Human health risks due to exposure to inorganic and organic chemicals from textiles: A review

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ABSTRACT

It is well known that a number of substances used in the textile industry can mean not only environmental, but also health problems. The scientific literature regarding potential adverse health effects of chemical substances in that industry is mainly related with human exposure during textile production. However, information about exposure of consumers is much more limited. Although most research on the health effects of chemicals in textiles concern allergic skin reactions, contact allergy is not the only potential human health problem. In this paper, we have reviewed the current scientific information regarding human exposure to chemicals through skin-contact clothes. The review has been focused mainly on those chemicals whose probabilities of being detected in clothes were rather higher. Thus, we have revised the presence of flame retardants, trace elements, aromatic amines, quinoline, bisphenols, benzothiazoles/benzotriazoles, phthalates, formaldehyde, and also metal nanoparticles. Human dermal exposure to potentially toxic chemicals through skin-contact textiles/clothes shows a non-negligible presence in some textiles, which might lead to potential systemic risks. Under specific circumstances of exposure, the presence of some chemicals might mean non-assumable cancer risks for the consumers.

Keywords: Textile industry; clothes; organic substances; trace elements; dermal exposure; human health risks

1. Introduction

The textile industry is the responsible for taking raw materials such as cotton or wool and spinning it into yarn, which is used later to create a fabric. All the processes involved in converting the raw material into a finished product - developing, producing, manufacturing, and distributing textiles - are included in the textile industry, which utilizes a number of types of fabrics, with two major categories, natural and synthetic. Natural fabrics are those that occur naturally from animals and plants, while synthetic fabrics are being created in a laboratory and are man-made.

China is the largest textile producing and exporting country in the world. In 2016, China was the top ranked global textile exporter with a value of approximately 106 billion US dollars, followed by the European Union (28 countries), with a value of 65 billion dollars. India, USA and Turkey would be the following with values of 16, 13 and 11 billion dollars, respectively (Statista, 2016). With respect to clothing, China and the European Union-28 were also the top two exporters in 2016, followed at great distance by Bangladesh, Vietnam, India, Hong Kong and Turkey. According to the World Trade Statistical Review (2017), the current dollar values of world textiles (SITC 65) and apparel (SITC 84) exports were in 2016, $284 billion and $443 billion, respectively.

As it happens with other industrial activities, textile industry has also environmental problems, being one of the oldest and most technologically complex of all industries. A number of substances used in the textile industry can mean not only environmental, but also health problems. Among the many chemicals whose presence has been detected in textile wastewater, dyes are among the most important pollutants (Brillas et al., 2015; Mohamed et al., 2016; Zare et al., 2018). Worldwide environmental problems associated with the textile industry are mainly associated with water pollution caused by the discharge of untreated effluent, as well as those due to the use of potentially toxic substances, especially during processing (Kan and Malik, 2013; Pattnaik et al., 2018).

The scientific literature regarding potential adverse health effects of chemical substances in the textile industry is mainly related with human exposure during textile production. Thus, examples of physical hazards associated with textile and clothing manufacture include fire risk, building construction, noise, temperature, humidity, unsafe machinery, dust and harmful chemicals. In contrast, the information about exposure of consumers is much more limited (KEM, 2014). There are numerous activities involved in the textile and clothing industry, going from the treatment of raw materials to finishing activities such as bleaching, printing, dyeing, impregnating, coating, plasticizing, etc. As result of these activities, the main chemical pollutants are dyes, which contain carcinogenic amines, metals, pentachlorophenol, chlorine bleaching, halogen carriers, free formaldehyde, biocides, fire retardants, and softeners (Brigden et al., 2012).

Most research about health effects of chemicals in textiles concern allergic skin reactions. Disperse dyes, used for staining synthetic fibers have been reported to be the most common causes of textile allergy, being contact allergy to disperse dyes a clinically relevant problem (Ryberg et al., 2006, 2009; Malinauskiene et al., 2013; Coman et al., 2014). However, contact allergy is not the only human health problem.

It is well known that humans are exposed to toxicants mainly through the diet (food and drinking water) and breathing (air pollution). However, for some chemicals dermal exposure should not be minimized. In relation to dermal exposure, although most chemicals added during the processes of manufacturing clothes are rinsed out, residual concentrations of some substances can remain and can be released during the use by the consumers (Luongo et al., 2014).

Based on the above, the main goal of this paper has been to review the current information regarding human exposure to chemicals through skin-contact clothes. The present paper is focused only on chemicals present in textiles in contact with the skin. For this reason, chemicals such as perfluorinated compounds, which are associated with specific clothes (i.e., waterproof) were not include in this review.

