BPZ, $> 98\%$), 4-cumylphenol (HPP, $> 99\%$), 2,4-dihydroxybenzophenone (DH-BP, $> 99\%$), estrone (E1, $> 99\%$), 17β -estradiol (E2, 98%), 17α -ethynyl estradiol (EE2, 98%), caffeine (CAF, 99%), 4-hydroxybenzophenone (H-BP, $> 97\%$), 2,2'-dihydroxy-4-methoxybenzophenone (DHM-BP, $> 97\%$), clofibric acid (CLA, 97%), ibuprofen (IB, $> 98\%$), naproxen (NP, 98%), ketoprofen (KP, $> 98\%$), diazepam (DZP, $\geq 98\%$), methylparaben (MePB, 98.5%), ethylparaben (EtPB, 99%), propylparaben (PrPB, 99%), butylparaben (BuPB, 99%), iso-butylparaben (iBuPB, $\geq 96.5\%$), benzylparaben (BePB, 99%), nonylphenol

(NONPH, 92%) and triclosan (TCS, 97%) and diclofenac (DF, 97%) from Sigma-Aldrich, Steinheim, Germany. The three transformation products of diclofenac: DFtp1, DFtp2 and DFtp3, were custom synthesized at the Faculty of Chemistry and Chemical Technology, University of Ljubljana (Ljubljana, Slovenia). Bisphenol B (BPB, > 99%) and mecoprop (MEC, 99%) were purchased from Dr. Ehrenstorfer GmbH, Augsburg, Germany and bisphenol Cl (BPCL2, 98%) and bisphenol PH (BPPH, 98%) from ABCR GmbH Karlsruhe, Germany. Carbamazepine (CBZ, 99%) was purchased from Acros Organics, New Jersey, USA, and iso-propylparaben (iPrPB, 99.2%) from Carbone Scientific, London, UK. Details about the 13 isotopically labelled surrogate standards, reagents and solvents used are given in Česen et al. (2018b).

Artificial wastewater was prepared according to Česen et al. (2015) and contained yeast extract (130 mg/L), casein peptone (130 mg/L), meat extract (130 mg/L), CH₃COONH₄ (317 mg/L), NH₄Cl (40 mg/L), K₂HPO₄ (24 mg/L), KH₂PO₄ (8 mg/L), CaCO₃ (100 mg/L), MgCO₃ (100 mg/L), NaCl (40 mg/L) and FeSO₄·7H₂O (5 mg/L). The yeast and meat extract was obtained from Biolife (Milan, Italy), NaCl from Carlo Erba (Milan, Italy) and all the other nutrients/minerals were from Merck (Darmstadt, Germany).

Calibration curves

Two sets of calibration curves for 48 emerging micropollutants were prepared as described by Česen et al. (2018b). It is important to note that the DOC content of artificial wastewater, although high (280 ± 14 mg/L), is comparable with that of raw wastewater (Česen et al. 2015) and is similar to that found in Slovenian hospital wastewater and WWTP influents (120–360 mg/L) as determined by Česen et al. (2015).

In the first calibration measurement, wastewater samples (300 mL) were spiked with the internal standard working solution (10–25 µL) and filtered through Whatman® glass microfiber filters, grade GF/F (< 0.7 µm, Whatman, USA). For the second calibration, the samples were additionally filtered through a Sartorius™ cellulose nitrate membrane filter (0.45 µm, Sartorius, USA). Extraction by Oasis HLB Prime (Waters, Massachusetts, USA), derivatization and analysis by GC-MS were the same for each set of calibrants. Two types of derivatives were prepared: trimethylsilyl derivatives using N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA, 98.5%, Sigma-Aldrich (Steinheim, Germany)) and (tert-butyl)dimethylsilyl derivatives (TBDMS) using N-(tert-butyl)dimethylsilyl-N-methyltrifluoroacetamide with 1% tert-butyl dimethylchlorosilane (MTBSTFA with 1% TBDMCS, 95 %; Sigma-Aldrich (Steinheim, Germany)). TMS derivatives were prepared for HPP, NONPH, BIS2, BPAF, DFtp3, H-BP, HM-BP, DHDPE, DH-BP, BP4,4,

BPF, BPE, BPA, DHM-BP, BPC, BPB, BPCL2, BPZ, E1, BPS, E2, BPAP, EE2, BPM, BPP, BPBP, BPPH and BPFL, while TBDMS derivatives were prepared for MePB, CLA, EtPB, iPrPB, IB, MEC, PrPB, iBuPB, BuPB, DFtp1, NP, TCS, KP, BePB, CBZ, DF and DFtp2. The derivatization procedure is provided in detail in Česen et al. (2018b). Caffeine, CNM and DZP were analysed underivatized. For each compound, six calibration points were obtained at concentrations relevant for real wastewater samples (1 to 5000 ng/L). All of the calibration data for each compound are presented in the Supplementary Material (Table S-I).

Gas chromatography/mass spectrometry analysis

Once derivatized, the sample extracts were analysed using electron impact gas chromatography-mass spectrometry (EI-GC-MS; Agilent 7890B/5977A, EI mode at 70 eV). The separation was achieved using a DB-5MS (30 m, 0.25 mm, 0.25 µm; Agilent, USA) capillary column with helium as the carrier gas in the constant flow mode (1 mL/min). The sample (1 µL) was injected in splitless mode at 250 °C. Selected ion monitoring (SIM) was used for quantitation as described in Česen et al. (2018b) where the ions selected are provided. Method validation data, recovery studies and limits of quantitation are given in Česen et al. (2018b) and the Supplementary material. Briefly, method accuracy, calculated as [(experimental value – spiked value) / spiked value] (*n* = 3; at 2nd and 5th calibration point) and expressed as %, was in the range from 2.59 to 66% at the 2nd calibration point with exceptionally high value for NP (179%) and in the range from 0.109 to 54.1% at the 5th calibration point. LOQ varied from 0.033 to 17.8 ng/L.

