

Evaluation of the presence of potential hazardous substances from plastic and textile fibre recycling

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Summary

Plastics are highly diverse and the most common materials used for packaging foodstuffs. However, the steadily increasing production of plastic with increasing amounts of fossil-based plastic waste causes severe environmental problems. Comparable with plastics, the textiles and apparel industry is one of the largest and fastest growing global industrial sectors owing to the greater productivity in mass production processes. In recent times, there is an increased awareness of the impacts of the existing linear supply chain of the textile and apparel industry. For plastics and textiles, the recovery of materials and energy, specifically through the application of recycling technologies, would greatly contribute to the vision of a circular economy model. The instalment of a circular economy could contribute to a more sustainable future for generations to come.

The successful recycling of plastics and textiles depends, apart from technical aspects, to a large degree on the safety of the products resulting from recycling. The safety of recycled products is a prerequisite for societal acceptance of recycled plastics and textiles. The transition to a circular economy of plastics and textile fibers will not be accomplished if no guaranteed safe products can be delivered to the market. The evaluation of the safety of recycled plastics and fibers is crucial, but a framework for evaluation of potential hazardous substances and associated risks for the consumer is virtually absent. More specifically, a legislative framework, risk assessment framework, and relevant testing strategies are urgently needed.

In this report the recycling and reprocessing of thermoplastic materials, composites and textiles have been reviewed and described. In the production of plastics and textiles many substances are used that are highly hazardous and therefore of significant concern for occupational health. During the recycling or the use of recycled materials these substances may be released to products or the environment. Plastics may be a source of contamination in the recycling process if they are mixed with other plastics and well known plastic additives have been found in children toys and food contact materials produced from recycled plastics. Since composites are rarely recycled no information was found about contaminants in recycled materials. For textiles it was found that the knowledge base surrounding substances problematic for recycling is very limited.

For the analysis of hazardous substances or non-intentionally added substances (NIAS) in recycled plastics or textiles two strategies are applied: targeted analytical methods for the analysis of predicted and known substances, and untargeted or screening methods to analyze unknown substances. Targeted analysis are performed using GC- and LC-MS based methods and dedicated substance libraries for identification. For untargeted analysis GC and LC techniques are used in combination with high resolution mass spectrometry (HRMS) techniques like Orbitrap or QTOF mass spectrometry. In untargeted analysis *in silico* tools are gaining importance in the identification of substances. Recent publications describe the use of so-called explorative methods, an untargeted analytical strategy to estimate the concentration and chemical structure of unknowns. However, a comprehensive analysis is not realistic and therefore a risk prioritization is required to identify the substances that most likely have adverse health effects.

The combination of bioassays with sensitive analytical techniques, so-called effect directed analysis, is another promising and efficient way of identifying unknowns and NIAS and their hazard to human exposure. *In vitro* bioassay based testing allows for a rapid evaluation of multiple toxicological endpoints. Positive sample extracts or fractions thereof can be further analyzed with GC- or LC-HRMS techniques to identify the toxic substances. Finally, safety assessment frameworks may be used for the detection and identification of unknown substances in complex samples. In such frameworks the number of analytes that have to be identified is reduced by using a threshold based on the threshold of toxicological concern (TTC). By identifying substances of highest concern, the resources available for experimental testing can be attributed in a more efficient way.

For a successful implementation of safe recycling processes and recycled products, there is an urgent need for comprehensive approaches for identification and quantification of hazardous substances, and to assess their safety. The first step in this process is method development for the identification and quantification of hazardous substances in recycled plastics and textiles. Currently such methods are virtually absent, especially for textiles. The literature review has revealed that targeted and untargeted mass spectrometric methods are needed. However, since many of the substances detected in such analyses may be NIAS or otherwise unknowns, identification is a difficult and time-consuming process. For efficient identification such techniques have to be combined with compound databases that may be compiled from different sources. Since it is unlikely that all detected substances can be identified an effect-directed method would be very helpful to detect and finally identify potentially hazardous substances. However, as with the other analytical techniques, effect-directed analysis and especially the coupling of the bio-assay and the instrumental technique is not standard and has to be developed. Finally, hazardous substance prioritization schemes and techniques as TTC and CoMSAS for risk assessment have not been used for recycled plastic and textile materials and so this is also a new playing field to be developed.

1 Introduction

Plastics are highly diverse and the most common materials used for packaging foodstuffs. In 2015, almost 20 million metric tons of plastic packaging were used in Europe (Plastics Europe, 2016), generating approximately 30 kg of plastic packaging waste per inhabitant per year (Eurostat, 2017). The steadily increasing production of plastic with increasing amounts of fossil-based plastic waste causes severe environmental problems. This includes a high energy demand during production, the consumption of fossil fuels and accumulation of plastic waste in landfills and natural environments. Approaches to slow-down the demand for virgin plastic have been developed although the recycling of plastic materials is currently achieved only for a small percentage of all plastic produced. The instalment of a circular economy could contribute to a more sustainable future for generations to come. This circular economy is based on three main pillars; stop littering by setting up waste management systems, circular use of materials and use of bio-based feedstock to produce virgin materials (Ellen McArthur Foundation, 2017a). Waste management systems and recycling technologies are in place or in development for paper and board and for some plastic waste (mainly food packaging materials), but many more carbon containing materials need developments towards circular use. The recycling and reprocessing of thermoplastic materials can generally be performed relatively easily from a practical and technological point of view (Soroudi and Jakubowicz, 2013; Ambrose et al., 2002; Maris et al., 2018). Two other important and more challenging material classes are composites and textiles.

Composites are a combination of a thermoset resin with a carbon fibre reinforcement. Thermoset materials are classified amongst the most difficult materials to recycle and therefore the recycling of composites is rare and focuses on the recovery and reuse of the carbon fibre reinforcement.

The textiles and apparel industry is one of the largest and fastest growing global industrial sectors, owing to increasing population, the rise in consumption, the diverse applications of textiles, and greater productivity in mass production processes. With a 1.3 trillion USD annual revenue in 2016 (Euromonitor International Apparel & Footwear, 2016), the global clothing industry is the largest consumer of textiles. Annual production has nearly doubled since 2000, surpassing 100 billion units in 2015 with apparel consumption expected to rise 63% by 2030. This increase is partly due to the fast fashion industry, which relies on shorter production cycles and style turnaround, often at lower prices, enabling a larger selection and choice for consumers (Ellen McArthur Foundation and Circular Fibres Initiative, 2017). In recent times, there has been great interest in increasing the reuse and recycling of textiles because of an increased awareness of the impacts of the existing linear supply chain of the apparel industry. Reuse refers to the utilization of a product in its original form while recycling refers to the conversion of waste into products. Recovery of materials and energy, specifically through the application of recycling technologies would greatly contribute to the vision of a circular economy model as proposed by the Ellen McArthur Foundation (Ellen McArthur Foundation and Circular Fibres Initiative, 2017a).

It is crucial to determine the safety of recycled products, and it's a prerequisite for societal acceptance of recycled plastics and textile fibres that these products are safe to use. A framework for safety (risk) evaluation of potential hazardous substances is needed, and state-of-the-art chemical analysis technologies are required for that. Next to known hazardous substances (e.g. BPA, PFASs, BFRs, dioxins), pigments and additives, also unknown substances (non-intentionally added substances, NIAS) need to be targeted. In all cases circular use could lead to accumulation of hazardous substances and new analyses strategies are needed especially for NIAS. The identification of NIAS has not been reported in recycled plastics, contrary to recycled paper (Peters et al., 2019). In this study an overview of the potential hazardous substances that arise from plastic and textile recycling will be made via literature research. It will be assessed if current analytical methods for the determination of NIAS and other substances in paper/board recycling can be extended to plastic materials. Finally, in-vitro testing approaches for the evaluation of toxic effects of recycled materials will be studied.

2 Recycling of plastics and textiles: Processes and contaminants

Plastic and textile waste can be recovered either by mechanical recycling (primary recycling substituting virgin materials in the same application and secondary recycling), by producing chemical building blocks (monomers, tertiary recycling), or the waste can be turned into energy (quaternary recycling) (ASTM, 2000; Hopewell et al., 2009). Recycling is most commonly achieved by mechanical and, to a much lower extent, by chemical processes. Mechanical recycling of plastics includes cleaning, grinding, remelting and regranulating steps (Ignatyev et al., 2014). During mechanical recycling, polymer backbones are partially degraded because shredding and heating will lead to breakage of intramolecular bonds resulting in a lower molecular weight distribution and changed mechanical and optical properties of the recycled polymer. Some types of plastic additives, e.g. plasticizers, antioxidants and stabilizers, may form unintended reaction products, thereby losing their original function. To compensate such unwanted changes, mechanical recycling processes often require the addition of virgin polymers and/or additives. The application of mechanically recycled plastic in contact with food requires special attention because it may not only contain degradation products of polymers or additives, but also incidental contaminants arising from previous use and misuse by consumers, cross-contamination from waste disposal, and environmental contaminants. Chemical recycling processes depolymerize plastics into monomers which are subsequently used for repolymerization of virgin-like materials (Geyer et al., 2016). Economic and ecological issues currently limit the large-scale application of chemical recycling processes.

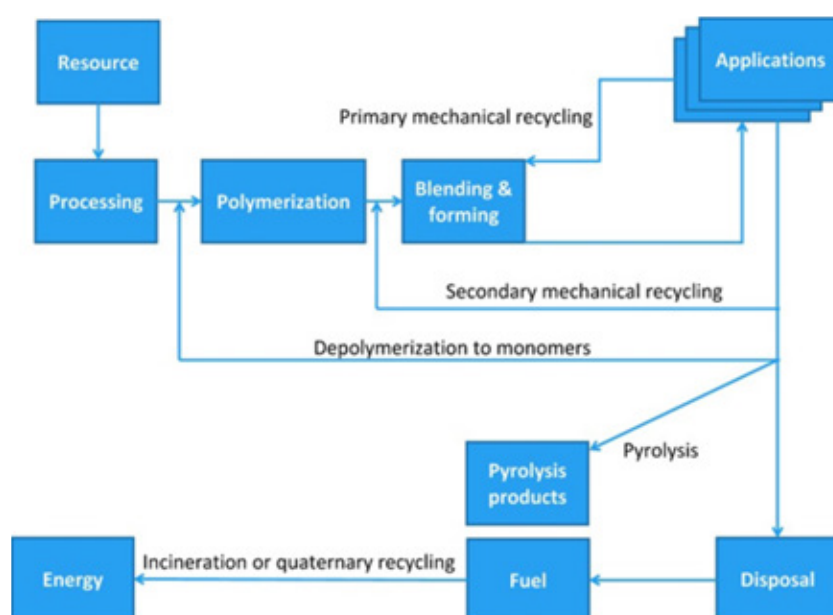


Figure 1 Most common recycling methods and their position in a lifecycle of an application (Ignatyev et al., 2014).

2.1 Recycling of thermoplast materials

The most recycled thermoplast material is polyethylene terephthalate (PET). It is completely recyclable by thorough washing and re-melting, or by chemically breaking it down to its monomers to make new PET resin (ILSI, 2017). Recycling of PET beverage bottles has become standard due to the relatively high inertness of PET, its resistance to higher temperatures, and the establishment of collection systems for food-contact grade PET. Several dozens of bottle-to-bottle PET (primary) recycling processes have been developed in the last 25 years and this is a good example of primary

recycling. PET can also be recycled into fleece as an example of secondary mechanical recycling (downcycling to a product with less value). Finally, PET can also be cleaved by some reagents, like water (hydrolysis), glycols (glycolysis) or alcohols (alcoholysis). According to the reagent used, different products are obtained. Hydrolysis is a recycling method that involves a reaction of PET with water in an acid (DeCarvalho et al., 2006), alkaline or neutral environment (Karayannidis and Achilias, 2002), leading to total depolymerization into its monomers. Chemical recycling of PET by glycolysis involves ethylene glycol insertion into PET chains to give bis(hydroxyethyl) terephthalate (BHET), which is a substrate for PET synthesis and other oligomers (Karayannidis and Achilias, 2007). Chemical recycling of PET by methanolysis involves PET degradation by methanol at temperatures between 180 and 280°C and pressures from 2 to 4 MPa with the main products being dimethyl terephthalate (DMT) and ethylene glycol (EG) (Yang et al., 2002).

