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# Are Melamine and Its Derivatives the Alternatives for Per- and Polyfluoroalkyl Substance (PFAS) Fabric Treatments in Infant Clothes?

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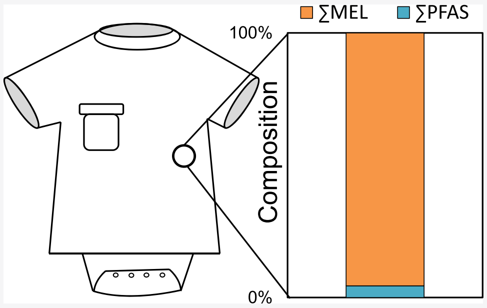

**ABSTRACT:** Per- and polyfluoroalkyl substances (PFAS) and melamine (MEL)-based compounds are used in textile finishing as grease, stain, and water repellents. Here, we investigated the occurrence of a large suite of PFAS and MEL compounds in 86 infant clothing items. The ∑MEL concentrations ranged from below the method detection limit to 250,000 ng/g with a median concentration of 78.2 ng/g, significantly higher ($p < 0.05$) than the ∑PFAS levels (1.22−203 ng/g; median 3.62 ng/g). MEL and its derivatives were most abundant in nylon clothes (median 32,800 ng/g), followed by organic cotton (median 6120 ng/g). In a simulated laundering experiment, the ∑MEL concentrations in clothing decreased on an average by ~60 and 90% when washed in cool (20 °C) and warm (50 °C) water, respectively. This removal rate increased to 97% when the samples were washed with a detergent. The estimated daily intakes of MEL and PFAS through dermal absorption from nylon clothes were three orders of magnitude higher than those from the non-nylon clothes and decreased by more than half for washed clothes. Our findings demonstrate that MEL-based compounds are abundant in infant clothing and suggest that this group of compounds could be used as potential PFAS replacements in textile finishing.

## INTRODUCTION

Fabric finishing is an important process in textile manufacturing and includes a variety of treatment applications used to impart specific functional properties to the material. More than 2500 chemicals are currently used in fabric finishing treatments,[1] including dyes, antioxidants, flame retardants, fiber purifiers, UV light absorbers, and grease, stain, and water repellents.[2,3] The latter are essential for oil-, stain-, and waterproofing fibers and fabrics and have been in use since the 1950s when textiles with enhanced water resistance and grease-proof properties were first introduced to the market.[4] The majority of these applications are fluoropolymer-based and contain per- and polyfluoroalkyl substances (PFAS) that are applied as surface coatings to fabrics or fibers, followed by polymerization and curing.[5] A number of PFAS-based textile coating agents are marketed under trade names such as Teflon, Stainmaster, NanoTex, GoreTex, and Unidyne. The two major PFAS compounds, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), have been found in various textiles, including carpets, rain jackets, gloves, and backpacks.[6−11] In addition, because of global restrictions on the production and use of persistent and toxic PFOS and PFOA, textile treatments using PFAS with shorter (<C8) carbon chains and nonionic (neutral) molecules, generally considered less environmentally persistent and bioaccumulative, have been increasingly used.[12,13] For example, surface coating finishes such as Scotchgard PM-3622, PM-490, and PM-930 use side-chain fluorinated polymers based on the derivatives of perfluorobutane sulfonyl fluoride,[14] which can degrade to perfluoro-1-butanesulfonic acid (PFBS, C4).[15] Neutral PFAS, such as fluorotelomer alcohols (FTOHs), especially those with six perfluorinated carbons, are used as cross-linking agents for textiles.[16] Both short-chain and neutral PFAS were found in textile impregnating treatments with levels reaching 13.2 mg/L.[17] As a result, dermal exposure from clothes and other textiles has been recognized as an important human exposure pathway to many PFAS.[3,18]

Considering the growing concerns regarding the toxicity of the entire PFAS family,[19] the textile industry has been working on implementing "green" strategies for textile finishing.[5] The results of a 2015 survey of 17 textile manufacturing companies indicate that 4 of these companies eliminated fluorine-based technologies in waterproof textiles and switched to a PFAS-free polymer technology to achieve water-repellent properties.[5] The Roadmap to Zero Discharge of Hazardous Chemicals (ZDHC) was launched in 2011 by a group of major apparel and footwear brands and retailers, aimed to lead the industry

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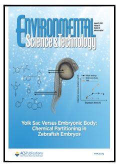

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toward zero discharge of hazardous chemicals by 2020.[20] According to the ZDHC report on durable water repellents, melamine (MEL) and its derivatives are the major group of nonfluorinated chemicals being increasingly used in waterproofed fabrics instead of PFAS.[20]

MEL has received global attention after a series of pet food and infant formula adulteration incidences that resulted in renal damage, and in some cases, renal failure and death of infants and pets.[21−23] However, it is less known that, in addition to food adulteration, MEL and its derivatives are also widely used as textile additives. MEL-based polymers were first introduced in the 1930s and have been used since then as fabric surface coating resins.[24] MEL-based polymers comprise a large group that includes MEL−formaldehyde, methylated MEL−formaldehyde, MEL−urea−formaldehyde, MEL−urea−phenol−formaldehyde, and other resins. Similar to PFAS, these MEL-based resins are used to enhance water-repellent and wrinkle-resistant properties of textiles[11,25] but are generally considered less toxic. In addition, MEL-based fibers can be used in flame-resistant protective clothing because of their low thermal conductivity, high flame resistance, and self-extinguishing properties.[26] Other MEL-based compounds, such as cyanuric acid (CYA), ammeline (AMN), and ammelide (AMD), are byproducts or impurities in the manufacturing of MEL[25] and can be used together with MEL to produce MEL-based resins. In addition, CYA is used as a disinfectant, bleaching agent, and fertilizer on its own.[27]

Clothing has been recognized as an important source of chemical exposures through dermal absorption from direct contact of clothes with skin.[28] Infants wearing clothing items that are in direct contact with skin, such as cloth diapers and onesies, may be at a higher risk from nearly constant exposure.[29] Even low-dose environmental exposures are of concern in the early-life period and can result in health effects resonating across the entire life span.[30] However, the number of studies on chemical exposures from infant clothes is limited.[31,32]

Here, we simultaneously measured two major groups of chemicals used as textile surface treatments, PFAS and MEL compounds, in a wide selection of infant clothing. We investigated the occurrence and distribution of 11 MEL derivatives and 40 ionic and neutral PFAS in infant clothing items purchased from local and online stores in the United States and assessed infants' dermal exposure to these chemicals from clothes. In addition, we conducted simulated laundering experiments to assess the release of MEL and PFAS compounds from clothing to the environment.