2. Flame retardants

In a review on the presence of additives in fibers and fabrics, which was published in the seventies of the last century, Barker (1975) assumed that all fibers and fabrics contained measurable amounts of contaminants and additives. It was concluded that while the levels of contamination of the fibers was –in general terms- quite low, significant concentrations of added chemicals were present at that time in fabrics treated for flame resistance, or for oil and water repellency, for example. Among the flame retardants traditionally used in the textile industry, polybrominated diphenyl ethers (PBDEs) have played an important role. PBDEs are a class of brominated flame retardants (BFRs) that are added to plastics, polyurethane foam, textiles, and electronic equipments in order to protect people from fires by reducing the flammability of these potentially combustible materials (Lorber, 2008). In recent years, PBDEs have become widespread environmental pollutants (Malarvannan et al., 2015; Guiguerno and Fernie, 2017), which have been incorporated in tissues of the general population (Schuhmacher et al., 2009, 2013; Ma et al., 2017; He et al., 2018). A number of studies have shown that, as for other persistent organic pollutants, dietary intake is the main route of human exposure to PBDEs (Lorber, 2008; Linares et al., 2015; Domingo, 2012; Domingo et al., 2008; Perelló et al., 2009). However, information on human exposure to PBDEs through the skin is very limited. Chen et al. (2009) measured the levels of various BFRs –including PBDEs- in children's toys purchased from South China. Higher exposures predominantly contributed through the mouthing pathway, being inhalation, dermal contact and oral ingestion less relevant routes of exposure associated with toys.

With respect to human exposure to BFRs through clothes, it is important to remark that clothing covers approximately 85% of the human skin, being able of acting as a barrier for environmental pollutants. However, clothing can be, in turn, a potential source of exposure to certain chemicals. Recently, Saini et al. (2016) investigated the role of clothing as a sorbent of indoor semivolatile organic compounds (SVOCs) and as source to outdoors through laundering. Phthalates, BFRs and organophosphate esters (OPEs) were measured. It was demonstrated that clothing acted as an efficient conveyer of soluble SVOCs from indoors to outdoors through accumulation from air, and then release during laundering. Clothes drying could also contribute to the release of chemicals emitted by electric dryers. These findings have implications for potential dermal exposure. In a subsequent study conducted by the same research group (Saini et al., 2017), the accumulation of phthalates and BFRs to cotton and rayon was assessed by deploying these fabrics indoors in 20 homes and 5 offices for 28 days and measuring uptake over 56 days. The results confirmed the accumulation of both gas-and particle-phase chemicals to cotton. It was concluded that this large sorptive capacity should have implications for fabrics as a chemical sink for SVOCs indoors, as well as for human exposure.

In order to better characterize the concentrations of PBDEs in lint, Schecter et al. (2009) determined the levels of these chemicals in household drier lint in the USA and Germany. It was found that despite being washed prior to drying, clothes might be a source of PBDE contamination of dryer lint, and they could serve as an indicator of indoor exposure to these pollutants. The authors suggested that the source of PBDEs in lint would be mainly derived from dryer electrical components and also dust deposition onto clothing.

Due to the increased regulatory interest in the restrictions of PBDEs and other flame retardants such as hexabromocyclodecane (HBCD), in recent years the use of alternative flame retardants has been unavoidable. In Japan, for treatment of textiles, HBCD and DecaBDE have been the most frequently used BFRs. As they have been incorporated as additives –without being covalently linked to the polymers to which these compounds are applied- they tend to migrate, becoming environmental pollutants, which can be then subjected to photolytic transformations. Based on this, Kajiwara et al. (2013) investigated the photolytic debromination and isomerization of the major components of HBCD and DecaBDE in flame-retarded curtains under natural sunlight. The concentrations of polybrominated dibenzofurans (PBDFs) in the textiles, formed as products of photodecomposition of DecaBDE, were 4–5 orders of magnitude lower than the levels of PBDEs. The authors remarked that PBDFs were formed as a result of sunlight exposure during normal use of textile products treated with DecaBDE. These results were in the same line than those of a previous study of the same research group, showing that fibers from the flame-retarded textiles could be an important component of indoor dust, and consequent of human exposure (Kajiwara et al., 2009). With respect specifically to the levels of PBDEs in various textiles treated with BFRs, Shin and Baek (2012) detected BDE-28, -66, -100, -119, -153, -197, -206, and -209 in all textile samples analyzed by HRGC/HRMS. In contrast, the congeners BDE-3, -7. -47, -49, -71, -99, -126, and -156 were not detected in any sample. The highest concentration corresponded to BDE-209. As a consequence of the wide use of PBDEs as flame retardants in a number of commercial items, including textiles and clothes, and their transference to the environment, the presence of these compounds in outdoor and indoor environments is evident (Lim et al., 2014). Recently, Ionas et al. (2015) determined the concentrations of PBDEs and organophosphate flame retardants in textile home furnishings, such as carpets and curtains from stores in Belgium. The levels of PBDEs were typically too low to impart flame retardancy. Only high levels of BDE-209 (11–18% by weight) were found.

