Rapid and cost-effective multiresidue analysis of pharmaceuticals, personal care products, and antifouling booster biocides in marine sediments using matrix solid phase dispersion

Q5

The corrections made in this section will be reviewed and approved by a journal production editor.

Q4Q1 Karina Lotz Soares[a,b,c,1], Adrià Sunyer-Caldú[d,1], Sergiane Caldas ~~Barbosaa~~Barbosa[c,1], Ednei Gilberto ~~Primela~~Primel[c,1], Gilberto ~~Fillmanna~~Fillmann[b,c,1], M. Silvia ~~Díaz Cruz~~Diaz Cruz, PhD[d,1,*] sdcqam@cid.csic.es

[a]Instituto de Oceanografia, Universidade Federal Do Rio Grande (IO -FURG), Av. Itália S/n, Campus Carreiros, C.P. 474, 96201-900, Rio Grande, RS, Brazil

[b]PPG Em Oceanologia, Universidade Federal Do Rio Grande (PPGO-FURG), Av. Itália S/n, Campus Carreiros, 96203-900, Rio Grande, RS, Brazil

[c]PPG Em Química Tecnológica e Ambiental, Universidade Federal Do Rio Grande (PPGQTA-FURG), Av. Itália S/n, Campus Carreiros, 96203-900, Rio Grande, RS, Brazil

[d]Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA), Severo Ochoa Excellence Center. Consejo Superior de Investigaciones Cientificas (CSIC), Jordi Girona 18 - 26, 08034, Barcelona, Spain

*Corresponding author.

[1]Present Address of Karina Lotz Soares: Postdoctoral fellow of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (PNPD-CAPES) at Programa de Pós-Graduação em Oceanologia (PPGO). Laboratório de Microcontaminantes Orgânicos e Ecotoxicologia Aquática (CONECO), IO, FURG, Rio Grande, RS, 96203–900, Brazil.

Handling Editor: Andreas Sjodin

Abstract

Currently, there are many contaminants of concern that need to be accurately determined to help assess their potential environmental hazard. Despite their increasing interest, yet few environmental occurrence data exist, likely because they are present at low levels and in very complex matrices. Therefore, multiresidue analytical methods for their determination need to be highly sensitive, selective, and robust. Particularly, due to the trace levels of these chemicals in the environment, an extensive extraction procedure is required before determination. This work details the development of a fast and cheap vortex-assisted matrix solid-phase dispersion-high performance liquid chromatography tandem-mass spectrometry (VA-MSPD-HPLC-MS/MS) method for multiresidue determination of 59 contaminants of emerging concern (CECs) including pharmaceuticals, personal care products, and booster biocides, in sediment. The vali~~o~~dated method provided high sensitivity (0.42–36.8 ngg^{-1} dw quantification limits), wide and good linearity (r^2 > 0.999), satisfactory accuracy (60–140%), and precision below 20% for most target analytes. In comparison with previous methods, relying on traditional techniques, the proposed method demonstrated to be more environmentally friendly, cheaper, simpler, and faster. The method was applied to monitor the occurrence of these compounds in sediments collected in Brazil, using only 2 g dw sediment samples, free-solid support, and 5 mL methanol as extraction solvent. The UV filter avobenzone, the UV stabilizer and antifreeze methylbenzotriazole, the preservative methylparaben, the fluoroquinolone antibiotic ciprofloxacin, and the biocides irgarol and 4,5-dichloro-2-octyl-4-isothiazolin-3-one were determined at concentrations in the range 1.44–69.7 ngg^{-1} dw.

Keywords: Matrix solid phase dispersion; Pharmaceuticals; Sunscreens; Booster biocides; Parabens; Sediment

1 Introduction

Pharmaceuticals and personal care products (PPCPs), and antifouling booster biocides comprise a large group of contaminants worldwide studied which are currently considered environmental contaminants of emerging concern (CECs). These substances have been increasingly investigated in water (Köck-Schulmeyer et al., 2019), sediment (Batista-Andrade et al., 2016)(Batista-Andrade et al., 2018), sludge (Cerqueira et al., 2018), and biota (Vieira et al., 2018b). Due to their physicochemical properties, some compounds have more affinity for the organic phase, having a greater tendency to be adsorbed onto sediments and the suspended particulate matter of the water column (Martins et al., 2018). Besides, they tend to bioaccumulate in aquatic organisms and thus have been investigated for potential ecotoxicity (Molins-Delgado et al., 2018a).

In recent years, PPCPs have been regarded as an important environmental issue since these compounds are widely used in human and veterinary medicine and represent an important group of high volume production products ~~CECs~~ (Čelić et al., 2018). Within this group, sunscreen agents, also known as UV filters (UVFs) deserve major attention for their increasing use as a protection against the harmful effects of the UV solar radiation (Molins-Delgado et al., 2018b). They are present in numerous hygiene and beauty consumer goods (cosmetics, sunscreens, and hair-style products, among others), and have many additional industrial applications (plastic, rubber, textile materials, etc) to protect the polymeric materials.

Concerning antifouling booster biocides, their use is directly related to marine biofouling, defined as a biological phenomenon characterized by the colonization and/or growth of organisms over surfaces submerged in seawater. To minimize the problems caused by biofouling, paints containing chemicals with biocidal properties were actively developed. More recently, booster biocides, such as diuron, irgarol, dichlofluanid, 4,5-dichloro-2-octyl-4-isothiazolin-3-one (DCOIT) and [(1,3-benzothiazol-2-yl)sulfanyl]methyl thiocyanate (TCMTB) deserve particular attention due to its potential to contaminate coastal areas (Thomas and Brooks, 2010), already under the pressure of tourism and its associated PPCPs' release.

To determine traces of organic contaminants in complex solid environmental matrices, the development of analytical methods is undoubtedly one of the current greatest needs. In this regard, analytical sample preparation procedures employed so far for organic contaminants determination in environmental solid samples apply techniques using a high amount of sample and solvents' volume, generating a lot of waste and requiring long and tedious extraction methods. Therefore, the application of multi-residue analytical methods, simple, cost-effective, fast, and minimizing the amount of reagents, sample, and solvents are preferred. The major challenge for the simultaneous determination of a wide range of organic contaminants in the environment results from the broad spectrum of physicochemical properties combined with the high complexity of the matrix sample. Furthermore, usually, they are present at low concentrations, thus requiring a pre-concentration step (Caldas et al., 2016).

In this regard, an interesting approach is the application of the matrix solid phase dispersion (MSPD) for extraction and purification in CECs analysis. This technique consists of mixing and blending solid or semi-solid samples with abrasive solid support and subsequent elution of the target compounds with a small volume of a suitable organic solvent (Barker et al., 1989). However, to make the technique more robust, less susceptible to errors, and environmentally friendly, last years, the original MSPD technique underwent some modifications. One of these modifications improving the selectivity of the original technique is vortex-assisted matrix solid phase dispersion (VA-MSPD). This approach consists of vortexing the mixture (sample plus solid support) with a few mL of an organic solvent. This approach reduces some drawbacks of the original technique such as the package of the mixture, making the technique simpler, cheaper, and more robust (Caldas et al., 2013). Besides, this miniaturization version of the technique can still be optimized to further reduce reagent and solvent consumption and waste generation (Soares et al., 2017).

In this context, the present study aimed to develop and validate a simple, rapid, and cost-effective method based on VA-MSPD and HPLC-MS/MS for the simultaneous multiclass analysis of 59 organic compounds of sound environmental relevance (www.epa.gov) and quite different physicochemical properties in sediment samples. The selected organic compounds encompass 3 categories: pharmaceuticals and metabolites, personal care products and degradation products, and antifouling booster biocides. A particular aim of this work was to highlight the advantages of the combination of VA-MSPD-HPLC-MS/MS as a compound-selective tool for the trace determination of CECs environmental contaminants. Finally, the validated method was applied to the determination of the target CECs in sediment samples from one of the largest South American Ports in Brazil.