Assessment of the additional filtration effect

Calibration measurements for each micropollutant were performed on samples of artificial wastewater filtered (300 mL) using glass fibre filters (C_{gf}). For each calibrant, the signal response ratio of a compound's target ion and surrogate target ion (value of peak area of the analyte relative to that of the surrogate standard) was calculated from the calibration curve (Supplementary material Table S-II). The results (response ratios) were then inserted into the equation for the second calibration equation (two-step filtration) in order to calculate (simulate) the corresponding hypothetical concentration (C_{gf+mf}). The C_{gf+mf}/C_{gf} ratio was then used to assess the effect of the additional filtration step on the analytical result (concentration); if $C_{gf+mf}/C_{gf} = 1 \pm$ method bias, no effect was observed (0), and the results from both calibrations were considered equal. When C_{gf+mf}/C_{gf} was $> 1 \pm$ method bias, the effect was positive (P), and if $< 1 \pm$ method bias, the effect was assumed to be negative (N) which both can happen if the surrogate standards do not mimic the interactions of the

analytes with the colloidal OC (filter) cake in a multi-residual run. Namely, four different cases exist:

- (1) loss of analyte due to interactions without loss of the surrogate standard resulting in a lowering of the signal response ratio for the same concentration and consequently positive effects on the analytical result for the same signal response ratio when calibration curves are compared;
- (2) loss of analyte and surrogate standard due to interactions resulting in P, N and 0 effects, depending on the magnitude of change in the analyte signal relative to the surrogate standard;
- (3) no loss of analyte or surrogate, resulting in no effect, and
- (4) loss of surrogate standard without the loss of analyte, which leads to an increasing signal response ratio for the same concentration and consequently a negative effect on the analytical result for the same signal response ratio when calibration curves are compared.

Furthermore, other subcases are possible if the organic carbon that reaches the GC system after SPE extraction and derivatization differs significantly between two-step filtration and one-step filtration procedure. For instance, this could result in a lower amount of OC in the sample and the GC liner producing a negative effect on the theoretical concentration for the same response ratio (e.g. increasing the signal response ratio for the same concentration due to less interaction with OC in the liner). The opposite situation, i.e. loss of analyte, can occur due to analyte interaction with the injector liner because of the lower OC content. However, this situation is unlikely to happen if the analytes are derivatized. Such a hypothetical situation could lead to positive effects on the theoretical concentration for the same signal to response ratio (loss of the signal at the same concentration).

A comparison of the abundances of the surrogate standards for both one-step and two-step filtration (Fig. S-I) revealed that significantly lower peak areas were obtained with a two-step filtration. Case 2 is, therefore, the most likely scenario, although case 4 is also possible.

Molecular descriptors

To perform the structure activity relationship (SAR) study of interactions between selected organic micropollutants and colloidal OC, the following seven molecular descriptors were used: molecular weight (MW; g/mol), hydrogen bond donor count (HBD), hydrogen bond acceptor count (HBA), rotatable bond count (RB count), topological polar surface area (TPSA;

\AA^2), distribution coefficient at pH = 7.4 (logD) and molar volume (MV; cm^3) (see Table S-III). The descriptors were taken from the open chemistry database PubChem¹ except for logD and MV, which were obtained from the ChemSpider database². These descriptors reflect the size of the molecule (MW and MV), ability to participate in hydrogen bonding (HBA and HBD), the flexibility of the molecules (RB count), lipophilicity of the molecule at given pH (logD) and the polarity of the molecule expressed as the sum of surface contributions of all electronegative atoms (oxygens, nitrogens and attached hydrogens) in a molecule (TPSA, \AA^2). The choice was made based on various literature findings where all or some of those descriptors were used for quantitative structure activity relationship (QSAR) studies of different phenomena where the possibility to interact with different surfaces or natural organic matter and DOC occurs. For example, Sadmani et al. (2014) investigated MW and logD in a study looking at the rejection of pharmaceutically active compounds and endocrine-disrupting compounds by nanofiltration. Also, Morin et al. (2018) included logD and polar surface area in their study of a pharmaceutical polar organic integrative sampler, and Torresi et al. (2017) included MV, RB count and topological polar surface area (TPSA) in their research involving the partitioning of micropollutants in biofilms. Since the importance of being able to create hydrogen bonds is incorporated in various polyparameter linear solvation energy relationships (pp-LSER) (Dickenson and Drewes 2010), we also included two related descriptors, HBA and HBD.

Statistical analysis

Statistical analysis used for SAR study was performed using the Statgraphics 18.0 software package. The difference between the distributions of effects at different concentration levels and among different compound classes was tested using the Chi-squared test. Categorical and discrete variables of organic micropollutants (HBD, HBA and RB count) are presented as frequencies, percentages and mosaic plots, while continuous variables (TPSA, logD, MW and MV) are presented as Box-and-Whisker plots. A non-parametric Kruskal-Wallis test with Bonferroni procedure for pairwise comparisons was used to assess statistically significant differences between descriptor values for each effect. Values $p < 0.05$ or $p < 0.01$ were considered statistically significant.

In addition, we checked to see if a linear correlation exists between effects and molecular descriptors for all of the analytes that experience either a positive or a negative effect. The values of effects ($C_{\text{gf}+\text{mf}}/C_{\text{gf}} < 1$ or > 1) observed at a defined concentration level were separately grouped and correlated with the seven descriptors (Tables S-IVa and S-IVb). Correlation matrices were calculated using Statistica®, version 13.3 (TIBCO Software Inc., 2017, USA). A Pearson

¹ <https://pubchem.ncbi.nlm.nih.gov/>, last accessed October 30, 2019

² <https://www.chemspider.com/Default.aspx>, properties predicted by ACD/Labs (2019) online, last accessed October 30, 2019

product-moment correlation coefficient (r) was used as a measure of the linear correlation between two variables: selected descriptor vs exact value of $C_{\text{gf+mf}}/C_{\text{gf}}$ ratio.