3. Trace Elements

The main toxic pollutants in textiles are dyes, which contain various chemicals with a well established toxicity. Among these, a number of toxic trace elements can be found in textile materials because they are frequently present in various textile processes. In addition, raw textile materials can also contain several trace elements. Metals -in textile products and clothing- are used for many purposes, such as metal complex dye (cobalt, copper, chromium, lead), pigments, mordant (chromium), catalyst in synthetic fabrics manufacture (antimony oxide), synergists of flame retardants (Sb_2O_3), antimicrobials (nanoparticles of silver, titanium oxide and zinc oxide), as well as like water repellents, and odor-preventive agents (Derden and Huybrechts, 2013; Muenhor et al., 2010; Simoncic and Tomsic, 2010; Stefaniak et al., 2014; Wöhrle et al., 2012). The relationship between trace elements and textiles may mean an important environmental problem for the textile industry, while the presence of certain toxic trace elements in clothing may also mean health hazards for the consumers. An exhaustive search of the scientific literature shows that human exposure to metals rarely produce morbidity, and very rarely mortality. However, a continued exposure to low levels of toxic elements such as As, Cd, Hg and Pb –among others- is related with a number of adverse effects (García-Esquinas et al., 2015; Jaishankar et al., 2014; Rodríguez-Barranco et al., 2014; Roy et al., 2011). In addition, various metals such as Cu, Co, Fe, Mn, Mo, or Zn, which are essential for humans, can be also dangerous at high exposure levels (Domingo, 1994, Lucas et al., 2015).

Based on the potential health risks derived from exposure to metals, the concentrations of these elements have been quantified in various textile materials. Tuzen et al. (2008) determined the concentrations of 6 trace metals (Cu, Cd, Zn, Mn, Fe and Ni) in various textile samples collected in Turkey. The levels of these metals were in the range of 0.10-0.25 μg/g for Cd and 3.55-34.3 μg/g for Fe, metals showing the lowest and highest values, respectively. Copper and Cd concentrations in the analyzed samples were higher than the limit values given by Oeko-Tex. In turn, Rezic and Steffan (2007) determined the levels of 17 trace elements in 16 textile samples of different origin. Results in the sweat extracts (minimum-maximum in μg/mL) were the following: Al 0.11-1.58, Cd 0.02-0.05, Cr 0.01-0.32, Cu 0.05-1.95, Mn 0.01-2.17 and Ni 0.05-0.10. Concentrations of other elements were below the respective detection limits. The concentrations of some trace elements were above the limits suggested by different ecological standards. Thus, Zn and Cd were found in cotton and polyester samples, Cr was detected in flax, silk and polyester samples, Cu was found in silk samples, and As was detected in silk and polyester samples. The same research group (Zeiner et al., 2007) also tested several analytical procedures for determining heavy metals in the textile industry, concluding that the method for an exact quantification of these elements should be selected depending on the analytical task. In a subsequent investigation of the same authors (Rezic et al., 2011), the concentrations of 28 trace elements (Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Hg, Mg, Mn, Mo, Na, Ni, Pb, Sc, Si, Se, Sn, Sm, Sr, Tl, V and Zn) were determined in raw textile materials (cotton, flax, hemp and wool) by inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave digestion of the samples. The levels of these elements ranged between <LOD for various elements, and 1170.2 mg/g for K in cotton. In flax, they ranged between <LOD for various elements and 86.6 mg/g for Mg; in hemp, between <LOD for various elements and 540 mg/g for Ca, and finally, between <LOD for various elements and 660 mg/g for Ca in wool. On the other hand, Matoso and Cadore (2012) measured the concentrations of Sb, As, Pb, Cd, Cr, Co, Cu, Ni and Hg in polyamide raw materials (pellets) and textiles used in sport T-shirts. The highest levels of trace elements were found for Cr in black fabrics, but the extractable content –using acid solution- was lower than the limits suggested by Oeko-Tex Standard 100:2017 Standards (OEKO-Tex, 2018).

