

The washout effect during laundry on benzothiazole, benzotriazole, quinoline, and their derivatives in clothing textiles

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Abstract In two previous papers, the authors have shown that benzothiazole, benzotriazole, quinoline, and several of their derivatives are widespread in clothing textile articles. A number of these compounds exhibit allergenic and irritating properties and, due to their octanol–water partition coefficient, are prone to be absorbed by the skin. Moreover, they are slightly soluble in water, which could make washing of clothes a route of emission into the environment. In the present study, the washout effect of benzothiazole, benzotriazole, quinoline, and some of their derivatives has been investigated. Twenty-seven textile samples were analyzed before, as well as after five and ten times of washing. The most abundant analyte was found to be benzothiazole, which was detected in 85 % of the samples with an average concentration of 0.53 µg/g (median 0.44 µg/g), followed by quinoline, detected in 81 % of the samples with an average concentration of 2.42 µg/g (median 0.21 µg/g). The average decrease in concentration for benzothiazoles was 50 % after ten times washing, while it was around 20 % for quinolines. The average emission to household wastewater of benzothiazoles and quinolines during one washing (5 kg of clothes made from polyester materials) was calculated to 0.5 and 0.24 g, respectively. These

results strongly indicate that laundering of clothing textiles can be an important source of release of these compounds to household wastewater and in the end to aquatic environments. It also demonstrates a potential source of human exposure to these chemicals since considerable amounts of the compounds remain in the clothes even after ten times of washing.

Keywords Benzothiazoles · Benzotriazoles · Quinolines · Clothing · Textiles · Garments

Introduction

Benzothiazoles and benzotriazoles are commonly used chemicals with a number of applications (Kloepfer et al. 2004; Weiss and Reemtsma 2005). Benzothiazoles are mainly used as vulcanization accelerators in rubber production (Ni et al. 2008), but have also been used as biocides and fungicides (Kloepfer et al. 2004). Both benzothiazoles and methylated benzotriazoles have been used as corrosion inhibitors in different antifreeze formulations (Weiss and Reemtsma 2005), while the 2-hydroxyphenyl derivatives of benzotriazoles (BUVs) are mostly used as ultra-violet (UV) stabilizers, e.g., in textiles and plastics (Kim et al. 2011; Nakata et al. 2009). In recent years, these compounds have frequently been detected in wastewater in populated areas (Matamoros et al. 2010; Reemtsma et al. 2006), in municipal wastewaters (Reemtsma et al. 2010), as well as in household wastewater not affected by road surface runoff (Kloepfer et al. 2005). The removal of benzothiazoles and benzotriazoles in wastewater treatment plants (WWTPs) has been examined in many studies, showing removal efficiencies of up to 80 % for benzothiazoles and up to 60 % for benzotriazoles (Asimakopoulos et al. 2013a; Kloepfer et al. 2005; Liu et al. 2012; Matamoros et al. 2010).

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Benzothiazoles and benzotriazoles have also been detected in urine samples collected from general populations in USA, Greece, Vietnam, Korea, Japan, China, and India (Asimakopoulou et al. 2013b), while BUVs have been found in fish (Kim et al. 2011), clams, oysters, and gastropods (Nakata et al. 2009). Although benzothiazoles and benzotriazoles occur widely in the environment, and have been found in humans and aquatic organisms, the toxicological and eco-toxicological information is scarce. It has however been shown that several benzothiazoles are acute toxic in various test systems (Reemtsma et al. 1995) and have allergenic and irritating properties (Fishbein 1991; Jung et al. 1988). Benzotriazole has shown both mutagenic and estrogenic properties in aquatic organisms (Tangtian et al. 2012) and BUVs have been found to bioaccumulate in birds, fishes, and invertebrates (Nakata et al. 2009) and in a recent study BUVs showed significant human aryl hydrocarbon receptor (AhR) ligand activity, potentially affecting the immune response similar to dioxins (Nagayoshi et al. 2014).

Besides benzothiazoles and benzotriazoles, quinoline and quinoline derivatives were also investigated in the present study. These compounds belong to the group of azaarenes, polycyclic aromatic hydrocarbons (PAHs), in which a carbon atom in the ring structure is replaced with nitrogen. Their principal sources are incomplete combustion of fossil fuels, effluents of several facilities processing oil shale or coal, and wood preservation treatment (Pereira et al. 1983). They have been found in air particulate matter, tobacco smoke, ground water, and lake and marine sediments (Drushel and Sommers 1966; Nielsen et al. 1986; Stedman 1968; Wakeham 1979). Quinoline and its oxidized derivatives were recently quantified in Dutch river sediments and Dutch coastal zone of the North Sea, with the 2-hydroxyquinoline showing the highest concentration (Brulik et al. 2013; de Voogt and Laane 2009). Two-ring azaarenes have also been detected in the Danshuei River sediments, in Taiwan (Chen et al. 2008). Owing its water solubility and low biodegradability, quinoline is considered as a persistent pollutant in ground-water and soil. There are various methods to remove quinoline and its derivatives from water, including adsorption (Bai et al. 2011), biodegradation (Lin and Jianlong 2010), photocatalytic oxidation (Jing et al. 2013), and photo- and biodegradation combined (Chang et al. 2014). Those methods have different removal efficiency, but almost all of them give minimal removal of the ammonium-N released during their degradation, which is a key water pollutant (Paerl et al. 2011). Theoretical and practical bases for treatment of wastewater that contain recalcitrant organic compounds containing N has recently been developed (Yan et al. 2014).

The main use of quinoline is the manufacture of other specialty chemicals, as moiety to pharmaceuticals (Mukherjee and Pal 2013; Vezmar and Georges 2000) and to dyes (Lam et al. 2012), and its presence in textile (Luongo et al. 2014) and in dye processing plants effluents has been reported in the literature

(Oliveira et al. 2007; Yuan et al. 2006). Even though no human studies on their carcinogenicity are available, tests involving acute exposure of mice have demonstrated quinoline and some of its methylated isomers to induce liver cancer (Hirao et al. 1976; La Voie et al. 1988). Mutatox™ test showed both quinoline and isoquinoline (Iso-Q) to be direct genotoxic (Bleeker et al. 1999) and ecotoxic (Neuwoehner et al. 2009) agents. Quinoline and several monomethyl derivatives have proven to be mutagenic in *Salmonella typhimurium* after metabolic activation (Eisentraeger et al. 2008; Nagao et al. 1977), whilst dimethylquinolines have been found to be moderately toxic in the aquatic environment (Birkholz et al. 1990). Despite the possible environmental and health impact, little attention has been given to heterocyclic PAHs, probably due to lower concentrations (1–10 %) comparing to those of the analogue homocyclic PAHs (Bleeker et al. 2001). However, literature data of the solubility for some azaarenes and PAHs shows that the former has a higher polarity, which could enhance their mobility in the environment and promote water contamination (Pearlman et al. 1984). Therefore, an understanding of the releasing processes from the possible sources into the aqueous system is needed.

In previous studies (Avagyan et al. 2015; Luongo et al. 2014), we have demonstrated that benzothiazole, benzotriazole, quinoline, and their derivatives are commonly occurring chemicals in clothing textiles on the Swedish retail market. Assuming that laundering of clothes may be a source of these compounds in household wastewater and eventually also to the aquatic environments, we have stressed the importance to further investigate the laundering effect of clothing textiles.

In the present study, the washout effect of the three classes of compounds, benzothiazoles, benzotriazoles, and quinolines were quantified in 27 textile clothes and their release into household wastewater was investigated. The study is of a global significance since most of the retailers and brands analyzed are available on the retail markets worldwide.