Results and discussion

Table S-II gives the measured effects of a second filtration (membrane) step on the analytical results. The results show that all three effects: positive (P), negative (N) and no effect (0), were observed.

Effects of analyte concentration

Figure 1 presents the distribution of effects by concentration for all organic micropollutants tested (six calibration points resulting in a total of 288 measurements). The results show that the observed effects vary with concentration, $\chi^2_4 = 21.004, p < 0.01$. Below 1 nmol/L (195 measurements), the most pronounced effects were positive (47.7%); at 1–10 nmol/L (70 measurements), the observed effects were mainly negative (48.6%), or no effect (32.9%), while at > 10 nmol/L (23 measurements), positive effects predominate (43.5%). All the positive effects mentioned are associated with an increase in the theoretical concentrations (for the same analyte peak area relative to its surrogate standard) which is a consequence of a reduced signal for the same concentration. The effect probably happens due to higher analyte loss in comparison with surrogate loss (if any) and the overall decrease in the signal response ratio. Negative effects associated with a decrease in the theoretical concentration (for the same analyte peak area relative to its surrogate standard) are a consequence of an increase in the signal for the same concentration due to both analyte and surrogate loss of such a magnitude that the overall signal response ratio increased (loss of analyte < loss of surrogate standard). Similarly, such negative effects could have occurred due to a lower organic carbon load in the injector liner when a two-step filtration was applied.

This organic carbon, when present in the liner, can contribute to analyte loss by sorption.

Only 20 compounds show one effect type regardless of concentration. Among them, positive effects on concentration result for the same analyte peak area relative to its surrogate were observed for BIS2, BPA, BPAP, BPE, BPZ, CAF, DFtp3, E2 and EE2. This finding means that those substances have a high affinity to interact with the colloidal OC cake. Their logD values vary over a wide range between 0.28 and 4.38. Zhu et al. (2012) reported similar molecular interactions between BPA and DOC in the water phase, the evidence for which was the observed negative effect on the extraction efficiency of SPME. In this study, exclusively negative effects of two-step filtration on hypothetical concentration result for the same analyte peak area relative to its surrogate standard were observed in the case of BePB, BPM, CNM, DFtp1, iPrPB, MEC, PrPB and TCS. They also have a relatively wide range of logD values (− 0.65–5.19) at pH 7.4 and mean that this descriptor cannot explain their behaviour. For CLA, KP and NP, there was no effect on analyte response at the concentration levels investigated, and their logD values ranged from − 0.88 to 0.45. These findings suggest that the distribution coefficient of compounds at pH 7.4 is not sufficient to elucidate the effects of an additional filtration step. These findings agree with those of both Wick et al. (2011) and Rostvall et al. (2018) who found that for certain (ad)sorption processes, logD was not sufficient to describe the mechanism.

For the remaining 28 organic micropollutants, the effect response changes with concentration. In a sub-group of 21 micropollutants, changes from no effect to a positive effect increase with increasing concentration. That means that stronger organic micropollutant/colloidal OC filter cake interactions are present at higher analyte concentrations and are related to increasing sorption of analytes on the colloidal OC filter cake. In contrast, in a second sub-group of seven compounds: H-BP, HM-BP, DH-BP, DHM-BP, BPBP, IB and CBZ (Table S-II), changes are from positive effect or no effect to a negative effect with increasing concentration which is related to lower losses of analyte at higher concentrations than

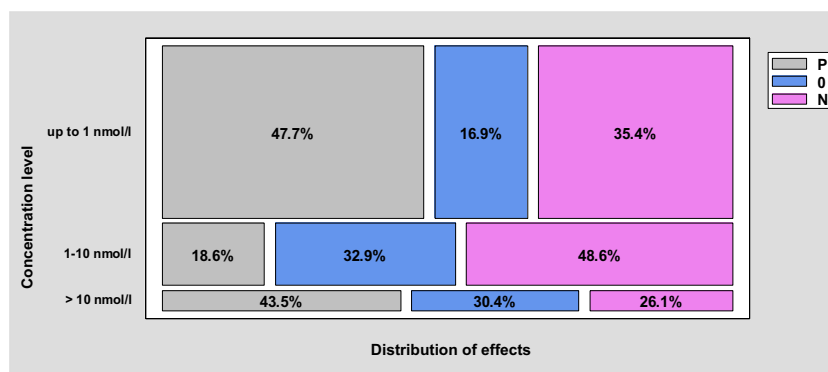


Fig. 1 Distribution of effects at three concentration levels: ≤ 1 , 1–10 and > 10 nmol/L (Chi-squared test : $\chi^2_4 = 21.004, p < 0.01$)

for the surrogate. One can speculate that competition with other micropollutants in the mixture at higher concentrations causes a displacement effect because interactions of those compounds with the colloidal OC are weak or repulsive. All these compounds, including all tested benzophenones, are polyaromatic except IB. Mostly, compounds also contain a keto group (except BPBP with hydroxyl groups, CBZ with an amide group and IB with a carboxylic group). Charge delocalisation by resonance could be the reason for the ease of displacement of those molecules from colloidal OC by the compounds that can form more stable hydrogen bonds. Even though their logD values are mostly ≥ 3 (the exceptions were IB and CBZ with logD values of 0.45 and 0.29, respectively), they were not “captured” by the colloidal OC cake collected in the filter when the concentration simultaneously increases for all 48 micropollutants. However, the signal also could be enhanced by reduced interactions with organic carbon in the injector liner because a significant portion of the organic carbon does not reach the injector when two-step filtration is applied.