2 Experimental

2.1 Standards and reagents

Analytical standards (Table 1S of the Supporting Information) of high purity (96–99.9%) were purchased from Sigma-Aldrich (Germany) and TCI (Belgium). Isotopically labeled analytical standards were obtained from CDN isotopes (Canada) and Sigma Aldrich (Germany). Florisil, alumina, silica, formic acid (98%), and ammonium acetate (≥96%) were supplied by Merck (Germany), C18 cartridges (500 mg) by Isolute (Spain), methanol (MeOH), ethanol (EtOH), and acetonitrile (ACN) ultra-gradient HPLC grade, ethyl acetate (EtAc) and dichloromethane (DCM) (~~both for~~ organic

residue analysis grade) by J.T. Backer (The Netherlands) and nitrogen (99,999%) and argon (99.995%) by Air Liquid (Spain).

Stock solutions of individual standards (1000 mg L^{-1}) and an intermediate stock solution containing all analytes (1 mg L^{-1}) were prepared in MeOH. Daily, standard work solutions were prepared at appropriate concentrations. All solutions were stored in the dark at −20 °C.

2.2 HPLC-(QqLIT)-MS/MS analysis

For the analytical determination, a 4000 Q TRAP™ hybrid triple quadrupole-linear ion-trap mass spectrometer (Applied Biosystems-Sciex; Foster City, Ca, USA), equipped with an HPLC system with an Alias autosampler was used. Target analytes were monitored in electrospray ionization under positive (ESI+) and negative (ESI-) modes.

The initial conditions selected to develop the method were based on previous studies (Gago-Ferrero et al., 2011a, 2013a; Serra-Roig et al., 2016). Chromatographic separation was performed using a Purosher® STAR® HR R-18 (50 mm × 2.0 mm, 5 µm) (Merck) column. The elution was performed at a flow rate of 0.3 mL min^{-1}. For the analysis in ESI+, a mixture of HPLC-grade water and MeOH, both with 0.1% formic acid, was used. In the ESI- mode, the mobile phase consisted of the same binary solvent combination containing 5 mM of ammonium acetate). The injection volume was 20 µL in both modes.

For improved sensitivity and selectivity, the tandem-MS detection was performed under selected reaction monitoring (SRM) mode, targeting the two major characteristic fragments of the precursor molecular ion for each analyte. The most abundant and the second most abundant transitions were used for quantification and confirmation, respectively, in line with the EU recommendation (Commission Decision, 2002/657/EC).

General operation conditions for the analysis were as follows: ESI+: capillary voltage, 5000 V; source T^a, 700 °C; curtain gas, 30 psi; ion source gas 1, 50 psi; ion source gas 2, 60 psi, and entrance potential, 10 V. ESI-: capillary voltage, −4000 V; source T^a, 500 °C; curtain gas, 20 psi; ion source gas 1, 50 psi; ion source gas 2, 60 psi, an entrance potential, −10 V (Gago-Ferrero et al., 2013b). All data were processed using the Analyst software V 1.4.2 (Applied Biosystems).

Once the chromatographic conditions were established, a chromatogram under total ion mode in both positive and negative electrospray ionization modes were recorded for a mixture standards solution in MeOH at 700 ng mL^{-1}. Fig. 1S illustrates the chromatogram in the positive mode and Fig. 2S in the negative mode, respectively. According to Figs. 1S and 2S, it is possible to observe that many compounds obtained close retention times or else, they co-eluted. The lack of resolution in a chromatogram can be a problem in liquid chromatography when coupled with traditional detectors such as UV since they are specific enough when spectral differences are small. However, the use of LC-MS/MS can circumvent these problems of chromatographic separation, since MS/MS and SRM mode used are highly selective.

2.3 Sample collection and TOC determination

Eight sediment samples were collected in Santos-São Vicente Estuarine System (SSES) (São Paulo) and a shipyard at Patos Lagoon Estuary (Rio Grande do Sul). Samples were collected at different depths, using a stainless steel "*Ekman*" grab, in areas under influence of maritime anthropogenic activities.

The sediments were lyophilized, homogenized and stored at −20 °C for subsequent analysis. The granulometry was determined according to Gray and Elliott (2014), whereas total organic carbon (%TOC) was measured, after de-carbonation of the sediment samples, using a TOC-L SSM 5000 A (Shimadzu) instrument (Kristensen and Andersen, 1987).

2.4 VA-MPSD extraction

To develop the method, the initial conditions were selected based on a previous study where VA-MSPD was applied for diuron, irgarol, TCMTB, and DCOIT extraction from sediments (Batista-Andrade et al., 2016). Considering that it was a multi-residue method, VA-MSPD was optimized to obtain recovery rates of 100 ± 40%, with relative standard deviation (RSD) below 20%.

2.4.1 Extraction solvent selection

The appropriate selection of the extraction solvent is a key factor in the development of sample preparation methods. In addition to its effectiveness, human and environmental toxicity must be considered as well (Anastassiades et al., 2003). In this work due to the different polarity of the selected compounds and based on a literature review, MeOH, EtOH, EtAC, and ACN were evaluated as extraction solvents.

2.4.2 Solid support selection

Materials used as solid support can have a simple abrasive role to ensure complete matrix disruption or can be selective materials enhancing the MSPD selectivity, allowing purification and extraction in the same step. A solid support is considered one of the most studied variables in the MSPD technique and its choice depends on the matrix, analytes of interest, and extraction solvent.

The success of C18 material as solid support is due to its removal capability for non-polar compounds, such as fatty substances and lipids, being recommended for matrices with fat content >2%. The potential interaction among non-polar analytes and the solid support occurs through van der Waals forces and the use of C18 or its combination with other materials, such as Primary Secondary Amine (PSA), to turn the sample preparation of matrices with high contents of fat more effectively.

Florisil is one of those materials used in MSPD to retain non-polar lipids, dyes, amines, hydroxyls, and carbonyls through polar interaction mechanisms, such as hydrogen bonds (Kurz et al., 2019).

In the present study, and according to a literature review, the solid supports C18, florisil, alumina, silica, and polymeric material (Strata-X) were tested.

In the optimized procedure, an aliquot of 2 g of freeze-dried sediment was spiked with 100 µL of a solution containing the isotopically labeled surrogate standard benzophenone-C13, left 30 min. to equilibrate and then manually ground in a mortar and pestle for 5 min. This mixture was transferred to a polypropylene tube, and 5 mL of the extraction solvent was added, vortexed for 1 min and centrifuged at 4000 rpm for 10 min. Before injection, the IS mixture (50 ng mL^{-1}) was added. Analyses were performed in triplicate, and each replica was measured 3 times.

2.5 Analytical validation

The method was validated following SANTE (2017) and INMETRO (2018). Method limits of detection and quantification (LODm and LOQm), calibration curves and linearity, accuracy, precision, and matrix effect (ME %) were evaluated. LODm and LOQm, were determined as the lowest compound concentration that yielded a signal-to-noise (S/N) ratio of 3 and 10, respectively. Analytical calibration curves were constructed and adjusted according to the individual response range of each compound. Accuracy was assessed by the recovery efficiency of each standard spiked in the blank sediment, determined in triplicate at three concentration levels (1xLOQ, 5xLOQ, and 10xLOQ), and measured 3 times (n = 9). Precision was calculated as the RSD (in %) for each concentration level, analyzed intra-day and inter-day. Matrix effect was evaluated by comparing the slopes of the analytical calibration curves prepared in MeOH and in the sediment extracts (matrix-matched calibration standards). All analytical calibration curves, as well as all validation tests, were carried out in the presence of the isotopically labeled IS mixture at 50 ng mL^{-1} (Table 1S).