Materials and methods

Chemicals and solvents

The benzothiazole, benzotriazole, and quinoline derivatives used in this study are listed in Table S1 in the Electronic Supplementary Material (ESM). Methanol and acetonitrile (ACN), both of HPLC grade, were purchased from Rathburn Chemicals Ltd. (Walkerburn, UK). Acetone, *n*-hexane, and dichloromethane (DCM) (purity >99.8 %) were acquired respectively from Fisher Scientific (Gothenburg, Sweden), Merck Millipore (Darmstadt, Germany), and Fluka/Sigma-Aldrich (St. Louis, MO, USA). Formic acid was purchased from Fluka/Sigma-Aldrich (Seelze, Germany). Water was purified using a Millipore Synergy 185 water purification system

equipped with a Millipak 0.22 μm membrane filter (Millipore Corp., Billerica, MA, USA).

The solid-phase extraction (SPE) cartridge used for the cleanup was an endcapped octadecyl Isolute[®] SPE-C18 (EC) with 200 mg stationary phase in a 3-ml cartridge (Biotage AB, Uppsala, Sweden).

Clothing textile samples

Twenty-seven textile samples purchased from ten retail stores in Stockholm between September and November 2014 were used for this study. The purchased clothes represented four worldwide, two European, and one Swedish brand. Thus, most of the purchased clothing were also available on the retail markets worldwide. The origin of manufacture was nine Asian countries and one European, and most of the textile garments were made from different polyester materials. The reason for this selection of textile material was that, in earlier studies, we have shown the target analytes are present to a greater extent in polyester materials compared to cotton based textiles (Avagyan et al. 2015; Luongo et al. 2014). Information about color, material, type, and manufacturing country is summarized in Table 1. Analyses were conducted in duplicate on the unwashed samples, as well after five and ten washing steps. The washing of the individual textile samples was performed using a commercially available washing machine (Logixx 8 VarioPerfect[™] Bosch, Germany) with a pre-set washing program of 40 °C for synthetic textiles. The washing program was as follows: 40 °C for 20 min with detergent, followed by rinsing with water for 20 min at 40 °C. The rinsing was necessary in order to remove residual chemicals coming from the detergent that may scatter on the fabric surface. The amount of detergent used (5–15 % anionic and non-ionic surfactant, Via Classic Color, Unilever Sverige AB, Sweden) corresponded to 2 % of the weight of the textile. Subsequently, the cleaned samples were water-extracted and finally dried at 40 °C for 40 min in a tumble dryer (Avantixx8 Sensitive, Bosch, Germany). The same washing procedure was repeated five times and ten times on a new, unused textile sample. The unwashed and washed dried fabrics were stored in individual bags at room temperature prior to all experiments.

Analytical method

The analytical methods for benzothiazole and benzotriazole derivatives and quinolines have been described in detail in two previous papers (Avagyan et al. 2013; Luongo et al. 2014). Briefly, 1.5–2 g of the textile was cut into 5×5 mm pieces and placed in test tubes. The internal standards were added, 2-methyl benzothiazole (MeBT) for the benzothiazole and benzotriazole analysis, and quinoline d₇ (Q-d₇) for quinoline analysis respectively. The benzothiazoles and benzotriazoles were then extracted from the textiles using 10 mL of 20 % acetone in DCM in an

ultra-sonication bath (Bandelin Electronic, Berlin Germany) for 20 min, while quinolines were extracted using pure DCM for 10 min. The extractions were repeated with fresh solvents and the two extracts were combined. For the benzothiazole and benzotriazole analysis, the extract was filtered using 0.2 μm Nylon filters; 0.2 mL purified water was added as a keeper prior the volume of the extract being reduced to 0.2 mL under a gentle stream of nitrogen. Methanol (0.3 mL) was added and the extract was filtered once again.

For the quinoline analysis, the combined extract was reduced in volume to 1 mL by evaporation under a gentle stream of nitrogen and filtered using SPE-C18 (EC) cartridge. The cartridge was washed with 5 mL hexane and 10 mL DCM prior the extract was loaded. Elution was performed by 10 mL of DCM, and the eluate subsequently reduced by evaporation to a volume of 1 mL.

Instrumental analysis

The benzothiazoles and benzotriazoles were analyzed on an Agilent high-performance liquid chromatography (HPLC) system consisting of an 1260 binary pump solvent delivery system, an 1100 degasser, and an 1100 autosampler (Wilmington, DE, USA) and an API QTrap[™] triple quadrupole mass spectrometer (PE Sciex, Toronto, ON, Canada) equipped with a TurboIon[®] electro spray interface used in positive ion mode.

The chromatographic separation was performed on a ACE 3 C8 microbore column (2.1 mm×50 mm, 5 μm particle size) equipped with a ACE 3 C8 guard cartridge, both from Advanced Chromatography Technologies (Aberdeen, Scotland). Pure water and acetonitrile with 0.10 % (v/v) formic acid were used as mobile phase A and B, respectively. The HPLC gradient program was set as follows: 0 min 35 % B, 2 min 35 % B, 5 min 95 % B, 25 min 95 % B, and 25.1 min 35 % B using linear ramps. The system was equilibrated for 10 min with 35 % B before each run.

The mass spectrometer (MS) parameters were set as follows: curtain gas (N₂): 20 psi, collision gas (N₂): medium, ion spray voltage: +5000 V, ion source gas (N₂): 20 psi, and source temperature 150 °C. The dwell time for each selected reaction monitoring (SRM) transition was set to 0.25 s. The analyte specific parameters are presented in Table S2 in ESM.

The quinoline analyses were performed on a gas chromatograph/mass spectrometer (GC/MS) system consisting of a 6890 N gas chromatograph, a 5975C mass spectrometer, programmable temperature vaporizer injector, and a 7683 autosampler (Agilent Technologies, Palo Alto, CA, USA). The temperature program for the vaporizer was 70 °C for 0.5 min followed by a ramp of 700 °C/min to 310 °C, which was maintained for 8 min. The GC column oven temperature program was 50 °C for 1 min followed by two ramps, 6 °C/min to 170 °C, and 20 °C/min to a final temperature of 300 °C, which was kept for 7 min. The column

Table 1 Textile samples; name, color, material, type and manufacturing country

Name	Color	Material	Type	Country
T-1	Turquoise	100 % Polyester	Female T-shirt	Cambodia
T-2	Jade green	100 % Silk	Pillow case	India
T-3	Black	100 % Polyester	Sport trousers kid	China
T-4	Blue	100 % Modal	Scarf	China
T-5	Violet	90 % recycled polyamide, 10 % Elastane	Tights	Italy
T-6	Blue	88 % polyamide, 12 % Elastane	Tights	Turkey
T-7	Beige	80 % Polyamide, 20 % Elastane	Hotpants	Sri Lanka
T-8	Black	80 % Polyamide, 20 % Elastane	Hotpants	Sri Lanka
T-9	Green	87 % Polyester recycled, 13 % Elastane	Male T-shirt	China
T-10	Green	73 % Polyamide, 18 % Polyester, 6 % Elastodiene, 3 % Elastane	Socks	China
T-11	Pink	Shell: 81 % Polyester, 19 % Elastane Lining: 100 % Polyester	Swimsuit baby	Indonesia
T-12	Pink	100 % Recycled Polyester	Female T-shirt	Thailand
T-13	Orange/Grey	87 % Polyester, 13 % Elastane	Skirt	Indonesia
T-14	Orange	100 % Polyester	T-shirt	Thailand
T-15	Grey/Black	88 % Polyester, 12 % Elastane	T-shirt	Unknown
T-16	Pink	95 % Polyester, 5 % Elastane	T-shirt	Unknown
T-17	Black	58 % Cotton, 39 % Polyester, 3 % Elastane	Trousers	Bangladesh
T-18	Black	100 % Polyester	Jacket	China
T-19	Black	97 % Cotton, 3 % Elastane	Trousers	Bangladesh
T-20	Black	67 % Viscose, 28 % Polyamide, 5 % Elastane	Trousers	China
T-21	Yellow-green	100 % Polyester	T-shirt kid	Indonesia
T-22	Light blue	85 % Polyester, 15 % Elastane	T-shirt kid	China
T-23	Cobalt	88 % Polyester, 12 % Elastane	Shorts	Vietnam
T-24	Blue	100 % Polyester	T-shirt kid	Unknown
T-25	Fuchsia	88 % Polyester, 12 % Elastane	Top	Sri Lanka
T-26	Blue	100 % Polyester	Shorts kid	China
T-27	Blue	100 % Polyester	Trousers	China

was a J&W DB5-MS capillary column (Agilent Technologies; 30 m, inner diameter 0.25 mm, film thickness 0.25 μ m). Helium was used as the carrier gas at a linear flow rate of 45 cm/s in constant-flow mode. The ion source temperature was set to 300 °C, and the quadrupole temperature to 150 °C. Ionization was done using electron ionization at 70 eV, and the analysis was performed in selected ion monitoring (SIM) mode.