## ■ MATERIALS AND METHODS

**Samples.** Eighty-six pieces of new finished infant clothing (sizes 0−12 months) from nine national brands were purchased from local stores in Bloomington and Indianapolis, Indiana, United States, and online in June 2019. The clothes were manufactured during 2017−2019 and included various categories such as shirts ($n$ = 13), pants ($n$ = 12), socks ($n$ = 12), cloth diapers ($n$ = 20), dresses ($n$ = 2), onesies ($n$ = 24), and outerwear ($n$ = 3) made of conventional and organic cotton, polyester, spandex, and nylon. The clothes were manufactured in nine countries, including Cambodia ($n$ = 6), China ($n$ = 38), India ($n$ = 6), Indonesia ($n$ = 5), Nicaragua ($n$ = 5), El Salvador ($n$ = 4), Thailand ($n$ = 2), the United States ($n$ = 10), and Vietnam ($n$ = 9). Table S3 includes the details of samples analyzed in this study, including fabric composition, clothing type, manufacturing origin, and year of production.

**Sample Treatment.** Three pieces of fabric (3 × 3 cm) were randomly cut out of each garment, finely cut, and mixed, and 100 mg of this sample was transferred into a 15 mL polypropylene tube and spiked with 50 ng of surrogate standards (Tables S1 and S2). The samples were then sonicated three times (1 h each) with 4 mL of methanol at room temperature. The supernatants were combined, solvent-exchanged to 500 μL acetonitrile with 5 mM ammonium formate buffer (95:5, v/v, pH = 4.0), filtered through a 0.2 μm nylon syringe filter, and spiked with 50 ng of internal standards (Tables S1 and S2).

**Simulated Laundering Experiments.** Laundering experiments consisted of a simulated washing process that included either washing without detergent in water at 20 and 50 °C or washing with detergent in water at 20 and 50 °C. Clothing items ($n$ = 4, all made of nylon) with the highest $\sum$PFAS and $\sum$MEL concentrations detected were included in these experiments. Fabric pieces (approximately 5 × 5 cm) cut from these selected clothing items were added to 400 mL of preheated high-performance liquid chromatography water at 20 and 50 °C, each in a separate beaker, and shaken in an incubator shaker at 150 rpm for 1 h. The clothing pieces were then squeezed to remove excess water and air-dried at room temperature covered with an aluminum foil in a fume hood. The experiment using a detergent was conducted in a similar way, but one drop of concentrated liquid laundry detergent was added to the water. The concentrations of MEL derivatives and PFAS were determined in washed fabric samples using the methods described above.

**Instrumental Analysis.** The complete list of the target compounds and surrogate and internal standards is given in Tables S1 and S2. The instrumental method for PFAS was previously reported[7] and is briefly described in the Supporting Information (Tables S1 and S2, and Figure S1). MEL and its derivatives were analyzed using an ultraperformance liquid chromatograph coupled with a triple-quadrupole mass spectrometer (Agilent 1290 Infinity II UPLC-6470 QQQ-MS). Chromatographic separation of MEL, CYA, AMN, and AMD was achieved on an Acquity UPLC HILIC column (50, 2.1 mm i.d., 1.7 μm thickness, Waters, Milford, MA). Ammonium formate buffer (mobile phase A) (5 mM, adjusted to pH 4.0 using formic acid) and acetonitrile (mobile phase B) were used as the mobile phases. The column temperature and the flow rate were 40 °C and 0.4 mL/min, respectively. The mobile-phase gradient was as follows: 0 min, 95% B; 5.6 min, 65% B; 9 min, 65% B; 9.1 min, 95% B; and 15.1 min, 95% B. The instrument was equilibrated for 4 min after every run, and the nebulizer, gas flow, gas temperature, capillary voltage, sheath gas temperature, and sheath gas flow were set to be 20 psi, 11 L/min, 260 °C, 3500 V, 300 °C, and 12 L/min, respectively. An Acquity UPLC BEH $C_{18}$ column (50, 2.1 mm i.d., 1.7 μm thickness, Waters, Milford, MA) was used for the separation of other MEL derivatives (Tables S1 and S2) at 40 °C. Mobile phases included 0.1% formic acid in water (mobile phase A) and 0.1% formic acid in methanol (mobile phase B), and the flow rate was 0.4 mL/min. The gradient was as follows: 0 min, 30% B; 0.5 min, 30% B; 3.5 min, 70% B; 8 min, 74% B; 14 min, 100% B; and 15.5 min, 100% B. The nebulizer, gas flow, gas temperature, capillary voltage, sheath gas temperature, and sheath gas flow were set to be 40 psi, 10 L/min, 260 °C, 3500 V, 375 °C, and 12 L/min, respectively.

