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Occurrence of and exposure to benzothiazoles and benzotriazoles from textiles and infant clothing

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HIGHLIGHTS

- Benzothiazoles (BTH) and benzotriazoles (BTR) were measured in infant clothing.
- BTHs were found in 86% of samples and BTRs were elevated in certain textiles.
- Polyester socks and graphics on clothing had elevated concentrations of BTR.
- Dermal exposure to BTR and BTH from textiles was several tens to hundreds of pg daily.

GRAPHICAL ABSTRACT

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ABSTRACT

Benzothiazoles (BTHs) and benzotriazoles (BTRs) are used in a wide range of applications, including rubber vulcanization and corrosion inhibition. Limited studies have reported the occurrence of BTHs and BTRs in textiles, including children's clothing. In this study, 79 textile samples (raw as well as tailored) collected in Albany, New York, USA, were analyzed to determine the occurrence of BTH, BTR and their seven common derivatives. BTH, 2-methylthio-benzothiazole (2-Me-S-BTH) and 2-hydroxy-benzothiazole (2-OH-BTH) were found in textiles at a detection rate (DR) of 86%, 54% and 19%, respectively. The DRs of tolyltriazole (TTR), BTR and 5-chloro-benzotriazole (5-Cl-BTR) in textiles were below 20%. Although BTH was the most frequently detected compound, BTR levels were elevated in certain textiles and the overall mean concentrations of BTR in textiles were higher than those of BTH. The concentrations of BTH in textiles ranged from 6.1 to 1120 ng/g. The highest concentration of BTR (14,000 ng/g) was found in a printed graphic of infant's bodysuit. On the basis of the measured concentrations, we calculated dermal exposure doses to BTHs and BTRs by infants. The dermal exposure doses were high from the use of socks (244 to 395 pg/kg·bw/d), and the exposure doses of BTHs and BTRs from textiles were as high as 3740 pg/kg·bw/d. Printed graphics on clothes, as well as socks, accounted for a major proportion of the exposure doses to BTHs and BTRs.

1. Introduction

The imperative need for textiles in every aspect of our lives is well known. Because textiles are used in various industries such as

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clothing/apparel, construction, home furnishings, automobile and others, the demand for them is constantly increasing, and the textile industry continues to grow significantly worldwide. Textile production comprises conversion of fiber (natural or synthetic) into yarn and then to fabric. Several chemicals are used in textile production to make textiles stronger and more versatile, and for the development of products that provide comfort, wellness, and freshness. A survey conducted by the Transparency Market Research firm in 2015 indicated that textile chemical market is expected to grow at 3.7% annually from its current U.S. market value of $21 billion globally (Transparency Market Research, 2016).

The production of fabric involves several steps that include scouring, bleaching, printing, dyeing, coating, sizing, and plasticizing, among others. A wide variety of chemicals are used in these processes. For example, dyeing involves application of color to textile substrates, mainly with synthetic organic dyes at elevated temperatures and pressures. During this process, along with dyes, many chemical aids such as surfactants, acids, alkali/bases, electrolytes, carriers, leveling agents, promoting agents, chelating agents, emulsifying oils, and softening agents can be applied to obtain a uniform depth of color with fastness. Different types of dyes and chemical additives are used to obtain preferred properties, including anti-fading, water proofing, softening, antistatic protection, soil resistance, stain release and microbial/fungal protection (Chequer et al., 2013). Many of these chemicals are used on textiles to gain these desired benefits, but they also contribute to human and environmental exposures.

Ongoing concerns about the use of chemicals in textiles have prompted increased research into sustainable alternatives. An increasing number of apparel brands and retailers are committing to remove hazardous chemicals from their supply chains (IHS Markit, 2016). In a recent report alerting consumers to dangerous chemicals in products from the European Union, 572 chemical-related notifications involving toys (37%), jewelry (20%) and clothing and textiles (13%) were identified (Chemical Watch, 2016). Other recent studies reported the occurrence of benzothiazoles (BTHs) and benzotriazoles (BTRs) in textiles from Sweden (Avagyan et al., 2015) and toxic metals in textiles from Spain (Rovira et al., 2015; Sungur and Gülmez, 2015; Rovira et al., 2017). A report by Greenpeace showed the presence of a wide range of endocrine disrupting chemicals in textiles, with nonylphenol ethoxylate concentrations as high as 17,000 μg/g (Greenpeace, 2014).

BTH and BTR are high production volume (HPV) chemicals that have a wide range of applications (Kloepfer et al., 2004). BTH and its derivatives (collectively referred to as BTHs) are commonly used in the vulcanization of rubber (Ni et al., 2008) and as biocides, fungicides, and corrosion inhibitors (Kloepfer et al., 2004). Laboratory animal studies have shown that BTHs are endocrine-disrupting chemicals (Hornung et al., 2015) and genotoxic (Yan et al., 2014). BTHs are also reported to be dermal sensitizers (Wang and Suskind, 1988). BTR and its derivatives (collectively referred to as BTRs) are also HPV chemicals, with an estimated annual production of over 9000 tons in the United States alone (Ferrey et al., 2013). BTRs are the commonly used corrosion inhibitors in deicing fluids for aircrafts, automotive antifreeze formulations, household detergents, and industrial cooling systems (Weiss and Reemtsma, 2005). Commonly known derivatives of BTRs include 4-OH-BTR, 5-OH-BTR, XTR and methylated tolyltriazoles (TTR) (Ferrey et al., 2013).