Quality assurance/quality control (QA/QC)

The method validation is described in detail elsewhere (Avagyan et al. 2013; Luongo et al. 2014) and shortly summarized in Table S3 in ESM. Briefly, for the benzothiazole and benzotriazole analysis, limit of detection (LOD) and method quantification limit (MQL) ranged from 1 to 36 pg injected and 13–108 pg/g textile, respectively. Coefficients of determination (R^2) were ≥ 0.99 for all calibration curves. Recoveries of the analytes from spiked textile matrices ranged from 69 to 102 %, and the relative standard deviations (RSDs)

of repeated experiments ranged from 4 to 18 %. MeBT has successfully been used as internal standard both for benzothiazole and benzotriazole derivatives (Avagyan et al. 2013), instead of, e.g., deuterated analogues of the analytes. Deuterated benzotriazole (d_4 -BTri), a commonly used internal standard for benzothiazole and benzotriazole analysis, has been reported to elute in the beginning of the chromatogram and may not be the most appropriate internal standard for all of the compounds (Herrero et al. 2013). In addition, methods have been developed for determination of MeBT, but it has not been detected in, e.g., water samples (Carpinteiro et al. 2012; Reemtsma 2000), neither in the clothing textiles investigated in this study.

For the quinoline analysis, LOD ranged from 0.4 to 3.4 pg injected, while MQL ranged from 1.1 to 4.9 ng/g. The recoveries of the analytes were more than 90 %, R^2 of all calibration curves were ≥ 0.99 , and RSDs ranged from 1 to 8 %. Quality control samples at two different concentration levels (70 and 700 ng/g) were included in each batch and analyzed in parallel with the samples. The relative error was below 15 % for all the

compounds at both levels, except in one case for the dimethyl derivatives at the lower concentration level when it reached 19 %. Blanks were run in parallel with the samples to assess the absence of contamination and eliminate the risk of carry over. In order to determine the homogeneity of the distribution of quinolines in the textile, three different spots (front, back, and sleeves) of three garments were analyzed; from each spot, a triplicate analysis was conducted. The RSD of the triplicate in one spot reached 7 %, and intra-spot deviation was up to 9 %.

Results and discussion

Benzothiazole, benzotriazole, and quinoline derivatives in clothing textiles

The 27 textile samples were investigated for their content of benzothiazoles, benzotriazoles, and quinolines; three groups

of compounds which appear to be frequent chemical residues in textile materials. The concentrations of each compound in the different garments are summarized in Tables 2 and 3 and shown in Figs. 1a, 2a, and 3 and Fig. S1a–S13a in ESM.

The most abundant of the target analytes was benzothiazole (BT), detected in 85 % of the 27 samples with an average concentration of 0.53 µg/g, with a range of 0.10 to 1.59 µg/g and a median of 0.44 µg/g (Fig. 1a). Sample T-14, an orange T-shirt made from 100 % polyester material, had the highest concentration of this analyte. The second most abundant compound was quinoline which was detected in 81 % of the samples (Fig. 2a).

Quinoline was always found to be present together with Iso-Q and several methylated quinoline derivatives, where quinoline itself constituted more than 50 % of the total amount of quinoline derivatives in each fabric. The average concentration was 2.42 µg/g, with a range of MQL–23.7 µg/g and a median of 0.21 µg/g. Sample T-25, a pink top made from

Table 2 Determined concentrations (ng/g) of benzothiazole and benzotriazole derivatives in clothing textile samples ($n=2$) before washing

	BT Mean (SD ^a)	BTri Mean (SD)	5-Ttri Mean (SD)	UV-234 Mean (SD)	UV-P Mean (SD)	UV-328 Mean (SD)
TS-1	1160 (118)	n.d. ^b	n.d.	140 (8.10)	n.d.	n.d.
TS-2	297 (83.4)	n.d.	n.d.	n.d.	n.d.	n.d.
TS-3	857 (42.3)	n.d.	34.8 (1.69)	n.d.	n.d.	n.d.
TS-4	229 (6.63)	n.d.	n.d.	n.d.	n.d.	n.d.
TS-5	99.4 (2.00)	40.0 (0.48)	25.1 (1.33)	99.7 (43.3)	244 (4.47)	n.d.
TS-6	231 (4.47)	n.d.	n.d.	n.d.	12.5 (2.01)	n.d.
TS-7	228 (12.6)	n.d.	n.d.	20.1 (1.01)	n.d.	58.3 (6.01)
TS-8	212 (71.1)	n.d.	n.d.	n.d.	22.5 (6.66)	47.8 (2.89)
TS-9	212 (51.6)	n.d.	n.d.	3800 (110)	n.d.	n.d.
TS-10	866 (90.4)	n.d.	n.d.	40.4 (30.0)	n.d.	n.d.
TS-12	789 (76.3)	n.d.	25.9 (2.95)	10.2 (1.02)	23.9 (3.16)	n.d.
TS-13	459 (38.7)	n.d.	n.d.	503 (30.0)	n.d.	60.0 (4.57)
TS-14	1590 (86.6)	n.d.	n.d.	20.2 (9.03)	18.7 (1.40)	85.3 (3.53)
TS-15	587 (15.8)	n.d.	n.d.	n.d.	18.0 (1.83)	n.d.
TS-16	846 (34.1)	n.d.	n.d.	194 (12.0)	16.3 (3.89)	n.d.
TS-17	447 (0.88)	n.d.	n.d.	5330 (170)	30.8 (0.70)	n.d.
TS-18	348 (4.70)	6.46 (5.13)	29.7 (0.22)	281 (11.0)	n.d.	n.d.
TS-19	133 (3.44)	122 (14.9)	n.d.	30.0 (5.05)	9.12 (1.13)	n.d.
TS-20	210 (2.76)	n.d.	n.d.	n.d.	n.d.	n.d.
TS-21	n.d.	n.d.	n.d.	579 (22.7)	n.d.	n.d.
TS-22	n.d.	25.0 (3.89)	n.d.	1460 (146)	13.3 (3.69)	n.d.
TS-23	741 (84.6)	n.d.	n.d.	6690 (338)	115 (1.88)	n.d.
TS-24	n.d.	n.d.	70.5 (2.76)	3870 (387)	n.d.	n.d.
TS-25	440 (17.6)	n.d.	n.d.	230 (11.0)	6.58 (3.88)	n.d.
TS-26	383 (33.2)	n.d.	n.d.	140 (69.9)	n.d.	n.d.
TS-27	831 (52.0)	n.d.	n.d.	170 (9.98)	16.7 (1.93)	n.d.