As for PET, mechanical recycling is the most used process for recycling polypropylene (PP), low-density polyethylene (LDPE) and especially high-density polyethylene (HDPE). The HDPE material is mechanically separated from the other plastics, shredded and melted down to further refine the polymer. The plastic is then cooled into pellets which can be used in manufacturing. Chemical recycling of polyethylene's involves pyrolysis, gasification, liquid-gas hydrogenation, viscosity breaking, steam or catalytic cracking, similar to those employed in the petrochemical industry (Schillias et al., 2018). Catalytic cracking and reforming facilitate the selective degradation of waste plastics. In particular, polyethylene has been targeted as a potential feedstock for fuel (gasoline) producing technologies. PE thermally cracks into gases, liquids, waxes, aromatics and char. There is a growing interest in developing value added products such as synthetic lubricants via PE thermal degradation. Polyurethanes (PU) are one of the most versatile groups of plastic materials, with a variety that stretches from flexible/rigid foams and thermoplastic elastomers to adhesives, paints, and varnishes. PU production is expensive compared with mass-produced plastic materials (e.g., polyolefin plastics), which is the reason for the development of recycling methods for PU wastes since the 1960s (Behrendt and Naber, 2009). As with the other plastics, recycling routes for PU can be divided into 'mechanical', 'chemical' and 'energy'. Mechanical recycling covers grinding, compression moulding, adhesive pressing and bonding of PU wastes. Chemical recycling covers two different technological routes: chemolysis and petrochemical type processes. The chemical route uses mostly hydrolysis, aminolysis or a glycolysis approach. Energy recovery refers to incineration of PU waste, decomposition (by pyrolysis or hydrogenation) and the combustion of products.

2.2 Recycling of thermoset materials and composites

Due to an increasing number of applications that use lightweight thermoset materials and restrictions on landfill solutions throughout the EU, the development of thermoset recycling strategies has accelerated in recent years (Yang et al. 2012). Mechanical recycling uses high force and shear to achieve a size reduction of the waste component into uniformly sized flakes. These flakes are treated with hammer mills or high-speed mills into finer products in the millimetre to micrometre range. A disadvantage of this approach is that the thermoset matrix and the carbon fibres are not treated separately and as such any orientational advantage of the filler material is lost. The powder obtained after mechanical grinding is generally only used as a filler in new, for example thermoplastic, materials (Bernardeau et al., 2018). Thermal recycling can be divided in aerobic and anaerobic combustion known as incineration and pyrolysis. Incineration leads to recovery of energy and in some processes to recovery of the glass and carbon fibres (Pickering et al., 2000). Pyrolysis will break down the thermoset matrix into lower molecular weight organic substances of which the chemical structure is related to the original material which can potentially be used as feedstock for further chemical processing (Yang et al., 2012; Al-Salem et al., 2017). Since the recovered carbon fibres are not affected by oxidation this leads to a higher quality recycled product and therefore pyrolysis is seen as the most optimal thermal recycling treatment for thermoset materials or composites. In chemical recycling a liquid medium is used to degrade and dissolve the thermoset matrix so the reinforcing carbon fibres can be regained. Similar as to pyrolysis, the degraded and dissolved organic substances can be reclaimed from the solvent and be re-used as molecular building blocks (Kuang et al, 2018; Sokoli et al., 2017). The cracking of the thermoset matrix, mostly flexible or rigid foam mixtures, produces a polyol which can be reintroduced into the PU raw material cycle. An issue is that the separation of organic substances from the solvent requires a lot of

energy and that the frequent use of hazardous solvents makes the impact of chemical recycling questionable (Shuaib and Mativenga, 2017).

2.3 Recycling of textiles

Textile recycling processes have long existed, but have been greatly influenced by factors such as high prices, volume, and availability of virgin raw materials, which have limited the ability to be integrated as established and economically viable operations. Processes such as re-spinning of post-industrial and post-consumer materials, pulping of cotton and linen, and non-woven material production have existed for centuries, with variations of such operations currently practiced. Comparable to the situation for plastics (schematically presented in Figure 1), four categories of recycling technologies exist and are summarized as follows (Wang, 2010):

- Primary: recycling material in its original form for recovery of equal value;
- Secondary: processing post-consumer product usually by mechanical means into product with different physical and/or chemical properties (mechanical recycling);
- Tertiary: processes such as hydrolysis and pyrolysis, in which waste is converted to basic chemical constituents, monomers, or fuels (chemical recycling);
- Quaternary (recovery): waste-to-energy conversion processes such as incineration of solid waste, or utilization of heat generated.

Specific to textile materials recovery, common processes include mechanical and chemical recycling methods. Mechanical recycling processes are categorized as a secondary recycling approach. Processes include: cutting of sorted fabrics for use as wiper rags, shredding and pulling of textile materials into fibres, re-bonding or re-spinning into new yarns or fabrics, melting and re-extruding, reblending (may include proportions of virgin material) or re-spinning to produce new yarns and threads, or textiles (Peterson, 2014). Chemical recycling processes are categorized as a tertiary recycling approach, and include processes in which the chemical structure of the material is either broken down partially or fully (depolymerization), followed by re-polymerization to virgin material, or through the dissolution and melting processes, from which the material is drawn or extruded into re-usable textile fibre (Peterson, 2014). Chemical recycling of cellulosic fibres has been developed with ongoing advancements in technology towards scale-up, while the recycling of synthetics (nylons and polyesters) include some full-scale developments, but is limited to a few suppliers. Nevertheless, developments in demonstrated technologies are expected to be advanced in the coming decades.

Mechanical recycling of polyester consists of a re-melt process (or melt recycling). The process consists of the following main steps (Arthur, 2017):

- Collection, sorting, separation, and removal of contaminants or non-target materials;
- Reduction of size – crushing, grinding, shredding, or pulling;
- Heating/re-melting, and extrusion into resin pellets;
- Melt extrusion into textile fibres;
- Processing of textile fibres to fabric.

The polyester recovered from mechanical recycling is often used in lower value applications, due to the loss of physical properties, degradation, and contamination during use cycles and processing. Post-consumer PET bottles are most often recycled into PET yarns. The chemical recycling pathways for PET have already been described in the previous section “recycling of thermoplast plastics” (2.1) and include processes which break down (depolymerize) the polymer into its components (monomers, oligomers, other intermediates). Chemical treatment in the recycling process may also facilitate the separation of PET from other materials, such as blended textile fibres (i.e. elastane or cotton), or dyes and chemical finishing, as well as the creation of other end products of equal value (Aguado and Serrano, 2007). The most common depolymerization methods include: hydrolysis, methanolysis, glycolysis, or hybrid routes.

The process for the mechanical recycling of nylon involves the same steps as that for polyester. Due to its lower melting temperature (compared to PET), nylon is highly susceptible to contamination by microbes, bacteria, and non-recyclable impurities remaining in the material, and thereby requires a

cleaning process prior to recycling (Muthu et al., 2012). Chemical recycling of nylons includes a depolymerization process followed by distillation to obtain and recover their monomeric constituents: caprolactam (for Nylon-6), and HMDA and adipic acid (for Nylon-6,6).

The mechanical recycling of cotton is well established and is applied to both pre- and post-consumer waste and generally entails the respinning of recycled material combined with virgin material without additional chemicals (Ellen McArthur Foundation, 2017b). The majority of chemical recycling processes of cotton is in the development stage or close to commercial adoption, and include either dissolution processes to recover the cellulosic fibres or depolymerization processes to generate other by-products. The chemical recycling process of cotton is based on the dissolution of cellulose. Two main routes which have been explored include the depolymerization of glucose monomers for use in other applications, or a polymer dissolution route where the separation and regeneration of cellulosic fibres occurs by use of solvents (Li-Carrillo, 2016).

3 Additives in plastics and textiles: Hazardous substances

Many substances used to make plastics, including packaging plastics, are highly hazardous and therefore of significant concern for occupational health. During the subsequent use, disposal and recycling of the plastics packaging, substances present in the plastic may transfer into products such as foods or cosmetics, or into the environment. Plastic recycling can also result in accumulation of hazardous substances in the recycled materials and therefore, a detailed assessment of substances associated with plastic packaging is necessary. Recently, a number of publications have emerged that give an overview of substances associated with plastics or plastic packaging. Stenmarck et al. (2017) have produced an overview that was based on reports from the Danish Ministry of the Environment and includes substances from the following lists of hazardous substances: The Danish EPA's list of undesired substances (LOUS), The SVHC Candidate List under REACH, The Norwegian list of priority substances, ECHA's Registry of Intentions, CMR-substances likely to be present in plastic toys, and recognized alternatives to problematic phthalates and BFRs. Hahladakis et al. (2018) categorized the most commonly used additives in plastics and plastic packaging (mostly food packaging) and described their uses, applications and properties. Groh et al. (2019) produced an overview of known plastic packaging-associated substances and their hazards. They compiled a database starting from the American EPA's Chemicals and Product Categories database and Ernest Flick's Plastics additives database and combining these with a number of further overviews and listings. In this study the overviews of the three references are combined into an overview of 238 most hazardous substances likely associated with plastic packaging. The list of these substances is given in Annex 1.

As with the plastics, an extensive amount of substances is used throughout the manufacturing stages of textiles, from textile fibre production, through to treating, dyeing, and finishing processes, often comprising 5-15% of a garment's weight (Safer Made, 2018). Substances may be used to provide colour and impart function to textiles. To convert raw materials into textiles, it has been cited that 8,000 different substances are used (Safer Made, 2018). Various substances have been identified to be toxic to human health and produce a multitude of effects on the environment, notably water pollution. Increased awareness and concern regarding effects of chemical usage in the industry has prompted widespread efforts to create and implement chemical management practices, identification systems, standards, policies, and legal requirements. There have also been extensive efforts towards new safe and sustainable chemistry and processes, as well as innovation around new or alternative substances. In the "Safer Chemistry Innovation in the Textile and Apparel Industry" report by Safer Made chemicals used in the textile sector were evaluated and organized into 43 classes of substances, and six broad substance groups which are: amines, dyes and residuals, halogenated substances, metals, monomers and solvents and process aids (Safer Made, 2018). The list of 43 classes of substances is given in Annex 2.

4 Contaminants in recycling plastics and textiles

Whereas in the northern part of the world plastics production, use and recycling is regulated to varying degrees, in many developing countries plastic recycling is often not controlled by an appropriate regulatory framework, and environmental protection is poorly enforced, resulting in significant contamination of the ambient environment in areas where plastic is recycled. Uncontrolled recycling can also result in the transfer of potentially harmful substances into recycled plastics. This section deals with contaminants in plastics and textiles as a possible result of recycling and environmental and human exposure aspects of recycling.

4.1 Contaminants in recycled plastic.

The application of recycled plastics is limited by two factors: The polymer purity and the molecular purity. The former restricts the use of recycled material to thick-wall applications with less mechanical demands. Most of the polymers are not compatible with each other, i.e. their blends have mechanical properties that are inferior to those of the pure constituents. Examples are PET impurities in PVC, in which solid PET lumps form in the PVC phase. This leads to significantly downgraded properties and consequently less-valuable end products (Hopewell et al., 2009). The molecular purity restricts the use of recycled plastics to non-food applications only. Only for recycled PET is the molecular contaminant limited and is re-use possible. Differently from PE, PP, PS and PVC, PET only absorbs very limited amounts of fat, mineral oil and other molecular materials. For the other materials it is questionable whether recycled material can be used as a food contact material (FCM). The collected used plastics waste are contaminated by e.g. oil/food/residues, and during recycling the materials will be treated with washing agents, solvents, and heated to >125°C. These new products potentially contain a wide range of molecular contaminants (i.e. residual contaminants and de-novo chemical reaction products resulting from treatments, the so-called non-intentionally added substances, NIAS). Information about what the nature of the molecular contaminants and NIAS in plastics is limited and will also often not be known by the manufacturer.

Additives fulfil a large variety of different functions in plastic polymers by improving production processes as well as appearance and performance of the final products. In Europe, around 600 substances are authorized as additives and polymer production aids for plastic FCMs (EC, 2011). Additives are generally substituted during recycling to compensate losses in functionality while residual additives and their breakdown products remain in the plastic material. Dutra et al. (2014) measured the migration of non-volatile and inorganic residual substances from post-consumer recycled PET, as well as from multilayer packaging material containing postconsumer recycled HDPE. Tests were carried out using food simulants. Several authorized plastic additives were measured in recycled PET, including the plasticizers di-isononyl adipate (DINA) and di-isononyl phthalate (DINP), the optical brightening agent Uvitex OP and the slip agent oleamide. Several inorganic contaminants, determined by inductively coupled plasma mass spectrometry, were found but all were below the acceptable levels. Keresztes et al. detected several phthalates in water samples from PET bottles with 20-30% recycled content. In contrast, these phthalates were not found, or only in low concentrations, in water samples from bottles composed of virgin PET (Keresztes et al., 2013). It's not so clear where these phthalates should come from since they are not needed as additives in PET. Results of Pivnenko et al. (2016), who analysed the levels of nine phthalates in plastic waste samples, seem to suggest that these phthalates were introduced into post-consumer PET as irregular external contaminants derived from other polymer types during the collection stage.