Table 1. Detection Frequencies (DF, %) and Median Concentrations of MEL-Based Compounds and PFAS in Infant Clothing (ng/g) [Calculated for Concentrations above the Method Detection Limit (MDL)]

| | cotton | | organic cotton | | cotton/polyester | | cotton/spandex | | polyester | | nylon | | overall | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DF | median | DF | median | DF | median | DF | median | DF | median | DF | median | DF | median |
| MEL | | | | | | | | | | | | | | |
| MEL | 95 | 36.4 | 100 | 20.8 | 95 | 43.7 | 61 | 16.6 | 64 | 9.70 | 100 | 17,300 | 85 | 35.7 |
| CYA | 58 | 48.8 | 100 | 5990 | 40 | 15.6 | 28 | 32.8 | 27 | 15.0 | 38 | 171 | 47 | 77.6 |
| AMD | 58 | 2.47 | 50 | 42.1 | 20 | 10.3 | 22 | 56.0 | 9 | 3.74 | 75 | 401 | 36 | 28.2 |
| AMN | 16 | 708 | <MDL | | 20 | 270 | 6 | 262 | 18 | 219 | 100 | 14,900 | 21 | 1530 |
| TBMMAT | 79 | 0.631 | <MDL | | 20 | 0.133 | 11 | 0.503 | 27 | 0.0835 | 100 | 50.3 | 37 | 0.451 |
| **∑MEL** | | **81.4** | | **6120** | | **61.1** | | **23.9** | | **6.20** | | **32,800** | | **78.2** |
| PFAS | | | | | | | | | | | | | | |
| Short-Chain Ionic | | | | | | | | | | | | | | |
| PFBA | <MDL | | 100 | 0.707 | <MDL | | <MDL | | <MDL | | <MDL | | 12 | 0.707 |
| PFBS | 11 | 0.0965 | <MDL | | 15 | 0.0769 | 6 | 0.162 | 9 | 0.0656 | 25 | 0.251 | 11 | 0.0775 |
| PFHxA | 26 | 0.116 | <MDL | | 35 | 0.107 | 44 | 0.0797 | 55 | 0.142 | 50 | 0.138 | 35 | 0.110 |
| PFHxS | 63 | 0.282 | 100 | 0.564 | 65 | 0.309 | 61 | 0.297 | 64 | 0.377 | 100 | 0.306 | 71 | 0.329 |
| PFHpA | 37 | 0.0777 | 20 | 0.0329 | 45 | 0.0845 | 33 | 0.0893 | 36 | 0.0696 | 38 | 0.0646 | 36 | 0.0765 |
| Long-Chain Ionic | | | | | | | | | | | | | | |
| PFOA | 68 | 0.704 | 90 | 0.610 | 65 | 0.662 | 67 | 0.517 | 64 | 0.739 | 50 | 0.671 | 67 | 0.614 |
| PFOS | 11 | 0.466 | <MDL | | 5 | 0.229 | <MDL | | <MDL | | <MDL | | 3 | 0.432 |
| PFNA | 16 | 0.140 | <MDL | | <MDL | | <MDL | | <MDL | | 25 | 0.184 | 6 | 0.157 |
| PFDA | 58 | 0.206 | 80 | 0.161 | 55 | 0.242 | 56 | 0.293 | 36 | 0.156 | 25 | 0.289 | 54 | 0.220 |
| PFUdA | 89 | 0.475 | 100 | 0.484 | 95 | 0.520 | 100 | 0.397 | 82 | 0.410 | 75 | 0.540 | 92 | 0.479 |
| PFDoA | 53 | 0.248 | 100 | 0.164 | 45 | 0.316 | 61 | 0.213 | 27 | 0.301 | 63 | 0.366 | 56 | 0.230 |
| PFTrDA | 79 | 0.242 | 90 | 0.198 | 65 | 0.261 | 83 | 0.268 | 73 | 0.266 | 13 | 0.493 | 71 | 0.242 |
| PFTeDA | 95 | 0.331 | 100 | 0.376 | 100 | 0.443 | 100 | 0.319 | 100 | 0.447 | 100 | 0.362 | 99 | 0.367 |
| PFHxDA | 100 | 1.07 | 100 | 0.855 | 100 | 1.47 | 100 | 1.04 | 100 | 1.39 | 100 | 1.39 | 100 | 1.17 |
| **∑ionic PFAS** | | **3.27** | | **4.02** | | **3.46** | | **2.91** | | **3.28** | | **3.54** | | **3.42** |
| Neutral | | | | | | | | | | | | | | |
| 6:2 FTOH | <MDL | | <MDL | | <MDL | | 6 | 1.84 | 27 | 17.3 | 38 | 149 | 8 | 27.1 |
| 8:2 FTOH | <MDL | | <MDL | | <MDL | | 17 | 10.4 | <MDL | | 63 | 56.7 | 9 | 27.2 |
| 10:2 FTOH | <MDL | | <MDL | | <MDL | | <MDL | | <MDL | | 25 | 12.2 | 2 | 12.2 |
| **∑neutral PFAS** | | | | | | | | **10.4** | | **17.3** | | **89.5** | | **41.9** |
| **∑PFAS** | | **3.27** | | **4.02** | | **3.46** | | **3.19** | | **3.28** | | **86.9** | | **3.62** |

The injection volume was 5 μL. The details of multiple reaction ion monitoring transitions, fragmentors, and collision energies for all analytes are provided in Tables S1 and S2.

**Quality Assurance and Control.** Procedural blanks ($n = 7$) and matrix spike recovery samples ($n = 7$) were analyzed with every batch of 12 samples. The average absolute matrix spike recoveries were 94 ± 18, 85 ± 19, and 65 ± 20% (mean ± standard deviation) for MEL, ionic, and neutral PFAS compounds, respectively. The average recoveries for MEL and PFAS surrogate standards in different fabrics are provided in Table S4. Blank levels of target compounds constituted less than 1% of the respective levels in samples, on an average. All data were blank-corrected by subtracting blank concentrations from sample concentrations. Method detection limits (MDLs) were set as 3 times the standard deviation of the target analyte levels detected in the blanks and ranged from 0.01 to 0.35 ng/g. For compounds not detected in the blanks, MDLs were based on a signal-to-noise ratio of three. Quantification of target analytes was performed by isotope dilution using calibration curves with concentration ranges of 1−500 ng/mL. Correlation coefficients in linearity tests were all >0.99, and samples with concentrations exceeding the linearity ranges were diluted to achieve the levels within the concentration ranges of the calibration curves.