^a Standard deviation

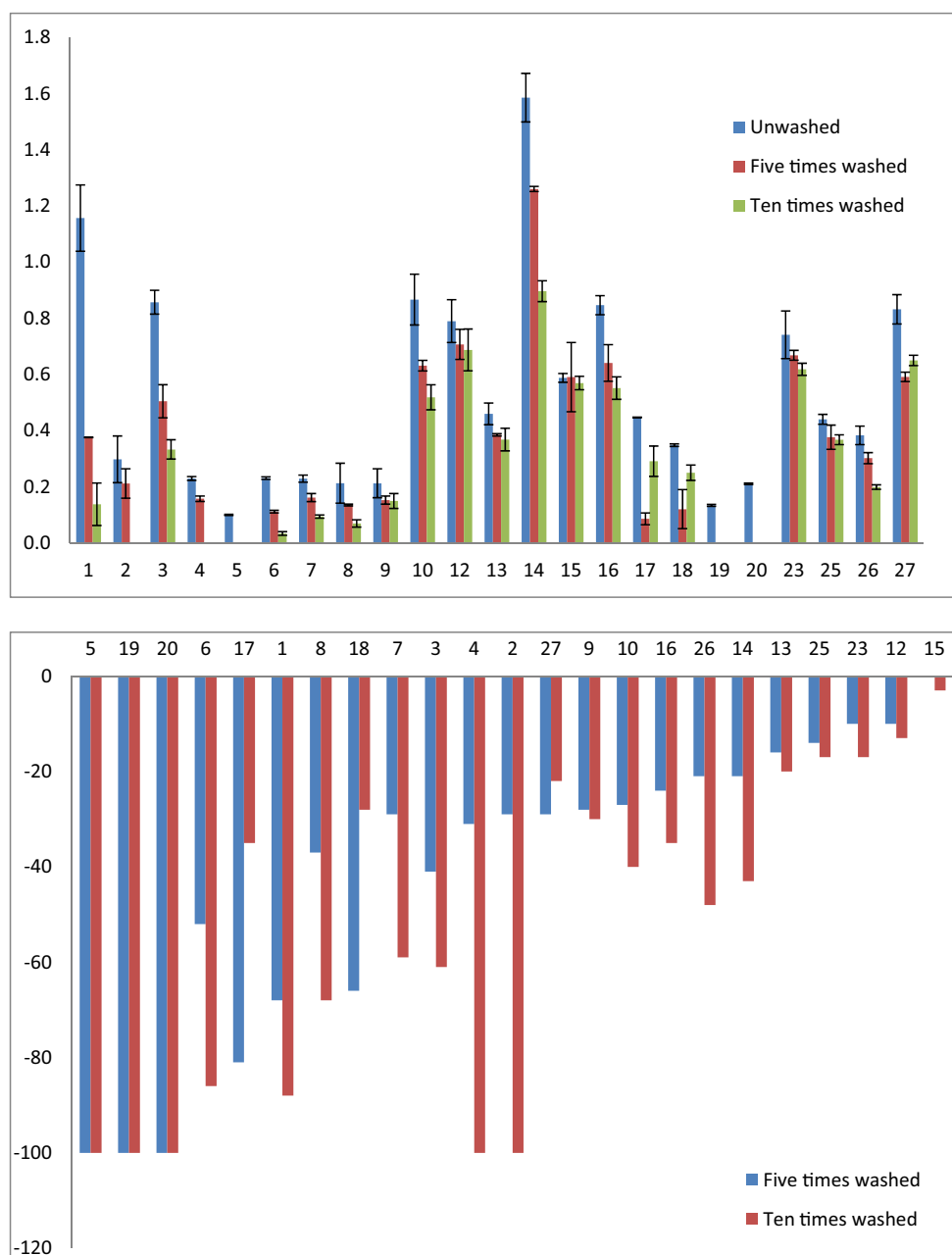
^b Not detected

Table 3 Determined concentrations (ng/g) of quinoline derivatives in clothing textile samples ($n=2$) before washing

	Quinoline Mean (SD) ^{a)}	IsoQ Mean (SD)	2-MQ Mean (SD)	8-MQ Mean (SD)	1-IsoMQ Mean (SD)	6-MQ Mean (SD)	3-MQ Mean (SD)	4-MQ Mean (SD)	2,4-DMQ Mean (SD)	2,6-DMQ Mean (SD)
TS-3	1280 (8.80)	448 (10.3)	158 (3.24)	81.9 (2.25)	23.7 (0.72)	263 (9.50)	106 (3.27)	162 (11.1)	39.8 (2.06)	125 (9.35)
TS-4	LOD	LOD	n.d. ^{b)}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TS-5	LOD	LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	LOD	LOD
TS-6	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
TS-8	LOD	LOD	LOD	LOD	LOD	LOD	LOD	n.d.	LOD	LOD
TS-9	1610 (26.8)	444 (10.9)	228 (6.06)	61.7 (1.44)	21.4 (0.50)	182 (5.50)	63.8 (1.79)	82.8 (3.12)	41.9 (1.53)	85.9 (3.64)
TS-10	193 (0.65)	115 (23.4)	36.6 (2.39)	18.4 (1.72)	9.3 (0.73)	24.8 (2.53)	12.4 (2.19)	9.3 (0.45)	18.0 (1.86)	11.4 (1.15)
TS-12	1860 (44.2)	445 (16.2)	216 (8.57)	57.0 (0.80)	15.6 (2.29)	219 (6.05)	75.8 (0.78)	87.4 (2.20)	42.3 (0.90)	77.7 (2.40)
TS-13	296 (7.54)	64.3 (3.06)	33.2 (1.06)	7.70 (0.14)	2.70 (0.17)	26.8 (1.29)	12.0 (1.08)	16.0 (0.17)	5.9 (0.44)	15.2 (1.15)
TS-14	3270 (357)	870 (94.4)	510 (65.1)	184 (24.6)	41.6 (6.05)	599 (77.9)	222 (30.5)	249 (29.4)	153 (22.2)	262 (35.1)
TS-16	852 (50.8)	198 (5.91)	141 (7.17)	56.2 (3.98)	11.6 (0.61)	113 (4.72)	43.7 (2.77)	49.7 (1.83)	26.7 (1.23)	55.3 (4.47)
TS-17	107 (1.78)	17.3 (0.28)	9.00 (0.39)	1.48 (0.18)	2.27 (0.57)	n.d.	3.11 (0.02)	n.d.	2.26 (0.02)	8.67(0.27)
TS-18	879 (92.6)	262 (25.1)	138 (17.6)	40.0 (5.54)	7.94 (2.01)	85.2 (10.2)	27.7 (3.97)	26.6 (3.53)	14.0 (2.23)	29.5 (3.71)
TS-19	12.4 (0.29)	1.51 (0.06)	2.01 (0.05)	0.29 (0.01)	2.48 (0.12)	2.13 (0.10)	0.35 (0.03)	n.d.	1.40 (0.07)	3.53 (0.21)
TS-20	6.17 (0.10)	2.86 (0.01)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.17 (0.12)	2.27 (0.03)
TS-21	58.1 (4.76)	12.8 (0.06)	6.59 (0.16)	3.29 (0.51)	11.4 (0.23)	15.0 (0.38)	2.30 (0.46)	8.94 (1.82)	13.9 (0.71)	13.6 (1.66)
TS-22	181 (5.77)	23.6 (1.03)	15.5 (0.31)	4.09 (0.22)	0.62 (0.09)	n.d.	2.41 (0.01)	n.d.	1.33 (0.15)	2.67 (0.39)
TS-23	335 (13.8)	67.7 (0.32)	31.4 (0.11)	9.10 (0.39)	4.53 (0.83)	128 (7.4)	31.2 (0.99)	244 (12.7)	4.94 (0.26)	24.4 (0.40)
TS-24	232 (9.93)	96.7 (1.60)	47.4 (1.00)	33.9 (1.06)	14.9 (0.59)	71.4 (0.87)	24.4 (1.00)	56.9 (1.14)	34.8 (2.56)	86.6 (4.14)
TS-25	23700 (445)	6830 (101)	4250 (91.1)	2260 (48.4)	454 (9.85)	5520 (122)	2090 (45.5)	2550 (72.2)	1150 (35.4)	1770 (40.0)
TS-26	18200 (173)	3250 (30.9)	1780 (22.8)	1220 (14.0)	86.2 (1.41)	1940 (8.02)	764 (9.08)	453 (1.26)	243 (8.09)	242 (6.48)
TS-27	168 (4.53)	31.5 (2.15)	12.0 (0.59)	3.10 (0.01)	1.18 (0.26)	9.25 (0.12)	3.25 (0.11)	3.84 (0.52)	2.37 (0.36)	10.4 (1.34)

^a Standard deviation^b Not detected

Fig. 1 **a** Determined concentrations ($\mu\text{g/g}$) of BT in the clothing textile samples ($n=2$). **b** Concentration decrease, given in percent, after five and ten washing steps



88 % polyester and 12 % elastane, had the highest concentration of quinoline and also contained benzothiazole at a concentration of $0.44 \mu\text{g/g}$. High quinolines levels, $18.2 \mu\text{g/g}$ of quinoline and $9.97 \mu\text{g/g}$ of quinoline derivatives, were also found in sample T-26, which was a pair of blue shorts in 100 % polyester material. In other samples, quinolines were detected in lower concentrations, ranging from 1 ng/g to $3.85 \mu\text{g/g}$.