A report from the Norwegian Environment Agency from 2013 outlined the presence of 43 substances potentially used in plastics and that are considered hazardous and which may be limiting the possibilities for plastic recycling (NEA, 2013). The report did not explicitly include NIAS potentially present in plastic products, waste plastics and recycled plastics. Thus, the list of substances actually

present in plastics can potentially be longer. Nevertheless, among the substances identified in the report main groups of substances included phthalates, toxic metals, brominated flame retardants (BFRs), poly-aromatic hydrocarbons (PAHs), etc.. Phthalates are mostly used as plasticizers in plastic production, with the largest share of the plasticizers market being attributed to polyvinyl chloride (PVC) production. Depending on their carbon chain length, phthalates are commonly divided into low and high molecular weight (i.e. LMW and HMW, respectively). LMW phthalates are prone to migration, making them more relevant for human toxicity. This has also resulted in restrictions on their use in selected applications in plastic materials (e.g., food-contact articles and children's toys) (EU, 2011). Di-iso-butyl phthalate (DiBP), di-(ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) are LMW phthalates found in the majority of plastics (Pivnenko, 2016). DEHP is the dominant phthalate found in relatively high concentrations (up to 2700 mg/kg) in the majority of the plastic samples. Several sources of plastics were evaluated for their phthalate content (Pivnenko et al., 2016). The results showed that virgin and recycled industrial plastics (group 1) have similar phthalate content. Furthermore, residual and source-segregated waste plastics and recycled household plastics (group 2) were also similar as to their phthalate content. On the other hand, group 1 and group 2 were significantly different, with group 2 having higher phthalate content. Based on the systematic statistical assessment of results for the evaluated samples, this could indicate that phthalates are added in later stages of plastic product manufacturing (labelling, gluing, etc.) and are not removed in the re-processing of plastics, making recycling a potential source of phthalates in products based on recycled waste material.

Different groups of contaminants, e.g. oligomers, additives and their degradation products, as well as substances derived from previous uses, have been reported in recycled plastic (Camacho and Karlsson, 2000; Dutra et al., 2011; Nerin et al., 2003). Flavor, odor and aroma substances from previous uses belong to common contaminants in post-consumer plastic packaging. The presence of citrus-based essential oils has been attributed to soft drinks stored in PET bottles (Bayer, 2002). According to the same reference other substances from food-grade PET used in non-food applications such as mouthwash, personal hygiene and household cleaners also contributed to the contamination of post-consumer PET. Similar substances were measured in recycled, but not in virgin HDPE (Camacho and Karlsson, 2000). Furthermore, 11 esters and 5 alcohols were only identified in recycled, but not in virgin HDPE and their origin was assigned to the previous use of the packaging, e.g. personal hygiene products or cleaning agents.

Oligomers are unintentionally formed by-products in the synthesis of plastics. Additionally, they may be generated during the recycling of polymers. Linear and cyclic oligomers have been measured in recycled PET with di- and trimers being the predominant species (Lopez et al., 2014). Acetophenone and benzaldehyde are oxygenated derivatives of styrene, which have been found in higher relative abundances in recycled than in virgin PS samples (Vilaplana, 2007). Kanwal et al. (2007) measured thermal degradation of PS after recycling and found increased levels of migration into vegetable oils at high temperatures.

Plastic samples, including waste and recycled plastic waste from households and industry, and virgin plastic were analysed for 15 selected metals. Samples of reprocessed household waste contained the overall highest concentrations of metals, potentially related to the use of metal-containing additives (e.g. fillers) to enhance the mechanical properties of plastic during recycling. While the elevated metal concentrations in the recycled plastic did not exceed legal limits, it is important to be aware that metal concentrations are higher in recycled plastic from household plastic waste and that a continuous increase in plastic recycling rates may lead to even higher metal concentrations in the future (Eriksen et al., 2018). In addition metal-containing additives have direct impact on the recyclability of plastics or even support the degradation of plastics (Pivnenko et al., 2016). In particular metal salts or oxides such as Fe_2O_3 , Cu_xO , ZnO and TiO_2 have been found to act as pro-oxidants and photo-oxidation catalysts (Shawaphun et al., 2010).

Contaminants can also be derived from non-food grade plastics by transfer of certain groups of additives into new recycled products, a problem especially with more sensitive use areas. For instance, brominated and phosphorous flame retardants and phthalates have been found in children toys from recycling (Chen et al., 2009; Ionas et al., 2014; Lee et al., 2014). Flame retardants have also been

measured in samples of black plastic FCMs and household products from the European market (Samsonek and Puype, 2013; Puype et al., 2015; Puype et al., 2017). Flame retardants are commonly divided into four groups in accordance to the main chemical constituent used, i.e. halogenated organic, phosphorus-containing, nitrogen-containing and inorganic (Birnbaum and Staskal, 2004). The largest market share is attributed to a subgroup of halogenated organic – brominated flame retardants (BFRs). The subgroup contains well-established BFRs produced in large volumes, i.e. hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA), as well as emerging phenol-based BFRs (e.g., 2,4-dibromophenol (2,4-DBP) and 2,4,6-tribromophenol (2,4,6-TBP)). While HDPE contained among the lowest concentrations of HBCD and TBBPA, packaging waste HDPE (both source-segregated and residual) also contained the highest concentrations of 2,4-DBP and 2,6-dibromophenol (2,6-DBP). In addition to the direct use of selected BFRs, relatively high concentrations of 2,4-DBP (240 ng/g), 2,6-DBP (250 ng/g) and TBBPA (7000 ng/g) in a sample could be attributed to thermal degradation of TBBPA and production of dibromophenols as by-products in recycling. Puype et al. (2015) analysed 10 selected food contact utensils (produced of recycled materials) of which seven contained a bromine level ranging from 57 to 5975 mg kg⁻¹. The BFRs that were present were TBBPA, decabromodiphenylether (decaBDE), decabromodiphenylethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE). In all cases when bromine was detected at higher concentrations, concurrently antimony was also detected, which confirms the synergetic use of antimony in combination with BFRs. Finally, the plastic recycling process may also influence the transformation of contaminants contained in the waste material being recycled. As an example, among the three isomers of HBCD measured, α -HBCD was found in relatively higher concentrations compared to β - or γ -HBCD (Pivnenko et al., 2017). This contradicted the common composition of commercial HBCD mixtures, where γ -HBCD is the dominant isomer. Since exposing HBCD to temperatures >100°C promotes the transformation of γ -HBCD to α -HBCD, temperatures commonly applied in thermoplastics re-processing (135-245 °C) can alter the diastereometric ratio of a HBCD mixture and explain the prevalence of the α -HBCD in samples of recycled plastics.

4.2 Contaminants in composites

Since composites are rarely recycled no information was found about contaminations in recycled composite material.

4.3 Contaminants in recycled textiles

It has been identified that substances found in textile materials have potential to impede recycling processes; however, the knowledge base surrounding substances problematic for recycling is limited, and specific impacts have not been characterized. In the current system, information regarding substances and quantities present in textile materials is not generally passed on to potential recycling companies. It would be greatly beneficial to advance the knowledge gaps in this area by improving traceability and the identification of substances in textile materials, and the examination and identification of substances which have been found to interfere with recycling technologies.

In addition to substances of concern there are emerging concerns related to plastic pollution caused by the textile and apparel industry. Synthetic textile fibres like polyester and nylon now dominate apparel. Synthetic polymers tend to persist in the environment and can end up acting as chemical pollutants as well as substrates that magnify the accumulation of other harmful substances in the ecosystem. An article published in Environmental Science & Technology connects plastic microfiber pollution in the marine environments with emissions from washing apparel made from synthetic textile fibres (Browne et al., 2011). Since (mechanically) recycled textile is expected to contain less strongly bound textile fibres this problem may increase with increasing textile recycling.

4.4 Environmental contaminants due to recycling processes

All four levels of plastic recycling, primary and secondary mechanical recycling, chemical recycling and thermal recovery, are currently implemented worldwide in a different degree to recycle and recover plastic waste. Depending on the type of process this may lead to contamination of the environment and exposure of humans. Moulding and extrusion are key stages in the mechanical material recycling of plastic waste that usually is operated at 200-300 °C, and in this temperature range a lot of hazardous substances such as toxic metals, volatile organic compounds (VOC), phthalates, polycyclic aromatic hydrocarbons (PAH), polybrominated diphenyl ethers (PBDE) and polybrominated dibenzo-p-dioxins and furans (PBDD/F) may be released. He et al. (2015) studied VOC emissions during the recycling of different types of plastics and found that especially styrene and other mono-aromatics were emitted during the recycling of ABS and PS plastics. Huang et al. (2013) showed that exhaust gases from plastic waste recycling granulation had an effect on the ambient environment. PAHs were detected inside and outside of the recycling granulation plants area while high levels of the phthalates DBP and DEHP were detected inside the plants. Tang et al. (2015) demonstrated that the surface soils and sediments in areas with plastic recycling plants are contaminated with Cd and Hg in concentrations of 0.36 and 0.41 mg/kg in the soils and 1.53 and 2.10 mg/kg, respectively, in the sediments. Tang et al. (2014) and Labunska et al. (2013) studied the emission of PBDE from plastic waste recycling and found that concentrations of these substances in soils, sediment, human hair and dust were higher in areas containing plastic waste recycling plants. PBDE concentrations in road dust samples from an area with intense mechanical recycling of plastic waste, were 10 to 100 times higher than normal background concentrations (Tang et al., 2016). The open burning of cables and other e-waste plastic resulted in the formation and release of complex mixtures of persistent organic pollutants including chlorinated and brominated dioxins and furans and dioxin-like polychlorinated biphenyls with often particular high levels of brominated and mixed halogenated dibenzofurans suggesting the combustion of PBDE-containing plastics as the principal source (Tue et al., 2016). Gu et al. (2017) investigated the environmental impacts from mechanical plastic recycling and made a sensitivity analyses to evaluate the potential environmental changes occurring by variations in operational process parameters. They concluded that specific focus should be given to the extrusion process, that plastic recycling activities should be centralised, and that material substitution achieved considerable environmental benefit.

5 Analytical and bioanalytical approaches for additives and NIAS identification in recycled plastics and textiles

The successful recycling of plastics and textiles depends, apart from technical aspects, to a large degree on the safety of the products resulting from recycling. The safety of recycled products is a prerequisite for societal acceptance of recycled plastics and textiles. The transition to a circular economy of plastics and textiles will not be accomplished if no guaranteed safe products can be delivered to the market. The evaluation of the safety of recycled plastics and textiles is crucial, but a framework for evaluation of potential hazardous substances and associated risks for the consumer is virtually absent. More specifically, a legislative framework, risk assessment framework, and relevant testing strategies are urgently needed.

5.1 Legislative framework

A legislative framework covering the safety of recycled products in a broad sense is lacking. The area of food contact materials (FCMs), and particularly the substance safety of plastic FCMs, is regulated in EC regulation 10/2011. This regulates a number of issues: (i) overall and specific migration limits (SMLs) for a wide range of substances; (ii) a list of approved monomers and additives, partly with restrictions and specifications and (iii) the obligation to consider also substances which are not added intentionally, so-called NIAS. This framework focusses on new plastic materials. When it comes to FCMs produced from recycled plastics (including packaging and e.g. kitchen utensils), the Commission Regulation (EC) No 282/2008 of 27 March 2008 on recycled plastic materials and articles intended to come into contact with foods regulates the requirements for recycling processes. The EC keeps a register for validated FCM recycling processes (EC, 2019a). Mainly PET plastics are being recycled for FCM use. It should be noted that the recycling process itself is regulated, rather than regulating contaminating substances. Apart from FCMs, a large amount of recycled plastics (LD-PE, HD-PE, PP, PS) is downcycled into other non-FCM products, including waste bins, flower pots, outdoor furniture and others. Because skin-contact may occur at several occasions with these materials, such materials should also be safe to use. There is currently no comprehensive EU legislation in place that covers the chemical safety evaluation of recycled products, both thermoplastic and also thermoset materials. When it comes to textiles, both cellulose based and polymer based, there are several initiatives to explore the possibilities to recycling of these products into new textiles (as discussed in chapter 2). Currently also here a regulatory framework for safety evaluation of the recycled textiles is lacking, whereas this is urgently needed given the material-to-skin contact of these materials. If we anticipate that future technological developments enable a better recycling of plastics and textiles into FCMs, recycled plastic products and textiles, then a legislative framework will facilitate a large scale implementation of plastic and textile recycling strategies in a circular economy.

