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Multi-pathway exposure modeling of chemicals in cosmetics with application to shampoo

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ABSTRACT

We present a novel multi-pathway, mass balance based, fate and exposure model compatible with life cycle and high-throughput screening assessments of chemicals in cosmetic products. The exposures through product use as well as post-use emissions and environmental media were quantified based on the chemical mass originally applied via a product, multiplied by the product intake fractions (*PiF*, the fraction of a chemical in a product that is taken in by exposed persons) to yield intake rates. The average *PiF*s for the evaluated chemicals in shampoo ranged from 3×10^{-4} up to 0.3 for rapidly absorbed ingredients. Average intake rates ranged between nano- and micrograms per kilogram bodyweight per day; the order of chemical prioritization was strongly affected by the ingredient concentration in shampoo. Dermal intake and inhalation (for 20% of the evaluated chemicals) during use dominated exposure, while the skin permeation coefficient dominated the estimated uncertainties. The fraction of chemical taken in by a shampoo user often exceeded, by orders of magnitude, the aggregated fraction taken in by the population through post-use environmental emissions. Chemicals with relatively high octanol-water partitioning and/or volatility, and low molecular weight tended to have higher use stage exposure. Chemicals with low intakes during use (<1%) and subsequent high post-use emissions, however, may yield comparable intake for a member of the general population. The presented *PiF* based framework offers a novel and critical advancement for life cycle assessments and high-throughput exposure screening of chemicals in cosmetic products demonstrating the importance of consistent consideration of near- and far-field multi-pathway exposures.

1. Introduction

Using cosmetics can lead to consumer exposure to chemical ingredients during use or general population exposure to chemicals emitted post-use to the environment (Bergfeld et al., 2005; Boxall et al., 2012). With limited human exposure data available for cosmetics (e.g. Koch et al., 2014), and potential for health risks associated with chemical exposures, modeling tools are needed to assess multi-pathway exposure to the variety of chemical-cosmetic combinations.

High-throughput screening (HTS) of exposures to chemicals, such as those used in cosmetics, is a risk prioritization strategy responding to the millions of product-chemical combinations on the market. In order to evaluate dozens to thousands of chemicals at a time, HTS relies on lower-tier models with high computational speed, interpretation of uncertainty, and readily available data such as national emission statistics (Isaacs et al., 2014; Shin et al., 2015; Wambaugh et al., 2013). SHEDS-HT (Isaacs et al., 2014) for example offers a comprehensive platform for exposure screening of consumer products including cosmetics. Unlike platforms such as Crème RIFM (Safford et al., 2015) and the Targeted Risk Assessment (TRA) tool (http://www.ecetoc.org/tra) that assume dermal exposure leads to 100% dermal absorption, SHEDS-HT estimates absorption based on a simplified linear scaling of the chemical-specific skin permeation coefficient without consistently coupling all exposure pathways in a mass balance equation system (i.e. probabilistic mass transfers and exposures are forced to unity in post-processing). Skin permeation coefficients are also used in the dermal exposure models of ConsExpo (Delmaar et al., 2005) and PACEM (Delmaar et al., 2014; Dudzina et al., 2015a), which can estimate aggregated exposure fractions for chemicals in cosmetics per unit mass of product used (Dudzina et al., 2015a) or per unit mass of chemical applied via a product (Delmaar et al., 2014). Platforms such as TRA, SHEDS-HT, ConsExpo, and PACEM can consider multiple exposure pathways and are suitable for risk-based assessment approaches. For comparative assessments based on multi-media, mass balance exposure models (Hauschild et al., 2008; Wambaugh et al., 2013) there is a need to consistently integrate multiple exposure

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pathways and mechanistically consider the competition between different transfer and loss processes. For cosmetic exposure in particular, the chemical mass permeating the skin and the mass volatizing that leads to inhalation are interdependent. Accounting for simultaneous volatilization and dermal permeation has been demonstrated as an important consideration by models that focus on dermal exposure (e.g. Kasting and Miller, 2006), but is currently missing from multi-pathway exposure screening assessments. Such dermal exposure models are not suitable for implementation in HTS or life cycle assessment (LCA) because of computational complexity (e.g. requiring numeric solutions) and unsuitable exposure metrics. Furthermore, none of the aforementioned exposure models have been used to estimate post-use emissions, which lead to ubiquitous contamination of aquatic environments including sources of drinking water (Kolpin et al., 2002; Pal et al., 2014), and subsequent environmental exposure pathways.