Effects of chemical class

Out of the 288 measurements, 168 belong to three classes of compounds: (i) 17 bisphenol type compounds (16 bisphenols with C- or S-link in between phenolic moieties and structurally similar 4,4'-bisphenol, 0.00283–21.902 nmol/L), (ii) seven parabens type compounds (0.05–32.862 nmol/L) and (iii) four benzophenone type compounds (0.04–5.045 nmol/L). The results (Fig. 2) reveal different effect distributions between classes I, II and III. The difference is statistically significant, $\chi^2_4 = 44.616, p < 0.01$, which means that bisphenols (class I) have a significantly higher abundance of positive effects than parabens (class II) and benzophenones (class III). Bisphenols have two or more phenolic structures that can interact with their π -electrons and via hydroxyl

groups creating hydrogen bonds with colloidal organic carbon. Alternatively, parabens, p-hydroxy benzoic acid esters, are monoaromatic compounds with less hydrogen donating groups that together can lead to fewer interactions with colloidal organic carbon. Their logD values are in a lower range (2.09–3.44) than the logD values for bisphenols (1.72–5.94). A significant difference between class II and class III was not confirmed. Class I compounds demonstrated mostly a positive effect (59.8%), while classes II and III reveal mostly a negative (71.4 and 50%, respectively) and no effect on analyte response (33.3 and 50%, respectively).

Further analysis of the distribution of effect types within each class was performed at different concentrations (Fig. 3a, b, c).

At the lowest concentrations (Fig. 3a), class I (98 measurements) revealed 58.2% positive effects and 25.5% negative effects. The difference is statistically significant, $\chi^2_4 = 36.881, p < 0.01$. Class II showed the most pronounced negative effects (94.1% of the 17 measurements), while 15 measurements of class III compounds had almost an equal distribution of effects.

When the concentration was increased to 10 nmol/L (Fig. 3b), only two measurements in class I showed a positive effect (100%), while in total, 18 measurements in class II showed no effects (to 33%) and negative effects (61%). Nine measurements in class III were negatively affected (77.78%).

At concentrations > 10 nmol/L (Fig. 3c), the only two measurements of bisphenol type compounds (class I) experienced a positive effect, while seven measurements of parabens had an almost equal distribution of effects (Fig. 3c). Class III was not measured at this concentration level. Also, a statistical analysis could not be applied at > 1 nmol/L due to the positive effect observed for all compounds in class I (Fig. 3b, c).

Overall, the results show that different classes of compounds have different affinities to OC in addition to concentration dependence. Certain compounds show higher sorption

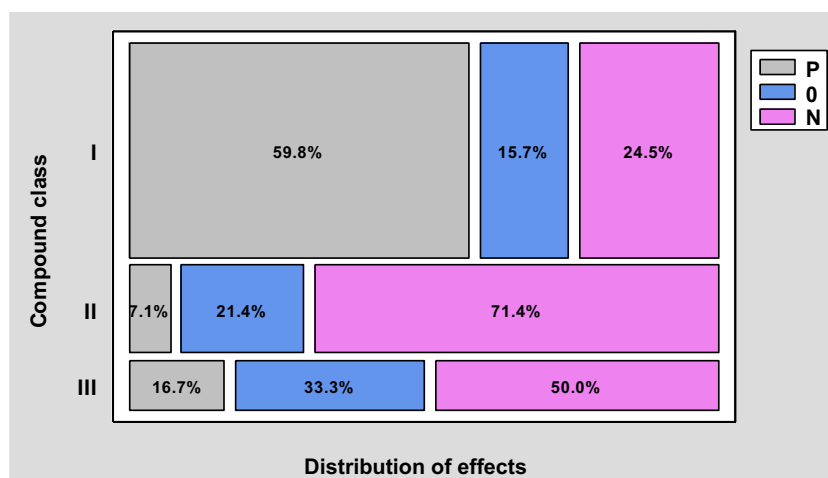


Fig. 2 Effect distribution between compound classes (Chi-squared test : $\chi^2_4 = 44.616, p < 0.01$)