To iterate the contaminating substances that may end up in the recycled product, they may comprehend a wide diversity:

- Polymeric contaminants, i.e. polymeric impurities (monomers, oligomers, polymeric fractions) from a different polymer than the intended product;
- Additives (e.g. pigments, stabilizers, catalysts, fillers...);
- Chemical contaminants originating from previous use (odors and flavours, residues);
- Neo-formed chemical contaminants which are generated during the chemical or physical recycling process where heat, chemicals and/or pressure were applied in the process from collection, cleaning and reprocessing of the polymer;
- Contaminants (VOCs) originating from the degradation of polymers (Yamashita et al., 2009);
- Contaminants coming from the mixed collection of waste polymers (e.g. chlorinated and brominated substances and phthalates from plastics) (Yamashita et al., 2009).

In the production of polymers and textiles, several substances are blended together to produce the intended polymer. These are called intentionally added substances (IAS). However, several non-intentionally added substances (NIAS) may occur in a recycled product, originating from the above mentioned contamination sources. Below, we will focus on testing methods for the detection of NIAS.

5.2 Methods for (recycled) plastics and textiles

The number of studies that designed methods specifically for analysis of contamination in recycled plastics is very limited. Only a small number of studies focussed on recycled polymers like PET, PVC, polyolefins and others. No studies were found on methods for contaminants in thermoset materials, for the reason that current thermoset materials are only recycled to a limited degree. For textiles no studies were identified that specifically focus on recycled materials. Because of specific methods for recycled polymers and textiles are limited or lacking, we discuss below methods that are used for non-recycled (i.e. virgin) polymers and products thereof. The same holds for textiles. Concerning paper recycling, which has a long history already, many analytical studies on targeted and untargeted methods have been published, as recently reviewed by Peters et al. (2019). Whenever we deemed such methods complementary, we have included them in below discussion.

5.3 Sample extraction and clean-up for NIAS in plastics

The first step in NIAS analysis is the release of the analytes from the plastic or textile matrix. The extraction method to be chosen depends on the nature of the analyte; volatile analytes require a different approach than non-volatile analytes. Several extraction techniques can be employed for that purpose, which are discussed below. For plastics intended as FCM leaching experiments can be conducted in relevant food simulants (e.g. demineralised water, 3% acetic acid, olive oil and 10% and 50% ethanol). These simulants serve as extractant and act and collect that analytes of interest. Once the migration time is completed, the migrant will be further processed for determination of the analytes of interest. Regulation (EU) No 10/2011 provides directions on how to perform migration studies. This regulation also provides specific migration limits (SMLs) for a range of substances. Although this regulation applies to virgin plastics only, the listed substances may become a NIAS once the used plastics are being recycled. It's is therefore that these migration experiments may be very well suitable also for determination of NIAS in FCMs made of recycled plastics, although once again it should be noted that the mentioned SMLs only apply to virgin plastics. Specific technical approaches may apply, and technical guidelines for testing of e.g. kitchen utensils are provided at the European Reference Laboratory (EU-RL) for FCMs (EC, 2019b).

Above migration experiments are specifically designed for FCMs, but recycled polymers with other destinations require different extraction approaches. Several solvent extraction techniques have been employed to extract contaminants from recycled plastics. Vilaplana et al. (2007) extracted low molecular weight compounds (e.g. VOCs) from recycled high impact polystyrene (HIPS) using microwave assisted extraction (MAE) using a n-hexane/isopropanol mixture (50%, v/v). Peters et al. (2019) recently reviewed the analytical approaches for identification of NIAS in paper and board FCM. Many of the sample preparation procedures discussed in that review can be applied for recycled matrices as well. These include liquid extraction approaches such as Soxhlet or other reflux extraction techniques, liquid solid extraction (LSE), ultrasound-assisted solvent extraction (UAE), often combined with some type of clean-up.

Volatile substances in recycled plastics may be extracted from the matrix using headspace, or a combination of headspace and solid phase microextraction (SPME), as demonstrated by Dutra et al. (2011) for volatile organic compounds (VOCs) in recycled PET and HDPE. They used this approach to evaluate the efficiency of VOC removal in the recycling process. Yamashita et al. (2009) used Tenax/Carboxen absorbent to capture VOCs from the waste plastic flakes, and used thermal-desorption (TD) coupled to GC-MS for determination. Ibarra et al. (2018, 2019) used purge and trap (volatiles) and acetonitrile extraction for the extraction of IAS and NIAS from films, laminates and PP FCMs.

5.4 Sample extraction and clean-up for NIAS in textiles

Many studies towards contaminants in the textile industry focus on the pollution of the production facilities, and have investigated the effluents from these facilities. Only limited studies focused on the development of methods for contaminants in the textiles themselves. Luongo et al. (2014) developed an extraction method for the determination of quinoline derivatives in from polyester, cotton and mixed textile fibre materials using UAE with dichloromethane, combined with solid phase extraction (SPE) clean-up. Although in this study the analytes were not necessarily marked as NIAS, these methods will apply in a similar way when these analytes are unintentionally present in recycled textile fibres. Avagyan et al. (2014) extracted benzothiazoles and benzotriazoles from textiles by UAE with a 20% acetone in DCM mixture. Detection of NIAS may also be feasible directly, using direct techniques that do not require extraction of the NIAS from the matrix. Those techniques detect the contaminants at the surface of the material, without the need for extraction, and can be applied as screening techniques. These will be discussed below in more detail.

5.5 Targeted methods detection

A range of methods have been reported for targeted analysis of substances, mostly based on chromatography combined with MS approaches. Various ionisation approaches are applied like electron impact (EI) for GC-MS and electrospray ionisation (ESI) for LC-MS/MS. Quadrupole and triple quadrupole approaches are most often applied as mass analysers, but the use of other analysers was also reported. Volatile and apolar substances are amenable to gas chromatography (GC). Garcia Ibarra et al. (2018, 2019) produced a list of intentionally added substances (IAS) and non-intentionally added substances (NIAS) (alkanes, aldehydes, alcohols, phthalates, citrates, adipates, phosphates, phenolic substances, diisocyanates, and fatty acids) in plastic packaging materials that were identified with GC in combination with single quadrupole MS. GC-MS was used by Dutra et al. (2011) and Yamashita et al. (2009) for the detection of VOCs, styrene trimers and aliphatics. Vilaplana et al. (2007) used GC-time of flight (ToF)-MS for the detection of contaminants in recycled and virgin HIPS.

Only a few studies investigated substances in textiles or fabrics, and most of them focussed on derivatives from AZO dyes because of their (suspected) negative health effects. Luongo et al. (2014, 2016) and Avagyan et al. (2014) used GC-MS for the determination of aromatic anilines and derivatives, quinolines, benzothiazoles and benzotriazoles in textile. Brüscheweiler et al. (2014) investigated derivatives from AZO dyes (aromatic amines) in textile products using LC-ESI^(+/-)-MS/MS. Abdallah et al. (2017) investigated BFRs in polyester textiles. Their detection methods were GC-MS for PBDEs, and LC-ESI⁽⁻⁾MS/MS for the separation and detection of HBCDD diastereomers in these samples.

5.6 Comprehensive suspect screening and non-target analysis

The studies on the identification of NIAS by MS approaches shows various levels of complexity, particularly on the methods used for identification. Fairly straightforward approaches involve the identification using a NIST library. Somewhat more complicated is the use of external databases such as SciFinder and Chemspider, or the use of a suspect list. The highest complexity is achieved when, with an exact mass as a starting point, substantial efforts are made to unravel the molecular composition of a NIAS, ultimately leading to a successful identification of the unknown substance. With the increasing level of complexity, the complexity of applied instrumentation and identification approach increase as well. Below, we will discuss examples of different approaches. As noted before, there are only limited studies on the investigation of recycled polymers, except for FCMs where some studies on recycling of polymers were reported.

Song et al. (2019) investigated NIAS markers that were discriminative towards recycled EPS versus virgin EPS. They employed HS-SPME-GC-MS for the analysis of VOCs, and used the NIST library for identification purposes, resulting in 99 identified substances, of which 17 substances (o-xylene, acetophenone, ethylbenzene, α -ethylstyrene, 2-phenylpropenal, propylbenzene, 2-phenyl-1-propene, undecanal, benzoic acid ethyl ester, 2-ethyl-1-hexanol, decanal, benzylcarboxaldehyde, isopropylbenzene, 2,4-diphenyl-1-butene, dodecanal, benzaldehyde, nonanal) were discriminative towards recycled EPS.

Martinez-Bueno et al. (2019) recently reviewed the use of high resolution accurate mass spectrometry (HRAMS) strategies for the identification of migrating substances (IAS and NIAS) in food contact materials. They identified 17 studies that applied HRAMS, mostly coupled to LC for this purpose, showing that the application of HRAMS is still in its infancy for studying migrants. The applied MS instruments were Q-ToF-MS and Q-OrbitrapMS interfaced to LC with ESI+ and ESI-. Only a small number of GC applications were reported using EI or APCI sources, connecting to above instruments. Several data acquisition strategies were reported, including Data Independent Acquisition (DIA) – full scan MS, DIA – all ion MS/MS, Data Dependent Acquisition (DDA) – Full MS-ddMS² and full scan MS. In DDA mode, the instrument performs the data collection using predetermined rules, switching between full-spectrum MS survey and a full-spectrum product ion (MS/MS) analysis dependent mode, in one chromatographic run. The switching is automatically controlled based on the predetermined rules: based on the intensity of the precursor ions observed; or based on other criteria such as isotope pattern, charge state or specific m/z values on an inclusion list or an exclusion list. In DIA, all ions within a selected m/z range (e.g. 50-150) are fragmented and analysed in a second stage of tandem MS. The switching between MS and MS/MS is automatically performed to obtain fragments for all precursor ions present. MS and MS/MS data of unknown substances are also acquired simultaneously in one chromatographic run. The DIA mode has significant advantages in identifying unknown substances compared with other acquisition methods, because no exclusion of peaks occur based on the predetermined criteria. In all ion fragmentation (AIF), MS/MS experiments can be performed at a low and higher collision energy, resulting in different fragmentation, and, when combined, in richer MS/MS spectra. This approach typically results in large number of hits (i.e. detected masses), and not all of them may be relevant. In two recent studies (Canellas et al., 2019; Vera et al., 2019), the use of ion mobility MS (IMS) was presented as a way to reduce background noise during acquisition, through drift-time alignment. Through this process, they demonstrated that matrix-interferences can be reduced substantially, leading to cleaner spectra. The next step after data acquisition is the reduction of the obtained 1000's of masses down to an appreciable number. This data reduction can be done on the basis of mass range, signal-to-noise threshold level, a minimum response threshold, PCA analysis of two or multiple samples, visual comparison to blank or reference sample and peak deconvolution. This should preferably result in a limited number of hits that will proceed to the next stage: the (tentative) identification of the peaks. The identification is done by the following procedures, or (often) combinations thereof: study of the fragmentation pattern, comparing fragmentation to *in-silico* fragmentation tools, confirmation by pure standards (when available), comparison to databases (e.g. ChempSpider, SciFinder), comparison to mass spectral databases (NIST, MassBank or mzCloud), studying isotope pattern, reducing mass tolerance, bibliographic search and background knowledge.

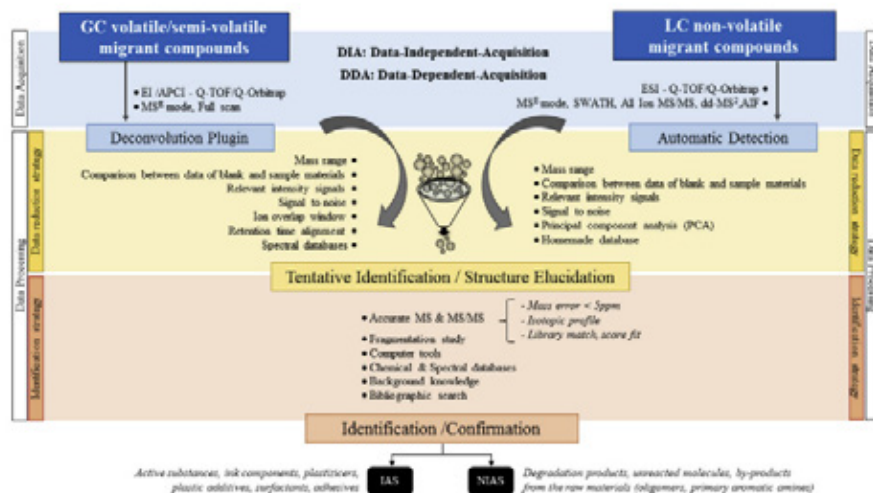


Figure 2 Schematic overview of the workflow for non-targeted identification of IAS and NIAS using HRAMS approaches. Figure taken from Martinez et al. (2019).

