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Concentrations of cyclic volatile methylsiloxanes in European cosmetics and personal care products: Prerequisite for human and environmental exposure assessment

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ABSTRACT

Low molecular weight cyclic volatile methylsiloxanes (cVMSs) are widely employed as emollients and carrier solvents in personal care formulations in order to acquire desired performance benefits owing to their distinctive physicochemical properties. Under current European legislation cosmetic ingredients such as cVMSs are required to be labeled on the product package only qualitatively, while for the assessment of environmental and consumer exposure quantitative information is needed. The aim of this study was therefore to measure concentrations of three cVMSs, namely octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) in 51 cosmetics and personal care products (C&PCPs) that are currently available on the European market. The list of selected articles comprised a variety of hair and sun care products, skin creams and lotions, deodorants including antiperspirants, liquid foundations and a toothpaste. The target compounds were extracted from the products with different organic solvents dependent on the product matrix, followed by gas chromatography analysis with flame ionization detection (GC–FID). D5 was the predominant cVMS with the highest mean and median concentrations in all the C&PCP categories. The median concentrations of D5, D6 and D4 were 142, 2.3 and 0.053 mg/g in deodorants/antiperspirants (n = 11); 44.6, 30.0 mg/g and below the limit of quantification (<LOQ; LOQ for D4 = 0.00071 mg/g) in cosmetics (n = 5); 8.4, 0.32 mg/g and <LOQ in skin care (n = 16); 9.6, 0.18 and 0.0055 mg/g in hair care (n = 10); and, 34.8, 0.53 and 0.0085 mg/g in sun care (n = 8) products, respectively. The calculated median aggregate daily dermal exposure to D4 and D5 from multiple C&PCPs was approximately 100 times lower than the current NOAEL derived from chronic inhalation rat studies.

1. Introduction

Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) are low molecular weight cyclic volatile methylsiloxanes (cVMSs) (short name: cyclosiloxanes) consisting of four, five and six –Si–O– structural units, respectively, which are arranged in a ring with two methyl groups attached to each silicon atom. In pure form cVMSs are colorless and odorless fluids. Either as single substances or as mixtures (e.g., referred to as cyclomethicone) they are extensively being used as carrier solvents and emollients in cosmetics and personal care product (C&PCP) formulations. Applications of cVMSs stem from their distinct physicochemical properties such as high vapor pressure, low surface tension, and a high degree of compatibility with many formulation ingredients. Manufacturers began incorporating silicone materials into cosmetics and grooming products in the late 1940s. However, it was not until the 1970s, when the U.S. consumer market of cVMS containing products grew rapidly (Goddard and Gruber, 1999). Since then cVMSs have become the basic ingredients in most personal care formulations, such as deodorants, hair care and skin care products.

According to the data provided by the Skin Deep Database, which encompasses more than 75,000 C&PCPs, over 16% of cosmetics and personal care products nowadays contain cVMSs, with D5 appearing to be by far the most widely used compound (EWG, 2012). Both D5 and D6 have been recognized as high production volume (HPV) chemicals by the Organization for Economic Cooperation and Development (OECD, 2007). According to the U.S. EPA (2002) their annual import and production in the United States of America increased by ten times in the last 25 years to more than 225,000 and 22,500 t, respectively. In Europe the amounts of D4, D5 and D6 used annually for personal care applications were estimated by the Environmental Agency of the

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United Kingdom in its recent environmental risk assessment reports (UK EA, 2009a,b,c) at 579, 17,300 and 1989 t for year 2004, respectively. The total trade volume of silicones in Europe reaches 2.5 billion Euros a year (CES, 2011).

Industrial manufacturing of cVMSs as well as direct usage of cVMS-containing C&PCPs by consumers can lead to significant emissions of cVMSs into air or wastewater (Gouin et al., 2013; Maddalena et al., 2011), which in combination with their large production amounts and high mobility results in these compounds being found globally in various environmental matrices including ambient air (Buser et al., 2013; Genualdi et al., 2011; McLachlan et al., 2010; Norden, 2005; Warner et al., 2010; Yucuis et al., 2013), indoor air and dust (Tuomainen et al., 2002; Lu et al., 2010), surface and sewage water (NILU, 2007; Sparham et al., 2008; Zhang et al., 2011), biota (Kaj et al., 2005a; NILU, 2007; Norden, 2005), as well as human tissue (Flassbeck et al., 2001; Hanssen et al., 2013; Kaj et al., 2005b; Kala et al., 1997; US EPA, 1987). Consumer exposure to cVMSs primarily occurs via direct use of personal care products (Health Canada, 2008) where dermal and inhalation exposure routes play the key role in building up the systemic dose with route specific uptake rates of 0.017–0.5% and 2%, respectively (Jovanovic et al., 2008; Reddy et al., 2003, 2007, 2008). Having collected and evaluated a large number of studies relevant to persistence, bioaccumulation and toxicity (PBT) properties of D4 and D5, the ECHA PBT Expert Group (ECHA, 2012) came to the conclusion that based on the available information, D4 meets the criteria for both a 'persistent, bioaccumulative and toxic' (PBT) and a 'very persistent and very bioaccumulative' (vPvB) substance in the environment. D5 fulfills the criteria for a 'very persistent and very bioaccumulative' (vPvB) substance due to its persistence in sediment and a high bioconcentration factor in fish.

