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From incremental to fundamental substitution in chemical alternatives assessment

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ABSTRACT

Several chemicals in consumer products are subject to binding or voluntary phase-out agreements that are based on international treaties such as the Stockholm Convention on Persistent Organic Pollutants or on regulatory frameworks such as the European Union's Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). To facilitate a phase-out process, alternatives assessment is commonly applied as an emerging approach to identifying chemicals (or materials, processes, and behavior changes) serving as substitutes. Polybrominated diphenyl ethers (PBDEs), long-chain poly- and perfluorinated alkyl substances (PFASs), and polychlorinated biphenyls (PCBs) are well-known cases of chemicals where substitution processes can be studied. Currently, there are various challenges in assessing, evaluating and effectively introducing chemical alternatives. These challenges are mainly related to similarity in chemical structures and, hence, similar hazard profiles between phase-out and substitute chemicals, leading to a rather incremental than fundamental substitution. A hampered phase-out process, the lack of implementing Green Chemistry principles in chemicals design, and lack of Sustainable Chemistry aspects in industrial processes design constitute additional challenges. We illustrate the various challenges in the process of phasing out and successfully substituting hazardous chemicals in consumer products and provide guiding principles for addressing these challenges. We propose an integrated approach of all stakeholders involved toward more fundamental and function-based substitution by greener and more sustainable alternatives. Our recommendations finally constitute a starting point for identifying further research needs and for improving current alternatives assessment practice.

1. Introduction

A wide range of chemicals is commercially used as ingredients in consumer products to provide specific functions in particular production processes, products, or product components. Examples are chemicals that increase material flexibility (plastic softeners), provide specific colors (dyestuffs and colorants), reduce flammability (flame retardants), increase surface hydrophobicity (impregnation agents), inhibit material degradation (antioxidants and UV absorbers), or prevent bacteria and fungi growth (preservation agents and biocides) (Dionisio et al., 2015; Fitzpatrick, 2004; Park et al., 2006; Cosmetic Product Notification Portal, 2013). Among these chemicals, there is a certain fraction with intrinsic hazardous properties, such as persistence in the environment, bioaccumulation potential and toxicity (PBT properties), or carcinogenic, mutagenic, and repro-toxic (CMR) properties, or the ability to interfere with the hormonal system (endocrine disruptors) (Strempel et al., 2012; European Chemicals Agency, 2012; World Health Organization, 2013; Trasande et al., 2015). Large-scale screening studies have shown that there may be several hundreds of chemicals with PBT properties among the several tens of thousands of chemicals in commercial use (Strempel et al., 2012; Scheringer et al., 2012; Gouin, 2010; Arnot et al., 2012). For many of these chemicals, however, no (complete) risk assessments are available (Anastas et al., 2010). As a result, there exist regulatory and non-regulatory lists indicating chemicals of concern with respect to human or environmental health. Such lists include e.g. the Candidate List of substances in articles from the European Chemicals Agency (2015), the list of hazardous Chemicals in Textiles from the Swedish Chemicals Agency (2014), the SIN list from the International Chemical Secretariat (2014), or the TEDX List of Potential Endocrine Disruptors (The Endorcrine Disruption Exchange, 2013).

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Some groups of chemicals have raised particular concerns, such as polybrominated diphenyl ethers (PBDEs) or long-chain poly- and perfluorinated alkyl substances (PFASs) (Scheringer et al., 2014), and have been regulated or are subject to voluntary phase-out programs. More specifically, commercial pentaBDE and octaBDEs are scheduled for global elimination and uses of perfluorooctane sulfonic acid (PFOS) are being restricted under the Stockholm Convention on Persistent Organic Pollutants (United Nations Environment Programme, 2009), and perfluorooctanoic acid (PFOA) and C_{11}–C_{14} perfluorocarboxylic acids are regulated in the European Union as PBT substances and very persistent, very bioaccumulative (vPvB) substances, respectively (European Chemicals Agency, 2014). Furthermore, all long-chain PFASs (substances with ≥7 perfluorinated carbons) are subject to voluntary phase-out programs of major producers of fluoropolymers and fluorotelomer-based products (Wang et al., 2014; United States Environmental Protection Agency, 2015a).

To facilitate the phase-out of hazardous substances, chemical alternatives assessment as a methodology for *informed substitution* can be applied, aiming at finding suitable (i.e. less hazardous) alternatives at the level of chemicals, materials or product designs (Hester and Harrison, 2013; Lavoie et al., 2010). Thereby, the substitution process should be based on functional use considerations (Tickner et al., 2015). A set of existing alternatives assessment tools has been compiled into the OECD Substitution and Alternatives Assessment Toolbox (http://www.oecdsaatoolbox.org). These tools typically combine to a different extent hazard and risk assessment with economic and technical feasibility and to date, most stakeholders and companies mainly apply such tools with focus on chemical-by-chemical substitution (Bergez-Lacoste et al., 2014; Eisenberg et al., 2013; Eliason and Morose, 2011; Howard, 2014; Toxics Use Reduction Institute, 2006; United States Environmental Protection Agency, 2014).