Below, two examples are presented of studies where (tentative) identification was performed on substances in FCMs. LC-ESI-Q-TOF-HRAMS was applied by Ramos et al. (2019) for the identification of migrants from multilayer FCM. They operated the instrument at 32.000 resolution FWHM, and applied a data-independent data-acquisition (DIA) mode (SWATH; Sequential Windowed Acquisition of All Theoretical MS). They obtained 3149 possibilities (unique masses), and reduced this number substantially by filtering strategies like selecting the most intense peaks only, through which they arrived ultimately at 21 possibilities that were in-depth investigated. The latter was done by in-silico fragmentation prediction, experimental fragmentation studies, search in MS databases (Metlin, MassBank, mzCloud) and bibliographic search. Through this approach, 26 substances were (tentatively) identified. Most substances were cyclic oligomers originating from PU adhesives. Some cyclic oligomers were reported for the first time in this study. A confirmation of some of the tentatively identified structures was not possible, because of the lack of standards, according to the Schymanski rules (see below). Martinez-Bueno et al. (2017) investigated NIAS from a nanofilm FCM by using LC-Q-Orbitrap-HRAMS, operated in the All Ion Fragmentation (AIF) mode, identifying the substances through a process of data reduction (e.g. intensity threshold, relative intensity, principle component analysis), followed by comparison of the fragments of each substance with a mass spectral library. Through this approach, the 4 NIAS were tentatively identified (N,N-diethyldodecanamide, N-[(9Z)-9-Octadecen-1-yl]acetamide, 1-Palmitoylglycerol and Glycerol stearate). For GC-Q-Orbitrap-HRAMS, they compared their fragments with the available NIST library, resulting in the identification of 3 additional substances (tripropylene glycol diacrylate, 10-Heneicosene and α -Tocopherol acetate).

Once a substance has been (tentatively) identified, it can be included in a home-made database for future reference. Samples analysed at later stage can be compared to the substances in this list, which facilitates and accelerates the identification process. This process is called 'suspect screening', and comprises the screening of sample extracts making use of lists with substances that have previously been identified or reported. Such lists ideally contain the name of the substance, possible synonyms, IUPAC name, identifiers (e.g. CAS number, EINECS number), chemical formula, exact mass and the nature of the identified substance (e.g. $[M+H]^+$, $[M+Na]^+$). Such lists can be generated by a single lab, or by multiple laboratories together on a shared platform. An example of these is the lists in the high resolution mass spectral database generated by the Norman network in the field of environmental pollution (<http://massbank.eu/MassBank/>).

During the (tentative) identification process, the criteria defined by Schymanski et al. (2014) can be used to indicate the confidence at which a substance is identified. These criteria originate from the environmental research field, but can be applied to any HRAMS identification process. These criteria are used to ease communication on the status of identification. Schymanski identified five levels of confidence. An increasing confidence in identification is supported by an increasing effort on the identification, as indicated in Table 1. The ultimate identification is achieved at level 1, where the

confirmation is obtained through measurement of a pure standard. In most cases however, the identification will finish at level 2 or 3, because of the lack of a pure standard.

Table 1 Confidence levels defined by Schymanski et al. (2014).

Level	Criteria
1	Confirmed Structure: Proposed structure has been confirmed with appropriate measurements of reference standard with MS, MS/MS and retention time matching. Ideally, a orthogonal method is used for conformation as well.
2	a Probable structure, Library: Matching literature or Library spectrum where match is unambiguous. b Probable structure, Diagnostic: No other structure fits experimental information.
3	Tentative candidate(s): Level where evidence exists for possible structure(s), but insufficient information available for exact structure match. (e.g. positional isomers).
4	Unequivocal molecular formula: Using spectral information (e.g. adduct, isotope ratio and/or fragment information) an unambiguous formula can be assigned.
5	Exact mass: Exact mass of substances of interest or the retention time of a specific characteristic fragment.

A framework for quantification of unknown substances, applied for paper packaging but also amenable for plastics, was developed by Pieke et al. (2017).

5.7 Instrumental (surface ionisation) screening techniques

Detection of NIAS may also be feasible directly, using direct techniques that do not require extraction of the NIAS from the matrix. Those techniques detect the contaminants at the surface of the material, without the need for extraction, and can be applied as screening techniques. A prerequisite for such techniques is that the contaminants can be released easily from the plastic/textile matrix without solvent transfer. Although such techniques potentially enable the direct (qualitative) characterisation of NIAS, no studies were found that applied such technologies.

5.8 Combining chemical analysis and bioassays

Complete information on which substances are in fact present in (recycled) plastics or textiles is, however, not possible to obtain: during the production and/or recycling of plastic and textile articles, side products are formed that can remain in the finished product. These NIAS are sometimes well characterized, but a full elucidation of all NIAS present in (recycled) plastics and textiles is currently neither technically nor economically feasible. Thus, recycled plastics and textiles may contain unknown substances that cannot be quantified or characterized in terms of their specific toxicity. As a consequence, the only way to assess if a plastic or textile transfers substances of concern into foods and/or the environment is to test overall migrant toxicity through the use of bioassays.

Bengtström et al. (2014) completed a study on an interdisciplinary strategy for the screening and identification of substances with potential adverse health effects in food packaging materials. A comprehensive extraction process, compatible with both chemical and toxicological analysis, was developed, which consisted of a purge-and-trap method for small volatile organic substances, and a boiling ethanol reflux system for semi- and non-volatile substances. The first step in this method is to test the FCM extracts for endocrine disruptive effects, genotoxicity, and metabolic effects of xenobiotics by in-vitro effect assays. The response from the Aryl Hydrocarbon Receptor (AhR) assay can be linked to these metabolic effects. Samples that are tested positive for these toxicity tests, are then subjected to an effect directed analysis (EDA) scheme (Figure 3).

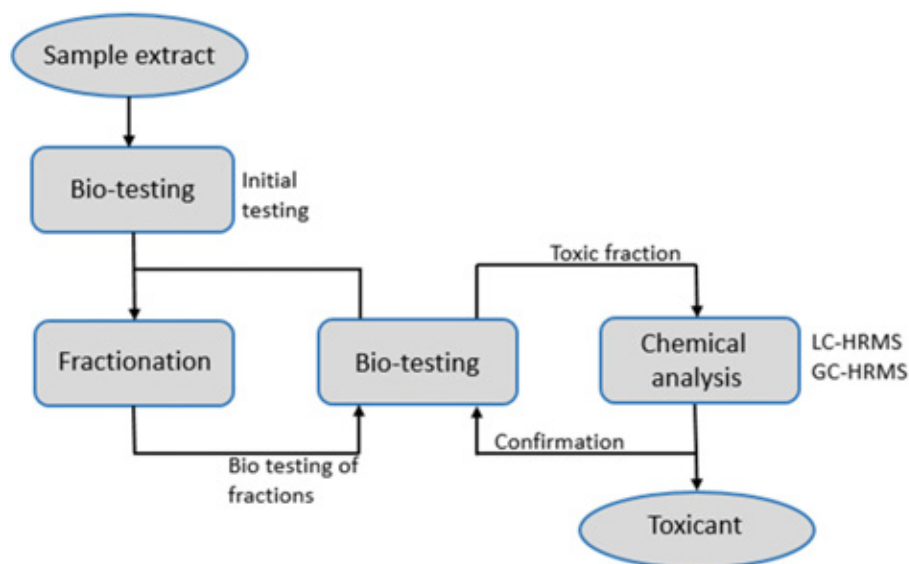


Figure 3 Effect-directed analysis (EDA) scheme for the identification of substances that exhibit an effect in a bioassay. Taken from Peters et al. (2019).

The aim of this approach is to narrow down the substances that potentially caused the response in the assay, and ultimately to identify the responsible substance causing the response. In this scheme a positive extract is fractionated by HPLC (e.g. on a C18 column along the polarity axis) and results in multiple fractions, and subjected to a second screening of cell assays. Specific fractions exhibited a response in the cell-assay, and directed towards the responsible bioactive substance. Secondly, the positive fractions were analysed by GC-QTOF-MS and UHPLC-QTOF-MS for identification of the bioactive substances. They faced problems with the availability of libraries for the UHPLC-QTOF-MS data, thus a large part of the tentative identification had to be performed manually, whereas the identification for the GC-QTOF-MS data could be automated. Following these difficulties, Bengtström created an accurate mass database containing about 2100 substances with reported use in paper and board, and which can be found in their report. The first step of tentative identification was a fully automated step of integration and deconvolution. Then, the quasi-molecular ions ($[M+H]^+$ or $[M-H]^-$) were located. The vendor specific software was used to find many suggestions for molecular formulas of a single m/z in the spectra, after which the isotope distribution was used to select the most matching one. They concluded that both isotope distribution and hits in the accurate mass database greatly increased the possibility of a correct tentative identification. In this study, the combination of bioassays with chemical analysis resulted in the identification of substances with endocrine disruptive effects, effects on the metabolism of xenobiotics, and mutagenic effects. Also, the concentration of the substances found in the extracts by chemical analysis, was successfully correlated in two of the three bioassays with the originally measured toxicological effect, thus proving the value of this combination.

In the area of environmental research, the fractionation part in EDA approaches was recently further innovated. Zwart et al. (2018) couples UPLC fractionation to a 384 wells fraction collector, allowing for 192 fractions without replicates (collected at 9 seconds interval), or a smaller number with replicates. The small sample volumes were applied to a agonistic and antagonistic androgen and estrogen receptor activity assay. Jonker et al. (2017) applied gas chromatographic (GC) fractionation of volatiles. The eluent of the GC column was diverted through a Y-splitter to the MS and to a the fraction collector. On the way to that fraction collector, the flow was directed to an inverted Y-piece where vaporized trap solvent is infused. The latter flow is directed outside the GC oven allowing subsequent condensation and stepwise collection of liquid fractions with trapped analytes on a 384-well plate for further application to assays.

Veyrand et al. (2017) performed a migration study on a plastic cup suspected to release the endocrine active substance 4-nonylphenol (4NP). The ethanol FCM extracts were divided into two parts, one for analytical and one for toxicological analysis. Chemical analysis of non-volatiles was performed by GC-MS for in full scan mode. Whereas LC-MS/MS was used for a targeted analysis on TNPP and 4NP, using

APCI for TNPP and ESI for 4NP. The ER α -CALUX and AR-CALUX assays were used for in vitro toxicological analysis. The leaching of 4NP was confirmed by LC-MS/MS and GC-MS together with a positive response in the bioassays, which meant an increase in both estrogenic and anti-androgenic activities. This study proves again how bioassays can give additional information to strengthen the results obtained from chemical analysis. Van Leeuwen et al. (2019) evaluated the in vitro (anti)estrogenic and (anti)androgenic potencies of a large number of BPA analogues (including BPS) and BADGE and BFDGE analogues and metabolites. They analysed a selection of drinking bottles and found traces of BPA and BPS.

Bradley et al. (2008) tested nineteen food contact materials according to a short-term test battery of in vitro bioassays developed by the Biosafepaper EU project, and combined this with detailed chemical characterisation by GC-MS. While these were paper and cardboard samples the method will work equally well for plastic and textile samples. The samples intended to be in contact with moist or wet foods were extracted with water, ethanol was used for paper and board holding fatty foods, and Tenax was used as a simulant for dry foods. Ethanol was used to extract the migrants from the Tenax for further testing by in vitro toxicity assays, as described by the Biosafepaper project (Groh et al., 2017). The water extracts were evaporated to dryness and the residue was redissolved in dry acetone, which was then derivatised by adding the silylation reagent N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). After another evaporation step, the residue was redissolved in dichloromethane and analysed by GC-MS, with EI and run in full scan mode (50-600 m/z). The ethanol extracts were analysed both with and without silylation. The derivatised extract was evaporated to dryness and redissolved in acetone before injection, with the same configurations for the MS, but scanned a mass range from 40 – 450 m/z. The ethanol extracts from the exposed Tenax were treated and analysed according to the same protocol as the regular ethanol extracts. Then, all extracts were subjected to the following cytotoxicity assays: total phenolic content (TPC) with HEP-2 and Hepa-1c1c7, the RNA synthesis inhibition test, and the inhibition of boar spermatozoan motility. The Ames test and the Comet assay were used to assess genotoxicity. Eventually, none of the water or Tenax extracts tested positive for cyto- or genotoxicity, however, all ethanol extracts responded positive to the cytotoxicity assays to some extent. Unfortunately, Bradley et al. (2008) could not assign the responses to any specific substance, although there seemed to be a correlation between the total amount of migrants and the degree of toxicity.