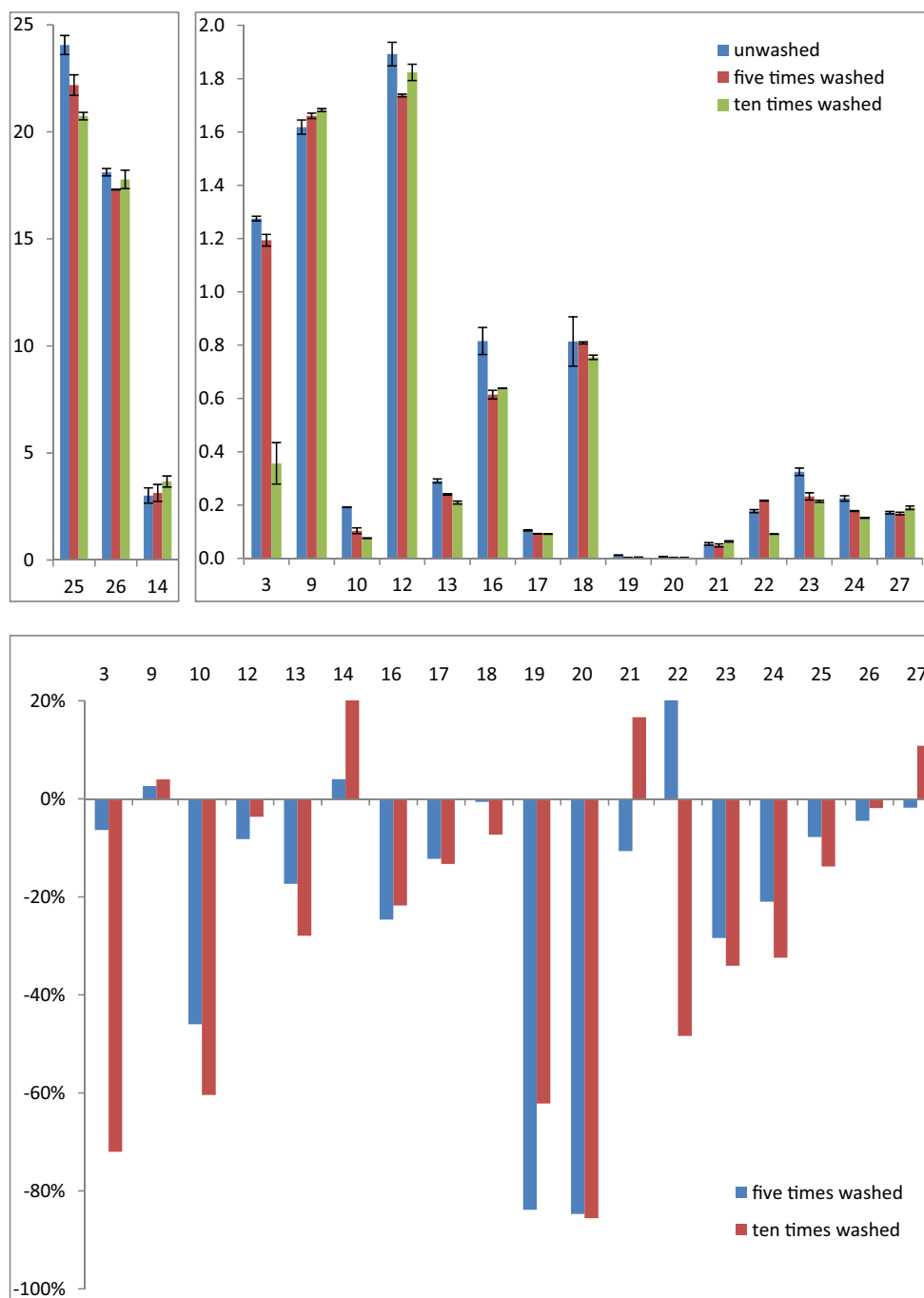
Two BUVs, the UV protection additives 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (UV-234) and 2-(benzotriazol-2-yl)-4-methylphenol (UV-P), were detected in more than 50 % of the samples with median concentrations of $0.19 \mu\text{g/g}$ and 18 ng/g garments, respectively (average of

$1.24 \mu\text{g/g}$ and 42 ng/g , respectively). 2-(2H-Benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (UV-234) reached a maximum concentration of $6.70 \mu\text{g/g}$ in sample T-23, a blue pair of shorts made of 88 % polyester and 12 % elastane. UV-328 and 1-H-benzotriazole (BTri) were detected in only four samples, and 5-methyl-benzotriazole (5-TTri) was found in five samples, with average concentrations of 63, 49, and 37 ng/g respectively.

Washout effect on the chemicals

In Fig. 4, the release of the chemicals from the textiles after five and ten laundry cycles is shown. The release of each compound from the investigated garments is shown in

Fig. 2 **a** Determined concentrations ($\mu\text{g/g}$) of quinoline in the clothing textile samples ($n=2$). **b** Concentration decrease, given in percent, after five and ten washing steps

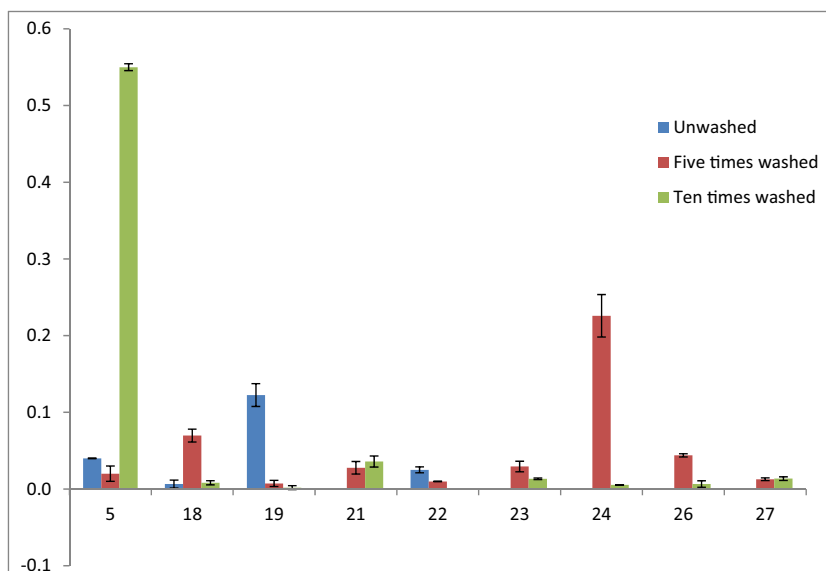


Figs. 1b and 2b and Fig. S1b–S13b in ESM and reveals a substantial difference in the behavior between the classes of compounds.

