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Ecotoxicity of two organic UV-filters to the freshwater caddisfly *Sericostoma vittatum*☆

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ABSTRACT

Organic ultraviolet filters (UV-filters) used for protection against radiation in personal care products and other materials (e.g. textiles, plastic products) are considered emerging contaminants of aquatic ecosystem. Benzophenone-3 (BP3) and 3-(4-methylbenzylidene)camphor (4-MBC) are the most commonly used organic UV-filters and have been reported in freshwater environments due to contamination through discharges from wastewater treatment plants and swimming pools or by direct contamination from recreational activities. Our aim was to evaluate the ecotoxicological effects of these UV-filters using the freshwater caddisfly *Sericostoma vittatum*' biochemical biomarkers and energy processing related endpoints (feeding behaviour, energy reserves and cellular metabolism). In laboratory trials, both compounds induced feeding inhibition of *S. vittatum* at 3.55 mg/kg of BP3 and at concentrations ≥2.57 mg/kg of 4-MBC, decreased carbohydrates content at 3.55 and 6.95 mg/kg of BP3 and 4-MBC respectively, and increased total glutathione levels at concentrations ≥1.45 and 1.35 mg/kg of BP3 and 4-MBC respectively. No significant effects were observed on endpoints associated with oxidative stress, antioxidant defences, phase II biotransformation or neurotoxicity after exposure to the two UV-filters. Our results show that environmental relevant concentrations of BP3 and 4-MBC, can negatively impact freshwater insects and demonstrate the importance of monitoring the ecological effects of organic UV-filters using non-model invertebrate species.

1. Introduction

Organic ultraviolet filters (UV-filters) absorb ultraviolet radiation (UVA-UVB) and are commonly used to protect skin from sun radiation and to protect a variety of materials from degradation. They are present in textiles, plastic materials, and in several personal care products such as sunscreens, lotions, shampoos and makeup products (Díaz-Cruz et al., 2008; Pedrouzo et al., 2011). After being used, these compounds can reach the aquatic ecosystems, namely streams and rivers by washing-off from skin and clothes of beachgoers during recreational activities, by discharges of swimming pools and sewage or due to insufficient removal of wastewater treatment plants (WWTP) (Brausch and Rand, 2011; Díaz-Cruz et al., 2008; Giokas et al., 2005; Golovko et al., 2014).

UV-filters have been detected worldwide both in surface and ground waters, as observed by several studies in Spain (Rodil et al., 2008; Román et al., 2011), Korea (Jeon et al., 2006), Switzerland (Giokas et al., 2005), Australia (Liu et al., 2012), and Japan (Kameda et al., 2011). UV-filters concentrations of up to 1040 ng/L were found in river waters (Kameda et al., 2011) and 4381 ng/L in lake waters (Rodil et al., 2009). Also, concentrations of up to 6812 ng/L (Tsui et al., 2014) and 621 ng/L (Román et al., 2011) were found in seawater and tap water, respectively. In solid matrices, UV-filters have been detected in concentrations of up to 0.128 mg/kg dry weight (dw) in sediments from coastal areas (Amine et al., 2012), 0.9 mg/kg (dw) in lake sediments (Rodil and Moeder, 2008), 27.7 mg/kg (dw) in sewage sludge (Plagellat et al., 2006), 0.635 mg/kg (dw) and 2.4 mg/kg (dw) in sediments from lotic ecosystems (Kameda et al., 2011; Gago-Ferrero et al., 2011).

Given its continuous application and consequent ubiquity in the

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environment, concerns of deleterious effects of UV- filters to aquatic biota have been raised and an evaluation of their ecotoxicity is vital (Sánchez-Quiles and Tovar-Sánchez, 2015; Tsui et al., 2014). It was demonstrated that UV-filters affected reproduction of several invertebrate species. As examples, reproduction of the oligochaete *Lumbriculus variegatus* was reduced after 28 days of exposure to 3-benzylidene-camphor (3-BC) and 3-(4-methylbenzylidene) camphor (4-MBC) (Schmitt et al., 2008), in the crustacean *Daphnia magna,* exposure to 3-BC during 21 days caused the reduction of number of neonates per adult (Sieratowicz et al., 2011), in the snail *Potamopyrgus antipodarum,* the number of unshelled embryos per snail increased after 56 days of exposure to 3-BC and 4-MBC (Schmitt et al., 2008) and in the snail *Melanoides tuberculata* the number of embryos per snail decreased after 28 days of exposure to ethylhexyl-methoxycinnamate (EHMC) (Kaiser et al., 2012). Delayed development was also observed in the dipteran *Chironomus riparius* exposed to Benzophenone-3 (BP3) and 4-MBC (Campos et al., 2017) while decreases of *D.magna* somatic growth were observed after 21 days of exposure to 4-MBC, 3-BC and EHMC (Sieratowicz et al., 2011). However, absence of effects during exposure to UV-filters were also reported. Exposure to octocrilene and butyl-methoxydibenzoylmethane (B-MDM) during 28 days did not affect the mean emergence time of *C. riparius* or the number of embryos per snail of *M. tuberculata* (Kaiser et al., 2012). Also, 21 days exposure to 4-MBC and BP3 has been shown to cause no effects on the number of neonates produced by *D. magna* (Sieratowicz et al., 2011).