**Data Analysis.** The removal rate of a chemical after the laundering experiment was calculated using eq 1

$$\text{Removal rate }(\%) = \frac{(C_{\text{before}} - C_{\text{after}}) \times 100\%}{C_{\text{before}}} \tag{1}$$

where $C_{\text{before}}$ is the concentration of a chemical in the fabric before laundering (ng/g) and $C_{\text{after}}$ is the concentration of a chemical in the fabric after laundering (ng/g).

Estimated daily intakes (EDIs, pg/kg body weight [bw]/day [d]) via dermal absorption of target chemicals from non-washed and washed clothing were calculated using eqs 2 and 3, respectively

$$\text{EDI}_{\text{non-washed}} = \frac{(C \times D \times \text{SA} \times F_{\text{mig}} \times F_{\text{contact}} \times F_{\text{pen}} \times N) \times T}{\text{BW}} \tag{2}$$

$$\text{EDI}_{\text{washed}} = \frac{(C \times (1 - \text{CC}/100) \times D \times \text{SA} \times F_{\text{mig}} \times F_{\text{contact}} \times F_{\text{pen}} \times N) \times T}{\text{BW}} \tag{3}$$

where $C$ is the median concentration of a chemical in the fabric (ng/g), $D$ is the density of the fabric (23.4 mg/cm$^2$), SA is the skin contact surface area (2040, 2310, 2660, and 3160 cm$^2$ for <1, 1−3, 3−6, and 6−12 month old infants, respectively),[33] $F_{\text{mig}}$ is the migration rate of a chemical to the skin per day (0.005/day),[34] $F_{\text{contact}}$ is the fraction of contact skin area (1, unitless),[34] $F_{\text{pen}}$ is the penetration rate of a chemical (0.01, unitless),[34] $T$ is the contact time between the fabric and skin (assumed to be 1 day),[18] $N$ is the average number of events per day (assumed to be 1/day),[18] BW is the body weight (4.8, 5.9, 7.4, and 9.2 kg for <1, 1−3, 3−6, and 6−12 month old infants, respectively[33]), and CC is the change in the concentration after laundering (%).

Basic and descriptive statistics were calculated using Minitab 19. Plots were generated using SigmaPlot 13 (Systat Software Inc.). Analysis of variance (ANOVA) was performed on log-transformed concentrations. The results of ANOVA are shown as letters; the concentrations of analytes sharing the same letters are not significantly different at $p < 0.05$.

## RESULTS AND DISCUSSION

**Melamine (MEL) and Its Derivatives.** Five out of 11 targeted MEL-based compounds were detected in clothing items analyzed in this study. The other six analytes (Table S1) were not detected and are not included in the further discussion. MEL was detected in 85% of the samples, while the rest of the compounds were detected in up to 47%. The ∑MEL concentrations ranged from <MDL to 250,000 ng/g with a median concentration of 78.2 ng/g (Table 1). Ammeline (AMN) was the most abundant chemical with a median concentration of 1530 ng/g [calculated for concentrations above the MDL], although it was detected only in 21% of the samples. AMN-based resins, such as the AMN−formaldehyde resin, can be used in textiles along with MEL-based resins, which can be a possible explanation for this finding.[35] The concentrations of cyanuric acid (CYA), MEL, and ammelide (AMD) (medians 77.6, 35.7, and 28.2 ng/g, respectively) were lower than those of AMN, but the concentrations of these MEL-based compounds were not statistically different from one another (Figure 1). 2,4,6-*Tris*[*bis*(methoxymethyl)amino]-1,3,5-triazine (TBMMAT) was detected in 37% of the samples and was the least abundant compound among MEL derivatives (median 0.451 ng/g).

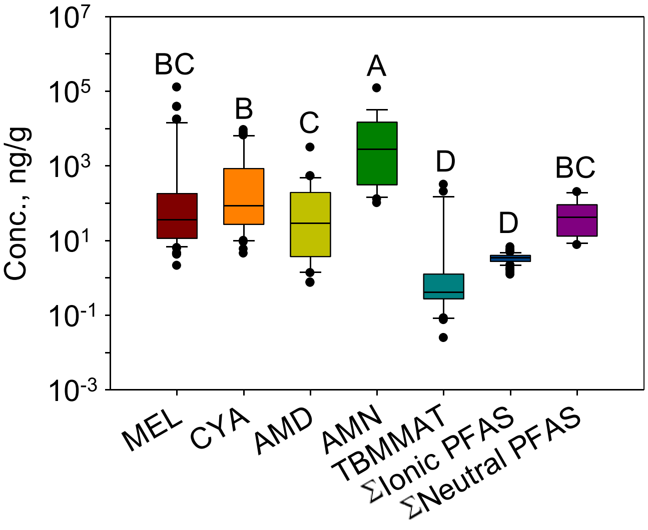

**Figure 1.** Concentrations of MEL and its derivatives, ∑ionic PFAS, and ∑neutral PFAS in infant clothes (ng/g). Concentrations are shown as boxplots representing the 25th and 75th percentiles; black lines represent the median; and the whiskers represent the 10th and 90th percentiles. The letters represent the results of ANOVA; concentrations are ranked from the highest to the lowest in alphabetic order, and boxes sharing the same letters are not significantly different at $p < 0.05$.