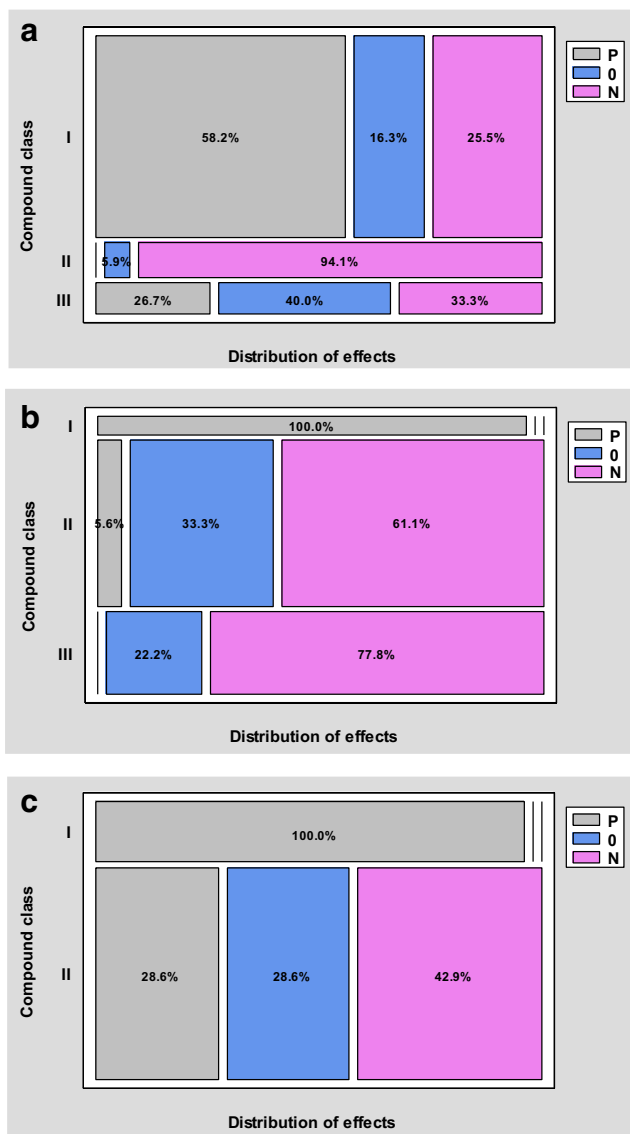


Fig. 3 Changes in effect distribution with compound class at different concentrations: **a** ≤ 1 nmol/L (130 measurements), **b** 1–10 nmol/L (29 measurements) and **c** > 10 nmol/L (9 measurements)

loads at higher concentrations, while the others are most probably displaced. From a comparative study, it was only possible to provide new information for parabens (class II) due to the limited number of samples for other compounds. It was shown that the affinity of parabens towards colloidal OC filter cake increases with increasing concentration (≤ 1 nmol/L to above 10 nmol/L). An abundance of a negative effect characteristic for parabens (Fig. 2, class II) changed significantly (94.1% to 61.1%) when the concentration increased from ≤ 1 to 1–10 nmol/L (Fig. 3a and b). Above 10 nmol/L, the number of negative effects was even lower (42.9%; Fig. 3c). The loss of these compounds during analysis, due to the interaction with the colloidal OC filter cake, can be expected with increasing concentrations above 1 nmol/L. This finding, together with a positive effect observed for bisphenols at

concentrations ≤ 1 nmol/L, is important also for wastewater treatment practitioners since strong interactions with OC can lead to the physical removal of organic pollutants by adsorption during different stages of wastewater treatment (flocculation and settling or biosorption). It must be noted that these findings are related to the high DOC content (280 ± 14 mg/L) used in this study and agree with Karthikraj et al. (2017) and Song et al. (2017) that sorption to sludge is a possible mechanism for parabens removal in WWTP due to their moderate hydrophilicity. Česen et al. (2018a) also confirmed the high removal of bisphenols in WWTPs and the importance of both mechanisms of biodegradation and sorption onto sludge.

Analysis of molecular descriptor distribution with effect type

Analysis of the distribution of three discrete (HBD, HBA and RB) and four continuous (TPSA, logD, MW and molar volume) molecular descriptors with effect type was performed for all the organic micropollutants with all 288 measurements (Tables 1, 2 and 3; Fig. 4). The majority of compounds with an HBD = 1 or 2 (Table 1) had negative and positive effects, while for positive effects were most pronounced for compounds ($> 70\%$) with an HBD = 2. A Kruskal–Wallis test was used to test the null hypothesis that the medians of the descriptor HBD within each effect type are the same. Since $p < 0.01$ ($H=24.4378$), the null hypothesis was rejected, meaning that there is a statistically significant difference. The Bonferroni procedure showed that substances experiencing a positive effect (loss of analyte $>$ loss of surrogate standard) have a significantly higher HBD value than in the case of a negative effect and no effect. This finding can be explained by the higher ability of substances with more hydrogen bond donor possibilities to interact stronger with colloidal OC, which resulted in increased analyte loss.

A similar distribution (Table 2) of negative and no effect types were observed for micropollutants with HBA = 2 and 3, while the highest number of positive effects was when HBA = 2. A Kruskal–Wallis test ($H = 44.1091$, $p < 0.01$) and Bonferroni procedure showed that micropollutants that exhibit a positive effect have a significantly lower value of HBA than both a negative and no effect. This result agrees with our previous findings related to HBD and means that substances that have a lower ability to accept hydrogen bond interact stronger with colloidal OC.

For the RB count descriptor (Table 3), negative and no effect cases are characterized by the frequent appearance of RB count = 2–4, while positive effects dominate when RB count = 2. Statistical analysis (Kruskal–Wallis test: $H = 17.0518$, $p < 0.01$) showed that those micropollutants that experience a positive effect have a significantly lower RB count than both negative and no effect, i.e. $N > P$: $p < 0.01$ and $O > P$: $p < 0.05$. This difference means that less flexible

Table 1 Frequency distribution of HBD by different effect types

Effect	No	HBD			
		0	1	2	
N	109	7.34%	50.46%	42.20%	
P	116	5.17%	24.14%	70.69%	
0	63	6.35%	58.73%	34.92%	

molecules will have a stronger interaction with colloidal OC (loss of analyte > loss of surrogate standard) and tendency to be “captured” while the interaction of those that are more flexible will be weaker.

Figure 4 shows effect type distribution of the continuous descriptors logD, molar volume, molecular weight and TPSA. For TPSA, significant differences exist between the median values of each group of compounds having different effects. For example, groups with negative and no effect have significantly higher TPSA values (46.5 Å) than the group (40.5 Å) that experiences a positive effect (Fig. 4a). That means that molecules containing more polar groups have a lower tendency to be captured by colloidal OC than those which have less polar groups. For the TPSA descriptor, one literature finding exists where a positive correlation is found with sorption on specific biofilm for organic cations (Torresi et al. 2017) while logD had limited reliability. In our study, we show that the positive effect group has a significantly higher MV median value (200 cm³) than the negative effect group (188 cm³) (Fig. 4c) underlying the significance of molecular size for interactions with colloidal OC. The median logD value is significantly lower for the no effect group (2.26) than for the positive (3.63) and negative effect (3.06) groups (Fig. 4b), which means that micropollutants with lower hydrophilicity have the highest tendency to interact with colloidal organic carbon

(median logD 3.63). In contrast, there are two possibilities to explain the difference in the median values of the no-effect group and the negative effect group. The first is that the group with a median logD 3.06 has a higher loss of surrogate in comparison with the analyte. The second explanation is interactions with OC, but in GC/MS liner where analyte loss will be lower since less OC present in the sample reaches the injector. No significant differences were observed between the median values of MW for all three effect groups.