3 Results and discussion

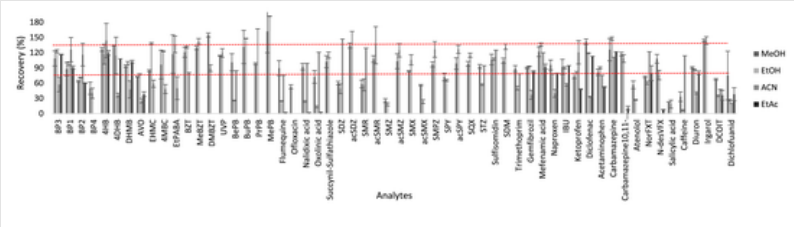
3.1 VA-MSPD extraction optimization

3.1.1 Selection of the extraction solvent

Five mL of MeOH, EtOH, EtAc, and ACN were individually tested in combination with 0.25 g of C18 material as solid support. The recovery efficiency for each solvent tested is shown in Fig. 1. It shows that when ACN and EtAc were evaluated, even though both have similar polarities, some compounds were scarcely recovered. When ACN was used as extraction solvent, average recoveries were below 70% for about 60% of the analytes and only 17% were between 60 and 140%. Besides, RSD were higher than 20% for most compounds. EtAc is often used in sample preparation procedures, since this solvent is considered non-mutagenic, non-bioaccumulative and more environmental friendly, however, when we used it, many matrix components were co-extracted. In addition, it was unsuitable for the extraction of more polar compounds, especially those with Log Kow values below 3. For moderately polar analytes, such as BP3, BP1, 4HB, 4DHB, DHMB, gemfibrozil, mefenamic acid, naproxen, diclofenac, atenolol and diuron, recovery rates ranged between 60 and 140%. It is known that polar compounds do not readily partition in this solvent, and significant amounts of Na_2SO_4 and/or polar co-solvents, such as MeOH and EtOH, have been used to improve the recovery rates (Anastassiades et al., 2003). However, to keep the method as simple and environmentally friendly as possible solvent mixtures were not tested in the present study.

alt-text: Fig. 1

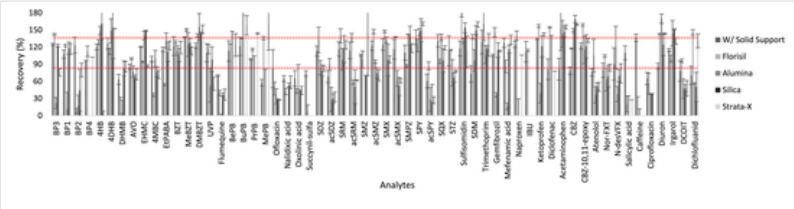
Fig. 1



Recovery rates of the target compounds after VA-MSPD extraction with four extraction solvents. Error bars represent RSD (%). Experimental conditions: 2 g dw sediment sample; 0.25 g C18 material as the solid support, and 5 mL of extraction solvent. One min. of vortex agitation and 10 min centrifugation at 4000 rpm, n = 9.

alt-text: Fig. 2

Fig. 2



Recovery rates of the target compounds after VA-MSPD extraction with four solid supports, and without solid support. Error bars represent RSD (%). Experimental conditions: 2 g dw sediment sample; 0.25 g C18 material as the solid support, and 5 mL of MeOH as extraction solvent. One min. vortex agitation and 10 min centrifugation at 4~~s~~000 rpm, n = 9.

When MeOH was employed in our optimization, average recoveries between 60 and 140% were obtained for ~~some~~ 64% of the compounds, providing the best extraction efficiency. This is likely because of the majority of the analytes in this study have medium to high polarity, from the most polar one (SPY: Log Kow0.05) to the most apolar one (EHMC: Log Kow 4.95). The effectiveness of MeOH as an extraction solvent in sample preparation techniques is linked to its ability to interact with polar compounds because it is a polar protic solvent. MeOH has high dielectric constant (ε), which is a good indicator of the higher probability of interacting with analytes of polar nature, favoring the extraction through the capacity of hydrogen bonding. In general, the dielectric constant is considered an important parameter to predict the behavior and to measure the polarity of a solvent (Cerqueira et al., 2018).

In previous studies, reported recovery rates for UVFs from sediments ranged from 80 to 125% when using pressurized liquid extraction (PLE) and MeOH as the extraction solvent. However, a larger volume of MeOH was used (25 mL) because the PLE technique requires a relatively large volume of extraction solvents as typically employs various extraction cycles for extended isolation (Gago-Ferrero et al., 2011).

When EtOH was evaluated, obtained recoveries were between 60 and 140% for 40% of the compounds. UVFs showed good recoveries, with RSD below 19%. Similarly to MeOH, EtOH is a protic polar solvent (with ε of 24.5), and likely because of this slightly less polar character, it provided lower recovery rates than MeOH.

Concerning antifouling booster biocides, MeOH, EtOH, ACN, DCM, and/or acetone have been used for the isolation of organic chemicals from sediment samples. However, the number of compounds as well as the chemical classes studied in these works is much lower than those included in our developed method. Moreover, the solvent volumes used were also larger than the MeOH volume used in the present study (5 mL).

In light of these results, MeOH was finally selected as the extraction solvent in the present study due to the best performance, reaching recovery rates between 79 and 120% for about 60% of the target analytes. To further improve the number of compounds with recoveries within this range, different solid supports were also assessed using MeOH as ~~an~~the extraction solvent.

3.1.2 Selection of solid support

Fig. 2 shows the recovery rates of each compound when different solid supports were evaluated. Besides, a sample without added solid support was also tested.

The obtained average recovery rates were between 60 and 140% for 22% of the compounds when Florisil was used. Some compounds, such as BP2, DHMB, and succinyl-sul~~ph~~fathiazole, showed average recoveries below 70%, and 61% of compounds showed values above 140%. Recovery rates between 75 and 114% for 17% of analytes were obtained when alumina was used as solid support. As observed for F~~f~~lorisil, most of the compounds showed recoveries out of the recommended range. Thus, considering that these compounds had not been extracted, the explanation could

be that i) these materials may be selectively interacting with the sample or, ii) the mechanical force applied during the technique was not able to break the original structure of the sample.

When silica was employed, the average recoveries were between 60 and 140% for 25% of analytes. Recovery rates above 140% were obtained for most polar compounds, such as some UVFs. The use of Strata-X yielded similar average recoveries than silica for some compounds (35%). Strata-X is a polymeric material with the presence of the pyrrolidine group and styrene in its structure. The presence of these two groups may favor the interaction with other compounds by hydrogen bonding or the possibility of interaction by π-π and dipole-dipole bonds, thus reducing extraction efficiency. Sulfonamides and booster biocides were recovered well beyond the acceptable range.

Overall, in the present study, we obtained recoveries between 70 and 120% for 71% of compounds when only the sediment sample (2 g dw) was macerated and MeOH (5 mL) was used as extraction solvent. This solid support-free VA-MSPD approach, assuming that the matrix itself, when macerated, can be considered abrasive, such as dried sediment, does not need the addition of solid support. This alternative extraction has scarcely been investigated so far, despite it appears an attractive alternative in sample preparation since it reduces the consumption of reagents and generates lower wastes.

Thus, according to the results, the solid support-free VA-MSPD was ~~chosen~~selected as the extraction technique since, besides providing the best recoveries among the tested configurations, it consumes ~~a~~ lower volume of reagents, generates fewer residues, consumes less time, and has the lower operative cost.

Despite the good performance obtained in this case, we must consider that the effectiveness of solid support-free extraction is directly related to the particular characteristics of the sediments analyzed. The sediment sample used in this study likely presents the content of inorganic substances such as carbon, magnesium, calcium, iron, aluminum, and silicon, which provide it with abrasive characteristics (Cerqueira et al., 2018). Also, there were practically no organic compounds that recovered below 60% when no solid support was used.

As the recommended recovery range was reached for 71% of compounds, and considering that it is a multiresidue method based on an extraction technique for analytes with very different physicochemical properties, other parameters that might influence the extraction and purification of the sediments were not further optimized. However, if the main goal of the study would be a specific chemical group of compounds with similar characteristics, we recommend for the improvement in the acceptable recovery range the optimization of other variables, such as the solvent volume, the amount of sample~~,~~ and solid support, and the blending time of the mixture solid sample plus solid support.

3.2 Method performance

The performance parameters of the validated method are shown in Table 1. Overall, LOQm ranged from 0.42 to 36.8 ng g^{-1} dw following those previously reported in studies analyzing PPCPs in soil and sediment (Batista-Andrade et al., 2016; Caldas et al., 2018). Regarding antifouling booster biocides, LOQm were comparable to the sediment quality guideline thresholds limit (Maximum Permissible Concentration – MPC) established by restrictive legislation on sediment quality criteria, Dutch authorities for instance, for diuron (9 ng g^{-1}) and irgarol (1.4 ng g^{-1}) (Crommentuijn et al., 2000). Depending on where the booster biocide is found, it can be classified as class IV “bad” for contamination.

alt-text: Table 1

Table 1

The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Method limits of detection (LODm) and quantification (LOQm), recovery rates (R%) and Relative Standard Deviations (±RSD)D%), for intra- and inter-day precision (%~~,~~ R) a the three concentration levels evaluated (1xLOQ, 5xLOQ, and 10xLOQ).