MEL concentrations in this study were comparable to those previously reported in textiles and infant clothes from the United States (Table S5, median 53 ng/g)[31] and benzothiazoles in unfinished textiles and infant clothing (median 51.1 ng/g).[36] These concentrations were higher than the concentrations of bisphenol-A (BPA) and bisphenol-S (BPS) in clothes from China (medians 26.9 and 7.38 ng/g, respectively)[37] but lower than the BPA levels detected in children's socks (median 396 ng/g),[29] BPS levels in pantyhose (median

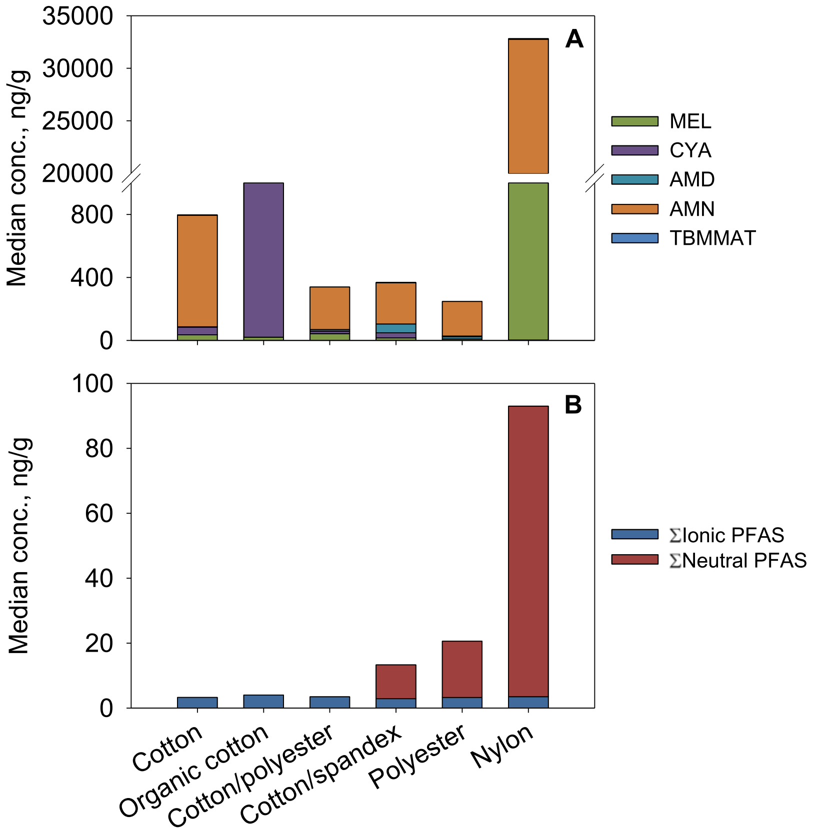

**Figure 2.** Median concentrations of (A) MEL-based compounds and (B) PFAS in different fabrics (ng/g).

1430 ng/g),[38] and phthalates in cotton infant clothing (690–2740 ng/g).[39]

When grouped based on the fabric type, the highest ∑MEL concentrations were found in clothing made of nylon ($n$ = 8) ranging from 6150 to 250,000 ng/g with a median concentration of 32,800 ng/g (Table 1). The ∑MEL levels in nylon and organic cotton were significantly higher ($p < 0.05$; Figure 2) than those in other fabric types including cotton, cotton mixed with polyester (cotton/polyester), cotton mixed with spandex (cotton/spandex), and polyester. The ∑MEL concentrations in other fabric types were statistically indistinguishable from one another. MEL and AMN were the most abundant chemicals found in nylon (medians 17,300 and 14,900 ng/g, respectively). The concentrations of these compounds in nylon were 2–4 orders of magnitude higher than those in other fabric types (Table 1), suggesting that MEL and its derivatives may be used in the manufacturing of nylon clothing to enhance water-repellent properties and thermal stability.[40−42] In fact, the process of using MEL–formaldehyde resins in nylon finishing for imparting water-repellent properties has been patented,[43] and the amount of MEL in nylon as a result of these treatments can reach up to 50% of a fabric's dry weight.[43] Hence, the high levels of MEL found in nylon samples may be due to the intentional use of MEL in this type of fabric.

Interestingly, organic cotton also had high ∑MEL concentrations ranging from 96.2 to 9220 ng/g (median 6120 ng/g). These ∑MEL concentrations mostly comprised of CYA with concentrations of up to 9120 ng/g, which was more than 2 orders of magnitude higher than that in conventional cotton (<MDL—471 ng/g). Commercial nitrogen-based fertilizers, such as urea, nitrolime, and ammonia-based natural fertilizers, contain high levels of CYA (up to 250,000 ng/g) relative to MEL (up to 90,400 ng/g)[44] and are used in growing organic cotton, which must meet strict federal regulations on the use of less toxic pesticides and fertilizers.[45] Heavy use of nitrogen-based fertilizers containing large amounts of CYA may result in plant uptake[44,46,47] and possibly contribute to CYA levels in organic cotton.

The ∑MEL concentrations in clothing labeled as 100% cotton ranged from 2.51 to 1770 ng/g with a median concentration of 81.4 ng/g. It has been reported that textiles labeled as "100% cotton" usually contain 77% cotton, 10% shrink-resistance resins, and 4% dyes and other additives.[1] The median concentrations of ∑MEL were 61.1, 23.9, and 6.20 ng/g for cotton/polyester, cotton/spandex, and polyester clothes, respectively. The ∑MEL concentrations in polyester and spandex clothing were statistically indistinguishable from each other, perhaps because of the limited sample size of each group.

When grouped based on clothing type (outerwear, diapers, dresses, onesies, pants, shirts, and socks), the highest ∑MEL concentrations were found in outerwear (median 70,800 ng/g; Figure 3 and Table S6). The outerwear items were made of nylon, which may be coated with MEL–urea–formaldehyde resins to increase the water-repellency and heat resistance of the fabric.[41,48] Cloth diapers were the second category that had high ∑MEL concentrations (median 4570 ng/g, Table S6), which is concerning considering that diapers are in close contact with skin and worn almost constantly during the first 12–24 months of life.