5.9 Safety assessment frameworks

The combination of bioassays with chemical analysis has shown to be very effective, although a chemical identification is necessary before toxicity can be linked to a substance. The threshold of toxicological concern (TTC) concept has been adopted within the European Union legislation as a tool to deal with unknown chemical substances (EFSA and WHO, 2016). The TTC concept uses tentative exposure data to determine whether intake of a substance is below an acceptable threshold of no concern, defined by assigning a Cramer class based on the chemical structure or so-called structural alerts. TTC is a preliminary assessment tool that has been applied in strategies to detect and evaluate NIAS as described by Koster et al. (2014) and Pieke et al. (2018a).

Koster et al. published an extensive report on a safety assessment strategy for detecting unknown NIAS in FCMs. The strategy enables one to distinguish toxicologically relevant from toxicologically less relevant substances by several toxicological assessments. The method is described as a complex mixture safety assessment strategy (CoMSAS), and uses several analytical and biological screening procedures that allow the exposure to NIAS to be estimated (Koster et al., 2015). CoMSAS is a decision tree method based on the TTC concept, and was applied by Koster et al. to 3 carton FCMs. The LOD of 10 $\mu\text{g/kg}$ food, that is generally required and used for the detection of migrants in FCMs, has been replaced by an exposure threshold of 90 $\mu\text{g/day}$, based on the TTC of Cramer toxicity class III substances. The new threshold is increased by nine times, which substantially reduces the group of components that must be identified. The identification of unknown substances is focussed only on those substances exceeding the threshold.

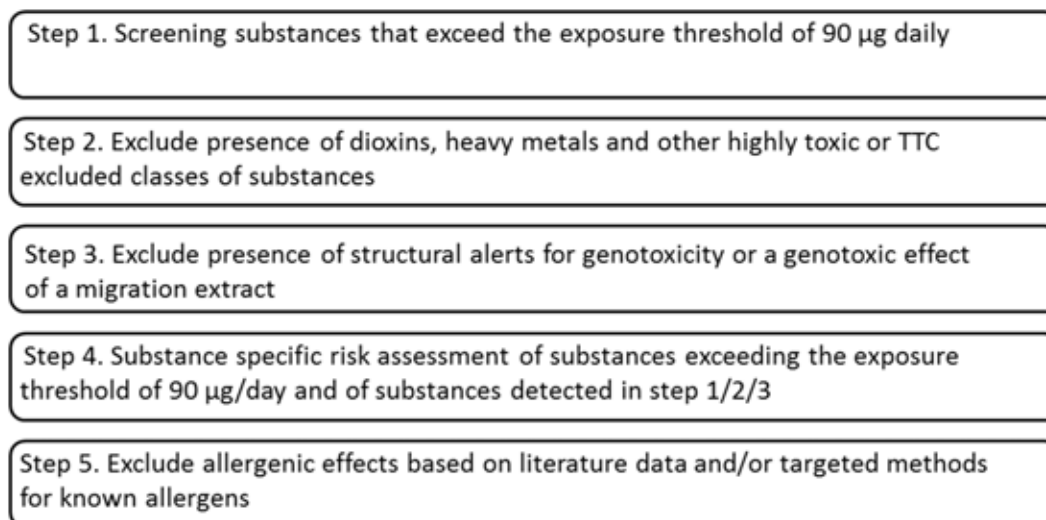


Figure 4 Complex mixtures safety assessment strategy (CoMSAS) (Koster et al., 2014).

The first step of the chemical analysis consists of a screening of substances in the migrate extract that exceed the exposure threshold of 90 µg/day, based on the TTC for Cramer class III substances. The analytical screening combines four different analytical techniques to ensure as many NIAS as possible are detected. The present evaluation includes (1) headspace GC-MS (EI) for volatile substances, (2) GC-MS (EI) for semi-volatile substances, (3) derivatisation of non-volatiles followed by GC-MS (EI) analysis, and (4) LC coupled to an evaporative light scattering detector (UV/ELSD) for analysis of non-volatiles. Since it is almost impossible to incorporate chemical standards, due to the large number of potentially present substances, detectors are used that give a uniform response so that a semi-quantitative estimate of the migration can be made. Whenever in LC-ELDS analysis a substance exceeds the threshold of 90 µg/day, it will be identified by GC- and LC-MS. After the analytical screening, an exclusion of known highly toxic substances and substances that are excluded from the TTC concept was performed as the second step. The presence of the following substances was examined: aflatoxin-like substances, N-nitroso substances, azoxy substances, polyhalogenated dibenzo-p-dioxins, -dibenzofurans and -biphenyls, steroids, non-essential metals, high molecular weight substances, and organophosphates and carbamates. The third step includes a genotoxicity assessment of the migration extract by means of a bioassay. The BlueScreen HC assay was chosen because of its sensitivity for gene mutations, clastogenicity and aneugenicity. When the bioassay presents a negative response, it can be assumed that there are no genotoxic substances present and further identification of substances is not required. When the bioassay does give a positive response for genotoxicity, additional work must be performed to identify the substance(s). Identification is then done by fractionation of the extract by size-exclusion chromatography (SEC), which results in a limited amount of substances per fraction, after which the fractions are submitted to a second bioassay. The fraction that then give a positive response for genotoxicity is further analysed. According to Leeman et al. (2015), the CoMSAS approach is the only one of its kind to assess unidentifiable NIAS until now. The introduction of an exposure threshold provides a pragmatic way for efficient screening for toxicological relevant NIAS in paper and board FCMS and reduces the effort the analytical chemist and toxicologist have to make in the whole process.

Another approach is proposed by Pieke et al. (2018a). They realized that a risk assessment of NIAS is most of the time not possible since much information is missing. This was also concluded by Muncke et al. (2017). Most NIAS do not have assigned chemical structures, concentration data or characterization of hazards. In a recent series of publications Pieke et al. (2017, 2018a, 2018b) described the use of explorative methods to determine NIAS in food contact materials and concluded that untargeted analytical strategies are useful to estimate the concentration and chemical structure of NIAS. However, a comprehensive analysis of all substances found via exploration is not realistic and therefore a risk prioritization is required to identify the substances that most likely have adverse health effects.

During the last years, *in silico* methods have received substantial attention which stimulated their development and made them become more interesting for the assessment of chemical hazards. *In silico* tools are essentially computer models, able to make predictions for a non-evaluated substance based on knowledge extracted from a collection of structurally related substances with experimental toxicity data. Quantitative structure-activity relationship (QSAR) modelling of chemical hazard may provide substitute toxicity data if testing is prohibitive, which has successfully been applied to FCM for hazard-based assessment and prioritization by Van Bossuyt et al. (2017) and by Pieke et al. (2018a). The widespread use of *in silico* tools, however, remains limited due to the non-flexibility of the current regulatory framework and the fact that uncertainty exists as to which *in silico* model is most suitable to assess a given substance for a particular endpoint. Therefore, the most promising application of *in silico* tools will be its use in priority setting upon screening of a large number of substances. A detailed characterisation of the complete toxicological profile of all substances in a non-targeted chemical analysis is not feasible from an economic and ethical (animal testing) point of view. By identifying substances of highest concern, the resources available for experimental testing can be attributed in a more efficient way.

6 Conclusions

The instalment of a circular economy will contribute to an increase in the recycling of plastics and textiles. The successful recycling of plastics and textiles depends, apart from technical aspects, to a large degree on the safety of the products resulting from recycling. The safety of recycled products is a prerequisite for societal acceptance of recycled plastics and textiles. The transition to a circular economy of plastics and textiles will not be accomplished if no guaranteed safe products can be delivered to the market. The evaluation of the safety of recycled plastics and textiles is crucial, but a framework for evaluation of potential hazardous substances and associated risks for the consumer is virtually absent. More specifically, a legislative framework, risk assessment framework, and relevant testing strategies are urgently needed.

In this report the recycling and reprocessing of thermoplastic materials, composites and textiles have been described, based on a (scientific) literature survey. In the production of plastics and textiles many substances are used, and several of these are highly hazardous and therefore of significant concern. During the recycling process or the use of recycled materials these substances may be released to products or the environment, and recycling workers and consumers can be exposed to these substances. A number of 238 hazardous substances associated with plastics and 43 classes of hazardous substances associated with textiles have been identified in this report. Plastics may also be a source of contamination in the recycling process if they are (accidentally) mixed with other plastics and well known plastic additives as phthalates and brominated flame retardants have been found in children toys and food contact materials produced from recycled plastics. Since composites are rarely recycled no information was found about contaminations in recycled composite material. For textiles there is only very limited information on hazardous substances for recycling and recycled end products. However, synthetic textile fibres like polyester and nylon can end up acting as chemical pollutants as well as substrates that magnify the accumulation of other harmful substances in the environment.

For the analysis of (hazardous) substances or NIAS in recycled plastics or textiles two strategies are applied: targeted analytical methods for the analysis of predicted and known substances, and untargeted or screening methods to analyse unknown substances. Targeted analysis are performed using GC-MS based methods for volatile substances and GC- and LC-MS based methods for semi- and non-volatile substances. For the identification of the targeted substances dedicated substance libraries are used. Untargeted analysis is performed to identify as many as possible substances in a migrate or extract, especially substances that cannot be predicted beforehand, which makes it a challenging task. This type of analysis is mostly done using GC and LC techniques in combination with high resolution mass spectrometry techniques like Q-Orbitrap or Q-TOF mass spectrometry. These high resolution accurate mass spectrometers are favoured because of the complexity of the sample extracts and are operated in various data acquisition modes (e.g. full scan, data-dependent acquisition) for untargeted analysis. Often software is used to generate elemental formulas for the accurate masses of the detected substance peaks, and identification is generally done with the help of substance libraries and databases.

In untargeted analysis *in silico* tools are gaining importance in the identification of substances. Recent publications describe the use of so-called explorative methods, an untargeted analytical strategy to estimate the concentration and chemical structure of unknowns. However, a comprehensive analysis of all substances found via exploration is not realistic and therefore a risk prioritization is required to identify the substances that most likely have adverse health effects. The combination of bioassays with sensitive analytical techniques, effect directed analysis, seems to be the most promising and efficient way of identifying NIAS and their hazard to human exposure. *In vitro* bioassay based testing allows for a rapid evaluation of multiple toxicological endpoints. In addition it allows the determination of a combined effect of all detected substances, including the unknowns, in a sample. Positive sample extracts or fractions thereof can be further analysed with GC- or LC-HRMS techniques to identify the

toxic substances. Future research is required into the selection of the bioassay. CoMSAS is an example of a successful approach for the detection and identification of unknown substances in complex samples. It combines the sensitivity of analytical techniques with the ability of testing for cytotoxicity, genotoxicity and endocrine disruptors in one method. The number of analytes that have to be identified is reduced by using a threshold based on the relevant TTC instead of using the generic migration limit or LOD of 10 µg/kg food. By identifying substances of highest concern, the resources available for experimental testing can be attributed in a more efficient way.

For a successful implementation of safe recycling processes and recycled products, there is an urgent need for comprehensive approaches for identification and quantification of hazardous substances, and to assess their safety. The first step in this process is method development for the identification and quantification of hazardous substances in recycled plastics and textiles. Currently such methods are virtually absent, especially for textiles. The literature review has revealed that targeted and untargeted mass spectrometric methods are needed. However, since many of the substances detected in such analyses may be NIAS or otherwise unknowns, identification is a difficult and time-consuming process. For efficient identification such techniques have to be combined with compound databases that may be compiled from different sources. Since it is unlikely that all detected substances can be identified an effect-directed method would be very helpful to detect and finally identify potentially hazardous substances. However, as with the other analytical techniques, effect-directed analysis and especially the coupling of the bio-assay and the instrumental technique is not standard and has to be developed. Finally, risk prioritization schemes and techniques as TTC and CoMSAS for risk assessment have not been used for recycled plastic and textile materials and therefore it is strongly advised to develop these schemes and techniques for this new playing field.