Analyte	LODm (ng g^{-1})	LOQm (ng g^{-1})	Precision (intra-day) R (%) ± RSD (%)			Precision (inter-day) R (%) ± RSD (%)		
			LOQ	5 LOQ	10 LOQ	LOQ	5 LOQ	10 LOQ
BP3	0.67	2.23	72.5 ± 23.4	75.8 ± 9.7	125.9 ± 0.7	111.2 ± 3.4	61.4 ± 0.6	102.2 ± 11.0
BP1	1.31	4.35	128.9 ± 20.7	129.8 ± 13.3	102.8 ± 7.5	128.5 ± 1.2	60.3 ± 10.1	115.0 ± 4.8
BP2	1.49	4.95	65.4 ± 1.2	74.0 ± 1.6	121.4 ± 4.9	79.0 ± 8.8	115.5 ± 0.3	34.0 ± 1.1
BP4	2.50	8.31	69.4 ± 21.5	69.3 ± 25.7	123.5 ± 33.1	56.2 ± 38.6	70.7 ± 29.4	121.5 ± 24.6
4HB	2.44	8.13	95.2 ± 20.0	130.8 ± 18.1	81.8 ± 5.0	86.1 ± 4.8	111.2 ± 1.5	124.6 ± 6.2
4DHB	2.02	6.71	63.4 ± 22.3	106.6 ± 26.1	68.8 ± 11.1	77.9 ± 6.7	101.3 ± 5.9	121.9 ± 6.3

DHMB	1.03	3.44	71.7 ± 21.1	64.8 ± 5.6	70.7 ± 8.6	112.9 ± 4.1	115.8 ± 9.8	149.9 ± 5.1
AVO	0.96	3.19	69.7 ± 10.0	94.0 ± 15.9	121.8 ± 12.2	91.5 ± 5.4	70.6 ± 12.2	123.5 ± 4.2
4MBC	0.49	1.65	120.7 ± 11.6	79.7 ± 14.8	66.2 ± 0.9	71.5 ± 1.1	100.2 ± 2.4	136.5 ± 3.8
EHMC	11.06	36.83	123.2 ± 4.5	87.2 ± 21.3	100.7 ± 1.1	62.2 ± 1.8	100.3 ± 1.2	80.7 ± 6.4
EtPABA	0.94	3.14	74.7 ± 19.4	61.3 ± 8.7	107.5 ± 10.3	53.6 ± 4.5	111.6 ± 12.0	69.6 ± 5.4
BZT	0.62	2.07	69.4 ± 17.6	124.9 ± 26.5	103.8 ± 26.0	116.6 ± 8.8	114.1 ± 1.5	113.6 ± 16.9
MeBZT	0.96	3.20	72.6 ± 12.8	78.6 ± 4.7	116.0 ± 23.7	88.4 ± 8.0	74.8 ± 7.5	69.9 ± 13.0
DMBZT	0.88	2.94	81.2 ± 3.4	65.5 ± 1.4	84.1 ± 49.8	95.9 ± 14.7	113.4 ± 4.0	81.3 ± 15.5
UVP	0.80	2.67	86.9 ± 16.5	75.8 ± 4.6	112.5 ± 8.9	55.0 ± 11.8	69.2 ± 21.5	118.4 ± 17.4
BePB	1.35	4.50	73.7 ± 8.1	111.8 ± 8.4	74.5 ± 7.0	63.7 ± 9.9	84.5 ± 2.2	110.3 ± 5.6
BuPB	0.94	3.13	73.0 ± 4.7	68.6 ± 7.5	70.2 ± 6.1	79.0 ± 9.5	95.8 ± 8.6	82.0 ± 0.8
PrPB	1.33	4.43	89.1 ± 5.0	94.5 ± 22.4	86.5 ± 11.1	86.0 ± 9.4	111.2 ± 8.3	53.1 ± 0.1
MePB	1.40	4.66	85.0 ± 6.8	78.4 ± 11.5	65.8 ± 17.2	69.9 ± 6.7	103.5 ± 0.3	89.1 ± 2.0
Flumequine	1.99	6.64	71.3 ± 7.7	75.6 ± 10.5	60.8 ± 9.7	77.5 ± 18.3	84.0 ± 8.0	124.8 ± 2.8
Ofloxacin	3.09	10.3	80.3 ± 4.2	130.5 ± 26.6	124.9 ± 12.4	99.6 ± 1.8	78.4 ± 15.2	78.7 ± 2 .2
Ciprofloxacin	0.62	2.07	136.5 ± 4.6	82.2 ± 10.0	72.2 ± 9.0	89.6 ± 19.0	122.2 ± 3.9	80.8 ± 2.0
Nalidixic acid	0.82	2.73	121.6 ± 6.0	123.3 ± 9.6	75.6 ± 11.5	122.8 ± 31.4	87.8 ± 7.3	95.8 ± 6.6
Oxolinic acid	0.54	1.79	80.7 ± 18.0	62.2 ± 24.8	75.0 ± 7.7	95.1 ± 21.0	121.4 ± 4.8	81.8 ± 1.8
Succinyl-sul~~ph~~fathiazole	0.32	1.07	84.8 ± 10.0	79.9 ± 4.2	122.8 ± 4.7	77.4 ± 1.5	69.4 ± 2.2	120.3 ± 4.6
SDZ	0.60	1.99	78.8 ± 18.9	102.9 ± 29.2	121.7 ± 20.5	129.9 ± 10.8	63.2 ± 12.5	104.2 ± 7.9
acSDZ	1.82	6.07	66.2 ± 10.8	124.7 ± 6.1	85.6 ± 13.8	115.7 ± 4.2	80.5 ± 13.0	97.7 ± 6.3
SMR	1.13	3.76	68.3 ± 17.3	122.4 ± 23.6	81.9 ± 24.4	80.2 ± 4.0	84.5 ± 12.2	122.4 ± 6.9
acSMR	0.22	0.72	121.3 ± 15.3	69.4 ± 5.3	99.9 ± 22.0	91.2 ± 25.4	54.9 ± 3.3	117.9 ± 21.3
SMZ	0.13	0.42	74.8 ± 9.0	70.0 ± 7.0	83.3 ± 11.3	99.8 ± 14.8	77.9 ± 11.2	95.8 ± 2.0
acSMZ	0.33	1.09	129.7 ± 20.6	89.5 ± 3.7	129.7 ± 5.8	80.6 ± 12.0	82.0 ± 16.6	125.7 ± 8.7
SMX	0.18	0.60	132.7 ± 6.3	78.3 ± 9.1	131.0 ± 5.8	68.6 ± 14.3	97.1 ± 12.4	145.7 ± 24.5
acSMX	0.41	1.37	124.4 ± 0.2	70.0 ± 6.6	105.4 ± 7.0	128.5 ± 23.2	73.0 ± 16.3	110.6 ± 8.1
SMPZ	0.16	0.53	68.7 ± 18.4	88.0 ± 3.0	122.3 ± 5.4	79.3 ± 9.9	89.5 ± 4.6	129.9 ± 20.4
SPY	0.26	0.86	57.9 ± 1.0	74.4 ± 3.3	111.6 ± 14.9	120.9 ± 2.9	88.8 ± 25.3	138.1 ± 18.9
acSPY	0.21	0.70	77.5 ± 4.4	49.3 ± 6.8	71.3 ± 0.1	117.2 ± 25.3	94.4 ± 5.6	81.1 ± 3.2
SQX	0.43	1.43	86.7 ± 8.5	97.6 ± 11.1	105.6 ± 20.0	88.8 ± 14.3	108.2 ± 17.6	156.5 ± 7.4
STZ	5.19	17.28	112.5 ± 2.4	72.6 ± 26.2	115.7 ± 8.7	128.7 ± 13.5	90.0 ± 23.5	101.7 ± 18.0
Sulfisomidin	5.70	18.99	75.4 ± 11.9	74.4 ± 26.3	65.7 ± 3.8	64.1 ± 3.7	79.0 ± 3.8	122.0 ± 0.2
SDM	1.54	5.14	62.4 ± 1.6	103.7 ± 4.3	91.8 ± 4.3	80.3 ± 16.1	99.9 ± 15.0	141.3 ± 15.3
Trimethoprim	1.56	5.20	88.9 ± 17.5	78.5 ± 16.7	98.8 ± 21.5	93.3 ± 8.1	120.7 ± 3.8	103.8 ± 11.5
Gemfibrozil	0.65	2.16	66.5 ± 11.2	68.3 ± 15.3	68.5 ± 5.8	131.3 ± 21.1	168.2 ± 2.0	136.3 ± 6.4
Mefenamic acid	1.16	3.86	135.7 ± 10.1	95.8 ± 9.3	123.1 ± 25.3	62.3 ± 2.5	83.1 ± 14.4	117.7 ± 17.0
Naproxen	0.47	1.58	123.5 ± 17.1	65.3 ± 5.4	112.0 ± 18.9	126.4 ± 5.1	69.6 ± 20.1	116.0 ± 12.9
IBU	1,66	5.54	84.4 ± 5.4	78.9 ± 17.5	111.8 ± 17.9	87.9 ± 25.3	131.3 ± 10.8	63.9 ± 10.5
Ketoprofen	0.36	1.21	57.6 ± 3.7	74.0 ± 10.9	106.5 ± 11.0	68.4 ± 7.4	68.3 ± 3.2	121.3 ± 22.7
Diclofenac	3.50	11.64	120.1 ± 4.2	111.5 ± 25.7	59.4 ± 17.9	62.0 ± 16.4	78.1 ± 23.1	89.2 ± 3.9
Acetaminophen	1.11	3.70	75.4 ± 7.4	74.8 ± 24.2	102.6 ± 27.2	86.8 ± 6.9	74.1 ± 16.5	111.9 ± 16.1
CBZ	1.87	6.24	64.0 ± 1.0	103.6 ± 12.8	103.2 ± 9.4	88.1 ± 1.4	93.4 ± 1.3	127.0 ± 24.7
CBZ-10,11-epoxy	5.04	16.80	63.0 ± 13.0	73.3 ± 13.5	109.3 ± 2.1	89.1 ± 1.8	82.1 ± 2.7	116.4 ± 5.2