The ∑MEL concentrations in clothes manufactured in the United States (median 6120 ng/g) were significantly higher than those from other countries ($p < 0.05$; Figure S2 and Table

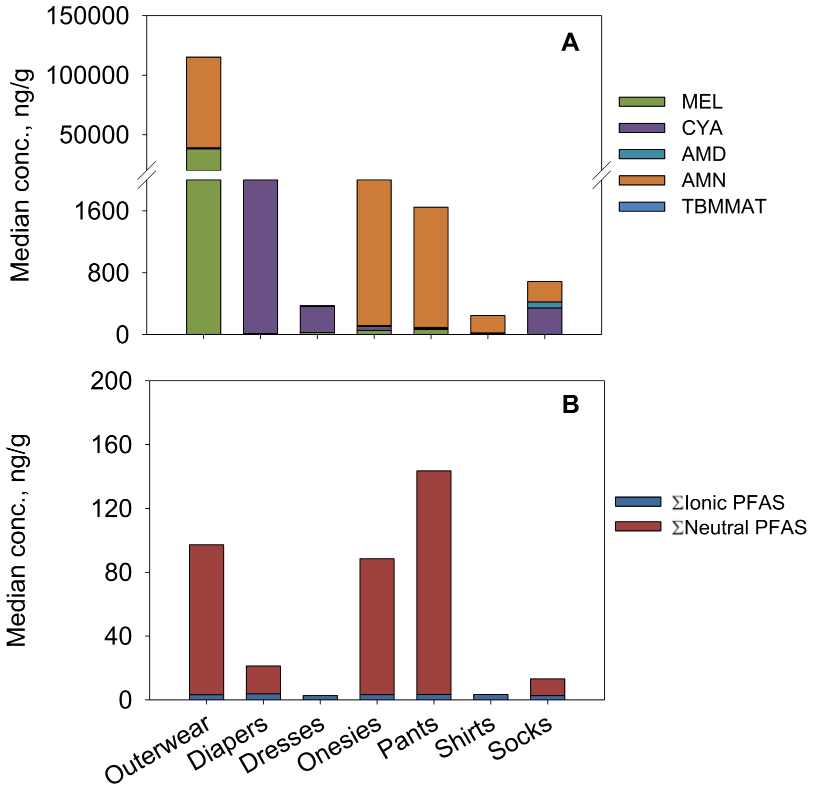

**Figure 3.** Median concentrations of (A) MEL-based compounds and (B) PFAS in different clothing categories (ng/g).

S7). However, it should be noted that because of the difficulty of finding clothes manufactured in the United States, these samples only included cloth diapers made of organic cotton. No significant differences in ∑MEL concentrations were found among clothing items manufactured in other countries. Overall, our findings suggest that fabric composition was the major factor affecting the concentrations of MEL-based compounds in infant clothing.

**PFAS.** Among 40 targeted PFAS, 17 were detected (Table 1). These included five short-chain (C4−C7) and nine long-chain (C8−C16) ionic PFAS. In addition, three neutral FTOHs were also detected (Table 1). Detection frequencies for these PFAS ranged from 2 to 100%, and at least, one PFAS was detected in each sample. The ∑PFAS concentrations (the sum of all 17 detected PFAS concentrations) ranged from 1.22 to 203 ng/g with a median concentration of 3.62 ng/g (Table 1), which was up to 3 orders of magnitude lower than the levels previously reported in performance clothes (2400−219,000 ng/g).[11,49] While FTOHs were detected at the highest levels among the measured PFAS (median 41.9 ng/g), they were found in only 2−9% of the samples. The FTOH concentrations in this study were up to 3 orders of magnitude lower than those reported for outdoor adult clothing (2380−219,000 ng/g).[11,32,49] Interestingly, perfluorooctane sulfonamides and perfluorooctane sulfonamidoethanols, the two PFAS groups that used to be applied in electrochemical fluorination textile treatment techniques before the 2000s,[50] were not detected in these samples.

In contrast, ionic PFAS were detected in most of the samples, but at lower concentrations. Overall, the median ∑ionic PFAS (3.42 ng/g) was up to 10 times lower than the median ∑neutral PFAS concentration (41.9 ng/g). Concentrations of ionic PFAS ranged from 1.22 to 6.45 ng/g and were similar to previous reports.[50,51] Long-chain (C11−C15) PFAS were frequently detected, also similar to previous studies.[5,10,52,53] The C16 homologue was the most abundant ionic PFAS at a median concentration of 1.17 ng/g. PFOS was detected in only 3% of the samples at a median concentration of 0.432 ng/g, while PFOA was found in 67% of the samples at a higher median of 0.614 ng/g. Short-chain ionic PFAS with 4−7 carbons were found in 11−71% of the samples, but at low concentrations (medians 0.0765−0.707 ng/g). The concentrations of long-chain ionic PFAS were significantly higher than the levels of the short-chain PFAS compounds (Figure S3, $p < 0.05$).

The highest ∑PFAS concentrations were found in clothing made of nylon (Figure 2, $p < 0.05$) and ranged from 4.23 to 203 ng/g with a median concentration of 86.9 ng/g (Table 1 and Figure 2). The ∑PFAS concentrations in nylon were dominated by FTOHs. Among FTOHs, 6:2 FTOH was the most abundant with a median concentration of 149 ng/g. In studies from the early 2000s, high FTOH levels (200,000−9,000,000 μg/L) were found in textile impregnating fluids[17] and in waterproofing products (up to 3.8% by weight).[54] The levels in our study were much lower compared to these earlier studies and suggest that PFAS in clothing items in this study were either added at much lower levels or due to the impurities in manufacturing processes or atmospheric deposition.