For BT, the decrease in concentration after washing ranged from 100 to 3 % with an average loss of 41 and 53 % after five and ten washing steps, respectively (Fig. 1b). In five samples, the loss of BT was 100 % after ten washes. These garments were made from different materials; hence, no conclusion regarding the high washout rate and type of material could be drawn. The UV protection additive UV-234 was found in 14

of the textile garments. When washed, the drop in concentration in the fabric was between 100 and 21 % with an average decrease of 60 % after 10 washings. Four of the textiles lost all their content of UV-234 additive and eight garments lost >80 % after ten washes. Thirteen of the garments contained UV-P, of which six had lost all of their content of this UV protection additive after ten washes. The average loss was close to 80 %, with a range of 100 to 11 %. UV-328 and 5-TTri were present in only four and five samples, respectively. They showed a similar behavior to UV-234 and UV-P, i.e.,

Fig. 3 Determined concentrations ($\mu\text{g/g}$) of BTri in the clothing textile samples ($n=2$)



with large variation in washout, some of the garments lost 100 % of the compound, while other textiles exhibited much smaller losses. BTri was detected in only 4 samples, with a concentration ranging up to $0.12 \mu\text{g/g}$ (sample T-19) (Fig. 3). However, after washing, this compound was detected in nine samples and the average concentration increased from 22 ng/g before washing, up to 50 ng/g after five washings, and 70 ng/g after ten washings. The reason for this is not known to us. In a

study by Janna and co-workers, it was shown that dishwashing formulations from the UK supermarkets contained both BTri and 5-TTri at concentrations on the order of several $\text{mg}/20 \text{ g}$ tablet or washing powder (Janna et al. 2011). Whether laundry detergents also may contain BTri could not be found in the literature. In this case, there was no BTri in the detergent. The large variation in concentration in the samples after the washing steps could possibly be due to

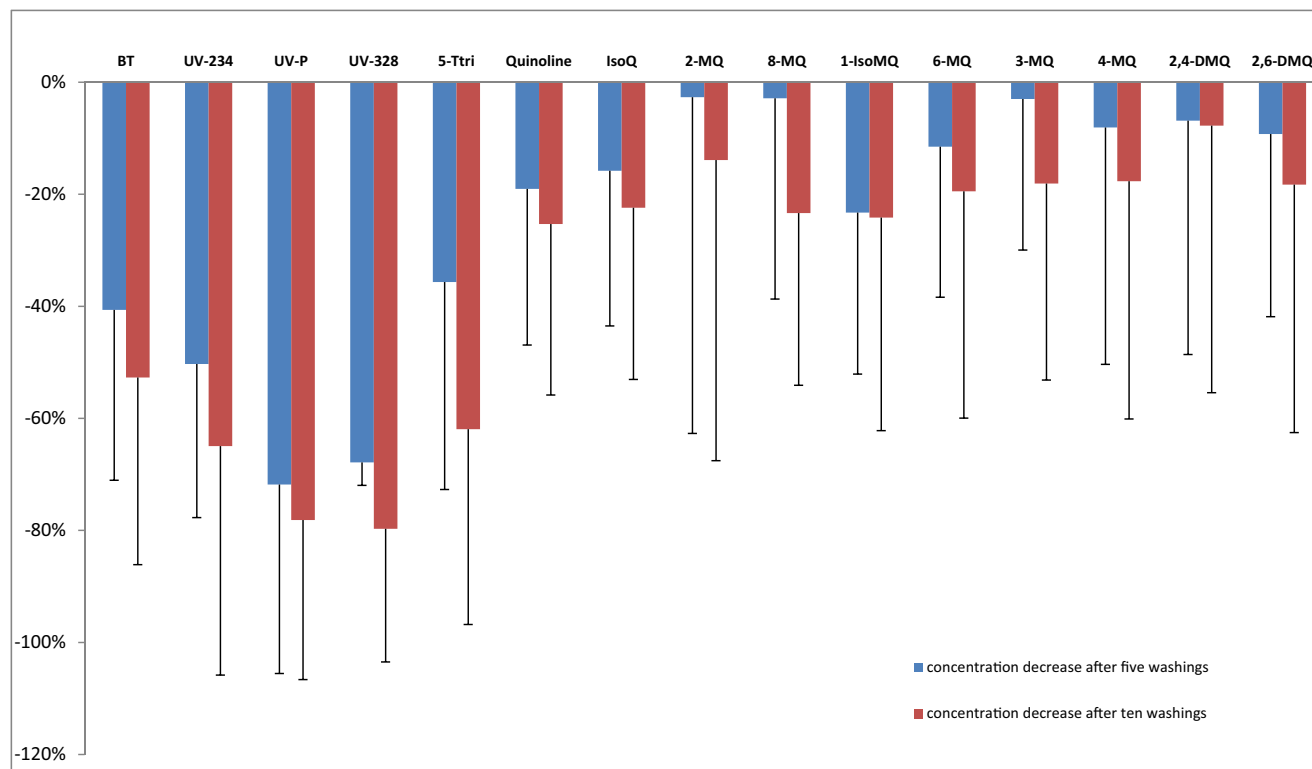


Fig. 4 Percentage of the average concentration decrease after five and ten washing steps of the investigated compounds, BTri not included (abbreviations as in Table S1)

the diverse fiber of the fabrics, retaining the compound from the detergent with different strength. Another explanation could be that BTri is formed during the washing procedure from other compounds, not investigated in this study.

Quinoline was subjected to a lower washout effect compared to BT. The average decrease of quinoline was 18 % after five and 24 % after ten washings (Fig. 2b). Only in one sample the loss reached up to 86 % (sample T-20), and in four samples, it was higher than 60 %. The average loss of Iso-Q and the other quinoline derivatives ranged from 5 % of 2,4-dimethylquinoline (2,4-DMQ) after five washings up to 30 % of 1-methylisoquinoline (1-iso-MQ) after ten. Sample T-3 and T-10 showed a large drop in concentration for all the quinoline derivatives. Sample T-9, T-12, and T-14 showed a slight increase, but this was within the error of the measurements.

Paired one and two-tailed *t* tests were used to statistically verify the decrease in the compound concentrations before and after washing at a 95 % significance level. For all the benzothiazoles and benzotriazoles, *p* was <0.05, and for quinoline, the paired *t* test gave a *p*<0.04. For the quinoline derivatives, *p* was >0.05, most probably due to their low concentrations. Two-factor ANOVA with replication and Tukey test were performed on the data; the results showed the means of unwashed samples to be significantly different from the means of five and ten times washed samples for all of the compounds, but no difference between the two sets of washed samples, except for quinoline. Moreover, no trend was observed in the loss of the compounds, which was clearly diverse in the different samples. Principal component analysis (PCA) on raw data, normalized, and/or scaled data did not reveal any correlation between loss of compounds and fiber material. The only noteworthy result was the difference between the washed and unwashed samples and difference in quinoline and BT concentration in the different samples.

Quinoline and benzothiazole are both slightly soluble in water. In spite of this similarity, their release from these textile garments was found to be diverse. It is most likely explained by a different use of the compounds and therefore a different interaction with the fabric. Benzothiazoles are mainly used as biocides and fungicides, and it is assumed that they are added to the final product to protect it from being affected by, e.g., mold during transportation. This suggests more of an interaction on the surface of the textiles. Quinolines on the other hand are included earlier in the manufacturing and are most likely byproducts from dyeing procedures using disperse dyes. Particularly, in the case of polyester garments, dyeing is performed at elevated temperatures and suggests that quinolines are more embedded to the fiber.

Clothing textiles are often washed more than five and ten times during their life cycle, and ideally, they should be washed 20 or 30 times for this study. However, limiting the investigation to five and ten washes, still demanding over 800

washings, clearly shows the release of these chemicals from the textiles.

Emissions to household wastewater

To make an estimate of the emissions, the average concentration of benzothiazoles and quinoline and their respective average loss during washing was used. For a laundry of 5 kg of clothes made from polyester materials, this corresponds to a release of 0.5 g of benzothiazoles and 0.24 g of quinoline to the environment by the household wastewater. Hence, the presence of the investigated compounds in products from retailers and brands available worldwide makes the emissions of these compounds to waterways through the washing of clothes an important domestic source, not only in Sweden. Although benzothiazole, benzotriazole, and quinoline derivatives are chemicals with a wide range of applications and have been detected in various aquatic environments worldwide, few studies have investigated the possible sources (Janna et al. 2011; Kloepper et al. 2005).