Atenolol	0.41	1.38	117.3 ± 0.6	92.0 ± 1.7	138.1 ± 1.5	69.8 ± 0.5	87.6 ± 7.3	53.2 ± 0.5
NorFXT	2.40	8.00	120.9 ± 17.7	93.4 ± 0.3	70.1 ± 14.7	129.5 ± 6.5	49.9 ± 1.6	101.3 ± 6.6
N-desVFX	1.17	3.91	71.0 ± 4.2	131.4 ± 16.4	66.3 ± 13.3	66.9 ± 5.1	51.8 ± 1.9	94.1 ± 6.5
Salicylic acid	1.42	4.72	87.9 ± 8.0	80.5 ± 4.4	98.8 ± 12.5	110.0 ± 20.0	67.4 ± 24.4	89.6 ± 11.0
Caffeine	0.89	2.96	88.9 ± 10.0	115.3 ± 0.4	122.3 ± 13.7	128.4 ± 0.4	90.0 ± 7.9	134.6 ± 4.7
Diuron	0.86	2.87	74.6 ± 6.3	123.9 ± 26.8	108.6 ± 3.2	77.2 ± 3.7	120.4 ± 0.9	102.4 ± 6.9
Irgarol	0.43	1.44	119.8 ± 5.0	92.3 ± 4.4	111.8 ± 27.8	81.2 ± 15.0	106.6 ± 19.4	138.1 ± 28.3
DCOIT	0.53	1.78	125.4 ± 2.3	116.9 ± 17.8	100.2 ± 2.4	95.0 ± 4.2	112.5 ± 4.2	93.1 ± 18.7
Dichlofluanid	0.75	2.48	71.6 ± 14.8	104.4 ± 26.3	86.6 ± 6.0	123.9 ± 2.7	85.7 ± 0.4	122.8 ± 4.3

The linear range was evaluated from 1 to 1000 ng mL^{-1}. Correlation coefficients (r^2) of analytical calibration curves ranged from 0.9979 to 0.9999 in MeOH, and from 0.9888 to 0.9999 in the sediment extract (matrix-matched standards), indicating good and wide linearity for all compounds (INMETRO, 2018).

The extraction efficiency of VA-MSPD was satisfactory, obtaining recovery rates between 60 and 140% (SANTE, 2017; INMETRO, 2018). Lower recoveries, below 60% were obtained for BP4, EtPABA, UVP, SPY, and ketoprofen. Generally, RSD values for intra-day and inter-day tested at three concentration levels were below 20% except for BP4 at 10xLOQm and nalidixic acid at 1xLOQm.

Concerning ME, by comparing the calibration curves in pure solvent and the sediment extract, 60% of compounds presented low to medium ME, mainly suppression of the signal. ME deemed to be low for signal suppression/enhancement of ±20%, the medium between ±20% and ±50%, and high for values higher than 50% or lower than −50% (Economou et al., 2009). Whenever ME is considered insignificant (less than or equal to 20%), calibration curves in the solvent can be used, avoiding the need for more laborious calibrations. However, in the presence of ME, some strategies should be done to appropriately compensate for signal changes and/or minimize the variability of results (Martins et al., 2016). The use of isotopically labeled IS provides a practical way of correction for any bias caused by the matrix that may affect the reliability of the instrument response factors. For multi-residue methods, as the developed one, the more deuterated internal standard used the better. However, deuterated standards are not available for every analytes and, whenever available are very expensive (SANTE, 2017). Thus, the quantification in the present study was done using at least one deuterated internal standard for each class of compound (Table 1S).

The developed VA-MSPD based method was intended for the analysis of a large number of analytes in sediment. Nevertheless, it may be applied to other solid environmental samples, such as soil and sewage sludge, once the characteristics of each matrix are considered. In general, and in comparison, with the previously published methods, the one developed in this work can simultaneously analyze 59 organic compounds while the previous ones limit the analysis to a specific and small group of substances with similar structures and/or properties. Furthermore, the method described in the present study is faster and cheaper, and more environmentally friendly.

4 Applicability of the method to the analysis of coastal sediment samples

Once validated, the analytical method was applied to analyze marine sediment samples. The analyzed sediments had ~~total organic carbon (~~TOC~~)~~ contents ranging from 0.9 to 3.5%, percentage of fines from 17.4 to 65.1%, and slightly distinct profiles of use (Table 2). Among the 59 analytes, only AVO (<3.2–7.8 ng g^{-1} dw), MeBZT (<3.2–3.5 ng g^{-1} dw), MePB (<4.7–69.7 ng g^{-1} dw), ciprofloxacin (<2.1–9.5 ng g^{-1} dw), irgarol (<1.4–2.2 ng g^{-1} dw) and DCOIT (5.0–41.1 ng g^{-1} dw) were detected (Table 3), although AVO, MeBZT, and ciprofloxacin were below LOQm only in one site. Disregarding any local input sources, since all of these sites are under the influence of maritime activities, sediment characteristics may also influence the amount of each contaminant accumulated in the matrix. The most contaminated sample (Alemoa) had the highest % of fines (65%) and TOC content (3.4%), whereas the less contaminated sediment (São Vicente 2) had one of the lowest percentage of fines (14%) and TOC (1.1%) (Table 2).

alt-text: Table 2

Table 2

The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Location, percentage of fines (% Fines), and total organic carbon (% TOC) of the sediment samples collected in Brazil at Santos-São Vicente Estuarine System (SESS) (São Paulo), Patos Lagoon Estuary (Rio Grande do Sul) and Rio Grande shipyard (Rio Grande do Sul).