When grouped based on clothing type, the highest ∑PFAS concentrations were found in pants (median 140 ng/g; Figure 3 and Table S6), followed by outerwear (median 93.8 ng/g). No significant differences in PFAS levels were found based on the clothing type and manufacturing origin (Figures 3 and S2).

A recent study from Zhu and Kannan measured ionic PFAS in infant clothing from the United States and reported a median concentration of ionic PFAS at 0.953 ng/g.[32] While

**Table 2.** $\sum$MEL and $\sum$PFAS Concentrations (Mean ± Standard Error, ng/g) before and after Laundering and the Removal Rate (%) as a Result of Washing[a]

| conditions | $\sum$MEL | removal rate | $\sum$PFAS | removal rate |
|---|---|---|---|---|
| before washing | 42,000 ± 9410 | | 119 ± 30.1 | |
| washing, 20 °C | 27,000 ± 23,200 | 56.6 ± 31.6 | <MDL | 100 |
| washing, 20 °C, detergent | 7400 ± 4900 | 86.2 ± 6.46 | <MDL | 100 |
| washing, 50 °C | 3090 ± 2960 | 95.4 ± 4.17 | <MDL | 100 |
| washing, 50 °C, detergent | 1800 ± 1610 | 97.2 ± 2.23 | <MDL | 100 |

[a] $\sum$MEL represents the sum of MEL and AMN concentrations as these two compounds were the most abundant in samples used for this experiment. MDL: method detection limit.

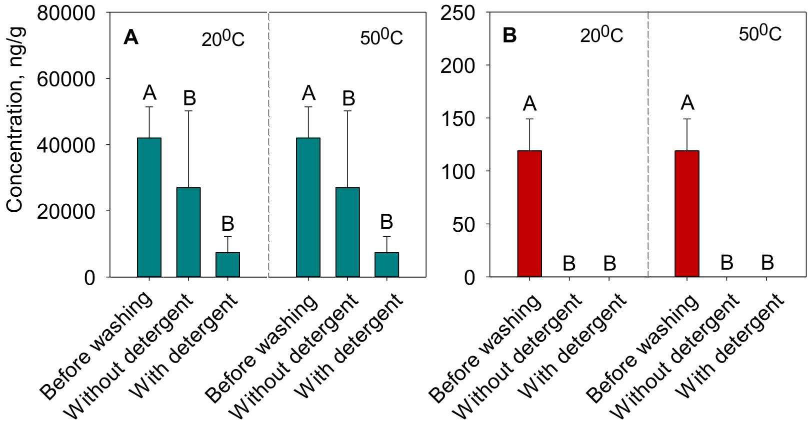

**Figure 4.** Mean (with standard errors) $\sum$MEL (A) and $\sum$PFAS concentrations (B) in clothes washed in different conditions (ng/g). The letters represent the results of ANOVA; the concentrations are ranked from the highest to the lowest in alphabetic order; and the bars sharing the same letters are not significantly different at $p < 0.05$.

neutral PFAS were not directly measured in the latter study, the total oxidizable precursor (TOP) assay was applied to test for possible PFAS precursors,[32] resulting in a 10-fold increase in the concentrations of the ionic PFAS after the TOP assay and suggesting that PFAS precursors were present in the analyzed clothing samples. Our study further supports these findings and suggests that these precursors may include FTOHs, which were found at high levels in several clothing items analyzed in this study.

Overall, both MEL derivatives and PFAS were found in all of the clothing items analyzed in this study. However, the detection frequencies and concentrations of MEL derivatives were significantly higher than those of PFAS ($p < 0.05$), suggesting potential higher use of MEL derivatives in textile production. There is a general trend in the textile industry to move away from using fluorine-based applications for grease-, stain-, and waterproof fabric finishing, while still achieving desired end results.[5] According to U.S. EPA's Chemview database, more than 30 companies have reported the use of MEL as a textile surface coating.[55] Interestingly, more than 15,000 patents on textile finishing using MEL-based compounds can be found as a result of a Google Patent search. The production volumes of MEL resins are not openly available, but the production amounts of individual MEL-based compounds that are used as components of these mixtures range from 23,000 to 120,000 tons/year in the United States.[55]

Our findings suggest that textiles can be a significant source of human exposure to MEL-based compounds. MEL has generally been recognized as a less toxic alternative for many textile finishing agents and specifically for long-chain PFAS.[20] However, the European Chemical Agency is currently considering classifying MEL as a bladder toxin and carcinogen.[56] In 2019, the International Cancer Research Agency (IARC) classified MEL as a possible carcinogen to humans.[57] The German Chemical Society considers MEL as a persistent, mobile, and toxic (PMT) compound similar to *tris*(2-chloro-1-methylethyl)phosphate and 1,4-dioxane.[58,59] When combined, MEL and CYA can crystalize in kidneys and induce renal damage and failure.[60−62] Recent studies found MEL and CYA in breast milk[63] and children's urine,[64] suggesting widespread exposure in early life. The urinary levels of MEL and CYA in children were higher than those in adults, indicating higher exposures in children,[64,65] and were suggestive of kidney damage at current exposure levels.[64]

**Simulated Laundering.** Clothing items with the highest $\sum$MEL and $\sum$PFAS concentrations were included in a simulated laundering experiment in order to evaluate the release of MEL and PFAS during the laundry process under different conditions, including washing with and without detergent in cool (20 °C) and warm (50 °C) water. $\sum$MEL and $\sum$PFAS concentrations in fabric decreased significantly after washing, especially when washed in warm water (Table 2). When washed in cool water, the average $\sum$MEL concentrations decreased on an average by ~60%, from 42,000 ± 9410 to 27,000 ± 23,200 ng/g (Table 2 and Figure 4), while when washed in warm water, the $\sum$MEL concentrations decreased on an average by ~95% to 3090 ± 2960 ng/g, which was significantly lower than the concentrations before laundering ($p < 0.05$). The $\sum$MEL concentrations decreased by an additional 30% when washed in cool water with detergent (7400 ± 4900 ng/g; Table 2 and Figure 4), indicating that the application of laundry detergent facilitates the release of MEL-based compounds from clothes into water. $\sum$MEL further decreased by only ~2% when

