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HOW CAN WE AVOID THE LOCK-IN PROBLEM IN THE SUBSTITUTION OF HAZARDOUS CHEMICALS USED IN CONSUMER PRODUCTS?

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Introduction

A wide range of chemical substances is used in consumer products for various purposes, including plastic softeners, dyestuffs and colorants, flame retardants, impregnation agents, antioxidants and UV absorbers, preservation agents and biocides, and many others. Among these chemicals, there is a certain fraction of substances with hazardous properties such as persistence, bioaccumulation potential and toxicity (PBT properties) or the ability to interfere with the hormonal system (endocrine disrupting chemicals, EDCs). Large-scale screening exercises have shown that there may be several hundreds of chemicals with PBT properties among the several tens of thousands of substances on the market^{1,2}. There are some groups of chemicals that have raised particular concerns such as polybrominated diphenyl ethers (PBDEs) or long-chain poly and perfluorinated alkyl substances (PFASs). These substances have been regulated or are subject to voluntary phase-out programs; specifically, penta- and octabrominated BDEs are scheduled for elimination globally under the Stockholm Convention on Persistent Organic Pollutants³; uses of perfluorooctane sulfonic acid (PFOS) are being restricted under the Stockholm Convention³, and perfluorooctanoic acid (PFOA) and C₁₁–C₁₄ perfluorocarboxylic acids are regulated in the European Union as PBT substances and vPvB (very persistent, very bioaccumulative) substances, respectively⁴. In addition, all long-chain PFASs (substances with seven or more perfluorinated carbons) are subject of voluntary phase-out programs conducted by major producers of fluoropolymers and fluorotelomer-based products^{5,6}. However, it has become evident that the replacements of these substances include chemically similar substances, i.e. brominated aromatic substances in the case of PBDEs and shorter-chain PFASs in the case of long-chain PFASs. These are two examples of a substitution process that leads to an incremental rather than a fundamental change in the structure of chemicals used in consumer products. Here we discuss the conditions for incremental and fundamental changes in the substitution process of chemicals.

Materials and methods

We investigate the chemical structures and the physicochemical properties of various types of chemicals and their replacements. Furthermore, we compare the properties of chemicals scheduled for phase-out and of their replacements to cutoff values defined for hazard properties under the Stockholm Convention and the European chemicals regulation, REACH. We discuss various aspects of the substitution process, including incremental vs. fundamental change, the influence of Green Chemistry on chemicals placed on the market, performance requirements, and challenges in the implementation of a phase-out and replacement of well established, widely used chemicals.

Results and discussion

Our results cover three areas: (i) challenges associated with the phase-out process of widely used chemicals for which an agreement on elimination has been reached, (ii) persisting use of old types of chemicals, and (iii) lack of green design in the development of new chemicals.

Challenges associated with the phase-out process of widely used chemicals for which an agreement on elimination has been reached. There are several challenges associated with the phase-out of hazardous chemicals widely used even if an agreement has been reached by an international treaty or by voluntary agreements by major companies. For example, PFOS has been listed in the Stockholm Convention. However, a wide range of exemptions for the use of PFOS have been granted since:

- a) Developing and transition countries are requesting for continuing the use of PFOS due to the lack of knowledge and technical capacity to phase in substitute chemicals. In addition they might not transition to chemicals newly patented, which may be more expensive than PFOS, which after the phase-out by the major manufacturer in North America is now produced by several companies in China (however at lower volume)^{7,8}.
- b) For some applications the phase-out seems to present challenges even in industrialized countries (e.g. for chromium plating) so that the EU and other industrialized countries have registered for exemptions for chromium plating although alternatives are on the market. Here some companies seem to be reluctant to use alternatives since the alternatives to PFOS have a similar structure and belong to the same chemical class (PFAS) and the toxicity assessments of the alternatives are not comprehensive. This uncertainty in combination with higher releases of the alternatives from the plating process (PFOS is easier to remove from the process by active carbon compared to the alternatives) seems to make it difficult to clearly decide on the benefit of a switch to these alternatives.

Therefore, PFOS might be used for an extended period of time in developing countries and even in industrialized countries.

Another case is long-chain PFAS. Here the US EPA has worked with eight leading chemical companies in the 2010/2015 PFOA Stewardship Program to reduce emissions and residual content of PFOA and long-chain PFASs by 95% by 2010, with the long-term goal to work toward elimination of long-chain PFASs by 2015⁵. However, there is limited incentive for other companies to join such a voluntary agreement. In fact, considering that the C8-based chemistries often have the most desirable performance characteristics, it is attractive for companies that are not party to the 2010/2015 PFOA Stewardship Program to increase their production of long-chain materials to meet continuing international market demands⁹.

Also decabromo diphenyl ether (DecaBDE), which degrades into lower-brominated PBDEs listed in the Stockholm Convention¹⁰, is still produced in large amounts in transition countries. Also for DecaBDE a voluntary phase-out has been negotiated by the US EPA with the major producers in industrialized countries¹¹. However, the major producers in developing/transition countries are not part of this agreement and might continue or even increase production if the other producers try to sell more expensive alternatives. Therefore it is a challenge to work in a global market with voluntary agreements for phase-out of hazardous chemicals in some countries. If these old hazardous chemicals have a good performance in their application that is similar (or even superior) to that of new (or existing) alternatives, a global phase out might take very long or might not happen at all.