Sampling site	Longitude (W)	Latitude (S)	Depth (m)	Brief description	% Fines	% TOC
Pier do Pescador	46° 18′ 10.82″	23° 59′ 30.75″	3.2	Entrance of the estuary (fishing boats) (by the main navigation channel)	17.4	0.9
Balsa	46° 17′ 40.27″	23° 59′ 15.40″	2.0	Intensive traffic of ferryboat used for vehicles and passengers (by the main navigation channel)	22.2	1.3
Terminal 1	46° 18′ 22.85″	23° 56′ 55.88″	7.0	Main mooring area of Santos Port	37.2	3.0
Terminal 2	46° 19′ 39.83″	23° 55′ 31.16″	6.0	Main mooring area of Santos Port/shipyard	32.5	2.7
Terminal 3	46° 22′ 9.11″	23° 55 ′7.56″	7.0	Main mooring area of Santos Port	39.4	2.8
Alemoa	46° 17′ 11.80″	23° 58′ 34.55″	4.5	Mooring area for Oil-based Transport Vessels	65.1	3.5
São Vicente 2	46° 25′ 30.36″	23° 57′ 7.24″	3.0	São Vicente estuary channel (near the mangrove swamps). Small fishing and leisure boats	14.8	1.1
Rio Grande shipyard	52° 04′ 07.04″	32° 03′ 15.09″	0.3	Oldest shipyard in the city. Few repair activities today and the presence of a fuel supply station	20.5	1.6

alt-text: Table 3

Table 3

The table layout displayed in this section is not how it will appear in the final version. The representation below is solely purposed for providing corrections to the table. To preview the actual presentation of the table, please view the Proof.

Concentrations (ng g^{-1} dw) of the target compounds in sediment samples collected in Brazil at Santos-São Vicente Estuarine System (SESS) (São Paulo), Patos Lagoon Estuary (Rio Grande do Sul), and Rio Grande (Rio Grande do Sul). LOQm, method limit of quantification for each analyte.

Analytes	LOQm (ng g^{-1})	Sediment samples							
		São Vicente	Alemoa	Pier pesca	Balsa	Tersminal 1	Terminal 2	Terminal 3	RG shipyard
AVO	3.19	<LOD_m	<LOD_m	<LOD_m	<LOD_m	<LOD_m	<LOD_m	<LOD_m	7.75
MeBZT	3.20	<LOD_m	3.48	<LOD_m	<LOD_m	<LOD_m	<LOD_m	<LOD_m	<LOD_m
MePB	4.66	12.63	69.69	44.19	12.09	38.00	21.30	36.56	5.79
Ciprofloxacin	2.07	<LOD_m	<LOD_m	<LOD_m	9.54	<LOD_m	<LOD_m	<LOD_m	<LOD_m
Irgarol	1.44	<LOD_m	<LOD_m	1.51	<LOQ_m	1.63	<LOD_m	1.55	2.18
DCOIT	1.78	11.55	6.50	5.02	6.70	10.42	7.46	41.14	9.18
∑Total		24.18	79.67	50.72	28.33	50.05	28.76	79.25	24.90

<LODm - below the limit of detection of the method; <LOQm - below the limit of quantification of the method for Irgarol.

AVO is a UVF present in many sunscreens, often employed as a substitute for the endocrine-disrupting BP3. Measurable levels of this contaminant were only detected in the sediment of Rio Grande shipyard (7.8 ng g^{-1} dw). The observed concentration was similar to previously reported values in soil and sediments, for instance from coastal areas of Hawaii, (<7 ng g^{-1} dw) (Mitchelmore et al., 2019).

Benzotriazoles are high production volume chemicals used in a wide range of industrial applications; as UV stabilizers in different plastic products, as corrosion inhibitors in detergents, and antifreeze or antifogging agents in automotive fluids (Molins-Delgado et al., 2015). Benzotriazole and MeBZT are the two UV-stabilizers most frequently detected in the environment, as they are poorly volatile and only partially removed during conventional wastewater treatment because of its high polarity and poor biodegradability (Liu et al., 2012; Asimakopoulos et al., 2013; Molins-Delgado et al., 2015, 2017). In this study, only MeBZT was detected in a single sediment sample, SSES (Alemoa - 3.5 ng g^{-1}dw), at the comparatively low levels to those found by Zhang et al. (2011) in sediments from China and the USA Similarly, MeBZT was detected but not quantifiable in river sediment samples from Iguaçu watershed, also in Brazil (Mizukawa et al., 2017). In contrast, they observed quite high concentrations of BZT (<LODm – 630 ng g^{-1}dw).

Due to the use and consumption of personal care products, pharmaceuticals, beverages, and other foodstuff containing parabens as preservatives, there is a continuous introduction into the environment, and thus parabens are ubiquitous in surface water and sediments worldwide. Methylparaben (MeP) and propylparaben (PrP) predominate, reflecting the composition of paraben mixtures in common consumer products (Haman et al., 2015). Their efficiency as fungicidal and bactericidal agent combined with its low cost, likely explains why parabens are so widely used (Soni et al., 2005). Many studies reported links between paraben preservatives and adverse effects observed in aquatic organisms (Dobbins et al., 2009), and highlighted its endocrine disrupting activity at environmentally relevant concentrations (Darbre et la., 2003; Golden et al., 2005).

In the present study, 100% of the sediments contained MePB (E number E218) in concentrations from 5.8 to 69.7 ng g^{-1}dw. MeP as well as EtP (E214), PrP (E216), BuP, and BzP have been found in sediment and sewage sludge samples of the USA, Japan, and Korea at a wider concentration range, from 0.70 to 95.7 ng g^{-1}dw (Liao et al., 2013).

Fluoroquinolones (FQs) are a class of antibiotics used in human and veterinary medicine. Due to their widespread application, and considering that they are only partially metabolized in the organisms and not completely removed in wastewater treatment plants, FQs such as ciprofloxacin, are one of the most detected antibiotics in the environment (Ziarrusta et al., 2018). Ciprofloxacin inhibits microorganisms and, therefore, can represent an important risk for the environment, especially for microbial ecology (Girardi et al., 2011). In the present study, ciprofloxacin was the only FQs detected in one single site of SSES (Balsa - 9.5 ng g^{-1}dw), which is an area of ferryboat operation and a mooring pier for boats and fishing boats. Also in Brazil, in mangrove sediment from the Paciencia River, (Maranhão Island) ciprofloxacin was the only antibiotic found in three out of the six samples analyzed, but at higher concentrations (56.55–70.45 ng g^{-1}) (Neves at al., 2018). These values are far below the recently reported concentrations of this antibiotic in river sediments from Kenia (4125-1275 ng g^{-1}) (Kairigo et al., 2020). This high pollution can be explained by the lower dilution effect and the higher impact of wastewater treatment plants discharges in rivers in comparison with the sea.

Regarding antifouling booster biocides, irgarol and DCOIT were detected in 75% and 100% of the samples, respectively, and at concentrations between 1.5 and 2.2 ng g^{-1} dw, and 5.0–41.1 ng g^{-1} dw, respectively. All sampling sites are within an estuarine system under the direct influence of maritime activities. This suggests that the presence of antifouling booster biocides may be related to the large flow of vessels that may be using these compounds in antifouling paint formulations. The current use of DCOIT is well known (Abreu et al., 2020). Its low water solubility (0.0065 mg L^{-1} a 25 °C) and high log K_{oc} (2.6–4.2) suggests the preferential partition in the suspended particulate matter from the water column and sediments. Although DCOIT has a short half-life in aquatic environments (Chen and Lam, 2017; Jacobson and Willingham, 2000) its presence may be explained by the continuous inputs in the region (Abreu et al., 2020; Chen and Lam, 2017), behaves as a pseudo-persistent contaminant due to its continuous release. Diuron and irgarol are more persistent than DCOIT in the environment (half-lives of 14 and 100 days in sediment, respectively), and their moderate log K_{oc} (2.3 and 3.3, respectively) indicate partition in both water and sediment. As a consequence of its toxicity for primary producers, their use has been restricted in many countries. In a previous study in Panamá, irgarol, diuron, and DCOIT were measured at concentrations between below 0.25 and 2.8 ng g^{-1} dw; 2.4 and 14.1 ng g^{-1} dw; and 2.4 and 81.6 ng g^{-1} dw, respectively (Batista-Andrade et al., 2016b). Lower values were reported by Abreu et al. (2020) for DCOIT, diuron, and irgarol ranging from below 0.2–75 ng g^{-1}, below 0.5–9.9 ng g^{-1}, and below 0.2 ng g^{-1}, respectively.

5 Conclusions

The present study developed and validated a multiresidue method based on vortex-assisted matrix solid-phase dispersion in combination with liquid chromatography-tandem mass spectrometry for the trace determination of 59 organic contaminants of emerging concern, including pharmaceuticals, personal care products, and biocides, in sediment. This techniques combination can be considered innovative and efficient in determining organic contaminants with a wide range of physicochemical properties in solid environmental matrices. The method used solely 2 g of sediment sample and 5 mL of extraction solvent. This approach provided limits of detection and quantification in the low ng g^{-1} dw range, which are below or similar to those reported in the literature for these analytes.