Human exposure?

The investigated chemicals are in most cases slowly released from clothes by washing, meaning that significant amounts remain in the clothes, even after ten times of washing. This indicates a chronic impact, not only on the aquatic environment, but possibly also regarding human exposure to these chemicals. In a study, Asimakopoulos and co-workers have showed the occurrence of benzothiazoles and benzotriazoles in humans from different countries, yet the effects on human health of these compounds are not clarified (Asimakopoulos et al. 2013b).

Conclusions

Three classes of compounds, commonly occurring in textile clothing, were investigated in 27 garments from different brands, of which most are available on retail markets worldwide. Benzothiazoles and quinolines were present in more than 80 % of the analyzed samples. In a single garment, the concentration of the investigated compounds all summed up exceeded 50 µg/g. Chemical analysis was performed on the clothes before and after five and ten times of laundering and revealed a considerable loss in the concentration of benzothiazoles and benzotriazoles. Several other studies have already shown that these compounds are common pollutants in municipal wastewater (Kloepper et al. 2005). These compounds have also been detected together with quinoline in the aquatic environment (de Voogt and Laane 2009; Ni et al. 2008). The study presented here points out that laundering is an important source of emissions to the environment of these

compounds, and that textiles can be a potential route to human exposure to a number of chemicals due to their high content in textile materials worn in close contact to the skin. In order to obtain a better understanding of the potential hazard for humans, further studies are needed regarding textile to skin transfer and uptake through the skin. This is a possible route of human exposure to chemicals has been demonstrated by skin uptake of tris(2,3-dibromopropyl)phosphate (Tris-BP) (Blum et al. 1978). Children sleeping in pajamas containing this chemical excreted its metabolite 2,3-dibromopropanol with the urine. The metabolite could still be excreted up to 6 months after ceased using pajamas containing Tris-BP. There is also need for more extensive screening of textile materials to obtain a knowledge base on chemicals that are actually present in clothing sold on the retail market worldwide.

Acknowledgments This study has been funded by Stockholm University.

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Electronic Supplementary Material

The washout effect during laundry on benzothiazole, benzotriazole, quinoline and their derivatives in clothing textiles.

Environmental Science and Pollution Research

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Table S3 LOD (pg/inj.), MQL in (pg/g) for benzothiazoles and benzotriazoles and in (ng/g) for quinolines, repeatability ($n = 5$) for benzothiazoles and benzotriazoles and ($n = 6$) for quinolines and recoveries of the analytes.

FIGURES

Fig. S1 a) Determined concentrations ($\mu\text{g/g}$) of UV-234 in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S2 a) Determined concentrations ($\mu\text{g/g}$) of UV-P in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S3 a) Determined concentrations ($\mu\text{g/g}$) of UV-328 in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S4 a) Determined concentrations ($\mu\text{g/g}$) of 5-TTri in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

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Fig. S8 a) Determined concentrations ($\mu\text{g/g}$) of 1-isomethylquinoline in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S9 a) Determined concentrations ($\mu\text{g/g}$) of 6-Methylquinoline in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S10 a) Determined concentrations ($\mu\text{g/g}$) of 3-Methylquinoline in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S11 a) Determined concentrations ($\mu\text{g/g}$) of 4-Methylquinoline in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S12 a) Determined concentrations ($\mu\text{g/g}$) of 2,4-Dimethylquinoline in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

Fig. S13 a) Determined concentrations ($\mu\text{g/g}$) of 2,6-Dimethylquinoline in the clothing textile samples ($n = 2$). **b)** Percentage of the concentration decrease after five and ten washing steps.

TABLES

Table 1 Investigated analytes; abbreviations, CAS-No., molecular weight (Mw) (g/mol) and supplier

Analytes	Abbreviation	CAS No.	Mw	Supplier
Benzothiazole	BT	95-16-9	135	Sigma-Aldrich, China
2-methyl benzothiazole	MeBT	120-75-2	149	Sigma-Aldrich, China
2-methylthio benzothiazole	MTBT	615-22-5	181	Sigma-Aldrich, Germany
2,2' -dithiobisbenzothiazole	MBTS	120-78-5	332	Sigma-Aldrich, Germany
N-cyclohexyl-2-benzothiazole sulphenamide	CBS	95-31-8	264	Sigma-Aldrich, USA
1-H-benzotriazole	BTri	95-14-7	119	Sigma-Aldrich, China
5,6-dimethylbenzotriazole	XTri	4184-79-6	147	Sigma-Aldrich, Germany
5-methyl-benzotriazole	5-TTri	136-85-6	133	Sigma-Aldrich, Japan
2-(benzotriazol-2-yl)-4-methylphenol	UV-P	2440-22-4	225	Sigma-Aldrich, USA
2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol	UV-328	25973-55-1	351	Sigma-Aldrich, USA
2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol	UV-234	70321-86-7	448	Sigma-Aldrich, USA

2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl) phenol	UV-327	3864-99-1	358	Sigma-Aldrich, India
Quinoline	Q	91-22-5 1	129	Merck, Germany
Isoquinoline	Iso-Q	119-65-3	129	Aldrich, Belgium
2- methylquinoline	2-MQ	91-63-4	143	Aldrich, China
3-methylquinoline	3-MQ	612-58-8	143	Aldrich, USA
4-methylquinoline	4-MQ	491-35-0	143	SAFC, USA
6-methylquinoline	6-MQ	91-62-3	143	Fluka, Sweden
8-methylquinoline	8-MQ	611-32-5	143	Aldrich, Japan
1-methylisoquinoline	1-iso-MQ	1721-93-3	143	Aldrich, USA
2,6-dimethylquinoline	2,6-DMQ	877-43-0	157	ICN· K&K, USA
2,4-dimethylquinoline	2,4-DMQ	1198-37-4	157	ICN· K&K, USA
Quinoline d ₇	Q d ₇	34071-94-8	136	Fluka, Sweden

Table S2 Analyte specific MS/MS parameters for the benzothiazoles and benzotriazoles

	Quantification transition	Confirmation transition	CE ^{a)} [eV]	DP ^{b)} [V]	EP ^{c)} [V]
BT	136 > 109	136 > 65	47	60	10
MeBT (IS)	150 > 109	150 > 65	34	13	10
MTBT	182 > 69	182 > 109	94	45	8.3
CBS	264 > 97	265 > 183	24	38	10
MBTS	333 > 167	333 > 109	36	46	8.0
BTri	120 > 65	120 > 92	31	48	10
5-TTri	134 > 77	134 > 79	37	66	10
XTri	148 > 77	148 > 91	40	80	10
UV-P	226 > 120	226 > 78	25	40	10
UV-328	352 > 282	358 > 212	29	59	7.5
UV-327	358 > 302	358 > 57	57	28	6
UV-234	448 > 370	448 > 199	30	58	9

^{a)} Collision Energy, ^{b)} Declustering Potential, ^{c)} Entrance Potential

Table S3 LOD (pg/inj.), MQL in (pg/g) for benzothiazoles and benzotriazoles and in (ng/g) for quinolines, repeatability ($n = 5$) for benzothiazoles and benzotriazoles and ($n = 6$) for quinolines and recoveries of the analytes