Additional analysis of the distribution of effect types within each class (data not shown) revealed that none of the descriptors was related to a specific effect type within the compound classes. For example, at a concentration level ≤ 1 nmol/L, all the bisphenols (class I, HBD = 2) showed all three measured effects. For HBA, the majority of bisphenols (81–91%) have an HBA = 2 and an RB count = 2 for each effect. Negative effects were observed when RB count = 2 (44%) and RB count = 4 (40%). The median values of continuous descriptors did not show any significant difference regarding effect type. Among the 17 measurements made for parabens (class II), 16 were negatively affected while among the 15 measurements for benzophenones (class III), a difference in the effect distribution concerning specific descriptors was observed only for HBD for those compounds showing N, P and 0 type effects (Table 4).

Table 2 Frequency distribution of HBA by effect type

Effects	No	HBA						
		1	2	3	4	5	8	
N	109	5.50%	33.03%	48.62%	4.59%	5.50%	2.75%	
P	116	10.34%	68.97%	15.52%	3.45%	0.00%	1.72%	
0	63	0.00%	34.92%	58.73%	4.76%	0.00%	1.59%	

Table 3 Frequency distribution of RB count by effect type

Effects	No	RB count								
		0	1	2	3	4	5	8	10	
N	109	6.42%	4.59%	28.44%	17.43%	34.86%	1.83%	0.92%	5.50%	
P	116	14.66%	5.17%	42.24%	18.10%	15.52%	0.00%	4.31%	0.00%	
0	63	0.00%	11.11%	25.40%	31.75%	25.40%	6.35%	0.00%	0.00%	

At concentrations > 1 nmol/L, either a smaller number of effects or no difference in the distribution of effects was observed.

For micropollutants showing only a single effect at all concentration levels (20 compounds, data not shown), there were no significant differences between continuous descriptors. Nine micropollutants were affected positively, three micropollutants remained unaffected and eight

micropollutants were negatively affected. No effect and negative effects were mainly related to those compounds which had an HBD = 1 (100% and 62.5%, respectively), while the group with the majority of compounds having an HBD = 2 (77.78%) experienced a positive effect. The same group containing the fewest number of compounds with an HBA = 2 experienced a positive effect, while mostly no effect or negative effects were observed when HBA = 3 (100% and 62.5%,

Fig. 4 Box and whisker plots of molecular descriptors for each effect type: **a** TPSA, **b** logD, **c** MV, **d** MW

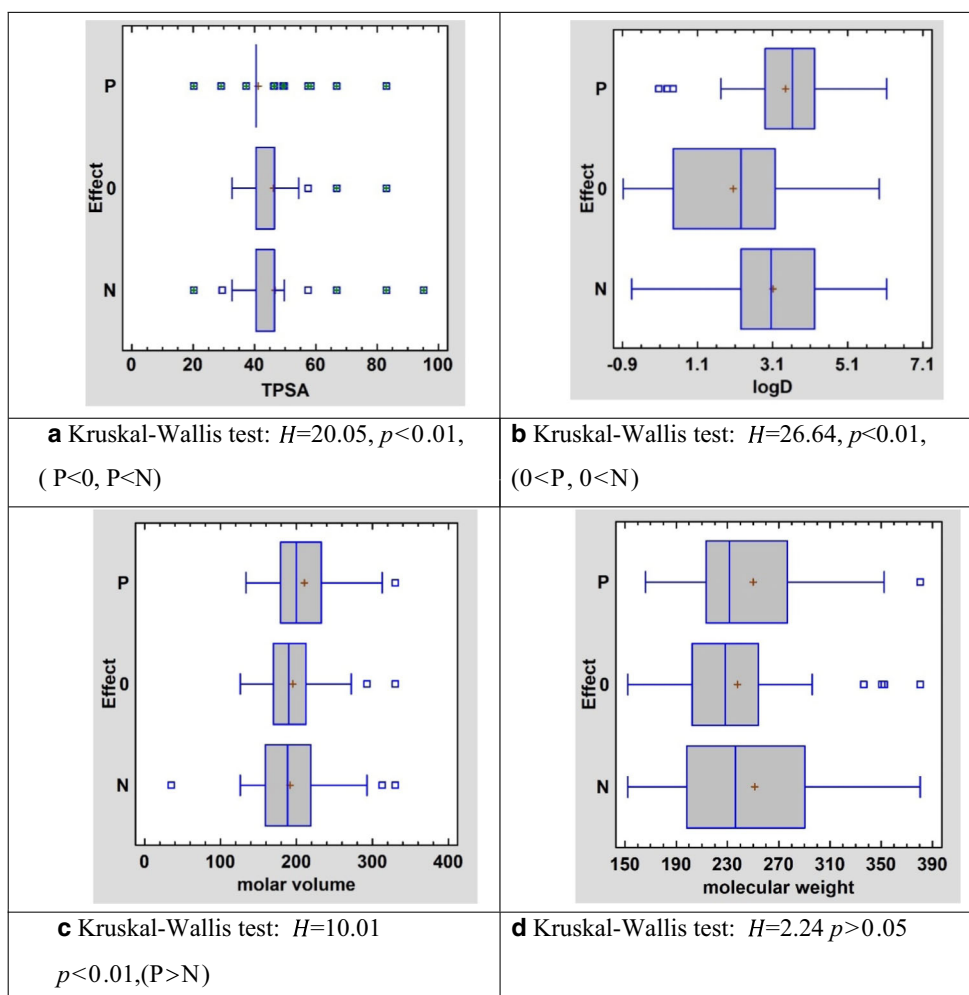


Table 4 Frequency distribution of HBD class III (benzophenones) with effect type

	HBD			Total
	0	1	2	
N	0.0%	20.0%	80.0%	5
P	0.0%	50.0%	50.0%	4
0	0.0%	66.7%	33.3%	6

respectively). Micropollutants showing positive effects had a RB count between 0 and 3 (44.4% RB = 2), while a no effect occurred 66.67% of the time when RB count = 3 and 33.3% when RB count = 4. Micropollutants experiencing a negative effect had a RB count of between 2 and 10.