It is well known that the main routes through which trace elements can reach the human body are ingestion and inhalation (Giné-Bordonaba et al., 2011). However, human exposure to metals through skin contact could also represent a non-negligible pathway for some elements and certain conditions of exposure. Based on this assumption, we recently conducted in our laboratory various investigations focused on determining the levels of a number of trace elements in clothes, as well as to assess the potential health risks for the consumers. In a first study (Rovira et al., 2015), the concentrations of Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sn, Sr, Tl, V and Zn were determined in various skin-contact clothes. The analyzed samples (T-shirts, blouses, underwear, baby pajamas and bodies) were made of cotton, polyamide, polyester, spandex, and viscose, being classified according to color, brand, and eco-labeled categories. High levels of Cr in polyamide dark clothes (605 mg/kg), Sb in polyester clothes (141 mg/kg), as well as Cu in some green cotton fabrics (around 280 mg/kg) were found. Interestingly, lower concentrations of Al and Sr were found in "eco" clothes, while no significant differences were noted in branded and unbranded clothing pieces. Moreover, Al and Sc levels were higher in clothes made in EU countries than in those made outside the EU. Although the non-carcinogenic and carcinogenic risks of dermal contact exposure for the consumers were –for most trace elements- below safe (HQ<1) and acceptable ($<10^{-6}$) limits, respectively, for Sb, the non-carcinogenic risk was above 10% of the safety limit (HQ>0.1) for dermal contact with clothes. In a second study (Rovira et al., 2017a), we aseessed the dermal contact exposure to 28 trace elements and the derived human health risks by analyzing the levels of these elements in 37 skin-contact clothes (T-shirts, blouses, socks, baby pajamas and bodies). To establish a more realistic exposure assessment, migration experiments were also conducted by determining the concentration of the same 28 elements in artificial sweat. Dermal exposure to trace elements for adult males and females, as well as for <1 year-old children, were calculated and the associated health risks were assessed. High concentrations of Zn (186–5749 mg/kg) were detected in zinc pyrithione labeled T-shirts, while high levels of Sb and Cr were found in polyester and black polyamide fabrics, respectively. In turn, an environmental scanning electron microscope (ESEM) confirmed the presence of Ag and Ti particles and aggregates in various clothes. All samples analyzed in that study fulfilled the parameters of the Oeko-Tex standard. However, four polyester samples exceeded the extractable Sb limit of TOX-Proof standard, which is set at 1.0 mg/kg. With respect to health risks, for polyester clothes, the mean HQs for Sb were 0.44, 0.40 and 0.13, for adult males, adult females, and children <1 year-old, respectively, with one polyester T-shirt reaching a value of 1.2. For the remaining analyzed trace elements and samples of clothes, non-carcinogenic and carcinogenic risks were considered as safe (HQ<1) and acceptable ($<10^{-5}$), respectively. We also detected ZnPT and Ag nanoparticles in some clothes. These substances with biocide activity could affect the natural skin microflora and, consequently, we concluded that they could lead to adverse effects on the human skin.

To the best of our knowledge, there was not any available scientific information on the presence of trace elements in commercially available home textiles, as well as on the potential adverse health effects of a continued exposure during their use. Therefore, the main goal of our third study (Rovira et al., 2017b) was focused on these objectives. For it, the levels of 28 trace elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo,Ni, Pb, Sb, Sc, Se, Sm, Sn, Sr, Ti, Tl, V and Zn) were determined in

78 samples of home textiles (towels, bedclothes and pajamas). Based on the fabric material, samples were classified into three categories: 100% cotton, cotton + synthetic and synthetic. Arsenic, Be, Cd, Sc, Se, Sm and Tl showed concentrations below their respective LODs in all samples. In turn, Hg, Mo and V were detected only in 2–4 items. The highest mean concentrations corresponded to Mg (142 mg/kg), Cu (32.8 mg/kg), Sb (26.9 mg/kg), Al (14.7 mg/kg), Fe (12.9 mg/kg) and Ti (10.9 mg/kg). However, after an individual assessment of the samples, the highest concentrations corresponded to Cu in a black (100% cotton) sample and to Mn in a brown (50% lyocell–50% cotton) sample, with concentrations of 1065 and 889 mg/kg, respectively. In agreement with the results of our previous studies (Rovira et al., 2015, 2017a), polyester items contained high levels of Sb, while Ti concentrations were also increased in synthetic fiber samples. On the other hand, textile color was a key issue because of the high levels of Cr, especially in polyamide black clothes, as well as those of Cu in colored (blue, green, red, and brown) clothes made of cotton. Regarding human health risks, the maximum HQ for almost all trace elements was well below 0.01. The only exception was Sb, whose HQs for dermal exposure due to the use of bedclothes/pajamas and towels were 0.4 and >1, respectively. Comparing with other daily activities, towels use, by towel to-hand-to-mouth effect, was the most relevant action leading to dermal exposure for most trace elements. In general terms, cancer risks did not exceed threshold levels, excepting Cr(VI), whose risk was above 10^{-5}.