Animal studies suggest that D4 and D5 exhibit rather similar toxicity profiles and may have direct and indirect effects on human health. These effects include the induction of uterine endometrial adenocarcinomas in rats following lifetime inhalation exposure with concentrations of D4 in air of several hundred parts-per-million (ppm) that correspond to an unrealistic exposure of more than 1500 mg/kg/day (Dow Corning Corporation, 2004, 2005), the increase in liver weight after subchronic oral and inhalation exposure of 100 mg/kg/day (Burns-Naas et al., 1998, 2002; Dow Corning Corporation, 1986; Jäger and Hartmann, 1991), and the decrease in fetal weight in pregnant rats treated over one week with gavage administration of 100 mg/kg/day dose of D4 (Falany and Li, 2005). The opinion of the European Scientific Committee on Consumer Safety (SCCS) on D4 and D5 present in cosmetics and personal care products (SCCS, 2010) summarizes the information on the toxicity profiles of these compounds and establishes the following critical effect levels for the safety evaluation: for both substances a no-observed-adverse-effect level (NOAEL) of 150 ppm from chronic inhalation exposure studies in rats and a lowest-observed-adverse-effect level (LOAEL) of 100 mg/kg/day from subchronic toxicity rat studies with oral dosing. On this basis the SCCS currently considers D4 and D5 safe for humans.

Although it is known that cVMSs are used in large amounts in consumer products, which therefore represent a large source of exposure for both humans and the environment, data on product concentrations are scarce. Concentrations of cVMS in C&PCPs were reported by Horii and Kannan (2008), Wang et al. (2009), and Lu et al. (2011). Their results were obtained for the North American (USA and Canada) and Asian (China and Japan) markets, but to the best of our knowledge no such data exist for Europe. In the above-mentioned studies, measured cVMS concentrations varied significantly across and within the product categories investigated and ranged between 0.01% in body washes and toilet soaps and 70% in deodorants. Voluntary reported data from the cosmetic industry on the approximate ranges of cVMS concentrations in C&PCPs (recently published by the Cosmetic Ingredient Review (CIR) Expert Panel (Johnson et al., 2012)) support the results for the American and the Canadian markets.

The objective of the present study was to measure the concentrations of cVMSs in selected cosmetics and personal care products that are currently available on the European market and are intensively used by consumers on a daily basis. Thus, we want to provide source data as a necessary input parameter for assessing environmental and human exposure. The products were selected based on the frequency of their use by Dutch consumers, as recently assessed by a questionnaire survey (Biesterbos et al., 2013). We determined concentrations of D4, D5, and D6 in 51 selected cosmetics and personal care products sold in Europe, including deodorants/antiperspirants, hair-care, skin care, and sun care products. The presence of at least one of the cVMSs of interest in an ingredient list of a product was the main inclusion criteria of this product into the study. The collected data was subsequently used in a preliminary worst-case scenario assessment of aggregate consumer exposure for D4 and D5 followed by comparison with biomonitoring data. Furthermore, the product concentrations of cVMSs determined in this study can serve as essential input data for environmental fate modeling, environmental exposure assessment, and validation of back-calculations of cVMS emissions based on the monitoring of the environmental media (Buser et al., 2013) as well as for life-cycle assessment.

2. Material and methods

2.1. Product selection

The cosmetics and personal care products (C&PCPs) for this study were selected on the basis of preliminary results of the questionnaire-based survey that investigated the use patterns of different C&PCP categories in the Netherlands (Biesterbos et al., 2012). We included consumer products of three to five most popular brands in each product category that (1) are the most intensively used by consumers considering both its frequency and amount of application, and (2) would contribute the most to consumer exposure to cVMSs because of potentially high concentrations of these compounds. The ingredient lists of selected products were examined for cVMSs' presence. Since the questionnaire data did not include full names of the products but only brand names we inspected the whole range of product names for each brand for every C&PCP category of interest. If none of the products in a brand included any of the cVMSs on its ingredients list, the brand was not further investigated. If none of the selected brands in a product category claimed to contain cVMSs, one random sample was chosen for verification.

In total 51 C&PCPs were analyzed. Among those, 46 products were purchased in retail stores in Utrecht, the Netherlands, in March 2011; all of these products were manufactured in Western Europe with the exception of one cream-deodorant produced in Canada and two stick-deodorants made in Russia. Another five products that matched the selected Dutch products by type and brand name were bought in Zurich, Switzerland, to compare cVMS concentrations by country of sale. The Swiss products were: hair repair spray, rinse-off hair conditioner, deodorant-stick, hand cream, and body lotion. All of these five product-pairs were made in the European Union. The stick-deodorants were both produced in Germany; the other four product-pairs were produced in different European countries.

The collected products can be grouped into five product categories comprised of 16 smaller subcategories (listed in brackets with n = number of products) including hair care products (hair repair spray, n = 4; rinse-off hair conditioner, n = 5; hair fixative spray, n = 1), deodorants including antiperspirants (stick, n = 4; spray, n = 5; cream, n = 1; roller, n = 1), skin lotions (body lotion, n = 4; face cream, n = 7; hand cream, n = 5), sun care products (sunscreen cream, n = 4; sunscreen spray, n = 3; aftersun cream, n = 1) and cosmetics (liquid foundations, n = 4; lipbalm, n = 1). The last product category contained only one item (toothpaste (n = 1)). Despite of no declared cVMS content, toothpaste was included in the analysis