The method was applied to investigate the target contaminants in marine sediment samples collected at two major ports in Brazil. The application in the environmental samples evidenced that solely 4 out of the 59 analytes of interest were found in the marine sediments. The preservative MePB and the antifouling booster biocide DCOIT were present in 100% of the samples. Irgarol was also frequently detected (75%). The sunscreen agents AVO and MeBZT, and the antibiotic ciprofloxacin were eventually detected (only in one sample each). The occurrence of these commonly detected contaminants, even at low ng g^{-1} levels, indicates the prevalent impact of the direct maritime activities and some urban inputs on the quality status of the selected coastal aquatic ecosystems of Brazil, which appears to be similar to those reported worldwide.

Declaration of competing interest

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

Acknowledgments

Q2 The authors thank M.P. Serra Roig (technician at IDAEA), FURG, CNPq, CAPES - Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CIMAR II No 1988/2014). G. Fillmann is research fellow of CNPq (PQ 312341/2013–0 and 314202/2018–8). K. L. Soares was a Ph.D. fellow of CAPES (N° 88881.185459/2018-01 ~~do~~ Programas Estratégicos - Portaria nº 19/2011) and is currently a research fellow of CAPES (N° 88887.369192/2019-00 ~~do Programa~~ PNPD/CAPES). M.S. Díaz-Cruz acknowledges the Generalitat de Catalunya (Water and Soil Quality Unit 2017-SGR-1404) and the Spanish Ministry of Science and Innovation (Project CEX 2018-000794-S).

Appendix A Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.129085.

Q3 Uncited references

Batista-Andrade et al. (2018); ~~Castro et al. (2011)~~; ~~ChemSpider,~~; ~~Córdova-Kreylos and Scow (2007)~~; ~~DrugBank,~~; ~~Mutavdžić Pavlović et al. (2017)~~; Soares et al. (2017).

References

The corrections made in this section will be reviewed and approved by a journal production editor. The newly added/removed references and its citations will be reordered and rearranged by the production team.

Abreu, F.E.L., Silva, J.N.L., Castro, I.B., Fillmann, G., 2020. Are antifouling residues a matter of concern in the largest South American port? J. Hazard Mater.. doi:10.1016/j.jhazmat.2020.122937.

Anastassiades, M., Lehotay, S.J., Štajnbaher, D., Schenck, F.J., 2003. Fast and easy multi-residue method employing ACN extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J. AOAC Int. 86, 412–431.

Asimakopoulos, A.G., Ajibola, A., Kannan, K., Thomaidis, N.S., 2013. Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece. Sci. Total Environ. 452–453, 163–171.

Barker, S.A., Long, A.R., Short, C.R., 1989. Isolation of drug residues from tissues by solid phase dispersion. J. Chromatogr. A 475, 353–361.

Batista-Andrade, J.A., Caldas, S.S., de Oliveira Arias, J.L., Castro, I.B., Fillmann, G., Primel, E.G., 2016. Antifouling booster biocides in coastal waters of Panama: first appraisal in one of the busiest shipping zones. Mar. Pollut. Bull. 112, 415–419.

Batista-Andrade, J.A., Caldas, S.S., Batista, R.M., Castro, I.B., Fillmann, G., Primel, E.G., 2018. From TBT to booster biocides: levels and impacts of antifouling along coastal areas of Panama. Environ. Pollut. 234, 243–252.

Caldas, S.S., Bolzan, C.M., de Menezes, E.J., Escarrone, A.L.V., Martins, C.d.M.G., Bianchini, A., Primel, E.G., 2013. A vortex-assisted MSPD method for the extraction of pesticide residues from fish liver and crab hepatopancreas with determination by GC–MS. Talanta 112, 63–68.

Caldas, S.S., Rombaldi, C., De Oliveira Arias, J.L., Marube, L.C., Primel, E.G., 2016. Multi-residue method for determination of 58 pesticides, pharmaceuticals and personal care products in water using solvent demulsification dispersive liquid-liquid microextraction combined with liquid chromatography-tandem mass spectrometry. Talanta 146, 676–688.

Caldas, S.S., Soares, B.M., Abreu, F., Castro, Í.B., Fillmann, G., Primel, E.G., 2018. Antifouling booster biocide extraction from marine sediments: a fast and simple method based on vortex-assisted matrix solid-phase extraction. Environ. Sci. Pollut. Control Ser. 25, 7553–7565.

Castro, Í.B., Westphal, E., Fillmann, G., 2011. Third generation antifouling paints: new biocides in the aquatic environment. Quim. Nova 34, 1021–1031.

Čelić, M., Gros, M., Farré, M., Barceló, D., Petrović, M., 2018. Pharmaceuticals as Chemical Markers of Wastewater Contamination in the Vulnerable Area of the Ebro Delta (Spain). Science of The Total Environment.

Cerqueira, M.B., Soares, K.L., Caldas, S.S., Primel, E.G., 2018. Sample as solid support in MSPD: a new possibility for determination of pharmaceuticals, personal care and degradation products in sewage sludge. Chemosphere 211, 875–883.

ChemSpider, Search and Share Chemistry.

Chen, L., Lam, J.C.W., 2017. SeaNine 211 as antifouling biocide: a coastal pollutant of emerging concern. J. Environ. Sci. 61, 68–79.

Córdova-Kreylos, A.L., Scow, K.M., 2007. Effects of ciprofloxacin on salt marsh sediment microbial communities. ISME J. 1, 585–595.

Crommentuijn, T., Sijm, D., Bruijn, J. De, Leeuwen, K. Van, Plassche, E. Van De, 2000. Maximum Permissible and Negligible Concentrations for Some Organic Substances and Pesticides. pp. 297–312.

Darbre, P., Byford, J., Shaw, L., Hall, S., Coldham, N., Pope, G., Sauer, M., 2003. Oestrogenic activity of benzylparaben. J. Appl. Toxicol. 23, 43–51.

Dobbins, L.L., Usenko, S., Brain, R.A., Brooks, B.W., 2009. Probabilistic ecological hazard assessment of parabens using Daphnia magna and Daphnia magna and Pimephales promelas. Environ. Toxicol. Chem. 28, 2744–2753.

DrugBank, DrugBank - Database.

Economou, A., Botitsi, H., Antoniou, S., Tsipi, D., 2009. Determination of multi-class pesticides in wines by solid-phase extraction and liquid chromatography-tandem mass spectrometry. J. Chromatogr., A 1216, 5856–5867.

Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2011. Fast pressurized liquid extraction with in-cell purification and analysis by liquid chromatography tandem mass spectrometry for the determination of UV filters and their degradation products in sediments. Anal. Bioanal. Chem. 400, 2195–2204.

Gago-Ferrero, P., Díaz-Cruz, M.S., Barceló, D., 2013a. Multi-residue method for trace level determination of UV filters in fish based on pressurized liquid extraction and liquid chromatography–quadrupole-linear ion trap-mass spectrometry. J. Chromatogr. A 1286, 93–101.

Gago-Ferrero, P., Mastroianni, N., Díaz-Cruz, M.S., Barceló, D., 2013b. Fully automated determination of nine ultraviolet filters and transformation products in natural waters and wastewaters by on-line solid phase extraction–liquid chromatography–tandem mass spectrometry. J. Chromatogr., A 1294, 106–116.

Girardi, C., Greve, J., Lamshöft, M., Fetzer, I., Miltner, A., Schäffer, A., Kästner, M., 2011. Biodegradation of ciprofloxacin in water and soil and its effects on the microbial communities. J. Hazard Mater. 198, 22–30.

Golden, R., Gandy, J., Vollmer, G., 2005. A review of the endocrine activity of parabens and implications for potential risks to human health. CRC Crit. Rev. Toxicol. 35, 435–458.

Gray, J.S., Elliott, M., 2014. Ecology of Marine Sediments. Oxford University Press.

Haman, C., Dauchy, X., Rosin, C., Munoz, J.F., 2015. Occurrence, fate and behavior of parabens in aquatic environments: a review. Water Res. 68, 1–11.

INMETRO, 2018. Orientação sobre validação de métodos analíticos DOQ-CGCRE-008, Revisão em julho de 2018.

