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UV-filters and musk fragrances in seafood commercialized in Europe Union: Occurrence, risk and exposure assessment

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ABSTRACT

In the framework of the FP7 ECsafeSeafood project, 62 seafood samples commercialized in Europe Union from several representative species – mackerel, tuna, salmon, seabream, cod, monkfish, crab, shrimp, octopus, perch and plaice – were analysed for residues of 21 personal care products (PCPs), including 11 UV-filters (UV-Fs) and 10 musk fragrances (musks). PCPs analysis were performed by Quick, Easy, Cheap, Effective Rugged, Safe (QuEChERS), combined with liquid-liquid extraction (LLE) or dispersive solid-phase extraction (dSPE), followed by gas chromatography-tandem mass spectrometry (GC-MS/MS). The results showed the presence in a wide range of samples of nine out of eleven UV-Fs compounds analysed, namely 2-ethylhexyl salicylate (EHS), 2-ethylhexyl,4-methoxycinnamate (EHMC), 4-methylbenzylidenecamphor (4-MBC), benzophenone-1 (BP1), benzophenone-3 (BP3), isoamyl-4-methoxycinnamate (IMC), 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (DHMB), homosalate (HS), and octocrylene (OC), whereas galaxolide (HHCB), galaxolide lactone (HHCB-lactone), and tonalide (AHTN) were the most found musks. The potential risks to human health associated with the exposure to eight of the more prevalent PCPs – EHS, EHMC, 4-MBC, BP1, BP3, IMC, HHCB, and AHTN - through seafood consumption were assessed for consumers from five European countries (Belgium, Ireland, Italy, Portugal and Spain). Results showed that the human exposure to UV-Fs and musks estimated from the concentration values found in seafood and the daily consumption of concerned seafood species, were far below toxicological reference values.

1. Introduction

The economic and industrial development of the world has rapidly increased in the last decades leading to a rise in threats to the oceans. Among these menaces, the organic contamination with personal care products (PCPs) has been of great concern in aquatic systems in the last few years (Halden, 2015), and their concentration in the oceans is likely to increase, particularly due to atmospheric temperature increase and ozone-depletion.

PCPs comprise a wide range of compounds such as UV-filters (UV-Fs) and musks, used in sunscreens to protect the skin against the harmful effects of ultraviolet radiation and in household products or cosmetics as fragrance ingredients, respectively. These compounds are widely employed, especially in developed countries for daily human

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hygiene and mostly end up in environmental waters. As a consequence, both UV-Fs and musks have been reported in surface waters (Homem et al., 2016; Tsui et al., 2014), ground water (Jurado et al., 2014; Pintado-Herrera et al., 2014), drinking water (Diaz-Cruz et al., 2012; Li et al., 2016), seawater (Magi et al., 2012; Panagiotou et al., 2009), and wastewaters (Cunha et al., 2015a; Homem et al., 2016; Kupper et al., 2004). Moreover, due to their lipophilic nature (log K_{OW} values between 4 and 8) and great stability in the environment, these compounds can easily bioaccumulate and biomagnify, reaching several trophic levels (Zhang et al., 2013). UV-Fs have been detected in various aquatic organisms, including fish (Gago-Ferrero et al., 2013), mussels, clams (Cunha et al., 2015b), and dolphins (Alonso et al., 2015), as well as in human fluids and tissues like breast milk (Rodriguez-Gomez et al., 2015), semen (Leon et al., 2010), and placenta (Valle-Sistac et al., 2016). The presence of musks have also been reported in fish (Cunha et al., 2015b), mussels (Trabalon et al., 2015), breast milk (Reiner et al., 2007) and human adipose tissue (Rimkus et al., 1994). Despite the importance of the above mentioned data, a large survey on the magnitude of PCPs contamination in fish consumed in Europe, a requisite to made an estimation of human intake of these compounds and associated risk, is missing as far as we know.

To date, numerous toxicological studies in aquatic organisms showed that several UV-Fs and musks exhibit endocrine disrupting properties (Downs et al., 2016; Kunz and Fent, 2006; Schlumpf et al., 2001). Yet, so far, the toxic effects in humans after such a prolonged low dose exposure to UV-Fs and musks have hardly been investigated. Kunz and Fent (2006) and Kunz et al. (2006) demonstrated that UV-Fs show anti-estrogenic, androgenic, and/or anti-androgenic activity through human estrogen and androgen receptor assays. The toxicity in aquatic organisms and also in humans raises legal and health concerns worldwide. Therefore, many regions (e.g., European Union (EU), The United States of America (USA), Japan and Australia) have UV-Fs and musks under strict legislation in terms of their manufacture and utilization in product formulation. For example, in EU a positive list of 25 organic UV-Fs is accepted in product formulations (1223/2009/EC, 2009), whereas these number is only 16 in USA, 26 in Australia, and 31 in Japan (Sanchez-Quiles and Tovar-Sanchez, 2015). Regarding environmental legislation, the levels of UV-Fs and musks are still not established. However, EHMC, was recently included in the Watch List as a priority pollutant in surface water under the Environmental Quality Standards Directive (2008/105/EC, 2013; Carvalho et al., 2015).

