



Assessing seasonal variation of synthetic musks in beach sands from Oporto coastal area: A case study[☆]



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ABSTRACT

Synthetic musk compounds are widely used in the formulation of several cosmetics, personal care and household products. Due to their massive and widespread use, together with some health concerns, they are considered emerging pollutants and have been detected in different environmental compartments.

This study focused on the evaluation of the concentration of synthetic musks (five nitro, five polycyclic and one macrocyclic musks) in beach sands, from Oporto coastal area (Portugal), contributing to the enhancement of the knowledge of levels, trends and behaviour of these compounds in this particular matrix. To accomplish this task, a QuEChERS methodology (“Quick, Easy, Cheap, Effective, Rugged, and Safe”) coupled to gas chromatography-mass spectrometry (GC-MS) was successfully used to determine synthetic musks from beach sand. The chosen methodology proved to be suitable, achieving satisfactory results for precision (relative standard deviation values below 15%), accuracy (average recovery of 97%) and limits of detection (below 38 pg g^{-1}).

Synthetic musks were detected in all 45 analysed samples, in concentrations ranging from 0.01 to 27 $\text{ng g}^{-1}_{\text{dw}}$. Tonalide (93%), exaltolide (89%) and galaxolide (76%) were the most commonly detected compounds, but also those detected in higher concentrations (up to 27 $\text{ng g}^{-1}_{\text{dw}}$). Musk ambrette, moskene, tibetene and xylene were not detected in any of the samples. Higher concentrations were as expected detected in the Summer (total average concentration of 9.21 $\text{ng g}^{-1}_{\text{dw}}$), namely in samples from Valadares Sul (29 $\text{ng g}^{-1}_{\text{dw}}$), Francelos (25 $\text{ng g}^{-1}_{\text{dw}}$) and Castelo do Queijo (25 $\text{ng g}^{-1}_{\text{dw}}$).

The preliminary environmental risk assessment study based on the determination of hazard quotients revealed that the presence of analysed compounds (tonalide, galaxolide and musk ketone) seems to pose no risk to the studied environmental compartment.

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1. Introduction

Synthetic musks are organic compounds produced in large quantities and extensively used in daily human life in a wide variety of cosmetics, personal care and household products (makeup, perfumes, body lotions, deodorants, soaps, shampoos, fabric softeners, air fresheners, etc.) as fragrances and fixative compounds (Mottaleb et al., 2012). They are usually classified according to their chemical structure in nitromusks, polycyclic, macrocyclic and alicyclic musks.

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Nitromusks were considered potential toxic compounds and most of them were phased out from the European cosmetic market, as musk ambrette (MA), musk moskene (MM) and musk tibetene (MT). Musk ketone (MK) and musk xylene (MX) are the only nitromusks that can still be used, but with some restrictions (European Parliament, 2009) because they are suspected of carcinogenic effects at high concentrations (Polo et al., 2007). Polycyclic musks dominate the global market, but recently there were some studies that indicate that such compounds may cause oestrogenic/anti-oestrogenic effects (Huang et al., 2016; Hu et al., 2011; Toivanen et al., 2008; Yamauchi et al., 2008). Macrocyclic musks were introduced in the market as an alternative to polycyclic ones. They present a similar structure to those of natural origin (i.e. large ringed ketones and lactones) and due to their relatively high cost of production they still represent only a small fraction of the market

(around 4%). Alicyclic musks, the fourth generation of musks, also known as linear musks (Arbulu et al., 2011), are still rarely used in personal care products.

Synthetic musks are continuously released into the environment through direct routes as recreational activities (e.g. swimming and bathing in beaches) (Groz et al., 2014) and indirect routes (mainly via effluents discharges from wastewater treatment plants - WWTPs) (Homem et al., 2015a). In fact, these emerging compounds have been detected in different environmental compartments, such as surface water (Hu et al., 2011; Clara et al., 2011; Villa et al., 2012; Lange et al., 2015), sea water (Nakata et al., 2012; Lee et al., 2014) and air (Kallenborn et al., 1999; Peck and Hornbuckle, 2006). Furthermore, due to their lipophilic, persistent and bioaccumulative nature, synthetic musks are easily adsorbed by particular organic matter, accumulating in soil and sediments (Zeng et al., 2008; Martinez-Giron et al., 2010; Hu et al., 2011; Wang et al., 2013; Chen et al., 2014; Huang et al., 2016). Few studies have been conducted to assess the occurrence of synthetic musks in sediment samples, especially in coastal sediments. In fact, only six studies were found on marine sediment (Rubinfeld and Luthy, 2008; Zeng et al., 2008; Sumner et al., 2010; Subedi et al., 2014; Lee et al., 2014; Huang et al., 2016) and none specifically in beach sands. For that reason, there is a lack of global monitoring data on sedimentary concentrations of these compounds.

Therefore, the aims of the present research were to investigate the application of a Quick, Easy, Cheap, Rugged and Safe (QuEChERS) extraction coupled to gas chromatography-mass spectrometry (GC-MS) analysis to determine synthetic musks (five nitro, five polycyclic and one macrocyclic musks) in beach sands. Furthermore, the results of this study will be important to characterize the musk residues in marine sediment (beach sand), to understand their distribution in the Oporto coastal area (Portugal) and to assess possible hazardous through a preliminary environmental risk assessment approach.

