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Inputs and distributions of synthetic musk fragrances in an estuarine and coastal environment; a case study

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Synthetic musks were determined in coastal environmental compartments along an estuarine transect indicating their ubiquitous occurrence in transitional waters.

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ABSTRACT

Synthetic musks are ubiquitous contaminants in the environment. Compartmental distributions (dissolved, suspended particle associated and sedimentary) of the compounds throughout an axial estuarine transect and in coastal waters are reported. High concentrations of Galaxolide® (HHCB) and Tonalide® (AHTN) (987–2098 ng/L and 55–159 ng/L, respectively) were encountered in final effluent samples from sewage treatment plants (STPs) discharging into the Tamar and Plym Estuaries (UK), with lower concentrations of Celestolide® (ADBI) (4–13 ng/L), Phantolide® (AHMI) (6–9 ng/L), musk xylene (MX) (4–7 ng/L) and musk ketone (MK) (18–30 ng/L). Rapid dilution from the outfalls is demonstrated with resulting concentrations of HHCB spanning from 5 to 30 ng/L and those for AHTN from 3 to 15 ng/L. The other musks were generally not detected in the estuarine and coastal waters. The suspended particulate matter (SPM) and sedimentary profiles and compositions (HHCB:AHTN ratios) generally reflect the distribution in the water column with highest concentrations adjacent to sewage outfalls.

1. Introduction

Traditionally, the focus of most environmental monitoring in water pollution control programmes has been devoted to the conventional priority pollutants, especially different groups collectively known as 'persistent, bioaccumulative and toxic' (PBT), 'persistent organic pollutants' (POPs) or 'bioaccumulative chemicals of concern' (BCCs). However, there has been a growing realisation of the occurrence of 'emerging' trace organic chemical pollutants in the environment (Daughton and Ternes, 1999). Many of these chemicals are not new and have been present in wastewaters for many decades, however, they are only now being recognised as potentially hazardous to the environment (Smital et al., 2004; Ellis, 2006). Their occurrence in receiving waters relates to the lack of removal processes in sewage treatment plants (STPs) which are designed principally to control suspended solids emissions and oxygen demand of the final effluent.

Amongst them, synthetic musk compounds first began to be identified in environmental samples over 20 years ago. Yamagishi et al. (1983, 1981) conducted probably the first comprehensive monitoring investigation which identified the nitro-musks, musk xylene and musk ketone in freshwater, fish, marine shellfish, riverwater and STP effluents. However, it was not until the late 1990s that similar studies of the polycyclic musks began to be undertaken regularly. The environmental occurrence and available datasets of musk fragrances have been reviewed by Rimkus (1999) and the analytical protocols recently by Bester (2009).

Synthetic musks are mainly components of personal care products and household cleaners. Musks are a class of fragrance ingredient which not only contribute to the distinctive odours of consumer products, such as perfumes, eau de toilette, shampoos, etc., but also serve to maintain the integrity of the products scent (Garcia-Jares et al., 2002; Reiner and Kannan, 2006). The term synthetic musk encompasses three chemical groups – nitro-musks, polycyclic musks and macrocyclic musks. Nitro-musks are comprised of methylated nitrates and acetylated benzene rings, whilst polycyclic musks are acetylated and highly methylated pyran, tetralin and indane skeletons (Daughton and Ternes, 1999; Bester, 2009). Macrocyclic musks are derived from natural

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odourants (Abramsson-Zetterberg and Slanina, 2002) and are large ringed (comprising often 10–15 carbons) ketones or lactones. The greater cost of preparing macrocyclic musks currently limits their more widescale usage (Abramsson-Zetterberg and Slanina, 2002). The production of all synthetic musks for use in consumer products is enormous. Between 1996 and 1998, production of HHCB and AHTN increased from 5600 tonnes/y to 8000 tonnes/y worldwide (Rimkus, 1999; Reiner and Kannan, 2006).