In a similar line to that of our recent studies (Rovira et al., 2015, 2017a,b), recently Nguyen and Saleh (2017) determined the levels of Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Sb, Se, Sr, Ti, V and Zn in 120 samples (63 cottons, 44 nylons and 13 polyesters) of different brands and colors of women undergarments manufactured in 14 countries. It was found that cotton samples were rich in Al, Fe and Zn, while nylon undergarments contained high levels of Cr, Cu and Al. In turn, polyester fabrics contained higher concentrations of Ni and Fe compared to cotton or nylon. China, Egypt and India were the countries for which the highest levels of trace elements were found in all fabrics. Chromium exceeded the Oeko-Tex limits in 35% of the samples, while Pb and Ni did it in 14% and 5% of the analyzed items, respectively. The authors recommended that the consumers should be aware of the potential health risks of the contents of these metals in their clothing.

4. Aromatic amines

Azo dyes represent the most important class of textile dyes. Although various aromatic amines (AAs) have been used as intermediates in the synthesis of azo dyes (Freeman, 2013), it is well known that AAs may have carcinogenic and genotoxic properties together with other toxicological effects, as well as allergenic potential (Brüschweiler et al., 2014; Brüschweiler and Merlot, 2017; Platzek, 2010). Moreover, dermal, systemic and bacterial biotransformation of azo dyes, can –in turn- release aromatic AAs (Stingley et al., 2010). According to this, the AAs that may release one of the 22 known carcinogenic AAs are currently banned from clothing textiles in the EU. Nevertheless, there are still an important number of gaps on the knowledge of the potential toxicity of non-regulated AAs.

To investigate the occurrence of azo dye cleavage products, Brüschweiler et al. (2014) collected 153 samples of colored or black clothing (T-shirts, underwear, sport clothes, scarves and clothes for children, which were purchased in the Canton of Bern, Switzerland. The most important criteria for sampling were direct contact with the skin, possible contact with sweat, as well as contact with sensitive skin. The 22 high priority non-regulated AAs of toxicological concern were analyzed. Eight of these 22 AAs were found in 17% of the samples, while in 9% of the samples, one or more of the AAs of concern were detected at concentrations >30 mg/kg. Finally, in 8% of the samples these AAs were found between 5 and 30 mg/kg, being the highest measured concentration 622 mg/kg of textile. The authors concluded that there was a major toxicity data gap for many of the AAs that can be cleaved from the 470 textile azo dyes. This means that the regulatory gap must be filled in a systematic and consistent manner. To fill this gap, in a recent study Brüschweiler and Merlot (2017) investigated the mutagenicity of 397 non-regulated AAs, which could be potentially released from the 470 known textile azo dyes. Thirty-six mutagenic AAs, via publicly available databases, were identified. In addition, 40 different AAs, that were found to be mutagenic (primarily in the Ames test), and are potentially released as cleavage products from approximately 180 parent azo dyes used in clothing textiles, were also identified. Based on these results, the authors concluded that not only exposure to single AAs, but also combined exposure to different mutagenic AAs in textiles must be considered for a complete exposure and health risk assessment, taking into account that mutagenic properties of AAs can mean a much higher concern than previously expected. Also in the same line, Nguyen and

Saleh (2016) investigated the levels of azo dyes and AAs in women under garment. Samples (120) of women underwear of different colors, fabric structures, origin, geographical locations of manufacture and brand names, were evaluated for their potential release of AAs to the skin. Low level mixtures of AAs were detected in 74 samples, but 18 samples had greater amounts of AAs than that recommended by the EU and China. The authors remarked the importance of analyzing AAs in garments.