For the case of chemical-by-chemical substitution, several studies have shown that the replacements of hazardous or phase-out substances may include structurally similar chemicals, e.g. brominated aromatic substances in the case of PBDEs (Howard, 2014; United States Environmental Protection Agency, 2014; Stieger et al., 2014; Bergman et al., 2012) and shorter-chain PFASs in the case of long-chain PFASs (Gomis et al., 2015; Wang et al., 2013b, 2015). These are two examples of a substitution process that leads to an *incremental* rather than a *fundamental* change in the structure of hazardous chemicals used in consumer products. However, incremental change in chemical structure of substitutes often leads to similar hazard profiles (Tickner et al., 2015; Gomis et al., 2015) and hampers the phase-out process of hazardous chemicals. To facilitate a successful phase-out process based on significantly reduced hazard profiles and improved environmental performance of consumer products containing substitute chemicals, a substitution process is required that is in line with Green Chemistry and sustainability principles. To address this need, we discuss in this paper the conditions for incremental and fundamental changes in the substitution process of chemicals within chemical alternatives assessments, give an overview of challenges along the substitution and phase-out process, and provide recommendations to shift from incremental to fundamental substitution in alternatives assessment practice.

2. Methods

We discuss different aspects and challenges of the phase-out agreement process for hazardous chemicals and of the process of assessing and evaluating potential replacements, hereafter referred to as substitutes or alternatives. Thereby, we primarily focus on chemical-by-chemical substitution as currently the most widely applied option in alternatives assessment of hazardous chemicals proposed for phase-out (Howard, 2014; Toxics Use Reduction Institute, 2006), and on incremental versus fundamental change in chemical structure. Along several examples of phase-out chemicals originally used in large quantities in consumer products and their alternatives, we specifically discuss when the problem of incremental change is likely to occur. For these cases, we explore how to strive toward more fundamental changes in chemical structures without the risk of burden shifting. We further discuss challenges in the phase-out and replacement of well established, widely used chemicals as well as performance requirements for alternative chemicals, and explore the influence of Green Chemistry and Sustainable Design on chemicals placed on the market. Finally, we highlight management needs for chemicals that can currently not be phased out.

For each step in the phase-out and substitution processes, we give indicative recommendations of how to address several related challenges to facilitate a shift from incremental to more fundamental substitution of hazardous chemicals in consumer products. These recommendations constitute a starting point for identifying research needs and for improving current alternatives assessment and chemical substitution toward a practice that is in line with Green Chemistry and sustainability principles.

3. Results and discussion

We identified several challenges and obstacles along the process of phasing out commercially used hazardous chemicals and substituting them by other chemicals in consumer products. Fig. 1 outlines the phase-out and chemical substitution process that follows the identification of a hazardous substance in one or more consumer products and depicts individual challenges along the pathway from ① concluding a phase-out agreement, ② creating an inventory of possible chemical alternatives, ③ assessing these alternatives, ④ selecting specific alternatives as potential "best-in-class" substitutes, and ⑤ implementing both phase-out of the hazardous chemical and introduction of the substitute chemical. Overcoming the phase-out and substitution challenges will help to systematically shift from an incremental substitution and hampered or blocked phase-out process that is often *current practice* (Fig. 1, left-hand pathway) to a more fundamental substitution process leading to actually phasing out hazardous chemicals, which we postulate as *recommended practice* (Fig. 1, right-hand pathway). In the following, challenges and potential solutions outlined in Fig. 1 will be discussed in the context of the actual phase-out process, the alternatives assessment procedure, different types of chemicals, and chemical design principles.

The question of incremental versus fundamental change, in particular, will be illustrated with several examples listed in Fig. 2. Examples 1–3 in this figure refer to the substitution of PCBs, PBDEs and long-chain PFASs and illustrate the problem of continued use of old types of chemicals (further detailed in Section 3.3), while example 4 addresses the lack of "green" design in the development of new chemicals, specifically referring to replacements of chlorofluorocarbons (further detailed in Section 3.4).

3.1. Challenges in the phase-out process of widely used hazardous chemicals

Challenges in phasing out hazardous chemicals in consumer products already start at the level of concluding a phase-out agreement (Fig. 1, ①), since such agreements often are voluntary and do not cover all relevant chemical manufacturers. An example is the very persistent long-chain PFAS, for which the United States Environmental Protection Agency (US EPA) has worked with eight