Seafood consumption, owing to its recognized value as part of an healthy diet, plays a significant role in the diet in many European countries, reaching a consumption of around 25,5 kg per capita per year on average in 2014 (Comission, 2016). Fish or seafood consumption has been reported to be the focal food category in the majority of food-related risk/benefit perception and communication studies from the past decades (Jacobs et al., 2015). Indeed, despite providing health benefits, mainly due to the presence of high value protein and $\Omega-3$ fatty acids, seafood consumption can lead to the exposure to certain environmental contaminants and in some cases (of high exposure) can induce health risks, e.g. for methyl mercury (Jacobs et al., 2017). Considering human exposure to UV-Fs and musks, a combination of exposure routes can occur: (i) through the diet, (ii) ingestion/inhalation via environment, and (iii) dermal/inhalation intake. The dietary route, especially through contaminated seafood consumption, plays an important role in the overall human exposure; however, risk analysis is difficult as there are still no admissible limits for the presence of both UV-Fs and musks in food. Nevertheless, in this study an attempt has been made to assess the exposure to both UV-Fs and musks via seafood consumption and to evaluate the potential risks for human health. So far, a similar study for musks is only available for Catalan populations (Trabalon et al., 2015), far from representing all the European population.

The current study, conducted in the framework of the European ECsafeSEAFOOD FP7 project, was focused on the monitoring of UV-filters and musk fragrances in seafood at European scale. Data obtained in this large survey were analysed to answer to the following questions: what are the fish species more exposed to musks and UV-F? what is the magnitude of the exposure? where are located the sites with higher PCPs levels? In addition, the potential risks for human health associated with the exposure to a selection of UV-Fs and musks through seafood consumption was assessed for adults from five EU countries, namely Belgium, Ireland, Italy, Portugal and Spain. For such purposes sixty-two samples of seafood consumed in Europe were collected, covering different habitats, wild vs. farmed organisms, and from EU or extra-EU production.

2. Experimental procedure

2.1. Standards and reagents for UV-filters

2-Hydroxy-4-methoxybenzophenone (BP3; 98% purity), and 2-ethylhexyl 4-(dimethylamino)benzoate (EPABA; 98% purity) were purchased from Alfa Aesar (Heysham, Lancashire, UK). 3,3,5-trimethylcyclohexyl salicylate (HMS; 98% purity) 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (DHMB, 99% purity) and isoamyl-4-methoxycinnamate (IMC, 95% purity) were purchased from TCI (Haven, Zwijndrecht, Belgium). Octocrylene (OC, 98% purity), 2-ethylhexyl 4-methoxycinnamate (EHMC, 100% purity), 2-ethylhexyl salicylate (EHS, 99% purity), hexyl 2-[4-(diethylamino)-2-hydroxybenzoyl]benzoate (DBENZO, 99% purity), 2,4-dihydroxybenzophenone (BP1, 99% purity) and 3-(4-methylbenzylidene)camphor (4-MBC, 98.5% purity), were purchased from Sigma-Aldrich (Steinheim, Germany). The internal standard (IS) Benzophenone-d10 (BPd_{10}-IS, 99 atom % D) was also purchased from Sigma-Aldrich.

Individual standard solutions of UV-filters were prepared in methanol (HPLC grade from Sigma-Aldrich) at concentrations of 2000 μg/mL. Working mixture solutions of 100 μg/mL were prepared in acetonitrile, solvent used in the extraction.

For QuEChERS extraction: acetonitrile (MeCN, gradient grade for HPLC; 78.6% purity), Z-sep+ and anhydrous magnesium sulfate (anhydrous $MgSO_4$; 99.5% purity) were purchased from Sigma-Aldrich; hydrochloric acid (HCl; 37%) and sodium chloride (NaCl; 99.5% purity), were purchased from AppliChem Panreac ITW Co. (Barcelona, Spain). To ensure efficient removal of residual water, anhydrous $MgSO_4$ was treated for 5 h at 500 °C in a muffle furnace. Liquid-liquid extraction solvents n-hexane (gradient grade for HPLC), *tert*-butyl methyl ether (MTBE, pro-analysis), and benzene (pro-analysis) were purchased from Merck (Darmstadt, Germany). Derivatization reagent N,O-bis(trimethylsilyl)trifluoroacetamide with 1% TMCS (BSTFA + 1%TMCS, 99% purity grade) was obtained from Fluka.

Ultra high purity Helium (99.999%) and nitrogen (99.99%) for GC-MS/MS were purchased from Gasin (Maia, Portugal).

2.2. Standards and reagents for musk fragrances

The six polycyclic musk fragrances: 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5*H*)-indanone (DPMI, cashmeran), 4-acetyl-1,1-dimethyl-6-*tert*-butylindane (ADBI, celestolide), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI, phantolide), 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane (ATII, traseolide), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-*(g)*-2-benzopyran (HHCB, galaxolide) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN, tonalide) were supplied by Promochem Iberia (Barcelona, Spain). 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-*(g)*-2-benzopyran-1-one (HHCB-lactone, galaxolidone) was provided by International Flavors & Fragrances Inc. (Barcelona, Spain). The nitro musk fragrances 2,4,6-trinitro-1,3-dimethyl-5-*tert*-butylbenzene (MX, musk xylene) and 1,1,3,3,5-pentamethyl-4,6-dinitroindane (MM, musk moskene) were purchased as 100 μg/mL individual solutions in