



Are natural compounds used in personal care products toxic for the aquatic environment?



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ABSTRACT

Natural substances are frequently used ingredients in personal care products. As the discharge of rinse-off products, like shampoos or soap, is mainly via the aquatic environment, the question is, whether these natural substances pose an environmental risk. More than a quarter of the natural substances which are listed in the "Inventory of ingredients employed in cosmetic products" (INCI list) are classified as dangerous for the environment with long lasting effects according to the European regulation on classification and labelling, e.g. various *Citrus* preparations, *Cupressus sempervirens* extract, *Picea excelsa* extract or *Pinus sylvestris* leaf extract. Some of the components responsible for the classification of natural substances as dangerous for the environment are e.g. limonene, pinenes or benzyl benzoate. Classification and labelling is a trigger for the registration requirements for natural substances according to the European regulation on chemicals (REACH), but so far only 5% of natural substances classified are registered. It must be assumed that there are more substances that should undergo the REACH process among the 703 natural substances that do not yet turn up in the data base of substances classified and labelled as hazardous (C&L inventory). Natural substances and personal care products receive special treatments in the European chemical legislation. The compilation of the classifications might question whether this special treatment is justified.

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1. Introduction

Many consumers consider personal care products that contain substances with natural origin as safe alternatives compared to purely synthetic products. Most natural substances derived from plants, animals, mushrooms or bacteria are complex mixtures of compounds belonging to various chemical substance classes. Many of their components are known for their potent physiological effects (Ramawat and Mérillon, 2013; Teuscher and Lindequist, 2010). The effects observed range from teratogenicity to photosensitization and facial eczema, pulmonary emphysema and abortion (Cheeke, 1985; Teuscher and Lindequist, 2010). Some natural substances, such as *Citrus* or *Eucalyptus* preparations are produced in production volumes above 1000 t per year in the European Union. The predominant amounts used and the knowledge about their potential physiological activity justify a closer look at these substances.

As the discharge of rinse-off personal care products, such as shampoo or soap, is mainly via effluents of wastewater treatment plants into the aquatic environment, the question is whether they exert negative effects on aquatic organisms. A previous study

(Klaschka, 2015) revealed that a considerable number of natural substances used in personal care products is classified as dangerous for the aquatic environment with long lasting effects, a result that was not at all to be expected. The objective of the present study is to explain this result.

Hazard assessment is a straightforward first approach to address this question. A hazard of a substance is defined as a possible source of danger, described through standardized classification and labelling as presented by the world wide globally harmonized system of classification and labelling of chemicals (GHS) (GHS, 2009) of the United Nations or the corresponding European counterpart, the regulation on classification, labelling and packaging of substances and mixtures (CLP-regulation) (EC, 2008). Classification is a very valuable tool which allows to identify hazardous substances through signal words, precautionary statements or pictograms. It must be applied to single hazardous substances, hazardous mixtures and products (e.g., pesticides, industrial chemicals, with the exception of personal care products). The classification of hazardous mixtures can be calculated on the basis of the classifications of the components according to the procedures determined in the CLP-regulation (EC, 2008). This was done in the present study for all natural substances where sufficient information could be found about the effects of their main components on the aquatic environment. Other hazardous effects

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on environmental organisms, which have not been incorporated in the hazard classification, are also addressed here. In addition, further legal restrictions concerning natural substances were analysed with the focus on the use in personal care products.

The cosmetic market is highly globalized. Sales in Europe make up for a third of the global market, and sales of natural cosmetics are especially increasing in Europe, two reasons which justify the focus on the European Union in this review. Several major features of the legal situations are congruent in the EU, the USA or in a developing country such as South Africa (Klaschka and Rother, 2013; Pauwels and Rogiers, 2007b). Furthermore, the natural substances considered here are common ingredients in natural personal care products and also used for other purposes such as fracking (e.g., 'sweet orange oil', 'terpenes and terpenoids', Halliburton, 2016) worldwide. Therefore, the basic scientific results and conclusions from this paper are relevant globally.