Except for studies from Sweden (Avagyan et al., 2013; Avagyan et al., 2015; Luongo et al., 2016), occurrence of BTHs and BTRs in textiles has not been thoroughly investigated. In our study, several textile products, including infant cloths (blankets, diapers and clothing) were collected from local stores in Albany, New York, USA, to determine the occurrence of BTH, BTR and their derivatives and to evaluate dermal exposure of these chemicals in infants and toddlers. This is the first study to report dermal exposure to BTH and BTR from textiles. 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.

2. Materials and methods

2.1. Chemicals standards

Benzothiazole (BTH, CAS# 95-16-9), 2-hydroxy-benzothiazole (2-OH-BTH, CAS# 934-34-9) and benzotriazole (BTR, CAS# 95-14-7) were purchased from Alfa Aesar GmbH & Co KG (Karlsruhe, Germany). 2-Methylthio-benzothiazole (2-Me-S-BTH, CAS# 615-22-5), 4-hydroxy-benzotriazole hydrate (4-OH-BTR, CAS# 26725-51-9), 4/5-methyl-1H-benzotriazole (TTR, CAS# 29878-31-7) and 5-chloro-benzotriazole (5-Cl-BTR, CAS# 94-97-3) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 5-Methyl-1H-benzotriazole (5-Me-1H-BTR, 98%), 2-amino-benzothiazole (2-NH_2-BTH, CAS# 136-95-8) and 5,6-dimethyl-1H-benzotriazole hydrate (XTR, CAS# 4184-79-6) were purchased from Acros Organics (Morris Plains, NJ, USA).

The isotope-labeled internal standards (ISs), d_4-BTH, d_4-BTR and d_6-Me-BTR, were purchased from Sigma-Aldrich (St. Louis, MO, USA). d_4-BTH was used as an IS in the quantification of BTH, 2-OH-BTH, 2-Me-S-BTH and 2-NH_2-BTH; d_4-BTR was used as an IS in the quantification of BTR, 5-Cl-BTR and 4-OH-BTR; d_6-MeBTR was used as an IS in the quantification of XTR and TTR. Methanol, dichloromethane, acetone and ethyl acetate were purchased from J. T. Baker (Phillipsburg, NJ, USA). Milli-Q water was purified by an ultrapure water system (Barnstead International, Dubuque, IA, USA).

2.2. Sample collection and analysis

Textiles were collected in April 2016 from various retail stores and supermarkets in Albany, New York, USA. A total of 79 samples were analyzed including raw textiles (fabrics) and infant (ages below 1 year) clothing. The textile samples were collected to represent various fabric types (e.g., cotton, polyester, and nylon), colors, and countries of origin. All raw textile ($n = 19$) samples originated from China, while the tailored infant clothing ($n = 40$) originated from China (23%), India (25%), Bangladesh (10%), Sri Lanka (5%), Vietnam (5%), Cambodia (20%), Salvador (5%) and Ecuador (7%). Among the clothing, three nylon newborn-size tights (94% with 6% spandex), thirteen 60% cotton/40% polyester blend bodysuits and a number of cotton or cotton/polyester blend pants, trousers, skirts, and shirts were analyzed. We analyzed two portions within tailored garments of five children's clothing that contained printed graphics/decorations. Nineteen (100% cotton) raw textiles with different colors were analyzed to examine the influence of the color of dyes on BTH and BTR concentrations. Fourteen types of polyester blend socks for newborns and infants (97–98% polyester with 1–2% spandex and up to 1% latex rubber) were analyzed (all originated from China). In addition, four pre-folded cloth diapers (100% cotton) and two infant blankets (100% polyester) were analyzed. A detailed list of samples analyzed in this study is provided in the supporting information (Table S1). The textile samples were stored in polyethylene bags in darkness until analysis.

Approximately 1.4 g portions of textiles were cut and placed in 15-mL polypropylene (PP) tubes. The samples were spiked with 50 ng of isotope-labeled internal standards (d_4-BTH, d_4-BTR and d_6-MeBTR). We then added 10 mL of a mixture of acetone and dichloromethane (v/v: 1/4), ultrasonicated for 20 min, centrifuged, and transferred the supernatant to another PP tube. The samples were extracted twice. Prior to evaporation, a mixture solvent of methanol and acetonitrile (5 mL; v/v: 1/1) was added to the extract. The extract volume was reduced to 0.3 mL under a gentle stream of nitrogen, and 0.7 mL methanol was added. We then filtered the extracts through a 0.2 μ nylon filter prior to instrumental analysis.

The samples were analyzed using an Agilent 1100 Series high performance liquid chromatography (HPLC) system (Agilent Technologies Inc., Santa Clara, CA, USA), interfaced with an Applied Biosystems API 2000 electrospray triple quadrupole mass spectrometer (ESI-MS/MS; Applied Biosystems, Foster City, CA, USA). A Zorbax SB-Aq