LCA—a common quantitative assessment technique to inform environmental risk minimization and sustainable production and consumption—generally accounts for post-use environmental emissions of cosmetic ingredients, and often assumes that a fixed fraction (e.g. 100%) of ingredients is emitted to freshwater (Koehler and Wildbolz, 2009). Life cycle impact assessment (LCIA) models used in LCA, estimate potential impacts on humans and ecosystems mediated by environmental *emissions* along product life cycle stages (e.g. manufacturing, use, disposal). Recent advances in HTS of exposures to environmental chemicals have also employed LCIA mass balance models (Shin et al., 2015; Wambaugh et al., 2013), thus underscoring the utility of models compatible with both HTS and LCIA despite their different goals. LCA-compatible methods to evaluate exposures occurring during product use are, however, not yet available, although exposure during use is a predominate exposure pathway for consumer products like cosmetics (Jolliet and Fantke, 2015). Recently, Jolliet et al. (2015) presented and illustrated examples of the product-specific chemical intake fraction (*PiF*) metric, which represents all incurred exposures per unit of chemical mass applied via a product, as the first necessary step towards developing methods for LCIA to include consumer product exposure. Models to estimate *PiF* have however not yet been operationalized to account for multi-pathway exposures to multiple chemicals. Existing modeling platforms are not appropriate for estimating *PiF*, because they are not mass balance-based across exposure pathways, they do not mechanistically account for volatilization as a competing process with dermal permeation, and they do not estimate post-use emissions and subsequent exposures. Further development of lower-tier mechanistic, mass balance-based, exposure models compatible with LCIA as well as HTS is needed to better assess potential impacts and risks related to chemical fate and exposure pathways originating from chemicals in cosmetic products (Jolliet and Fantke, 2015).

In this study, we address these research gaps and aim to (1) develop a consistent, LCA-compatible, mass balance framework coupling multi-pathway fate and exposures to chemicals in dermally applied cosmetics; (2) analyze fate and exposure pathways during and after use for an exposure duration relevant for cosmetic use; (3) quantify product intake fractions (*PiF*s) and intake rates for a case study of chemicals in a shampoo product and account for uncertainty propagation; and (4) apply the model to determine exposure to multiple chemicals in shampoo and to identify predominant exposure pathways and data gaps.

2. Methods

2.1. Cosmetic product intake fraction framework and exposure pathways

The presented framework is applicable to non-medical, dermally-applied products regardless of their functions (e.g., beautification, hygiene, etc.), referred to as cosmetics (European Union, 2009). We built the framework based on the product intake fraction (*PiF*, Jolliet et al., 2015) metric to quantify consumer exposure to chemicals in cosmetics via use and general population exposure mediated by post-use environmental emissions (Table 1). *PiF* is defined as the fraction of the *chemical mass* applied in a cosmetic product that is eventually taken in by all exposed persons, with the dimensionless units of kilogram chemical taken in versus kilogram chemical initially applied via the cosmetic. Thereby, *PiF* accounts for exposures during the use stage that are missing in LCIA methods (Jolliet et al., 2015) which are restricted to estimating the emissions-based intake fraction, *iF* (Bennett et al., 2002). The modeling strategy for *PiF* is determined by the nature of the product (e.g. if applied on the skin), and like *iF*, model results are dependent on chemical behavior (e.g. volatility), meaning each chemical has its own *PiF* and *iF*. Consistent with *iF*, but for the amount of chemical applied rather than emitted, *PiF* multiplies the amount of chemical applied in a product to yield the human *intake* (not *uptake*) at the exposure interface—for example, permeation into the stratum corneum, not uptake into the blood stream. As the outermost epidermal barrier, stratum corneum intake is recommended for exposure assessments (Cleek and Bunge, 1993).