Personal care products enter STPs and the aquatic environment through a variety of direct and indirect routes. For example, directly from showering, bathing or cleaning and from industrial wastes, and indirectly from leaching at landfill sites (Slack et al., 2007). It is the 'down-the-drain' route that is considered to be the primary environmental pathway for polycyclic musks into aquatic systems (Salvito et al., 2004; Reiner et al., 2007; Horii et al., 2007). Because of this, recent studies have examined concentrations of AHTN and HHCB in influents and effluents at STPs in Europe and North America (Simonich et al., 2002; Artola-Garicano et al., 2003; Ricking et al., 2003; Peck and Hornbuckle, 2003; Bester, 2009), sewage sludge (Stevens et al., 2003; Difrancesco et al., 2004) and organisms (Muller et al., 1996; Gatermann et al., 1999; Kannan et al., 2005). With increasing concern for personal care and health, the production and use of many of these emerging contaminants has increased, thus increasing their discharge into the environment (e.g. rivers, lakes, coasts), as reflected by recent studies (Peck and Hornbuckle, 2006; Moldovan, 2006). At present, however, very few studies have looked in detail at concentrations in suspended particulate matter (SPM) and sediments (Winkler et al., 1998; Rimkus, 1999).

The present research examines the occurrence of seven synthetic musks [Galaxolide® (HHCB), Tonalide® (AHTN), Phantolide® (AHMI), Celestolide® (ADBI), Musk Ketone (MK), Musk Xylene (MX) and Pentadecanolide®], in surface waters, SPM and sediments through an axial transect of the Tamar Estuary (UK) and the adjacent coastal environment, in order to assess the sources, distributions and fates in transitional waters. Extracts of final effluent samples from the major STPs discharging in the area, as well as estuarine and coastal water samples were analysed by programmable temperature vaporisation (inlet)-gas chromatography mass spectrometry (PTV-GC/MS) to establish the occurrence of musks from STP outfalls to estuarine and coastal waters.

2. Materials and methods

2.1. Area of study and sampling strategy

The Tamar Valley is located on the southwest peninsula of Cornwall and Devon, UK (Fig. 1). Altogether, the River Tamar and its tributaries drain over 1700 km^2 (Evans et al., 1993). Anthropogenic influences on the Tamar estuary include: agricultural land runoff, drainage from disused mining sites (Langston et al., 2003); and discharges from STPs serving the city of Plymouth and the surrounding areas. Other contaminant inputs occur from commercial and military shipping activities in the area.

The sampling strategy was developed and refined following a preliminary pilot study on the 21st June 2007, where surface water samples collected at 5 stations in the Tamar estuary demonstrated the occurrence of synthetic musk fragrances. On the 16th July 2007, further samples were collected at 11 stations covering an axial transect in the lower part of the Tamar estuary. These included sites adjacent to the sewage outfall at Ernesettle STP (station 2) through the estuary to the estuary mouth at West Mud (station 9). Two coastal stations were also sampled (stations 10 and 11 at Barn Pool and Plymouth Sound, respectively). Samples were collected at high tide and low tide in June and July, respectively, in order to estimate any influence of the tidal regime in the study area. Surface water samples (2 L) were obtained at 2 m depth with 2.5 L Winchester amber glass bottles using a custom-made stainless steel and Teflon sampling device. Surface sediment samples were collected using a Van Veen grab adjacent to STP outfalls (stations: 2, 3, 4, 8 and 11). Lastly, final effluent samples (1 L) were collected at the 4 main STPs which discharge into the Tamar and Plym estuaries, as well as to Plymouth Sound, surrounding the estuarine and coastal stations, on the 21st July 2007. Fig. 1 shows the locations sampled in both June and July 2007.

Samples were taken in triplicate at selected stations to evaluate the variability of the measurements in the field. Field blanks were also analysed. Samples were processed within 24 h on return to the laboratory.

2.2. Chemicals

High-purity standards including 1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (MX, Musk Xylene), 1-*tert*-butyl-3,5-dimethyl-2,5-dinitro-4-acetylbenzene (MK, Musk Ketone), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-(g)-2-benzopyrane (HCCB, Galaxolide®), 7-acetyl-1,1,3,4,4,6-hexa-methyltetraline (AHTN, Tonalide®), 4-acetyl-1,1-dimethyl-6-*tert*-butylindane (ADBI, Celestolide®), (1,1,2,3,3,6-hexamethyle-indan-5-yl)-ethanone (AHMI, Phantolide®) and AHTN-d_3 were purchased from Qmx Laboratories (UK). 1-oxa-2-cyclohexadecanone (Pentadecanolide®), Chrysene-d_{12}, and Pyrene-d_{10} were purchased from Sigma–Aldrich (UK). All solvents, including dichloromethane, hexane, acetone, methanol and ethyl acetate were of analytical/HPLC grade from Rathburn Chemicals Ltd. (UK) and were used without further purification. Trace analysis grade hydrochloric acid (37%) and nitric acid (70%) were purchased from Fisher Scientific (UK).