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Annex 1 An overview of 238 hazardous substances likely associated with plastic packaging

Substance	CAS	Function	Plastic type
Antimicrobial substances			
3-iodo-2-propynyl-N-butyl carbamate	55406-53-6	antimicrobial	
arsenic and its compounds	7440-38-2, 7778-39-4, 58-36-6, 15	antimicrobial	Plastisiced PVC, PUR, LDPE, PESs
bis(tributyltin)oxide (TBTO)	56-35-9	antimicrobial	PUR foam, other polymers (unspecified)
dichlorophen	97-23-4	antimicrobial	
ethyl 4-hydroxybenzoate	120-47-8	antimicrobial	
fentin acetate	900-95-8	antimicrobial	
fentin hydroxide	76-87-9	antimicrobial	
methyl 4-hydroxybenzoate	99-76-3	antimicrobial	
naphthenic acids, copper salts	1338-02-9	antimicrobial	
organic tin compounds (tributyltin, triphenyltin, dibutyltin, dioctyltin)	76-63-1, 76-87-9, 379-52-2, 639-5	antimicrobial	PUR foam, PVC, paint
propyl 4-hydroxybenzoate	94-13-3	antimicrobial	
silver sodium hydrogen zirconium phosphate	155925-27-2	antimicrobial	
thiram (tetramethylthiuram disulfide)	137-26-8	antimicrobial	
triclosan	3380-34-5	antimicrobial	PE, PP, PVC, PES fibres, PA fibres
ziram (zinc bis(dimethyldithiocarbamate))	137-30-4	antimicrobial	
Blowing agents			
butane	106-97-8	blowing agents	
C,C'-azodi(formamide) (ADCA)	123-77-3, 97707-96-5	blowing agents	PVC, PE, epoxy resins
chloromethane, methyl chloride	74-87-3	blowing agents	PS, PE, PP, PUR, phenol resins, acetylcellulose foam
fluorinated greenhouse gasses (HFCs, PFCs and SF6)	811-97-2, 354-33-6, 420-46-2, 75	blowing agents	PUR foam, PS foam, phenolic foam
isobutane	75-28-5	blowing agents	

Colorants and Pigments			
4,4-methylenedianiline	101-77-9	colorant	
4-methyl-m-phenylenediamine	95-80-7	colorant	
5-methyl-2-phenyl-1H-indole	13228-36-9	colorant	
cadmium and its compounds	7440-43-9, 10108-64-2, 542-83-6,	pigment	PVC (stabiliser), all plastics (pigment)
chromium and its compounds	1333-82-0, 7778-50-9, 7789-09-5,	pigment	PVC, PE, PP etc
chromium trioxide	1333-82-0	colorant	PE etc
cobalt(II) diacetate	71-48-7	pigment	PET
disodium 3,3'-[(1,1-biphenyl)-4,4'-diylbis(azo)bis(4-aminonaphthalene-	573-58-0	colorant	
disodium 4-amino-3'-[(4'-[(2,4-diaminophenyl)azo][1,1-biphenyl]-4-yl)amino-	1937-37-7	colorant	
disperse Yellow 32	2832-40-8	colorant	Yellow coloured plastics
lead and its compounds	75-74-1, 78-00-2, 301-04-2, 1072-	pigment	PVC (stabiliser), all plastics (pigment)
lead chromate	7758-97-6	pigment	All plastics
lead chromate molybdate sulphate red (C.I. Pigment Red 104)	12656-85-8	pigment	All plastics
lead sulfochromate yellow (C.I. Pigment Yellow 34)	1344-37-2	pigment	HDPE, LDPE, PVC, CA, PP
malachite green hydrochloride, malachite green oxalate	569-64-2, 18015-76-4	colorant	Green coloured plastics.
solvent Yellow 143	842-07-9	colorant	Yellow coloured plastics

Flame retardants			
1,2,5,6- tetrabromocyclooctane (TBCO)	3194- 57-8	flame retardant	EPS
2,4,6- tribromophenyl allyl ether	3278-89-5	flame retardant	EPS
2-ethylhexyl diphenyl phosphate	1241-94-7	flame retardant	
6H-dibenz[c,e][1,2]oxaphosphorin, 6-oxide (DOPO)	35948-25-5	flame retardant	Epoxies
aluminium diethylphosphinate	225789-38-8	flame retardant	Epoxy, PA, PBT, PET, TPU
aluminium hydroxide	21645-51-2	flame retardant	EVA, PE, thermosets
ammonium polyphosphate (NH ₄ PO ₃) _n	68333-79-9	flame retardant	PE, PP
antimony trioxide	1309-64-4	flame retardant	Various plastics
BFRs PBDEs (PeBDE, OBDE, DBDE, HBCDD, TBBPA)	32534-81-9, 32536-52-0, 1163-19	flame retardant	ABS, EPS, HIPS, PAs, PBT, PE, PP, epoxy, PES, PUR, PU
bis(3-chloro-1-propyl)(1-chloro-2-propyl) phosphate	137888-35-8	flame retardant	
bis(hexachlorocyclopentadiene) cyclooctane	13560-89-9	flame retardant	CPE, engineering thermoplastics, HIPS, PE, PP, therm
bisphenol A bis-(diphenyl phosphate) (BAPP)	181028-79-5	flame retardant	PPE (high impact) and HIPS
boric acid	10043-35-3	flame retardant	PS, PVC, synthetic rubber
decabromodiphenyl ethane (DBDPE)	84852-53-9	flame retardant	CPE, Engineering thermoplastics, HIPS, PE, PP, therm
diphenyl cresyl phosphate	26444-49-5	flame retardant	HIPS (flame retardant), PVC (plasticiser)
ethylene (bistetabromophthalimide) (EBTEBPI)	32588-76-4	flame retardant	HIPS, PP, PP, PBT, OPET, PC, engineering thermoplasti
hexabromocyclododecane (HBCDD) and all major diastereoisomers	25637-99-4, 3194-55-6, 134237-5	flame retardant	EPS, XPS, HIPS, polymer dispersions on textiles
magnesium hydroxide	1309-42-8	flame retardant	EVA, PA, PE, PP
melamine cyanurate	37640-57-6	flame retardant	Polyacrylate, PBT, TPU, UP
melamine polyphosphate	15541-60-3	flame retardant	Epoxy resins, phenolic based composites, polyacryla
molybdenum trioxide	1313-27-5	flame retardant	PES, PVC
N-alkoxy hindered amine reaction products	191680-81-6	flame retardant	PE, PP
organo phosphates (TCPP, TDCPP, TPP)	13674-84-5, 1067-98-7, 13674-87	flame retardant	PUR (foam)
phosphonate oligomer, polyphosphonate	68664-06-2	flame retardant	Thermosets
phosphoric acid, diethyl-, aluminium salt	225789-38-8	flame retardant	Epoxies
poly-(m-phenylene methylphosphonate)(Fyrol PMP)	63747-58-0	flame retardant	Epoxies
poly(phosphonate-cocarbonate)	77226-90-5	flame retardant	Engineering plastics (and elastomers)
red phosphorus	7723-14-0	flame retardant	Epoxy resins, polyacrylate, polyacrylate 66, PP
resorcinol bis-diphenylphosphate	125997-21-9	flame retardant	PPE-HIPS, PC-ABS
sodium borate, decahydrate	1303-96-4	flame retardant	
sodium tetraborate, anhydrous	1330-43-4	flame retardant	
sodium tetraborate, pentahydrate	12179-04-3	flame retardant	
TDCP (tris[2-chloro-1-(chloromethyl)ethyl] phosphate)	13674-87-8	flame retardant	PUR
tetrabromobisphenol A bis (2,3-dibromopropyl) ether (TBBPA-DBPE)	21850-44-2	flame retardant	ABS, HIPS, Phenolic resins, epoxy-laminates
tetrabromobisphenol A bis (allyl ether)	25327- 89-3	flame retardant	EPS
tetrachlorophthalic anhydride	117-08-8	flame retardant	
tetrakis(2,6-dimethylphenyl)-m-phenylene biphosphate	139189-30-3	flame retardant	Styrene based plastics
triphenyl phosphate	115-86-6	flame retardant	
triphenyl phosphate (TPP)	115-86-6	flame retardant	PPE-HIPS, PC-ABS, CA
tris(2-chloro-1-methylethyl) phosphate	13674-84-5	flame retardant	
tris(2-chloroethyl) phosphate	115-96-8	flame retardant	
tris(tribromoneopentyl) phosphate (TTBNPP)	19186-97-1	flame retardant	PP
tris(tribromophenoxy) triazine (TTBPTAZ)	25713-60-4	flame retardant	ABS, HIPS
trixyl phosphate	25155-23-1	flame retardant	
zinc borate	1332-07-06, 138265-88-0	flame retardant	PUR, PVC, EVA, PE, PP

Monomer or intermediate			
(epoxyethyl)benzene	96-09-3	monomer or intermediate	
1,1-dichloroethylene	75-35-4	monomer	Saran
1,2,3-trichloropropane	96-18-4	monomer or intermediate	
1,2-epoxy-4-epoxyethylcyclohexane	106-87-6	monomer	Epoxies
1,2-epoxybutane	106-88-7	intermediate	Epoxies
1,3-bis(2,3-epoxypropoxy)benzene	101-90-6	monomer or intermediate	Epoxies
1,3-butadiene	106-99-0	monomer	HIPS
1,4-diaminobutane (Putrescine)	110-60-1	intermediate	Nylon-4,6
1,4-dichlorobenzene	106-46-7	monomer	PPS
1,5-naphthylenediamine	2243-62-1	intermediate	PUR
2-((2-aminoethyl)amino)ethanol	111-14-1	monomer or intermediate	
2-chlorobuta-1,3-diene	126-99-8	monomer or intermediate	
4-(1,1,3,3-tetramethylbutyl)phenol, (4-tert-Octylphenol)	140-66-9	monomer or intermediate	Phenol resins
4,4'-diaminodiphenylmethane (MDA)	101-77-9	intermediate	Epoxies coatings and composites, and the high-perform
4-tert-butylphenol, 2,6-di-tert-butylphenol	98-54-4, 128-39-2	intermediate	Phenolic resins, PC
acrylamide	79-06-01	intermediate	Polyacrylamide, polyacrylonitrile copolymer
acrylonitrile	107-13-1	monomer	ABS, SAN, ASA
allyl 2,3-epoxypropyl ether	106-92-3	intermediate	Epoxies
aziridine	151-56-4	monomer or intermediate	
biphenyl	92-52-4	monomer or intermediate	
bisphenol A (BPA)	80-05-07	monomer	PC, epoxy resins, phenoplast cast resin, PVC, rigid PU
bisphenol F (BPF)	620-92-8	monomer or intermediate	
bisphenol S (BPS)	80-09-1	monomer or intermediate	
butyl 2,3-epoxypropyl ether	6-8-2426	intermediate	Epoxies
chloroethylene	75-01-4	monomer or intermediate	
epichlorohydrin	106-89-8	monomer or intermediate	
formaldehyde	50-00-0	monomer	Melamine, phenolic resins, acetal resins, POM
formaldehyde, oligomeric reaction products with aniline	25214-70-4	intermediate	Epoxies resins, high performance polymers
glycidyl methacrylate	106-91-2	monomer or intermediate	
hexahydro-2-benzofuran-1,3-dione and similar compounds	85-42-7, 13149-00-3, 14166-21-3	intermediate	Epoxies resins
hexahydromethylphthalic anhydride and similar compounds	25550-51-0, 19438-60-9, 48122-1	intermediate	PESs, plasticisers manufactured from the substance,
hydrazine	302-01-2, 7803-57-8	intermediate	PUR
imidazole	288-32-4	intermediate	PU and epoxy
isooctyl acrylate	29590-42-9	monomer or intermediate	
methylene diphenyl diisocyanate (MDI), toluene-diisocyanate, TDI	26447-40-5, 5873-54-1, 101-68-8	intermediate	PUR
methyloxirane (propylene oxide)	75-56-9	monomer or intermediate	PUR, thermoplastics
m-phenylenediamine	108-45-2	monomer or intermediate	
naphthalene	91-20-3	monomer or intermediate	
phenol	108-95-2	monomer	Bakelite (phenol-formaldehyde)
styrene	100-42-5	intermediate	PS, ABS, SAN, EPS, glassfiber reinforced products (st
trizinc bis(orthophosphate)	7779-90-0	monomer or intermediate	
vinyl acetate	108-05-4	monomer	PVA, VA/AA, PVCA
zinc	7440-66-6	monomer or intermediate	
zinc chloride	7646-85-7	monomer or intermediate	
zinc sulphate	7733-02-0	monomer or intermediate	