5. Quinoline, bisphenols, benzothiazoles and benzotriazoles

Quinoline and derivatives, bisphenols (BPAs), benzothiazoles (BTHs) and benzotriazoles (BTRs) are chemicals used in a wide range of applications, including clothing textile articles. Quinoline, a heterocyclic aromatic organic compound, and its derivatives are extensively used in the textile industry for the manufacture of dyes. Some of them are skin irritants and/or also probable human carcinogens. The presence of these substances has been reported in textile materials (Yang et al., 2013; Luongo et al., 2014, 2016a). The concentrations of quinoline and 10 quinoline derivatives were measured in 31 clothing samples of different types: from T-shirts and jeans to dresses. They represented different colors, materials, brands, countries of manufacture, and prices (Luongo et al., 2014). Quinolines were detected in 29 of the 31 analyzed samples, with quinoline contributing up to around 50% of the total amount of quinolines. The highest levels was 1.9 mg in a single garment, a result that cannot be minimized taking into account that the skin is exposed to a large surface area of clothing, as well as the potential health risks of these compounds. In a subsequent study conducted by the same research group (Luongo et al., 2016a), again 10 quinoline compounds were determined in textiles made of cotton, polyamide (> 70%) and polyester. Quinoline was detected in all samples at levels between 0.06 and 6.2 μg/g. As quinoline and isoquinoline are classified as carcinogens, the authors pointed out the importance of collecting data on this potential source to daily human exposure through the skin.

With respect to BTHs and BTRs, Avagyan and co-workers (2015) analyzed the concentrations of 11 derivatives of these families of compounds in 26 clothing samples –including items for babies, toddlers and children- of various textile materials, colors and manufactured in 14 different countries. Eight of the 11 analyzed compounds could be detected in the clothing samples, which demonstrated that clothes could be a route of human exposure to BTHs and BTRs. These substances are genotoxic, can act as endocrine disruptors, and may be dermal sensitizers -exhibiting allergenic and irritating properties- among other toxic effects (Ginsberg et al., 2011; Oda et al., 2008). The sample with the highest concentration of BTH contained 8.3 mg of this chemical, while it could be also detected (22 µg/g) in a baby body made from "organic cotton" equipped with the "Nordic Ecolabel" ("Svanenmärkt"). In general terms, the levels of BTHs were much higher than those for BTRs. Another study performed in the same laboratory (Luongo et al., 2016b), showed that the average emissions to household wastewater of benzothiazoles and quinolines during one washing (5 kg of clothes made from polyester materials) were 0.5 and 0.24 g, respectively. Taking into account that notable amounts of these compounds remained still in the clothes even after 10 times of washing, these results corroborated that clothes are a potential source of human exposure to BTHs, BTRs and quinolines.

Recently, Liu et al. (2017) determined the occurrence of benzothiazole benzotriazole and 7 common derivatives in a total of 79 textile samples, including raw textiles (fabrics) and infant clothing (blankets, diapers and clothing). The concentrations of BTHs and BTRs were examined on the basis of fabric type (e.g., cotton, polyester, and nylon), countries of origin, and colors. BTH was the most frequently detected compound. However, the concentrations of BTR were elevated in certain textiles, with the highest concentration of BTR (14,000 ng/g) found in a printed graphic of infant's bodysuit. The overall mean levels of BTR in the analyzed textiles were higher than those of BTH. Dermal exposure of these chemicals in infants was also evaluated. It was found to be high from the use of socks (244 to 395 pg/kg·bw/day), being the exposure doses of BTHs and BTRs from textiles as high as 3740 pg/kg·bw/day from a themed graphic imprint on the chest portion of a bodysuit. The same investigators also analyzed 77 textiles and infant clothing pieces to determine the occurrence of bisphenols, including bisphenol A (BPA) and bisphenol S (BPS), benzophenones, bisphenol A diglycidyl ethers (BADGEs) and novolac glycidyl ethers (NOGEs) (Xue et al., 2017). Various samples of fabric types (e.g., cotton, polyester, nylon), colors, and countries of origin, were collected. They included raw textiles, cloth diapers, blankets, and clothing marketed for infants aged < 1 year. The results showed that BPA and BPS occurred in 82% and 53% of the textile samples, with mean concentrations of 366 and 15 ng/g, respectively. In turn, benzophenone-3 (BP3) was found in 70% of the samples at a mean concentration of 11.3 ng/g. Finally, among the 11 BADGEs and NOGEs analyzed, BFDGE was the predominant compound, with a mean concentration of 13.6 ng/g.

