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Review

Analytical approaches for the determination of personal care products and evaluation of their occurrence in marine organisms

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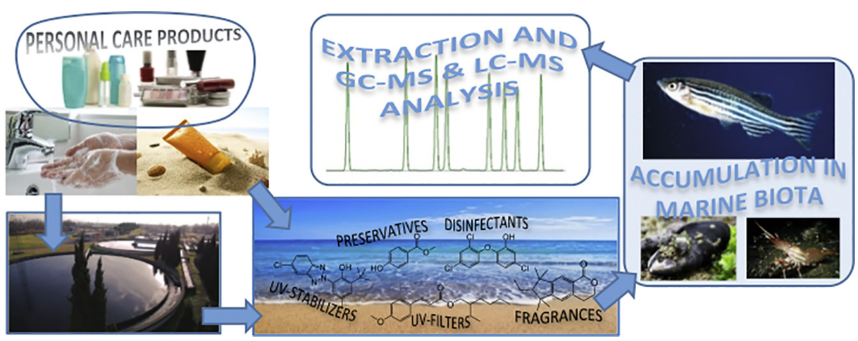
HIGHLIGHTS

- Literature since 2010 on PCP analysis and occurrence in marine biota is reviewed.
- Methods are critically compared, focusing on the complex solute-matrix interactions.
- Concentrations and detection frequencies of PCPs in various organisms are discussed.
- Reviewed data showed significant differences in PCP occurrence among world's areas.
- A limited dataset on PCPs in biota from different world's areas is herein evidenced.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination of the aquatic environment caused by multiple human activities may exert a negative impact on all living organisms. Several contaminants of emerging concern such as personal care products (PCPs) are continuously released into the aquatic environment where they are biologically active and persistent.

Abbreviations: 3-BC, 3-Benzylidene camphor; 3,4 DHB, 3,4-Dihydroxybenzoic acid; 4-HB, 4-Hydroxybenzoic acid; 4-MBC, 4-Methylbenzylidene camphor; ABDI, Celestolide, 1-[6-(1,1-Dimethylethyl)-2,3-dihydro-1,1-dimethyl-1H-inden-4-yl]-ethanone; ACN, Acetonitrile; AHMI, Phantolide, 1-(2,3-Dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl)-ethanone; AHTN, Tonalide, 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene; ATII, Traseolide, 1-[2,3-Dihydro-1,1,2,6-tetramethyl-3-(1-methyl-ethyl)-1H-inden-5-yl]7-ethanone; ATTN, Versalide, 1-(3-Ethyl-5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)-ethanone; AVO, Avobenzone; BP-1, Benzophenone-1; BP-2, Benzophenone-2; BP-3, Benzophenone-3; BP-6, Benzophenone-6; BP-8, Benzophenone-8; BP, Benzophenone; BuP, Butyl-paraben; BzP, Benzyl-paraben; DCM, Dichloromethane; DPMI, Cashmeran; ECs, Emerging compounds; EHMC, Ethylhexyl methoxycinnamate; EHS, 2-Ethylhexyl salicylate; ESI, Electrospray ionization; EtP, Ethyl-paraben; GC, Gas chromatography; GPC, Gel permeation chromatography; HeP, Heptyl-paraben; HHCB, Galaxolide, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran; HMS, Homosalate, (3,3,5-trimethylcyclohexyl) 2-hydroxybenzoate; HRMS, High-resolution mass spectrometry; HSSE, High Speed Solvent Extractor; IAMC, Isoamyl-4-methoxycinnamate; iBuP, Isobutyl-paraben; iPrP, Isopropyl-paraben; LODs, Limits of detection; MA, Musk Ambrette; MAE, Microwave assisted extraction; MeOH, Methanol; MeP, Methyl-paraben; MK, Musk Ketone; MM, Musk Moskene; MS, Mass spectrometry; MS/MS, Tandem mass spectrometry; MSPD, Matrix solid phase dispersion; MT, Musk Tibetene; MX, Musk Xilene; OC, Octocrylene; OD-PABA, 2-Ethylhexyl 4-dimethylaminobenzoate; OH EtP, Ethyl protocatechuate; OH MeP, Methyl protocatechuate; PCPs, Personal care products; PhP, Phenyl-paraben; PLE, Pressurized liquid extraction; PrP, Propyl-paraben; PSA, Primary and secondary amine; QuEChERS, Quick, Easy, Cheap, Effective, Rugged and Safe; SPE, Solid phase extraction; TCC, Triclocarban; TCS, Triclosan; UAE, Ultrasound assisted extraction; UHPLC, Ultra high performance liquid chromatography; UV, Ultraviolet; UV-9, 2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl) phenol; UV-234, 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenyl-ethyl)-phenol; UV-320, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-phenol; UV-326, 2-(5-Chloro-2-benzotriazolyl)-6-tert-butyl-p-cresol; UV-327, 2,4-Di-*t*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-phenol; UV-328, 2-(20-Hydroxy-30,50-di-tert-amylphenyl)-benzotriazole; UV-329, 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol; UV-531, 2-Hydroxy-4-octyloxybenzophenone; UVF, UV filters; UVS, UV light stabilizers; UV-P, 2-(2-Hydroxy-5-methylphenyl)-benzotriazole; WWTPs, Wastewater treatment plants.

