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Occurrence, profile and spatial distribution of UV-filters and musk fragrances in mussels from Portuguese coastline

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ABSTRACT

The increasing production and consumption of Personal Care Products (PCPs), containing UV-filters and musk fragrances, has led to its widespread presence in the aquatic environment which can cause harmful effects to the aquatic organisms due to its intrinsic toxicity. This study aims to evaluate the degree of contamination of wild mussels along the entire Portuguese coastline, continually exposed in their habitat to different contaminants. For this purpose, approximately 1000 mussel specimens were sampled during one year in seven different locations, along the Portuguese coastline. Simultaneous quantification of five UV-filters and seven musks in mussels was achieved by a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction procedure combined with dispersive liquid-liquid microextraction (DLLME) followed by gas chromatography with mass spectrometry (GC–MS) analysis.

Ten out of the twelve target analytes were found in the analysed samples, highlighting the presence of AHTN (tonalide), EHS (2-ethylhexylsalicylate) and EHMC (2-ethylhexyl 4-methoxycinnamate) in all positive samples (93%).

Overall, the results obtained indicate a widespread contamination of wild mussels along Portuguese coastline, all over the year. UV-filters were more frequently detected (90%) than musk fragrances (70%) and also quantified at higher levels, with average total concentrations reaching 1155.8 ng/g (dw) against 397.7 ng/g (dw) respectively. A high correlation was observed between the most densely populated and industrialized locations and the higher levels of musks and UV-filters found. In other hand, lower levels of PCPs were found in protected areas. As expected, an increase in UV-filters levels was observed after the summer, likely due to the intense period of recreational activities.

1. Introduction

Personal Care Products (PCPs) designate a group of chemicals used in different products, such as toothpaste, shampoo, cosmetics, sunscreens and body lotions, etc. (Daughton and Ternes, 1999). Among PCPs, UV-filters and musk fragrances are massively employed, especially in the developed countries, in skin protection and daily human hygiene (Giokas et al., 2007; Boxall et al., 2012) and their consumption is expected to rise as a demand of the society (Brausch and Rand, 2011). UV-filters are used to protect our skin against nocive effects from UV radiation, being incorporated not only in sunscreens but in a variety of other products (lipsticks, body and hair creams, lotions, etc.) (Balmer et al., 2006). UV-filters often used in PCPs include different families of

compounds like camphors (i.e. 4-methylbenzylidene camphor, 4-MBC), benzophenones (i.e. 2-hydroxy-4-methoxybenzophenone, BP-3), cinnamates (i.e. 2-ethylhexyl 4-methoxycinnamate, EHMC), among others (Ramos et al., 2016). Musk fragrances are a group of odoriferous compounds widely applied not only in PCPs but also in washing and cleaning agents (Bester, 2009). According to their chemical structure, musks are usually classified in nitromusks (i.e. musk moskene, MM), polycyclic (i.e. galaxolide, HHCB), macrocyclic (i.e. ethylene brassylate, MT) and alicyclic musks (romandolide) (Posada-Ureta et al., 2012).

These so called “emerging contaminants” are among the most commonly detected compounds in surface waters throughout the world (Daughton and Ternes, 1999; Rainieri et al., 2016), being released into the environment directly through normal human usage and indirectly

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through domestic and industrial wastewater discharges, at levels greater than pharmaceuticals (Giokas et al., 2007; Boxall et al., 2012; Homem et al., 2015). UV-filters and musk fragrances have already been recognized as important organic contaminants (Regulation, 2009) because of their high frequency detection in aquatic environments (Giokas et al., 2004, 2005; Poiger et al., 2004; Kasprzyk-Hordern et al., 2008; Lee et al., 2010; Moeder et al., 2010; Silva and Nogueira, 2010; Nakata et al., 2012; Jiang et al., 2014; Tsui et al., 2014; Liu et al., 2010) and also the endocrine disruptive activity and adverse effects on fecundity and reproduction observed in different aquatic organisms (Witorsch and Thomas, 2010; Krause et al., 2012; Kim et al., 2014; Schreurs et al., 2004; Coronado et al., 2008; Kinnberg et al., 2015; Kunz and Fent, 2006; Weisbrod et al., 2007). So, attention should be given to monitoring environmental levels and potential toxicity to aquatic organisms (Boxall et al., 2012; Jiang et al., 2014).

Indeed, UV-filters and musks have common physical-chemical characteristics such as the presence of more than one ring in the molecular structure, high lipophilicity (log K_{OW} values between 4 and 8) and stability against biotic degradation (Kupper et al., 2006). As a result they tend to accumulate in tissues of aquatic organisms such as crustaceans (Cunha et al., 2015a; Ziarrusta et al., 2015; Picot Groz et al., 2014) and fishes (Balmer et al., 2005; Duedahl-Olesen et al., 2005; Gago-Ferrero et al., 2015; Ramirez et al., 2009), even reaching higher trophic levels such as marine mammals (Gago-Ferrero et al., 2013; Nakata, 2005) and aquatic birds (Fent et al., 2010). Marine mussels are filter feeders that are able to retain complex mixtures of chemical pollutants, being widely used as bioindicator species (Beyer et al., 2017). So far, few studies assessing different UV-filters and musks in wild mussels were carried out. Recently, Cunha et al. (2018) found average levels of EHS, 4-MBC, BP-3, EHMC and IMC in mussels below 15 ng/g (dw), similar to those reported previously in mussels from different European spots where BP-3 and 4-MBC were detected always below the limit of quantification of the method (20 and 5 ng/g respectively) (Cunha et al., 2015b). However, Picot Groz et al. (Picot Groz et al., 2014) reported levels of EHMC up to 1765 ng/g (dw) in wild mussels collected in the southern of Portugal. Concerning musks levels, HHCB reached concentrations up to 42.0 ng/g (dw), AHTN levels up to 81 ng/g (dw) and not detected levels for ADBI and nitromusks were reported (Cunha et al., 2015a; Ziarrusta et al., 2015; Saraiva et al., 2016). Notwithstanding, the simultaneous monitorization of these contaminants in wild mussels along an entire coastline of a country was not yet performed, as far as we know.