To preserve versatility of application and model flexibility and to enable comparison across exposure pathways, the total *PiF* (PiF^{tot}) was differentiated into five components discerning life cycle stages as well as exposure pathways and routes (indicated by superscripts); Eq. (1) follows as

$$PiF^{tot} = \underbrace{PiF^{use,d,aq} + PiF^{use,inh} + PiF^{use,d,g}}_{\text{use stage},PiF^{use}} + \underbrace{PiF^{dis,inh} + PiF^{dis,ing}}_{\text{disposal stage},PiF^{dis}}. \quad (1)$$

Three exposure pathways were considered for the product use stage (near-field), i.e. dermal permeation originating from the aqueous solution on the skin surface ($PiF^{use,d,aq}$), and if volatilized from the skin surface, inhalation ($PiF^{use,inh}$) and dermal permeation via transfer from the gaseous phase ($PiF^{use,d,g}$). Two environmentally-mediated pathways (far-field) were considered for the disposal stage (i.e. after product use), i.e. inhalation of ambient air ($PiF^{dis,inh}$) and ingestion of freshwater, fish and other food items ($PiF^{dis,ing}$), aggregated for all members of the general population. *Far-field* refers to indirect exposure to post-use emissions mediated through environmental pathways, which includes exposures via food, water, and air. *Near-field* refers to direct (dermal permeation via application on skin) and indirect (e.g. inhalation)

Table 1
Calculation of the cosmetic product intake fraction (*PiF*) for the relevant exposure pathways with respect to life cycle stages.

Life cycle stage	Exposure pathways	Equation	
Use	Dermal, aqueous	$PiF^{use,d,aq} = \frac{k_{p,s}}{k_{p,s}+k_{p,a}} \times [1-e^{-(k_{p,s}+k_{p,a})\times t_d}]$	(4)
	Inhalation	$PiF^{use,\ inh} = f_{p,a} \times iF_a^{inh}$	(5)
	Dermal, gas	$PiF^{use,\ d,\ g} = f_{p,a} \times iF_a^{d,\ g}$	(6)
	Where	$f_{p,a} = \frac{k_{p,a}}{k_{p,s}+k_{p,a}} \times [1-e^{-(k_{p,s}+k_{p,a})\times t_d}]$	(7)
Disposal	Inhalation	$PiF^{dis,inh} = \sum_{j=1}^{n} (f_{p,j} \times iF_j^{inh})$	(8)
	Ingestion	$PiF^{dis,ing} = \sum_{j=1}^{n} (f_{p,j} \times iF_j^{ing})$	(9)

$k_{p,s}$ (h^{-1}), product-to-skin transfer rate constant, is a function of the skin permeation coefficient, K_p^{aq} (m h^{-1}) (SI Section S1), transfer through the aqueous film, φ_w (m h^{-1}) (SI Section S2), and the product thickness, h (m), where $k_{p,s} = (h/K_p^{aq} + h/\varphi_w)^{-1}$; $k_{p,a}$ (h^{-1}), product to indoor air transfer rate constant, is a function of φ_w (m h^{-1}) and the transfer from the aqueous film to the air, φ_a (m h^{-1}) (SI Section S2), and product thickness h (m), where $k_{p,a} = (h/\varphi_a + h/\varphi_w)^{-1}$; t (h), exposure duration prior to wash-off; $f_{p,a}$ (−), emitted fraction from the product to indoor air; iF_a^{inh} (−), intake fraction due to inhalation of indoor air (SI eq S3a); $iF_a^{d,g}$ (−), intake fraction due to dermal permeation from contact with the gaseous phase in indoor air (SI eq S3b); $f_{p,j}$ (−), emitted fraction from the product to environmental compartment j (SI Section S3), where emission to freshwater is a function of the remaining amount washed-off after use and sent to the treatment plant, $f_{p,tp} = \exp(-(k_{p,s}+k_{p,a})\times t_d)$; iF_j^{inh} (−), inhalation intake fraction estimated by USEtox for releases to environmental compartment j (SI Section S3); iF_j^{ing} (−), ingestion intake fraction estimated by USEtox for releases to environmental compartment j (SI Section S3).