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This work reviews the current knowledge, provided by papers published after 2010 and indexed by SciFinder, Scopus, and Google search engines, about the determination and occurrence of PCPs in marine biota. Analytical methodologies have been critically reviewed, emphasizing the importance of green and high-throughput approaches and focusing the discussion on the complexity of the solute-matrix interaction in the extraction step, as well as the matrix effect in the instrumental determination. Finally, the worldwide distribution of PCPs is surveyed, taking into account the concentrations found in the same organism in different marine environments. Differences among various world areas have been highlighted, evidencing some critical aspects from an environmental point of view.

Contents

1. Introduction

In recent years, pollution of aquatic environment is of great concern as it potentially adverse affects human health or ecosystem security. This is due to the large variety of suspect pollutants that have harmful effects over aquatic life. In fact, the 2030 Agenda for Sustainable Development of the UN has a key topic named “life below water” (*United Nations General Assembly, Resolution 25 September*, 2015), and one aspect of this topic is the reduction of marine pollution affecting aquatic organisms. There is considerable evidence of the negative effect that the occurrence of a broad spectrum of compounds, both natural and synthetic, has produced on aquatic life. The list of suspected contaminants is long, so humans and animals are likely to be exposed not to a single agent, but to a mixture of multiple compounds (Backhaus et al., 2011; Petersen et al., 2014).

There are regulatory frameworks to manage potential sources of pollution that require monitoring of a number of “priority” organic contaminants in the aquatic environment (*2013/39/EC Directive of the European Parliament and of the Council of August 2013*, n.d.). Other compounds (e.g. 2-ethylhexyl 4-methoxycinnamate and butylated hydroxytoluene) have been recently included in the watch list of substances to be monitored in the European Union within the topic of water policy (*2015/495 Commission Implementing Decision*, 2015). However, there are a huge number of contaminants (largely organic compounds) that are not currently subject to the same degree of regulation in Europe. The same situation occurs elsewhere in the world. The US Environmental Protection Agency (EPA), has recently promoted studies aimed at identifying constituents of personal care products (e.g., cosmetics, soaps, hair sprays and shampoos) with potential endocrine disrupting activity, so as to include them in the contaminant candidate list (CCL-3). The constituents under examination are phthalates, parabens, ultraviolet (UV) filters, synthetic polycyclic musks, and antimicrobials. While some threshold values have already been established for some organic micropollutants, guide values are not yet available for these emerging contaminants (ECs), due to the lack of knowledge on the environmental toxicity, impact and behavior, as well as limited monitoring data. Moreover, from an ecotoxicological point of view, a realistic scenario should consider that ECs are present in the environment as a complex mixture of components, thus posing a possible risk of increased toxicity owing to synergism or antagonism phenomena (Bebianno and Gonzalez-Rey, 2015).

For this reason, ECs should be considered as compounds of particular environmental concern. This term is used not only for newly developed chemicals, but also for compounds that only recently been have classified as contaminants (*CDC, Third national report on human exposure to environmental chemicals*, 2005; Lapworth et al., 2012). ECs include a wide array of different compounds, as well as metabolites and transformation products. Among “new” organic pollutants, personal care products (PCPs) are a worrying group of compounds, due to their toxic effects on aquatic biota (Hall et al., 2007; Tolls et al., 2009). Currently, some of these pollutants are considered pseudo-persistent owing to their continuous release into the environment. PCPs may be absorbed by the body and excreted or washed off after their application and a significant amount of these products goes down the drain and enters in wastewater treatment plants (WWTPs). The effluents of these systems are considered the greatest input to aquatic environment contamination by anthropogenic pollutants, and particularly of recalcitrant PCPs (Brausch and Rand, 2011). The environmental fate of these substances depends mainly on their physicochemical properties, that play an important role in the occurrence in marine environment, such as water solubility, adsorption behavior, volatility and degradability, which is affected by microorganisms (biological degradation) present in WWTPs, surface waters, and soils.

PCPs are present primarily at trace levels in the environment. However, recent studies have indicated that many of them are environmentally persistent, bioactive, and exhibit high bioaccumulation potential in aquatic organisms (Cortez et al., 2012). Moreover, numerous PCPs (including triclosan, paraben preservatives and ultraviolet filters) evidenced endocrine disrupting effects in aquatic organisms and thus