Dermal BPA exposure doses from textiles ranged from 201 pg/kg bw/day for 6–12 months old infant to 248 pg/kg bw/day for newborns, while BP3 exposure doses ranged between 6.17 and 7.62 pg/kg bw/day. Dermal BPA exposure doses from some textiles were as high as 7280 pg/kg bw/day for newborns. Among the analyzed clothes, most BPA exposure in infants corresponded to socks. The authors of these studies concluded remarking the need for further investigations on the sources and levels of exposure of the chemicals that are present in textiles (Liu et al., 2017; Xue et al., 2017).

6. Phthalates

Phthalates, a wide range of chemical compounds, are mainly used as plasticizers in plastics (especially PVC) to increase softness and flexibility. PVC prints are one of the uses of phthalates in textile industry; plasticized PVC that could lead to long periods of direct skin contact. It should be taken into account that final consumers of textiles with printed PVC are children, who are the most vulnerable group to these endocrine disrupting compounds due to their developmental status (Martinez et al., 2018). A clear example of this is the study conducted by Pedersen and Hartmann (2004), who analyzed phthalate content in children clothes. Phthalates were detected in all the garments tested (19 samples), with levels (sum of all phthalates) between 1.4 mg/kg and 200,000 mg/kg (around 20% of the weight of the sample). The phthalates found at higher amounts were DEHP, DINP, and DHP ((Pedersen and Hartmann, 2004). In turn, Negev et al. (2018) found phthalate (mainly DEHP and DINP) levels in nylon sheets, crib mattress and diaper-changing mats above 0.1% by mass, the standard set by EU Commission Regulation (EC No 552/2009). Similar results (levels >0.1%) were obtained in a study conducted by Li et al. (2015), suggesting that textiles should be monitored for these compounds.

7. Formaldehyde

The International Agency for Research on Cancer (IARC) classifies formaldehyde as human carcinogenic to humans (Group 1) (IARC, 2012). For a long time, textiles and clothes have been treated with formaldehyde releasing compounds and resins in order to improve the anti-creasing properties (Aldag et al., 2017). In 1950s and 1960s, the durable press chemical finishing were based on urea–formaldehyde resin and melamine/formaldehyde resin, which released considerable amounts of formaldehyde to clothes (5000 to 12000 ppm: 0.5-1.2%) (de Groot et al., 2010a). These high formaldehyde concentrations leaded to the report of a number of cases of contact dermatitis (de Groot et al., 2010a,b). Nowadays, durable press finishes are based on modified dimethylol dihydroxyethyleneurea, which releases less formaldehyde (de Groot et al., 2010b). Various studies have determined formaldehyde levels in clothes. Novick et al. (2013) analyzed 20 cloth items detecting formaldehyde only in 3 of them. However, levels of 2 out these 3 detected items (3172 and 1391 ppm) were 40 fold higher than the concentrations established by international textile regulations. According to Novick et al. (2013), washing and drying procedures reduced formaldehyde concentrations between 26% and 72%. The US Government Accountability Office (USGAO, 2010) performed a study with 180 textile items. Thirty-five out 180 free formaldehyde samples were detected, while 10 of them exceeded the regulatory standard (75 ppm in non-baby direct contact with skin clothes), with values between 75.4 and 206.1 ppm. In turn, Piccini et al. (2007) analyzed 221 samples of clothes and linen. It was reported that in 89% of them formaldehyde levels were below 30 ppm, while in 97% of them the concentrations were below 75 ppm. Only three items exceeded the level of 100 ppm, with a maximum value of 163 ppm. Differences according to the manufacture country and the shops where the samples had been purchased were found (Piccini et al., 2007).

8. Nanoparticles

In recent years, the use of metal nanoparticles has meant a tremendous boom for many industrial sectors. The ability of manufacturing novel nanomaterials have led to an increased production and use of engineered nanoparticle (ENPs) and engineered nanomaterials (ENMs). Among these, ENPs of metals are increasingly used in the textile industry (Som et al., 2011; Montazer et al., 2014; Yetisen et al., 2016) The antimicrobial activity of silver-ENP and the UV-absorption of titania-ENP are good examples of this use (Windler et al., 2013; von Goetz et al., 2013; Lombi et al., 2014). However, mobilization and migration of ENPs from the textile into human sweat can result in dermal exposure to these chemicals and their aggregates and agglomerates (NOAA) (von Goetz et al., 2013). Silver is one of the elements mainly used in metal nanoparticles. The use of nanoscale Ag in textiles is one the most often mentioned uses of nano-Ag. However, the form of Ag present in the textiles remains largely unknown as product labeling is insufficient (Lombi et al., 2014). In relation to this, it has been reported that for Ag-NOAA, its potential dermal exposure from textiles is comparable in magnitude to the major source of Ag-ENP, which are dietary supplements (von Goetz et al., 2013).