Persisting use of "old" types of chemicals. If the phase-out of a particular chemical identified as hazardous takes place, the substitution process may result in just an incremental rather than a fundamental change of the type of chemical used. Considering several specific groups of halogenated chemicals, we identify three archetypal cases of an incremental change: A) Polychlorinated biphenyls (PCBs) are being replaced by chlorinated paraffins (CPs) in many applications. The historical global production of PCBs from 1930 to 1995 is approximately 1.5 million tonnes¹². The current annual production of CPs is more than 0.5 million tonnes¹³, which means that the overall production of CPs exceeds that of PCBs by a surprisingly large factor. This is also supported by field data showing that CP concentrations in lake sediments already strongly exceed PCB concentrations¹⁴. B) PBDEs are being replaced by a wide range of other brominated aromatic compounds^{15,16}. C) Long-chain PFASs are being replaced by a wide range of fluorinated alternatives with shorter perfluorinated chains¹⁷.

All three cases show a substitution process where the basic chemical structure is largely maintained. On the one hand, this is plausible because it is this chemical structure that generates the desired properties and performance of the chemicals. On the other hand, this incremental change constitutes a problem because also the unwanted properties of the chemicals being replaced may show up in the replacements. For this type of substitution process, where the basic chemical structure is maintained, we propose the term "lock-in" problem.

A particular challenge connected with the lock-in problem is that not much specific information about the chemicals used as replacements is available in the public domain^{16,17}. Many of the replacements are chemicals that have been on the market for many years. However, because they were not used in large quantities before they were proposed as replacements of chemicals for which a phase-out has been decided, their properties and

environmental fate have not been investigated in much detail. Manufacturers of these chemicals are in possession of chemical-specific information, but in most cases this information is not publicly available. In the cases of PBDEs and long-chain PFASs, the replacements are diverse groups of substances for which a detailed investigation of their hazardous properties and environmental fate would require large efforts and financial resources. This indicates that publicly funded research is unlikely to provide a sufficient basis for the hazard and risk assessment of many replacements. In this situation, there are two options: in the absence of detailed information on the properties, toxicity, and environmental fate of the replacements, the replacements may be assumed to have unwanted properties similar to those of their predecessors; this assumption derives from the chemical similarity of replacements and chemicals being phased out. The other option is that the manufacturers of the replacements generate the information that is required for a detailed and comprehensive hazard and risk assessment of the replacements¹⁶. The information should not only be shared with regulatory bodies, but also be made publicly accessible. In principle, the second option is the intention of the European chemicals regulation, REACH. However, information provided under REACH has turned out to be inaccurate in many cases and it is currently unclear to what extent the data provided by the database of the European Chemicals Agency can be considered comprehensive and reliable^{16,18,19}.

Lack of Green Design in the development of new chemical products. Large scale screening of chemicals on the market shows that there is a fraction of 2 to 3% of potential PBT chemicals among a set of 95.000 commercially relevant chemicals, and approximately 50% of these potential PBT chemicals are halogenated (14% fluorinated, 31% chlorinated, 9% brominated)¹. A separate investigation of the former “new” chemicals on the European market (chemicals that were introduced in the period 1982–2006) shows that (i) the fraction of potential PBT chemical in this particular group is even higher than in the entire set investigated, namely around 5%, and (ii) that the fraction of fluorinated chemicals is much higher in the potential PBT chemicals from this group than in the potential PBT chemicals from the entire set (29% fluorinated, 13% chlorinated, 1.5% brominated)¹. These observations lead to two conclusions: (i) Within the former “new” chemicals of the EU, there is evidence for a more extensive use of fluorinated moieties, compared to the former “existing” chemicals of the EU. Chemicals with fluorinated moieties have been found to be particularly prone to exceed the screening criteria for Persistent Organic Pollutants under the Stockholm Convention². (ii) In this group of relatively new chemical products, no influence of the principles of Green Chemistry, in particular the principle of rapid degradability as a requirement for “green” chemical products, is (yet) visible. Generally, a life-cycle perspective on chemicals and the products and processes the chemicals are involved in needs to be introduced. This is important especially in green product design involving chemical substitution in order to avoid burden shifting from one undesired property to another between substituted and replacement chemicals, but also to avoid burden shifting from specific environmental impacts (e.g. bioaccumulation in the food chain) to other impacts (e.g. groundwater contamination) and from one location to another if the replacement chemicals involve different manufacturing or processing steps.

In conclusion, it is important to establish new strategies for introducing novel types of chemical structures in markets that are dominated by a certain type of chemistry. A first aspect of this is that more research into new types of chemical structures that are in agreement with the principles of Green Chemistry, in particular: low toxicity and no persistence, is needed²⁰. Chemical research needs to investigate systematically to what extent it is possible to reconcile the needs for technical performance in defined applications with the requirement that, according to the principles of Green Chemistry, chemical products should be degradable and not highly toxic. What should be done in cases where these two requirements cannot be fulfilled at the same time? A second aspect is that in cases with lock-in problems there is often competition between established manufacturers and their well-known products, on the one hand, and other, often small and/or new companies with products that are not yet established, on the other hand. What guidelines and what kind of support are needed for this process to take place in a productive way? Finally, how can a comprehensive comparative assessment of various environmental aspects be incorporated into chemical substitution design, and how can this assessment be performed in spite of substantial data gaps and uncertainties? This process needs an integrated approach of all stakeholders involved, in particular the chemical industry, industrial downstream users of chemicals, regulatory authorities, the research community, and various Non-Governmental Organizations.

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