Table 3. EDIs (pg/kg bw/day) of ∑PFAS, MEL, and CYA via Dermal Absorption from Clothing (Not Washed and Washed at Different Temperatures with Detergent) for 0−1, 1−3, 3−6, and 6−12 Month Old Infants (Based on Median Concentrations)

| | not washed | | | | washed, 20 °C, detergent | | | | washed, 50 °C, detergent | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| age (months) | 0−1 | 1−3 | 3−6 | 6−12 | 0−1 | 1−3 | 3−6 | 6−12 | 0−1 | 1−3 | 3−6 | 6−12 |
| Non-Nylon | | | | | | | | | | | | |
| ∑PFAS | 1.64 | 1.51 | 1.39 | 1.33 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MEL | 15.0 | 13.8 | 12.7 | 12.1 | 2.07 | 1.91 | 1.75 | 1.67 | 0.0580 | 0.0534 | 0.0491 | 0.0469 |
| CYA | 29.2 | 26.9 | 24.7 | 23.6 | 4.02 | 3.71 | 3.40 | 3.25 | 0.113 | 0.104 | 0.0953 | 0.0911 |
| Nylon | | | | | | | | | | | | |
| ∑PFAS | 44.5 | 41.0 | 37.6 | 36.0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| MEL | 8.590 | 7.910 | 7.260 | 6.940 | 1.190 | 1.090 | 1.000 | 958 | 33.2 | 30.6 | 28.1 | 26.8 |
| CYA | 85.1 | 78.4 | 72.0 | 68.8 | 11.7 | 10.8 | 9.93 | 9.49 | 0.329 | 0.303 | 0.278 | 0.266 |

washed in warm water with detergent (1800 ± 1610 ng/g). Similar levels of MEL released into wastewater were reported for MEL-based tableware[66−68] and may be attributed to high solubilities of MEL and its derivatives (3.24−1000 mg/L).[54]

In contrast, PFAS were completely washed out after laundering in cool water without detergent and were not detected in any of the samples after washing (Table 2 and Figure 4). Strong migration of PFAS has also been reported in previous studies.[9,52] Leaking of chemicals from clothing to water during laundry is significantly correlated with a chemical's $K_{ow}$.[69] For example, as much as 80% of organophosphate esters with log $K_{ow} < 4$ leaked from clothing to water in a simulated laundry experiment, while the leakage rate was only 10% for brominated flame retardants with log $K_{ow} > 6$.[69] The high release rates for both MEL and PFAS suggest that treated clothes and other textiles can be an important source of these chemicals to wastewater treatment plants and eventually to surface waters.

**Exposure Assessment.** EDIs of ∑PFAS, MEL, and CYA via dermal absorption from clothes for 0−1, 1−3, 3−6, and 6−12 month old infants are presented in Table 3. The ∑PFAS EDI from non-nylon clothes ranged from 1.33 to 1.64 pg/kg bw/d, which was 10−20 times lower than that for MEL and CYA. For nylon clothes, these EDIs increased to 36.0−44.5 pg/kg bw/d. The MEL EDI from nylon clothes was about 3 orders of magnitude higher than that from non-nylon clothing. The highest PFAS, MEL, and CYA EDIs were estimated for 0−1 month old infants, suggesting that newborns are the highest exposure risk group. The EDIs from infant clothing for BPA were estimated as 201−248 pg/kg bw/d[29] and were similar to the EDI for MEL from non-nylon clothes in this study (12.1−15.0 pg/kg bw/d) and much lower than the MEL EDI from nylon clothes (6940−8590 pg/kg bw/d). The EDIs for MEL and CYA via dermal absorption were up to 4−100 times lower than those from breastfeeding, consumption of infant formula, and dust ingestion (Table S8).[63,70,71] The EDIs calculated using concentrations in clothes after washing decreased by more than half for MEL and CYA and 100% for ∑PFAS. Lowest EDIs were determined in samples washed with detergent at 50 °C, suggesting that laundering in warm water using a detergent could be a suitable way to reduce dermal exposure to chemicals in clothes, but it raises concerns about the fate of these chemicals in wastewater treatment processes.

**Limitations and Implications.** This study has several limitations. The sample size of each fabric and clothing type was limited, especially for clothes made of nylon. Further studies on different categories of nylon clothing are needed to verify our findings of high levels of MEL in this fabric type. The absorption of PFAS and MEL-based compounds from the indoor environment onto textiles cannot be ruled out but was not evaluated in this study. In addition, the laundering experiment was performed using nonverified simulators, and no repeat washes were performed. The extraction methods used in this study did not include different exhaustive extraction methods (e.g., TOP assay), which may result in underestimation of the nonextractable MEL and PFAS compounds.

Nevertheless, this is the first comprehensive study that reports two groups of textile additives, MEL and PFAS compounds, in infant clothing. All clothing items analyzed in this study had significantly higher levels of MEL-based compounds than PFAS, suggesting a potential use of MEL and its derivatives in infant clothes and possibly other textiles. Although MEL-based formulations are considered as safe PFAS alternatives by the textile industry, the European Chemical Agency[56] and the International Cancer Research Agency have recently listed MEL as a possible human carcinogen.[57] Clearly, further research is needed on risks associated with existing environmental exposures to this group of chemicals.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c03035.

> Target analytes; sample details; summary of previously published data on emerging contaminants in textiles; representative chromatograms of FTOHs; concentrations of MEL-based compounds and PFAS in different categories of clothing items; details of exposure assessment; and PFAS composition in clothes (PDF)

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### Notes

The authors declare no competing financial interest.

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