2. Material and methods

2.1. Chemicals and materials

All polycyclic musks standards (cashmeran, DPMI; celestolide, ADBI; galaxolide, HHCB; phantolide, AHMI and tonalide, AHTN) were obtained with a purity of 99% from LGC Standards (Barcelona, Spain), with the exception of HHCB, which contains 25% of diethyl phthalate (DEP). LGC Standards also provided 10 mg L⁻¹ solutions in cyclohexane of the nitromusks tibetene (MT) and moskene (MM). Musk ambrette (MA) and musk ketone (MK) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) with 99% e 98% purity, respectively. 100 mg L⁻¹ solution in acetonitrile of musk xylene (MX) was purchased from Sigma-Aldrich (St. Louis, MO, EUA), as well as exaltolide (EXA; ≥95% purity). The surrogate standards musk xylene-d₁₅ and tonalide-d₃ were acquired from Dr. Ehrenstorfer GmbH (Augsburg, Germany) as individual 100 ng μL⁻¹ solutions in acetone and iso-octane, respectively. From these standards, individual stock solutions of 10 g L⁻¹ were prepared in cyclohexane and then, a final mixed stock solution was prepared in acetonitrile. All solutions were preserved at -20 °C in the absence of light.

For the QuEChERS preparation, sodium acetate were purchased from Sigma-Aldrich, PSA and DSC-18 from Supelco (Belleville, PA, USA) and anhydrous magnesium sulphate from Panreac (Barcelona, Spain). The MgSO₄ was baked at 450 °C overnight before use. All solvents used, namely acetonitrile and cyclohexane, were acquired from VWR (Fontenay-sous-Bois, France) with analytical grade.

2.2. Sampling area

Samples were collected from 23 different beaches along the Oporto's coastal area, in an extension of about 35 km, according to Fig. 1. Some additional information about the sampling points can be found in Table S1 (Supporting Information).

Samples were collected in the end of Summer (September 2013) and in the end of Winter (March 2014). During that Summer, the average temperature was around 20 °C, 71% of humidity and 0.2 mm of precipitation, while in the Winter the temperature was around 11 °C, 84% of humidity and 0.3 mm of precipitation. Dry sand samples were collected in three equidistant points along the beach (about 1 m above the high tide level) at a 5 cm depth, after removing impurities such as stones and gravels (mesh 18–50). Sand was placed in sterile plastic bags in a cooler for transport to the laboratory, where they were kept at -20 °C until extraction.

2.3. Sample extraction

The analytical methodology used in this work (QuEChERS-GC-MS) was based on a previously developed by Homem et al. (2013). In brief, 5 g of sample was weighted into disposable polypropylene conical tubes and spiked with the mixture of surrogate standards (AHTN-d₃ and MX-d₁₅ at 5 ng g⁻¹). Then, 3 mL of acetonitrile was added and the mixture was vortexed for 3 min and sonicated for 10 min in an ultrasonic bath with 40 kHz (J.P. Selecta, Barcelona, Spain). Afterwards the first QuEChERS, consisting of 2400 mg of MgSO₄ and 750 mg of NaCH₃COO was added to the tube and the mixture was once more vortexed for 3 min and then, centrifuged at 3700 rpm (2280 g) for 10 min. The supernatant was transferred to a tube containing the second QuEChERS (180 mg of MgSO₄, 60 mg of PSA and 30 mg of C₁₈) and the procedure mentioned above was repeated. The resulting supernatant was placed in an amber conical vial and it was dried under a gentle nitrogen stream and reconstituted in 50 μL of acetonitrile before GC-MS analysis. All the samples were analysed in duplicate.

2.4. Instrumental analysis

A Varian Ion Trap GC 240-MS system (Walnut Creek, CA, USA) was used for the chromatographic analyses. The detector operated in the electron ionization (EI) mode (70 eV) and the system was controlled by Varian MS workstation v. 6.9.3 software. For the separation of the target compounds, a J&W CP-Sil 8 CB capillary column (50 m × 0.25 mm i.d., 0.12 μm) from Agilent Technologies (Santa Clara, California, EUA) was used. Helium (99.999%), at a constant flow of 1.0 mL min⁻¹, was employed as a carrier gas. The oven temperature was held for 1 min at 60 °C and then, programmed to increase at 6 °C min⁻¹ to 150 °C (hold for 10 min), then 6 °C min⁻¹ to 225 °C and finally 20 °C min⁻¹ to 300 °C (hold for 2.5 min), with a total analysis time of 45 min. 1 μL was injected in splitless mode, with the split valve closed for 5 min. Temperatures of manifold, ion trap, and transfer line were maintained at 50, 250, and 250 °C, respectively and the filament emission current was set at 50 μA. For quantitative analysis, the selected ion storage (SIS) mode was applied and the retention times and the quantifier/qualifier ions used were shown in Table 1.

2.5. Moisture content

The moisture content of the beach sands was determined weighing 5 g of each sample, which was placed in a thermostatic oven at 80 °C. Samples were weighed every 24 h, until constant mass was verified. The mass difference corresponds to the amount of water.

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