2.3. Extraction of coastal, estuarine and final effluent samples

Samples were filtered through 1.2 μm GF/C filters (Whatman, UK) and were acidified to pH 2.5–3 with pure hydrochloric acid in order to preserve the samples. Prior to solid phase extraction, samples were spiked with 40 μL of a solution containing isotopically labelled internal standards AHTN-d_3 and Chrysene-d_{12} (10 ng/μL). Sample extraction was performed using (500 mg) OASIS® HLB cartridges (Waters, Hertfordshire, UK) using a VacMaster® SPE manifold. Cartridges were conditioned with 5 mL of a mixture ethyl acetate-dichloromethane (1:1), followed by 5 mL methanol, and finally 10 mL of deionised water (Milli-Q®) at pH 3. The samples (1 L or 2 L) were drawn, under vacuum, through the cartridge at a regulated flow rate of 10 mL min^{-1}. Following extraction, the cartridges were dried using N_2 gas and subsequently eluted (under gravity) with 12 mL of a mixture of ethyl acetate, dichloromethane and methanol (2:2:1). The extracts were passed through pre-packed sodium sulphate columns (2.5 g Na_2SO_4 cartridges, Kinesis Ltd., UK) to remove any residual traces of water. A clean-up step was employed when examining sewage final effluent samples. Extracts were eluted through 2 g of 2,3-dihydroxypropoxypropyl (DIOL, International Sorbent Technology, Kinesis Ltd., UK) cartridges conditioned with 5 mL of a mixture of ethyl acetate, dichloromethane and methanol (2:2:1). Extracts were recovered by gravity with 8 mL of the solvent mixture. Extracts were reduced in volume using N_2 gas to approximately 300 μL and transferred to GC micro-vials and further reduced to 100 μL prior to injection into the PTV-GC/MS.

2.4. Extraction of SPM and sediment samples

SPM was recovered from estuarine, coastal and final effluent water samples by filtration (1–2 L). The GF/C filters containing the suspended material were dried in a 40 °C oven for 30 min, then weighed, placed in sintered thimbles and spiked with 40 μL of internal standard solution (AHTN-d_3 and Chrysene-d_{12}). A Soxhlet apparatus was employed to perform 12 h extraction cycles with 200 mL of a mixture of hexane and dichloromethane (1:1). The extracts were concentrated to approximately 1 mL using a rotary evaporator. Anhydrous sodium sulphate (Na_2SO_4, Sigma–Aldrich, UK) was added to the extracts to remove residual traces of water and were subsequently filtered through glass wool to remove any residual particulate matter. The extracts were further reduced using N_2 gas to approximately 300 μL, transferred to GC micro-vials and were finally reduced to 100 μL prior to PTV-GC/MS analysis

Sediment samples were freeze-dried using an LSL Secfroid Freeze-drier apparatus (LSL Secfroid, Aclens, Switzerland) and sieved through 250 μm metal mesh. 3 g of sediment were placed in sintered thimbles containing glass wool and spiked with 40 μL of the internal standard solution (10 ng/μL). Soxhlet extraction conditions were the same as for SPM extractions. Sodium sulphate (Na_2SO_4) was added to the extract to remove residual water and the extracts were concentrated to approximately 1 mL using a rotary evaporator. A matrix clean-up step was employed for sediment extracts, which were eluted (by gravity) through conditioned (5 mL hexane) neutral alumina cartridges (International Sorbent Technology, Kinesis Ltd., UK) using 5 mL of ethyl acetate. Activated copper was added to the extracts to remove sulfur. The extract was then reduced using nitrogen gas to approximately 300 μL. In addition, a second internal standard (Pyrene-d_{10}) was added to the extract before the instrumental analysis.

2.5. PTV-GC/MS determination

Analyses were performed using an Agilent 6890 Gas Chromatograph interfaced with an Agilent 5973N Mass Spectrometer fitted with an inert source (Agilent Technologies, Germany). Instrumental control, data acquisition and quantification were performed using Agilent ChemStation software. A capillary column HP-MS 5 (30 m × 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, Agilent, USA) was used to separate the target analytes. A large volume injection (LVI) technique using a programmable temperature vaporiser (PTV) inlet was used to inject 20 μL of the sample extracts into the GC/MS. The initial inlet temperature was 40 °C. A solvent vent mode program was set up with a vent flow of 250 mL min^{-1} for 0.20 min (vent time). The splitless purge time was 0.80 min and the inlet temperature was ramped to 280 °C at 650 °C min^{-1}. The helium carrier gas flow was maintained at