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Concentrations of synthetic musk compounds in personal care and sanitation products and human exposure profiles through dermal application

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Abstract

Synthetic musks, such as 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran (HHCB), musk ketone (MK) and musk xylene (MX), are used as an alternative for natural musk. Due to their widespread use, these synthetic compounds turned up in different environmental compartments, such as wastewater, human and animal tissues. Yet, little is known about their distribution and occurrence in personal care and household products, information needed in order to evaluate the different human exposure routes. This paper gives an overview of the synthetic musk levels in six different product categories: body lotions, perfumes, deodorants, hair care products, shower products and sanitation products. Especially body lotions, perfumes and deodorants contained high levels of synthetic musks. Maximum concentrations of HHCB, AHTN, MX and MK were 22 mg g^{-1}, 8 mg g^{-1}, 26 μg g^{-1} and 0.5 μg g^{-1}, respectively. By combining these results with the average usage of consumer products, low-, medium- and high-exposure profiles through dermal application could be estimated. HHCB was the highest contributor to the total amount of synthetic musks in every exposure profile (18–23 700 μg d^{-1}). Exposure to MK and MX did not increase substantially (10–20-fold) between low- and high-exposure profiles, indicating that these compounds cover a less broad range. In comparison, exposure to HHCB and AHTN increased up to 10 000 fold between low- and high-exposure.

Keywords: Synthetic musk; HHCB; AHTN; Contamination level; Personal care products; Human exposure

1. Introduction

Synthetic musks are used as an alternative for the natural musk and comprise a broad variety of structurally heterogeneous compounds (Sommer, 2004). The nitro musks, such as musk ketone (4′-*tert*-butyl-2′,6′-dimethyl-3′,5′-dinitroacetophenone, MK), musk xylene (1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, MX) and musk ambrette, dominated the market for many years. Due to photoallergic reactions elicited by musk ambrette and the bioaccumulative properties of MK and MX, the use of nitro musks declined significantly in the 1990s (Rimkus, 1999). This was paralleled by an increase of polycyclic musks, a second group of synthetic musks which comprises several high-volume use products, such as 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran (HHCB). The low cost synthesis and increased resistance to light and alkali were the main reasons for their extensive use. However, reports on the presence of polycyclic musk in water, fish and human samples (Fromme et al., 1999; Gatermann et al., 1999; Rimkus, 1999; Dsikowitzky et al., 2002; Kannan et al., 2005) damped enthusiasm and caused production levels to decrease. Nevertheless, these compounds are still largely used in various personal care products, sanitation products and fragrances (Reiner and Kannan, 2006). The

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macrocyclic musks, a third group of synthetic musks, exhibit outstanding stability, fixation and high quality odor, but their expensive production has limited the economical importance (Sommer, 2004).

As mentioned in other papers (Rimkus and Wolf, 1994; Bauer et al., 2005), the lipophilic nature and widespread use of synthetic musks, make these products interesting subjects for new research. These properties are mainly important when considering the toxicology of synthetic musk compounds in man and animals. Although the available data are incomplete, the European Union established maximum authorized concentrations for MK and MX (0.03–1% MX and 0.042–1.4% MK depending on the consumer product), mainly due to the induction of metabolizing enzymes and their carcinogenicity (Brunn et al., 2004). EU also gave opinions on the safe use of polycyclic musks, AHTN and HHCB, which seem to be less toxic (Brunn et al., 2004). Synthetic musks have consistently been detected in air samples (Peck and Hornbuckle, 2006) and samples from the aquatic environment such as water (Rimkus and Wolf, 1994; Moldovan, 2006), sediments (Winkler et al., 1998; Dsikowitzky et al., 2002; Stachel et al., 2005) and fish (Rimkus and Wolf, 1994; Gatermann et al., 1999; Wan et al., 2007). However, fewer reports were released on the human exposure to synthetic musks (Kannan et al., 2005; Reiner and Kannan, 2006). Therefore, further studies are needed to examine the different routes of exposure.

In order to assess human exposure through the use of personal care products, we subdivided our research into two different objectives. The first aim was to determine the distribution of the most important synthetic musk compounds in a variety of personal care products. We included two high-volume production polycyclic musks, namely AHTN and HHCB, as well as the superseeded MX and MK to support evolutionary changes in the use of synthetic musks. The second aim was to assess three human exposure profiles (low, medium and high exposure) to these contaminants through dermal application. For this purpose, we combined distribution data of musks in the investigated personal care products with information concerning the use of these products.

2. Materials and methods

2.1. Samples

Personal care products and sanitation products ($n = 82$) were obtained through cooperation of several volunteers. The samples were divided into six categories: sanitation products ($n = 14$), perfumes ($n = 19$), deodorants ($n = 4$), hair care products ($n = 12$), shower and bath products ($n = 18$) and body lotions ($n = 15$). A detailed description is given in Table 1.

2.2. Standards and reagents

AHTN (Tonalide®), HHCB (Galaxolide®), MK and MX standards were of 98.5%, 51%, 98% and 99% purity, respectively. All standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) at concentrations of 10 mg/l in cyclohexane. Labeled d_3-AHTN was used as internal standard (100 mg/l in iso-octane) and had a purity of 99% (Dr. Ehrenstorfer). All solvents used for the analysis (*n*-hexane, dichloromethane-DCM) were of SupraSolv grade (Merck, Darmstadt, Germany). Na_2SO_4 (Merck) was pre-washed with hexane before use. Silica SPE cartridges (Bond Elut-SI, 500 mg, 3 ml) were obtained from Varian (Palo Alto, USA).

2.3. Chemical analysis

All samples were subjected to the same method although procedures could differ somewhat from group to group. For example, perfumes did not undergo extraction because they were completely soluble in hexane. Internal standard concentrations differed (50, 100 and 200 ng) according to the expected analyte concentrations. Only 50 ng IS was added to hair care, shower and sanitation products, while

Table 1
Overview of the investigated personal care products, where "*n*" is the number of samples in each category

Categories		*n*	Categories		*n*
Perfumes ($n = 19$)	Eau de toilette	7	Lotions ($n = 15$)	Body lotion	4
	Perfume	7		Day cream	2
	After shave	5		Calming lotion	1
Shower ($n = 18$)	Liquid hand soap	4		Peeling	1
	Hand gel	1		Hand cream	3
	Bath foam	2		Cleansing cream	1
	Shower gel	10		Body milk	2
Hair care ($n = 12$)	Shampoo	10		Body cream	1
	Conditioner	2	Sanitation ($n = 14$)	Dishwashing liquid	2
	Styling gel	3		Detergent	5
	Styling milk	1		Degreaser	3
Deodorants ($n = 4$)	Spray deodorant	4		Fabric softener	1
				Glass cleaner	2
				All purpose cleaner	1