2. Materials and methods

The so-called 'INCI list' is the European list of around 8500 ingredients with the official nomenclature in personal care products, published in the Commission Decision 96/335/EC (EC, 2006a) 'establishing an inventory and a common nomenclature of ingredients employed in cosmetic products'. Substances were selected from this list, which originate clearly from a specific organism indicated by its scientific name as described previously (Klaschka, 2015). These substances were compared with the entries in the classification and labelling inventory, the so-called 'C&L inventory'. This is the official European on-line database of classification and labelling information on notified and registered substances received from manufacturers and importers (so-called notifiers) according to the CLP-regulation (EC, 2008) on the basis of the European regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) Title XI (EC, 2006b). Substances subject to registration or any other dangerous substance as covered by Article 1 (EC, 1967) and placed on the market should be notified and included in the inventory (EC, 2006b, Whereas (113)). Classification and labelling is an ongoing process, leading to a continuous update of the data base 'C&L inventory'. Data used in the current study were collected from August 2013 until July 2015. Various notifier groups classified many substances differently. It was decided in this investigation to consider only the classifications by the majority of notifiers. The biggest effort in the study was the search for the information on the chemical identity of components and their percentages in a natural substance in publically available sources. This information was collected from data bases, scientific textbooks, material safety data sheets by manufacturers, safety assessments, REACH registrations and other scientific literature (see also Pauwels and Rogiers, 2007a). The classifications of the natural substances was calculated following the procedures set up by the ECHA guidance document for mixtures (ECHA, 2009) in accordance with the CLP-regulation (EC, 2008).

3. Results and discussion

3.1. 181 Natural substances in the INCI list are classified due to their hazardous effects on the aquatic environment with long lasting effects

According to the REACH-regulation (EC, 2006b, Whereas (113)), manufacturers and importers of chemical substances have to notify the classification and labelling following the CLP-regulation (EC, 2008) to the European Chemicals Agency (ECHA) regardless of the production volumes. The CLP-regulation provides for two

approaches: On one hand, the harmonized classification applies predominantly on effects of high concern, like carcinogenicity, germ cell mutagenicity, toxicity for reproduction as well as on substances which are persistent, bioaccumulative, and toxic. The harmonized classification leads to partial classifications. On the other hand, self-classification for all other hazardous properties is effectuated by the manufacturer, importer, or downstream user and notified to the ECHA.

Classifications for natural substances used in personal care products were gathered from the C&L inventory. All classifications found are self-classifications. In many cases, the classifications by various notifier groups differed. Several substances were classified by only one company and not classified by many others. The differences could be the consequences of slightly different compositions or contaminations of the natural substances, of different data bases used, of the application of calculation methods instead of measured test data, or of different classification approaches following the precautionary principle or following strategic reasons. It cannot be excluded that some classifications are over- or under-classifications (too severe or too weak classifications). Notifiers need to make sure that their self-classifications are correct. If the classifications differ between notifiers, notifiers should make an effort to find a joint solution (EC, 2006b, Art. 41). It is not the purpose in the current study to validate which classification is right or wrong. For pragmatic reasons, the classification which the clear majority of companies agreed upon is used in this study, whenever the self-classifications of various companies differ. In most cases, the majority is clear, although there are cases, where one consortium of notifiers does not classify or label at all, whereas the other consortium of a similar size does. For example, *Brassica nigra* extract was not classified by 29 notifiers, whereas 28 notifiers classified it with H226, H301, H311, H315, H319, H330, H335, H400, and H410.

The INCI list contains 1358 natural substances, most of them are herbal products, others are of animal, fungal or bacterial origin. Out of these, 655 appear in the C&L inventory, where 182 (28%) natural substances are classified as hazardous for the aquatic environment (Table 1), with 181 for long lasting effects (Klaschka, 2015). H400 is based on data for acute toxicity only, whereas H410, H411, H412 and H413 are based on data on acute and chronic toxicity, on degradability or on the potential for bioaccumulation. Some examples of classified natural substances are given in the footnotes of Table 1. This table also shows the numbers of the majority of notifiers who submitted the same classification and labelling information for a certain substance in the C&L inventory. The numbers of notifiers range between 1 to over 800 notifiers, e.g. 836 (*Anthemis nobilis* extract), 843 (*Salvia sclarea* extract), 845 (*Cedrus atlantica* extract), 891 (*Mentha arvensis* extract), 905 (*Eucalyptus globulus* extract), 981 (*Melaleuca alternifolia* oil). Although the numbers of notifiers do not allow to deduce the production volumes, they show the abundance of companies involved in the classification and labelling of these natural substances. Ingredient lists of a selection of natural cosmetics on the German market revealed that they contain natural substances classified as hazardous for the aquatic environment, for example various *Citrus* preparations, *Chamomilla recutita* extract, *Lavandula angustifolia* oil, *Rosmarinus officinalis* oil, or *Salvia officinalis* leaf extract. This shows that these substances are not only potential ingredients listed in the INCI list, but they are indeed in use and can reach the aquatic environment (Klaschka, 2016).

No harmonized classifications for these natural substances are available so far, and none of the natural substances appear in Annex VI of the CLP-regulation, which is the list of harmonized classification and labelling of hazardous substances. However, several single compounds, which can be isolated from plants (as indicated in the brackets) and which are highly toxic, are listed in

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