Given the increasing importance in the textile industry of metal nanoparticles in general, and silver nanoparticles in particular, the concern regarding their environmental and human health risks has also increased in parallel. Because of the great importance of these issues, an exhaustive revision of this topic has not been included in the current paper. We feel that this subject is worthy of an additional and exhaustive specific review. However, for those interested in the topic, information is available in some recent papers (León-Silva et al., 2016; Voelker et al., 2015; Tang et al., 2015; Som et al., 2011; McGillicuddy et al., 2017).

9. Conclusions

Most chemicals that have been added during the processes of converting fabrics into textiles are rinsed out. However, this does not prevent that residual levels may remain in the finished products, which -in turn- can be released during the use by the consumers. Although there are important control measures for many hazardous compounds employed in the EU, the continuing relocation of textile production to countries with fewer environmental restrictions and work standards, the complex raw material supply chains, as well as the large numbers of operators involved in the different production steps, makes that a strict control on the presence of some toxic chemicals in textiles in general, and in clothes in particular, is indeed very difficult. On the other hand, the rapid changes in fashion trends also lead to fluctuations in the types of prints, dyes, and other kinds of chemicals that are being used during the production processes (Fransson and Molander, 2013; Luongo et al., 2014). In 2012, Brigden and co-workers published an interesting report on the presence and in some cases concentrations of hazardous chemicals (nonyl phenol ethoxylates, carcinogenic amines, and phthalates) in branded textile products on sale in 27 countries. The results suggested the necessity of develop robust policies to force the elimination of such chemicals from manufacturing processes of textiles, and consequently, in the finished products (Brigden et al., 2012).

In the present paper, we have reviewed the presence of various potentially toxic chemicals in textiles. The review has been mainly focused on those chemicals whose probabilities of being detected in clothes were rather higher. Among these, flame retardants have been included. Flame retardants are incorporated into potentially flammable materials, including textiles, to prevent/inhibit combustion. PBDEs, HBCD, organophosphorus compounds and bisphenol A have been extensively used in the textile industry as flame retardants. The concentrations of these substances reported in a number of studies suggest that dermal exposure may be a non-negligible way of human exposure to these toxic compounds. Although the dietary intake is the main route of human exposure to flame retardants, followed by inhalation (Domingo, 2012; van der Veen and de Boer, 2012; Linares et al., 2015), without a deep knowledge on the importance of exposure through the skin, the risks of dermal exposure should not be discarded/dismissed (Abdallah and Harrad, 2018; Abdallah et al., 2015). A similar conclusion can be also drawn for the presence of trace elements in clothes (Rizzi et al., 2014). Thus, we have found that the non-carcinogenic risks of Sb were above 10% of the safety limit (HQ > 1) for dermal contact route, due to exposure with skin-contact clothes (Rovira et al., 2015). With respect to azo dyes and aromatic amines (AAs), contact allergy to textile dyes is well known (Ryberg et al., 2009; Isaksson et al., 2015; Malinauskiene et al., 2013; Coman et al., 2014). In addition, the scientific information above reviewed indicates that, for example, the presence of mutagenic AAs in textile azo dues is of much high concern than previously expected (Brüschweiler and Merlot, 2017). Similarly, the occurrence in clothes of other potentially harmful organic compounds such as quinolines, BTHs, BTRs, or bisphenol A, is also an issue of concern that requires further research on their presence in textiles (Luongo et al., 2014, 2016a). Recently, it has been even reported that perfluorinated compounds such as PFOS and PFOA, with a well known toxicity (Domingo and Nadal, 2017; Lóez-Doval et al., 2014; Kingsley et al., 2017), migrate from textiles, which could mean a significant direct and indirect source of human exposure to these chemicals (Supreeyasunthorn et al., 2016). Also, the information on human dermal exposure from textiles that contain metal (mainly silver) nanoparticles is still limited (Stefaniak et al., 2014; Tulve et al., 2015; Bianco et al., 2015, 2016).

In summary, the results of the current review focused mainly on the health risk assessment of human dermal exposure to potentially toxic chemical through skin-contact textiles/clothes, show a non-negligible presence of various chemicals in some textiles, which might lead to potential systemic risks. Even under specific circumstances of exposure, it might mean non-assumable cancer risks for the consumers. Therefore, we recommended elucidating which are being the chemicals of most concern in terms of dermal exposure through clothing. Studies should be conducted in order to prevent potential human health risks for the consumers, including the adult population, but very especially babies and children.

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