Stabilisers			
1,3,5-tris(oxiranylmethyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	2451-62-9	stabilizer	
1,4-benzenediol, 2,5-bis(1,1-dimethylethyl)-	88-58-4	stabilizer	
2-(2H-benzotriazol-2-yl)-4-(tert-butyl)-6-(sec-butyl)phenol	36437-37-3	stabilizer	Formaldehyde resins
2-(2'-hydroxy-3,5'-di-t-amylphenyl)benzotriazole	25973-55-1	stabilizer	Formaldehyde resins
2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-phenol	3864-99-1	stabilizer	Formaldehyde resins
2,2',4,4'-tetrahydroxybenzophenone	131-55-5	stabilizer	
2,4-dihydroxybenzophenone	131-56-6	stabilizer	
2,4-di-tert-butylphenol	96076-4	stabilizer	
2-benzotriazol-2-yl-4,6-di-tert-butylphenol	3846-71-7	stabilizer	Formaldehyde resins
2-ethylhexanoic acid	149-57-5	stabilizer	PVC and as residue in PUR products
2-ethylhexyl 10-ethyl-4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannatetracarboxylate	15571-58-1	stabilizer	
2-hydroxy-4-methoxybenzophenone	131-57-7	stabilizer	
2-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol	3896-11-5	stabilizer	Formaldehyde resins
butylated hydroxyanisole (BHA)	25013-16-5	stabilizer	
butylated hydroxytoluene (BHT)	128-37-0	stabilizer	
dibutyltin dichloride	683-18-1	stabilizer	PVC, PUR
dibutyltin dilaurate	77-58-7	stabilizer	
diphenylamine	122-39-4	stabilizer	
DMT EHMA, DMTC etc.4	57583-35-4, 15571-58-1, 77-58-7	stabilizer	
N-2-naphthylaniline, N-phenyl-2-naphthylamine	135-88-6	stabilizer	PE, EVA, PIB
triphenyl phosphite	101-02-0	stabilizer	
tris(nonylphenyl)phosphite, TNPP	26523-78-4	stabilizer	PVC, LLDPE, HDPE
zinc oxide	1314-13-2	stabilizer	

Plasticisers			
1,2-benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (Di)	71888-89-6	plasticiser	PVC, one-component PURs and acrylics
1,2-benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters	68515-42-4	plasticiser	PVC (mainly), foamed urethane
1,4-benzenedicarboxylic acid, bis(2-ethylhexyl) ester	6422-86-2	plasticiser	
2,2',6,6'-tetrabromobisphenol A	79-94-7	plasticiser	
acetyl tributyl citrate (ATBC)	77-90-7	plasticiser	PVC etc
alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins-SCCP)	85535-84-8, 108171-26-2, 287-47	plasticiser	PVC, rubber, elastomers, textile fiber cover
benzyl butyl phthalate (BBP)	85-68-7	plasticiser	PVC, PMMA, PA, thermoplastic PES
bis (2-ethylhexyl)phthalate (DEHP)	117-81-7	plasticiser	PVC, PMMA, ABS, PA, PS, thermoplastic PES
bis(2-methoxyethyl) phthalate (DMEP)	117-82-8	plasticiser	Nitrocellulose, acetyl cellulose, PVA, PVC and PVDC
di (2-ethyl-hexyl) terephthalate (DEHT)	6422-86-2	plasticiser	PVC etc
di-allyl phthalate	131-17-9	plasticiser	
dibutyl phthalate (DBP)	84-74-2	plasticiser	PVC, PP, PVA-based adhesives, plasticiser-solvent
dicyclohexyl phthalate (DCHP)	84-61-7	plasticiser	
di-ethyl phthalate	84-66-2	plasticiser	
dihexyl phthalate	84-75-3	plasticiser	
diisobutyl phthalate (DiBP)	84-69-5	plasticiser	PVC, PS, nitrocellulose, celluloseether, polyacrylate
di-isodecyl phthalate	26761-40-0	plasticiser	
di-isoheptyl phthalate	71888-89-6	plasticiser	
diisononyl adipate (DINA)	33703-08-1	plasticiser	PVC etc
diisononyl-cyclohexane-1,2-carboxylate (DINCH)	166412-78-8	plasticiser	PVC etc
di-isooctyl phthalate	27554-26-3	plasticiser	
dimethoxyethyl phthalate	117-82-8	plasticiser	
DINP, DIDP, DPHP, DEP, DIPP, DHP5	68515-48-0/28553-12-0, 68515-4	plasticiser	PVC and other plastic materials including PVA, cellulose
di-octyl phthalate	117-84-0	plasticiser	
dipropylene glycol dibenzoate (DGD)	27138-31-4	plasticiser	PVC etc
di-undecyl phthalate	3648-40-0	plasticiser	
glycerol triacetate (GTA)	102-76-1	plasticiser	PVC etc
medium-chain chlorinated paraffins, C14-17	85535-85-9	plasticiser	Soft plastic, PVC, and PES
short-chain chlorinated paraffins, C10-13	85535-84-8	plasticiser	
sulfonic acids, C10 – C18-alkane, phenylesters (ASE)	91082-17-6	plasticiser	PVC etc
tributyl phosphate	126-73-8	plasticiser	Cellulose based plastics etc
trimethyl pentaryl diisobutyrate (TXIB)	6846-50-0	plasticiser	PVC etc

Solvents			
(R)-p-mentha-1,8-diene	5989-27-5	solvent	
1,1,2-trichloroethane	79-00-5	solvent	Teflon
1,2,3-trichloropropane	96-18-4	solvent	Hexafluoropropylene
1,2,4-trimethylbenzene	95-63-6	solvent	other hydrocarbon
1,4-dioxane	123-91-1	solvent	Cellulose based polymers
1,6-hexanediol diglycidyl ether	16096-31-4	solvent	Epoxies, chlorinated vinyl resins
2-methoxyethanol	109-86-4	solvent	Epoxy resins and polyvinylacetate
benzene	71-43-2	solvent	
cyclohexane	110-82-7	solvent	
dichloromethane	75-09-02	solvent	PC
dimethylformamide	68-12-2	solvent	Polyacrylonitrile, PUR and polyvinylchloride
dipentene	138-86-3	solvent	
distillates (petroleum), hydrotreated heavy naphthenic	64742-52-5	solvent	
distillates (petroleum), hydrotreated heavy paraffinic	64742-54-7	solvent	
distillates (petroleum), hydrotreated middle	64742-46-7	solvent	
heptane	142-82-5	solvent	
naphtha	8030-30-6	solvent	
naphtha (petroleum), heavy alkylate	64741-65-7	solvent	
naphtha (petroleum), hydrotreated light	64742-49-0	solvent	
naphtha (petroleum), light alkylate	64741-66-8	solvent	
petrolatum	8009-03-8	solvent	
solvent naphtha (petroleum), light aromatic	64742-95-6	solvent	
stoddard solvent	8052-41-3	solvent	
trichloroethylene	79-01-6	solvent	PVC
Accelerator			
zinc bis(diethyldithiocarbamate)	14324-55-1	accelerator	
zinc bis(dibutyldithiocarbamate)	136-23-2	accelerator	
disulfiram (tetraethylthiuram disulfide)	97-77-8	accelerator	
di(benzothiazol-2-yl) disulphide	120-78-5	accelerator	
2-mercaptobenzothiazole	149-30-4	accelerator	

Surfactant			
(Z)-9-octadecenamide	301-02-0	surfactant or its degradation product	
(Z)-octadec-9-enylamine	112-90-3	surfactant or its degradation product	
2-[2-[2-[2-(4-nonylphenoxy)ethoxy]ethoxy]ethoxy]ethanol	7311-27-5	surfactant or its degradation product	
4-nonylphenol, branched, ethoxylated	127087-87-0	surfactant or its degradation product	
4-tert-octylphenol	140-66-9	surfactant or its degradation product	
ammonium pentadecafluorooctanoate	3825-26-1	surfactant or its degradation product	
dimethyldioctadecylammonium chloride	107-64-2	surfactant or its degradation product	
isononylphenol ethoxylate	37205-87-1	surfactant or its degradation product	
N-dodecyl-2-pyrrolidone	2687-96-9	surfactant or its degradation product	
nonoxynol-1	26027-38-3	surfactant or its degradation product	
nonylphenol	25154-52-3	surfactant or its degradation product	
nonylphenol, branched, ethoxylated	68412-54-4	surfactant or its degradation product	
nonylphenol, ethoxylated	9016-45-9	surfactant or its degradation product	
perfluorinated alkylated substances (PFAS); PFOS, PFOA and similar compounds	15166-06-0, 2395-00-8, 24216-05	surfactant or its degradation product	PTFE, FEP, PVDF
perfluorooctanoic acid	335-67-1	surfactant or its degradation product	
phenol, 4-nonyl-, branched	84852-15-3	surfactant or its degradation product	
p-nonylphenol	104-40-5	surfactant or its degradation product	

Annex 2 An overview of 43 classes of hazardous substances used in the textile sector

Substance	Function	Application
Amines		
Amines	Auxiliaries including surfactants, dispersants and softeners, or as process chemicals or precursors for other materials	Various manufacturing processes
Aryl amines	In polyurethanes and as decomposition products of azo colorants	Mills
Quaternary ammonium compounds (DTDMAC, DSDMAC, DHTDMAC)	Disinfectants, cleaners, antimicrobial treatments	Finishing
Dyes and residuals		
Azo-dyes (arylamine releasers)	Dyes	Dye houses
Hypochlorite	Bleaching	Dye houses, denim finishing
Naphthalene	Common residual found in synthetic leather tannins, and in dye dispersing agents that use naphthalene sulfonate derivatives	Leather production, dye houses
Polyaromatic hydrocarbons (PAH)	Residual in carbon black, dyes, rubber and other petrochemical products	Dye houses
Sensitizing disperse dyes (ZDHC for subset of known sensitizers, or GHS codes H317, H334, R43, R42)	Dyes for synthetic fibres including polyester, acetate and polyamide	Dye houses
Titanium dioxide	Pigments	Dye houses
Halogenated chemicals		
Chlorinated and non-chlorinated MIT, CMIT	Antimicrobial and preservative for formulated products	Chemical manufacturers
Chlorinated benzenes	Solvents and fibre swelling agents in dyeing process	Dye houses
Chlorophenols	Hide preservation	Leather processing
Halogenated flame retardants	Flame retardants	Fabric finishing
Per- and poly-fluorinated compounds	Durable water repellency and stain repellency	Fabric finishing
Short chain chlorinated paraffin	Leather conditioners	Leather production
Triclosan and triclocarban	Antimicrobial fabric treatment	Fabric finishing

Metals		
Arsenic	Some pesticides/defoliant for cotton; can be a contaminant in other materials and dyes	Cotton farms
Cadmium	Some pigments and coating	Many parts of the supply chain based on function
Cadmium (PVC stabilizer)	Stabilizer in PVC	
Antimony (catalysts)	PET catalyst	Various manufacturing processes
Chromium (leather)	Tanning agent	Mills
Chromium (wool)	Mordant for mordant dyes used for dark shades of wool	Dye houses
Lead	Plastics, paints, unks, pigments, surface coatings	Mills
Mercury	Present in pesticides; can be found as a contaminant in caustic soda. Mercury compounds may be used in paints	Many parts of the supply chain based on function
Nano silver	Antimicrobial fabric treatment	Fabric finishing
Organotin compounds	Plastics/rubbers (polyurethane), inks, glitter, some adhesives, heat transfer materials	Rubber production, shoe manufacturing, printing
Monomers		
Acrylamides	Manufacture of resins, sealants, binders, thickeners, fibres	Various manufacturing processes
Acrylonitrile, acrylates and methacrylates	Production of acrylic yarns (85% acrylonitrile, with the balance often being acrylates.methacrylates)	Acrylic yarn manufacturing
Bisphenols including BPA, halogenated bisphenols, epoxy resins	Residual in epoxy resins or polycarbonates	Shoe manufacturing, outdoor equipment manufacturing
Butadiene and styrene	Synthetic rubbers, monomers for ABS	Shoe manufacturing, outdoor equipment manufacturing
Epoxide and epoxide precursors like ethylene oxide, propylene oxide, epichlorohydrin	Epoxy resins and adhesives	Shoe manufacturing, outdoor equipment manufacturing
Formaldehyde and other short-chain aldehydes	Wrinkle-free coatings	Fabric finishing
Isocyanates	Monomers in polyurethane production and as cross-linkers in fabric finishing	Polyurethane production, shoe production, finishing
Ortho-phthalates	PVC plasticizers for screen printing and coatings	Non-woven manufacturing and printing
Vinyl chloride and vinylidene chloride	Waterproof plastic impregnated fabrics, artificial leathers	Non-woven manufacturing and printing

Solvents and process aids		
Alkyl-phenol Ethoxylates	Cleaners and detergents	Mills
Aromatic solvents	Synthetic leather and manufacturing and can be found in cleaners and ink solvents	Leather and dye houses
Bezene and o-, p- or m-cresol	Solvents used in processing and/or adhesives	Shoe manufacturing, outdoor equipment manufacturing
Carbon disulfide	Rayon and other cellulosic manufacturing	Rayon fibre production
Chlorinated cleaning solvents	Dry cleaning, spot cleaning, scouring	Garment manufacturing
DMF	Swelling/foaming for polyurethane non-woven	Materials and chemical suppliers
Glycols	Solvents in finishing, cleaning, printing and adhesive processes	Fabric finishing, garment manufacture
N,N-dimethylacetamide (DMAC)	Solvent for elastane and polyurethane coatings; adhesives	Material and chemical suppliers

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