Nevertheless, due to their physico-chemical properties, namely an elevated K_{ow} and low water solubility, organic UV-filters tend to accumulate in biota and sediments (Brausch and Rand, 2011; Rodil and Moeder, 2008) especially near fluvial beaches, coastal areas and effluents, which calls for an ecotoxicological evaluation of these compounds using non-model benthic species. This assessment should comprise responses at different levels of biological organization in order to provide clues to organismal and population level effects.

Thus, the main objective in this study was to address the potential effects of organic UV-filters present in sediments using the freshwater caddisfly *Sericostoma vittatum* (Rambur) as a test species. *S. vittatum* is widely distributed in streams and rivers across the Iberian Peninsula with an important role in the fragmentation of allochthonous organic matter in streams (Campos et al., 2014; Feio and Graça, 2000). Additionally, *S. vittatum* has been used previously in ecotoxicity studies (Campos et al., 2014, 2016; Pestana et al., 2009b) and given their close contact to sediments and detritivore feeding habits is a potential indicator of sediment contamination by lipophilic compounds such as organic UV-filters. This ecotoxicological evaluation is focused on feeding rate as an organismal endpoint, and on sub-cellular endpoints including energy reserves, energy consumption and biochemical parameters measured on *S. vittatum* larvae exposed to a gradient of environmentally relevant concentrations of organic UV-filters.

Feeding inhibition has been recognized as a general stress response to different contaminants, used as a early warning indicator and a complement to traditional parameters such as growth and reproduction especially important when dealing with organisms with a long life-cycle (Maltby et al., 2002; Pestana et al., 2007). Feeding behaviour has thus been used as an ecotoxicological relevant endpoint in a variety of aquatic invertebrate detritivores organisms including caddisflies (Campos et al., 2016; Pestana et al., 2009b; Rodrigues et al., 2016). Furthermore, energy parameters can be also used to better understand the long-term effects of altered energy intake and expenditure (respiration/detoxification). This is because detoxification processes, decrease food intake and assimilation and also, metabolic changes contribute for altered energy homeostasis in organisms under stressful conditions (De Coen and Janssen, 2003; Moolman et al., 2007; Sokolova et al., 2012; Sokolova, 2013). In this sense, we have also assessed effects of UV-filters exposure on energy reserves in terms of sugars, lipids and protein contents, as well as, energy consumption by measuring the activity of ETS (electron transport system) as a proxy for cellular metabolism.

Moreover and since it is known that UV-filters can increase the production of Reactive Oxygen Species (ROS) and induce alterations in antioxidant defences and/or cause oxidative damage (Gao et al., 2013; Liu et al., 2015) biochemical biomarkers chosen as sub-organismal endpoints in the present study included lipid peroxidation (LPO); antioxidant enzymes (catalase - CAT), phase II biotransformation enzyme (glutathione-*S*-transferase - GST) and non-enzymatic antioxidant defences (total glutathione - tGSH).

Finally, we also assessed the effects of UV-filters exposure on Acetylcholinesterase activity (AChE) as indicator of neurotoxicity. Despite no information on effects of UV-filters on AChE, this enzyme activity has been linked with behavioural parameters such as feeding and locomotion (Mesquita et al., 2011; Xuereb et al., 2009) and effects using AChE activity as indicator of neurotoxic have been reported to emergent contaminants (Mesquita et al., 2011), namely in caddisflies species (Pestana et al., 2014; Pradhan et al., 2016).

For this ecotoxicological assessment we selected BP3 and 4-MBC, that correspond to different classes of UV-filters (benzophenones and camphor derivatives, respectively) which are two of the most frequently detected UV-filters in the aquatic environment (Balmer et al., 2005; Gago-Ferrero et al., 2011; Kameda et al., 2011; Ramos et al., 2015).

2. Methods

2.1. Caddisflies collection and maintenance

S. vittatum larvae (size: 18.99 (± 3.87 (SD)) mg wet weight) were collected from a low order stream in central Portugal (40°06′N, 8°14′W) using a hand net. Organisms were maintained under laboratory conditions (20 ± 1 °C and light-dark cycle of 16:8 h) during one week, in American Society for Testing Materials hard water medium (ASTM) (ASTM, 1980), previously burnt (500 °C for 4 h) inorganic fine sediment (<1 mm) and alder leaves (*Alnus glutinosa*) as food which were previously conditioned during one week in 1500 mL of local river water with aeration and in laboratory conditions (20 ± 1 °C, 16:8 h light: dark photoperiod).

2.2. Chemicals

2-hydroxy-4-methoxybenzophenone (or benzophenone-3, BP3; CAS No. 131-57-7; purity ≥98%) and 3-(4-methylbenzylidene) camphor (4-MBC; CAS No. 36861-47-9, purity ≥98%) were obtained from Sigma-Aldrich (Portugal). Physico-chemical properties are presented in Table 1. Stock solutions and subsequent gradient of UV-filters experimental solutions of both compounds were prepared in ethanol (96%) due to low water solubility (Table 1).

2.3. Sediment dosing

Artificial sediment was composed of 75% inorganic fine sediment (<1 mm), 20% kaolin, 5% α-cellulose and 0.1% calcium carbonate. Tests were conducted using 180 mL glass vessels and each replicate contained 50 g dw of sediment. Ten mL of UV-filter solutions (prepared in ethanol) were used to dose the sediment which were mixed thoroughly and then allowed to evaporate during 24 h. To prepare the solvent controls 10 mL of 96% ethanol