Jacobson, A.H., Willingham, G.L., 2000. Sea-nine antifoulant: an environmentally acceptable alternative to organotin antifoulants. Sci. Total Environ. 258, 103–110.

Kairigo, P., Ngumba, E., Sundberg, L., Gachanja, A., Tuhkanen, T., 2020. Contamination of surface water and river sediments by antibiotic and antiretroviral drug cocktails in low and middle-income countries: occurrence, risk and mitigation strategies. Water 12, 1376.

Köck-Schulmeyer, M., Postigo, C., Farré, M., Barceló, D., de Alda, M.L., 2019. Medium to highly polar pesticides in seawater: analysis and fate in coastal areas of Catalonia (NE Spain). Chemosphere 215, 515–523.

Kristensen, E., Andersen, F., 1987. Determination of organic carbon in marine sediments: a comparison of two CHN-analyzer methods. J. Exp. Mar. Biol. Ecol. 109, 15–23.

Kurz, M.H., Batista, J.L.d.S., de Oliveira, L.G., Hoff, R., Martins, M.L., Gonçalves, F.F., 2019. Clean-up procedure development and method validation for pesticide residues analysis in carrots. Food Analytical Methods 12, 282–292.

Liu, Y.S., Ying, G.G., Shareef, A., Kookana, R.S., 2012. Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant. Environ 165, 225–232.

Martins, M.L., Rizzetti, T.M., Kemmerich, M., Saibt, N., Prestes, O.D., Adaime, M.B., Zanella, R., 2016. Dilution standard addition calibration: a practical calibration strategy for multi-residue organic compounds determination. J. Chromatogr. A 1460, 84–91.

Martins, S.E., Fillmann, G., Lillicrap, A., Thomas, K.V., 2018. Ecotoxicity of organic and organo-metallic antifouling co-biocides and implications for environmental hazard and risk assessments in aquatic ecosystems. Biofouling 34, 34–52.

Mitchelmore, C.L., He, K., Gonsior, M., Hain, E., Heyes, A., Clark, C., Younger, R., Schmitt-Kopplin, P., Feerick, A., Conway, A., 2019. Occurrence and distribution of UV-filters and other anthropogenic contaminants in coastal surface water, sediment, and coral tissue from Hawaii. Sci. Total Environ..

Mizukawa, A., Molins-Delgado, D., de Azevedo, J.C.R., Fernandes, C.V.S., Díaz-Cruz, S., Barceló, D., 2017. Sediments as a sink for UV filters and benzotriazoles: the case study of Upper Iguaçu watershed, Curitiba (Brazil). Environ. Sci. Pollut. Res. 24, 18284–18294.

Molins-Delgado, D., ~~Silvia Díaz-Cruz~~Díaz-Cruz, ~~M.~~M.S., Barceló, D., 2015. Removal of polar UV stabilizers in biological wastewater treatments and ecotoxicological implications. Chemosphere 119 (874), S51–S57.

Molins-Delgado, D., Távora, J., ~~Silvia Díaz-Cruz~~Díaz-Cruz, ~~M.~~M.S., Barceló, D., 2017. UV filters and benzotriazoles in urban aquatic ecosystems: the footprint of daily use products. Sci. Total 877 Environ. 601–602, 975–986.

Molins-Delgado, D., del Mar Olmo-Campos, M., Valeta-Juan, G., Pleguezuelos-Hernández, V., Barceló, D., Díaz-Cruz, M.S., 2018a. Determination of UV filters in human breast milk using turbulent flow chromatography and babies' daily intake estimation. Environ. Res. 161, 532–539.

Molins-Delgado, D., Muñoz, R., Nogueira, S., Alonso, M.B., Torres, J.P., Malm, O., Ziolli, R.L., Hauser-Davis, R.A., Eljarrat, E., Barceló, D., 2018b. Occurrence of organic UV filters and metabolites in lebranche mullet (Mugil liza) from Brazil. Sci. Total Environ. 618, 451–459.

Mutavdžić Pavlović, D., Ćurković, L., Grčić, I., Šimić, I., Župan, J., 2017. Isotherm, kinetic, and thermodynamic study of ciprofloxacin sorption on sediments. Environ. Sci. Pollut. Res. 24, 10091–10106.

Neves, M., Silva, G., Brito, N., Araújo, K., Marquesa, E., Silva, l., 2018. Aqueous ultrasound-assisted extraction for the determination of fluoroquinolones in mangrove sediment by high-performance liquid chromatography and fluorescence detector. J. Braz. Chem. Soc. 29 1 São Paulo Jan. 2018.

SANTE, 2017. Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticide Residues and Analysis in Food and Feed.

Serra-Roig, M.P., Jurado, A., Díaz-Cruz, M.S., Vázquez-Suñé, E., Pujades, E., Barceló, D., 2016. Occurrence, fate and risk assessment of personal care products in river–groundwater interface. Sci. Total Environ. 568, 829–837.

Soares, K.L., Cerqueira, M.B.R., Caldas, S.S., Primel, E.G., 2017. Evaluation of alternative environmentally friendly matrix solid phase dispersion solid supports for the simultaneous extraction of 15 pesticides of different chemical classes from drinking water treatment sludge. Chemosphere 182, 547–554.

Soni, M., Carabin, I., Burdock, G., 2005. Safety assessment of esters of p-hydroxybenzoic acid (parabens). Food Chem. Toxicol. 43, 985–1015.

Thomas, K.V., Brooks, S., 2010. The environmental fate and effects of antifouling paint biocides. Biofouling 26, 73–88.

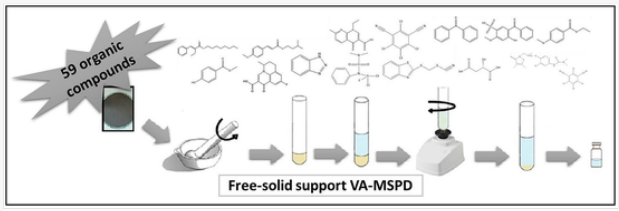
Vieira, A.A., Caldas, S.S., Kupski, L., Tavella, R.A., Primel, E.G., 2018. Extraction of chlorothalonil, dichlofluanid, DCOIT, and TCMTB from fish tissues employing the vortex assisted matrix solid-phase dispersion. Microchem. J. 143, 92–98.

Zhang, Z., Ren, N., Li, Y.F., Kunisue, T., Gao, D., Kannan, K., 2011. Determination of benzotriazole and benzophenone UV filters in sediment and sewage sludge. Environ. Sci. Technol. 45, 3909–3916. doi:10.1021/es2004057.

Ziarrusta, H., Mijangos, L., Irazola, M., Prieto, A., Etxebarria, N., Anakabe, E., Olivares, M., Zuloaga, O., 2018. Ciprofloxacin by-products in seawater environment in the presence and absence of gilt-head bream. Chemosphere 197, 560–568. doi:10.1016/j.chemosphere.2018.01.069.

Graphical abstract

alt-text: Image 1



Highlights

- A method for 59 emerging organic contaminants analysis in sediments was developed.
- Matrix solid phase dispersion allowed limits of quantification of 0.42 ngg^{-1}dw.
- The validated method was applied to analyze marine sediments from Brazil.
- Detected analytes were measured at concentrations between 1.44 and 69.69 ng g^{-1}dw.

Appendix A Supplementary data

The following is the Supplementary data to this article:

Multimedia Component 1

Multimedia component 1

alt-text: Multimedia component 1

Queries and Answers

Q1

Query: Please confirm that the provided email “sdcqam@cid.csic.es” is the correct address for official communication, else provide an alternate e-mail address to replace the existing one, because private e-mail addresses should not be used in articles as the address for communication.

Answer: OK

Q2

Query: Have we correctly interpreted the following funding source(s) you cited in your article: CNPq, Brazil; Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil?

Answer: Yes

Q3

Query: Uncited references: This section comprises references that occur in the reference list but not in the body of the text. Please position each reference in the text or, alternatively, delete it. Any reference not dealt with will be retained in this section. Thank you.

Answer: Corrected. Two uncited references were introduced. The others were deleted.

Q4

Query: Please confirm that given names and surnames have been identified correctly and are presented in the desired order and please carefully verify the spelling of all authors' names.

Answer: Yes

Q5

Query: Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact p.das@elsevier.com immediately prior to returning your corrections.

Answer: Yes