Correlation analysis: effect response vs molecular descriptor

A linear correlation analysis was performed separately for all tested organic micropollutants that experienced a positive or negative effect. Data were grouped according to concentration (Tables S-IVa and S-IVb). Selected Pearson's correlations between observed effect response and molecular descriptors, for five or more compounds tested at the same concentration level, appear over a wide range (Tables 5 and 6). A significant correlation depended on the number of observations (Bevington 1969). For substances that experienced a negative effect, an acceptable correlation between MV and the actual value of the negative effect was observed at 0.3, 2 and 5 nmol/L as well as between logD and a negative effect at 2 nmol/L. For the four other concentration groups: 0.01, 0.2, 1 and 3 nmol/L, there was no correlation between negative effect type response and molecular descriptor.

In the case of a positive effect, an acceptable correlation between MV, MW and the actual value of the positive effect was observed at 0.01 nmol/L for the group consisting of various types of molecules: BPE, HPP, BIS2, EE2 and E2. In this case, the MW ranged between 200.23 and 296.4 g/mol and MV between 165.7 and 244.5 cm³. The correlation is positive, which means the larger the molecule, the larger the interaction with colloidal OC. At concentrations of 0.02 and 0.1 nmol/L, rotatable bond count had significant correlation. Two groups are found where the RB count descriptor, which is related to molecule flexibility, correlates negatively with interaction with colloidal OC. Increasing the flexibility of the molecule lowers the loss of analyte in comparison with the loss of the surrogate. Both groups mainly consist of bisphenols including other estrogenic compounds, other phenolic structures and one benzophenone type compound. The first group includes BPAP, BPP, BPCL2, BPZ, EE2, BPB, E2, BPE, HPP and the second one H-BP, EE2, E2, BPAP, BPCL2, BPC, BPZ, BPPH, BPS, BPB, BPP, BPE, HPP, BIS2, BPF, E1, BPAF. In both groups, the RB count was in range 0–4.

Table 5 Pearson's correlation coefficient for molecular descriptors vs negative effect response obtained at different concentrations (significant correlation coefficients italicized)

Concentration level nmol/L	MW	HBD	HBA	HBA	RB count	TPSA (Å ²)	logD pH = 7.4	Molar volume (cm ³)	No of compounds	Comment
0.01	0.06	n.a. ^a	-0.03	-0.46	n.a. ^a	-0.23	-0.45	6	6	No significant correlation
0.2	0.01	0.24	0.61	-0.25	0.53	-0.30	-0.54	5	5	No significant correlation
0.3	0.65	0.84	-0.42	-0.85	-0.04	0.19	0.97	5	5	Significant correlation only in case $r > 0.88$, compounds DFtp1, BPPB, BPM, CNM, TCS $C_{(gf+mf)}/C_{(gf)} = 382.335 - 0.504$ molar volume, $r = 0.9706$
1	0.47	0.20	-0.26	-0.33	-0.18	-0.01	0.29	7	7	No significant correlation
2	-0.01	0.52	0.49	-0.68	0.58	-0.93	0.91	5	5	Significant correlation only in case $r > 0.88$, compounds CNM, DHM-BP, DFtp1, MEC, DH-BP $C_{(gf+mf)}/C_{(gf)} = 5.869 - 8.224$ logD, $r = 0.9302$ $C_{(gf+mf)}/C_{(gf)} = 52.076 + 2.58.507$ molar volume, $r = 0.9108$
3	-0.40	0.61	0.29	-0.52	0.32	-0.16	0.60	9	9	No significant correlation
5	0.74	-0.36	-0.14	0.45	-0.56	-0.07	0.90	5	5	Significant correlation only in case $r > 0.88$, compounds MEC, DH-BP, H-BP, DF, TCS $C_{(gf+mf)}/C_{(gf)} = 144.606 + 68.317$ molar volume, $r = 0.9004$

^aThe descriptor value was the same for all compounds

Table 6 Pearson's correlation coefficient for molecular descriptors vs positive effect response obtained at different concentrations (significant correlation coefficients italicized)

Concentration level mmol/L	MW	HBD	HBA	RB count	TPSA (Å ²)	logD pH = 7.4	Molar volume (cm ³)	No of compounds	Comment
0.01	0.98	0.46	0.46	-0.87	0.46	0.28	0.89	5	Significant correlation only in case <i>r</i> > 0.878, compounds BPE, HPP, BIS2, EE2, E2 <i>C</i> _(gf+mf) / <i>C</i> _(gf) = 200.988 + 3.424 MW, <i>r</i> = 0.9752 <i>C</i> _(gf+mf) / <i>C</i> _(gf) = 178.204 + 2.438 molar volume, <i>r</i> = 0.8940
0.02	0.27	0.20	0.20	-0.74	0.20	-0.21	0.22	9	Significant correlation only in case <i>r</i> > 0.666, compounds BPAP, BPP, BPCL2, BPZ, EE2, BPP, E2, BPE, HPP <i>C</i> _(gf+mf) / <i>C</i> _(gf) = 2.730 - 0.108753 RB count, <i>r</i> = 0.7362
0.1	0.37	0.15	-0.18	-0.53	-0.07	0.19	0.42	17 (in total 19 measurements)	Significant correlation only in case <i>r</i> > 0.456, compounds H-BP, EE2 (two measurements), E2 (two measurements), BPAP, BPCL2, BPC, BPZ, BPPH, BPS, BPP, BPE, HPP, HPP, BIS2, BPF, E1, BPAF <i>C</i> _(gf+mf) / <i>C</i> _(gf) = 2.444 - 0.0994 RB count, <i>r</i> = 0.5299
0.2	0.35	-0.25	-0.09	-0.17	-0.24	0.27	0.29	20	No significant correlation
0.3	0.39	0.32	-0.52	0.16	-0.32	0.45	0.51	6	No significant correlation
0.4	0.12	-0.40	-0.15	-0.36	-0.40	0.22	0.18	10	No significant correlation
0.5	-0.11	0.12	-0.45	-0.68	-0.42	0.81	-0.16	6	No significant correlation