The main objective of the present work was to provide a comprehensive status of the contamination levels of UV-filters and musk fragrances in wild mussels collected along the entire coastline of Portugal.

Twelve compounds were selected based either in their detection frequency and/or high consumption, seven musk fragrances (galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI), musk moskene (MM), musk xylene (MX), musk ketone (MK) and ethylene brassylate (MT)) and five UV-filters (4-MBC, BP-3, EHMC, isoamyl 4-methoxycinnamate (IMC), and 2-ethylhexyl salicylate (EHS)).

The extraction of these contaminants from a complex matrix like mussels requires a pre-concentration and a clean up steps previous to the analysis in order to achieve low limits of detection (LODs) and eliminate some potentially interfering compounds. QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction, a “green” analytical approach, with phase partition between an organic solvent, usually acetonitrile (MeCN) and water, enhanced by salt addition to increase ionic strength, gathers unique features, namely low volume of solvent with consequent low waste production, and has been successfully applied to mussels (Cunha et al., 2015a; Picot Groz et al., 2014; Daniele et al., 2016). Based in previous works developed by Cunha et al. (2015a), a procedure including QuEChERS extraction, combined with DLLME (dispersive liquid-liquid micro extraction), which is characterized by a quick extraction by the combined action of an extractor and a dispersive solvents in a aqueous solution (simple operation and

quickness with only few microliters of organic solvent extractor) translating in high enrichment factors of the analytes, followed by gas chromatography with mass spectrometry (GC-MS) was validated to enable the simultaneous extraction of UV-filters and musk fragrances from wild mussels.

2. Material and methods

2.1. Standards and reagents

The internal standards (IS) Chrysenes-d₁₂ (CSd₁₂-IS1) and Benzophenone-d₁₀ (BPd₁₀-IS2) both with purity > 98%, were also purchased from Sigma-Aldrich.

Acetonitrile (MeCN), methanol (MeOH), acetone, all HPLC grade, were obtained from Sigma-Aldrich. Individual standard solutions of the UV-filters, polycyclic musks and musk ketone (2000 mg/L, 4000 mg/L, 1000 mg/L, respectively) were prepared in MeOH. MX and MM, which were supplied directly at a concentration of 100 mg/L in MeCN, were used as received. Working mixture solutions of 100 mg/L were prepared in MeCN, the solvent used in the extraction.

Extractive solvent trichloroethylene (C₂HCl₃) and carbon disulfide (CS₂) were high purity solvents for GC analysis obtained from Fluka (Neu-Ulm, Germany). The sorbents sulphate magnesium (MgSO₄) and sodium chloride (NaCl), and the derivatization agents N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and acetic anhydride, were obtained from Sigma-Aldrich.

Water was prepared by purifying demineralized water in a “Seradest LFM20” system (Seral, Ransbach-Baumbach, Germany). Ultrahigh purity Helium (99.999%) for GC-MS was purchased from Gasin (Maia, Portugal).

Plastic material was avoided and all the glassware was previously rinsed with acetone. In each batch of samples, a procedural blank (i.e. a sample prepared as described in 2.3 using water) was extracted to verify the background contamination.

2.2. Sampling

In order to evaluate the presence of UV-filters and musk fragrances in wild mussels, along the Portuguese coastline, approximately 1000 mussel specimens (*Mytilus galloprovincialis* and *Mytilus edulis*), were hand-collected during one year (2015) in seven different locations of the coastline (including the intertidal zone and the bathymetry of 70 m) (see detailed information regarding sampling points at Supplementary Figure (S1) and (Cunha et al., 2017)).

From North to South, seven different locations were sampled: Viana do Castelo beach (Viana do Castelo city with 270.8 population/Km²), Leça da Palmeira beach (Oporto city with 2783.5 population/Km²), Vagueira beach (Aveiro city with 389.3 population/Km²), Algés and Costa da Caparica beaches (Lisbon city with 5066.4 population/Km²), Aljezur beach (Aljezur city with 17.4 population/Km²) and Faro beach (Faro city with 301.7 population/Km²) (INE, 2014).

Each location was sampled in January, March, May, July and October. For each sampling campaign in each different location, a pool of 25 individual organisms of similar size was collected, in order to reduce the intrinsic variability (age, size, health status and environmental conditions) (Gonzalez-Fernandez et al., 2015), resulting in a total of 30 composite samples (edible content) (Supplementary Table 1 ST1).

Each composite sample was grinded, homogenized, and frozen at –80 °C before being freeze-dried for 48 h at –80 °C and low pressure. After that, the lyophilized samples were once more homogenized and kept at 4 °C until analysis. This procedure is usually applied for aquatic biota samples prior to PCPs analysis (Cunha et al., 2015a; Gago-Ferrero et al., 2012a).

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