Given that correlations exist for some compound groups, but not others suggest that specific structural elements could contribute to their interaction with colloidal OC. However, we could not elucidate the contribution of structural characteristics by analysing only these seven selected descriptors. Rostvall et al. (2018) also showed that different groups of molecular descriptors were relevant for describing adsorption of not only different classes of compounds but also for different sorbent types. For example, the removal of perfluoroalkyl substances correlated with MW, logD, logKow, topological molecular surface area while other micropollutants, including parabens, correlated with the ratio of apolar and polar surface areas. Sadmani et al. (2014) also found that MW and logD are descriptors governing rejection of neutral pharmaceuticals by nanofiltration membrane in the presence of natural colloids and without humic substances. Namely, due to strong hydrophobic interactions with natural colloids accumulated on the membrane surface, rejection of neutral pharmaceuticals significantly decreased. The neutral pharmaceuticals were captured in the loose cake layer, unable to diffuse back due to increased solute partitioning (hydrophobic-hydrophobic interactions).

Conclusions

In summary, a second membrane filter added between a glass fibre filter and the SPE cartridge for highly DOC-loaded water samples (280 ± 14 mg/L) can have either a positive or negative effect on the GC/MS analytical result due to differential losses of analyte and surrogate resulting from their differential interaction with colloidal OC (0.45–0.7 μm). The influence of this added filtration step during sample preparation must be taken into account even when matrix-matched calibration is performed. The reason is that the effect type (positive, negative or no effect) can change with concentration which was shown for 28 out of the 48 compounds tested. For 21 compounds, increasing concentration increased sorption on the colloidal OC filter cake. In contrast, certain polyaromatic structures prone to charge delocalisation by resonance (four benzophenones tested together with BPBP CBZ) and IB showed the opposite effect. Most likely, these compounds could be easily displaced from colloidal OC cake by the other compounds that form stronger bonds. The remaining 20 compounds showed only one effect. Namely, higher analyte losses were observed for BIS2, BPA, BPAP, BPE, BPZ, CAF, DFtp3, E2 and EE2 due to filter membrane cake interactions when compared with BePB, BPM, CNM, DFtp1, iPrPB, MEC, PrPB and TCS. These compounds experienced an increase in signal response when a second membrane filtration step was included. Clofibric acid, ketoprofen and naproxen were unaffected. Broad ranges of logD values are characteristic of each of these groups confirming the literature findings that this descriptor is

not sufficient to explain analyte-organic carbon interactions. Among the three major compound groups (parabens, bisphenols and benzophenones), both bisphenols and parabens showed affinity towards colloidal OC. This finding is also relevant for water treatment practice since (ad)sorption processes during wastewater treatment can result in their physical removal.

Statistical analysis of molecular descriptor distribution for different effect types revealed that organic micropollutants most likely to be captured by colloidal OC filter cake are larger in volume, have significantly higher ability to donate hydrogen atom via a hydrogen bond, are less flexible and have a lower topological polar surface area. This finding has implications for water treatment where such compounds in addition to compounds which have strong hydrophobic interactions are expected to be removable together with colloidal OC (e.g. by (ad)sorption, flocculation, membrane filtration). The median logD value is significantly lower for the no-effect group than for positive and negative effect groups which can be the consequence of their interaction either with colloidal OC in filter cake or with OC that reached the injector liner, respectively. Pearson's correlations between all observed positive and negative effect response and molecular descriptors confirmed that molar volume, logD, molecular weight and rotatable bond count correlate at specific concentrations for certain groups of analytes. It was also not possible to elucidate additional structural elements within these groups from the descriptors used in this study, and future studies should include a more extensive data set of both chemical classes and descriptors. Finally, the chemical and physical nature of organic carbon (thickness of the colloidal OC cake, the content of aromatics) will also determine types of interactions with different compounds. For this reason, detailed colloidal organic carbon characterisations are needed.

Authors' contributions The study was conceptualized, designed and coordinated by IIT, EH. IIT was the principal investigator and prepared the draft article. ZL performed the statistical analysis and TDS performed the SAR analysis. Chemical analysis was performed by MČ. MB was responsible for data calculation and curation. The manuscript was written by IIT, ZL, TDS, DH and EH, while all contributing authors made paper revisions under the mentorship of IIT.

Funding This work was supported by the Bilateral Cooperation Agreement between the Republic of Serbia and Slovenia (2016-2017) and a grant from the Ministry of Education, Science and Technological Development (Grant No. 451-03-68/2020-14/200125). Authors received the ARRS financial support (Programme group P1-0143 and Projects L1-7544, N1-0047, J2-8162, L7-1848). The authors also received the financial support from EMPIR WFD-EDC project.

Data availability All data generated or analysed during this study are included in this published article and its supplementary information files

Compliance with ethical standards

Competing interest Not applicable.

Ethical approval Not applicable.

Consent to participate Not applicable

Consent to publish Not applicable

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