	LOD ^{a)}	MQL ^{b)}	Repeatability RSD ^{d)} (%)	Recoveries Mean (%) (RSD %)
Benzothiazoles				
BT	20	60	7	94 (1.1 %)
MTBT	26	79	13	102 (1.5 %)
MeBT (IS)	9			
CBS	36	108	5	90 (2.2 %)
MBTS	12	37	18	77 (0.7 %)
Benzotriazoles				
BTri	29	87	4	95 (1.6 %)
5-TTri	18	55	5	87 (0.6 %)
XTri	33	100	8	92 (0.5 %)
UV-P	10	30	15	76 (0.3 %)
UV-327	19	58	13	70 (0.7 %)
UV-328	14	44	14	69 (0.7 %)
UV-234	1	13	11	102 (3.9 %)
Quinolines				
Q	0.8	1.1	1.5	101 (4%)
Iso-Q	3.4	4.9	2.1	86 (7%)
2-MQ	0.4	1.8	2.1	91 (3%)
4-MQ	1.0	0.6	1.9	91 (4%)
1-iso-MQ	2.1	3.0	2.7	89 (9%)
6-MQ	0.7	1.1	3.3	88 (5%)
3-MQ	1.1	1.6	3.1	93 (11%)
8-MQ	1.0	1.5	3.6	90 (8%)
2,4-DMQ	1.7	1.7	5.1	87 (5%)
2,6-DMQ	1.2	2.6	6.2	106 (5%)

^{a)} Limit of detection, ^{b)} Method quantification limit, ^{c)} Relative standard deviation

FIGURES

Fig. S1 a) Determined concentrations ($\mu\text{g/g}$) of UV-234 in the clothing textile samples ($n = 2$)
b) Percentage of the concentration decrease after five and ten washing steps

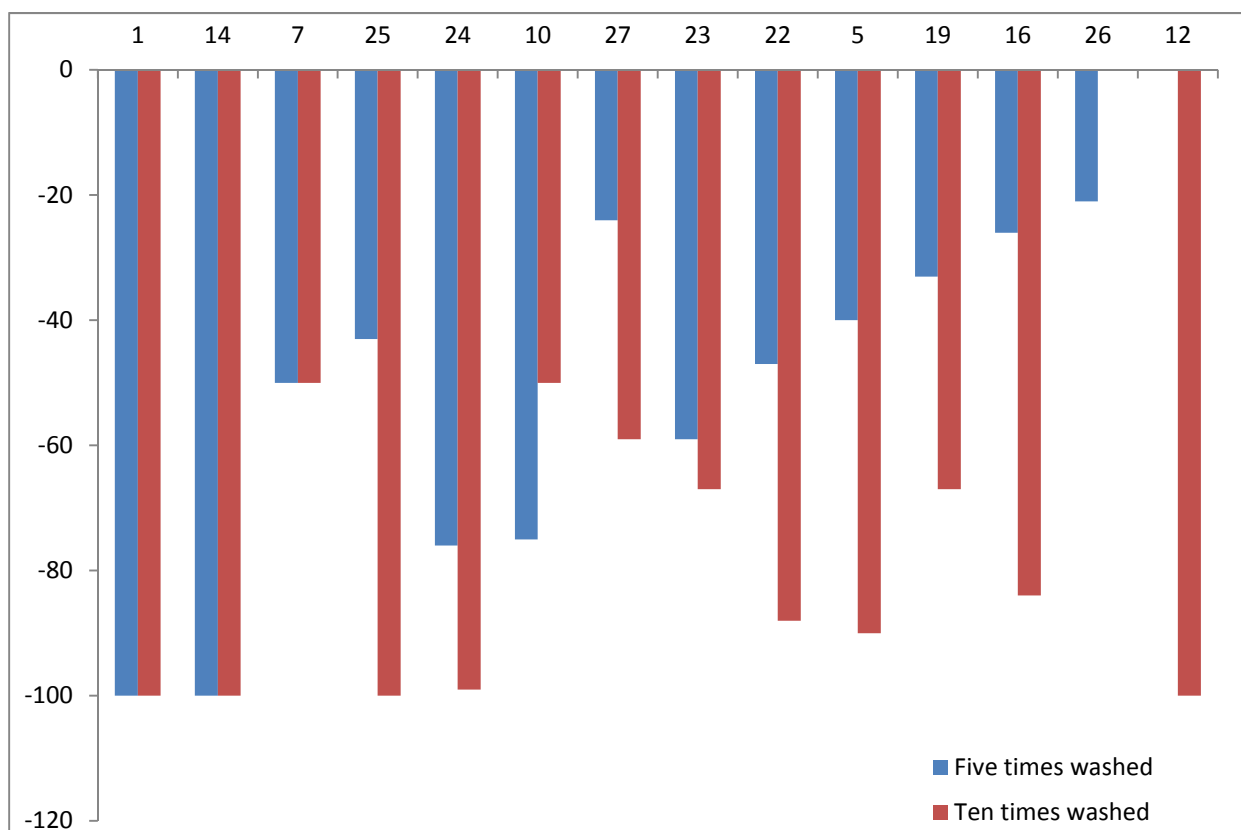
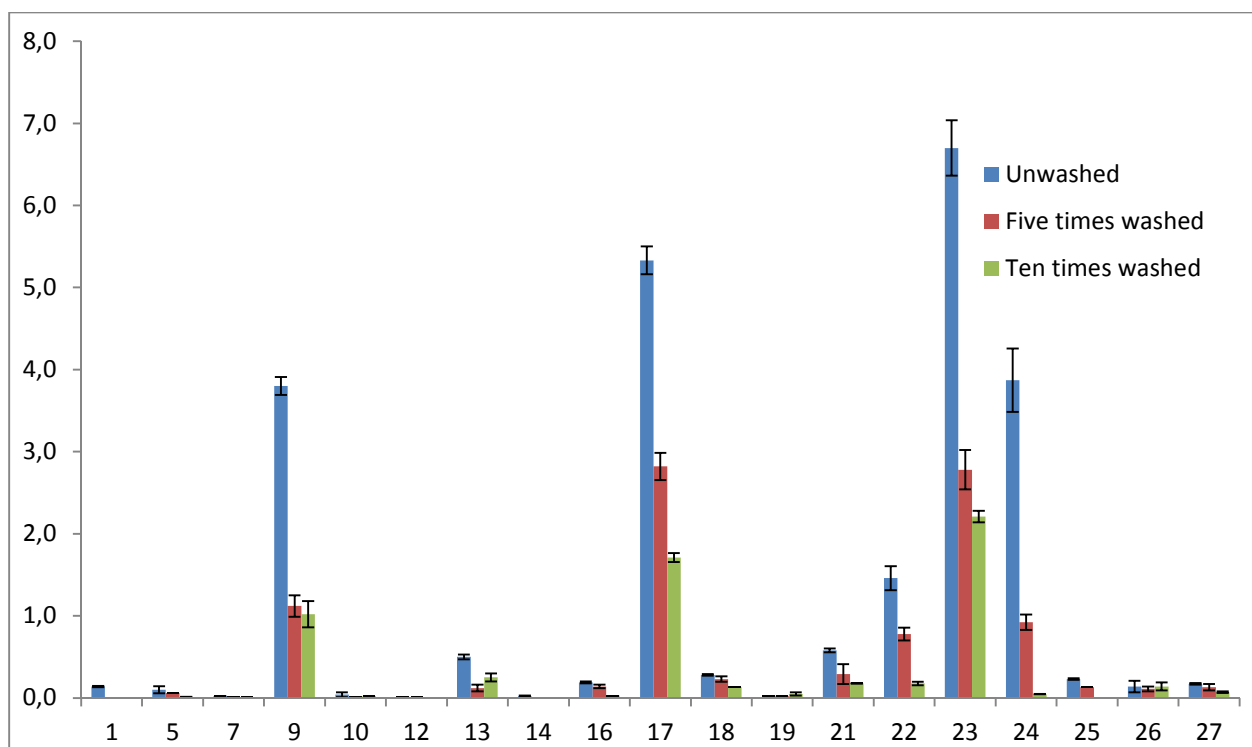


Fig. S2 a) Determined concentrations ($\mu\text{g/g}$) of UV-P in the clothing textile samples ($n = 2$)
b) Percentage of the concentration decrease after five and ten washing steps

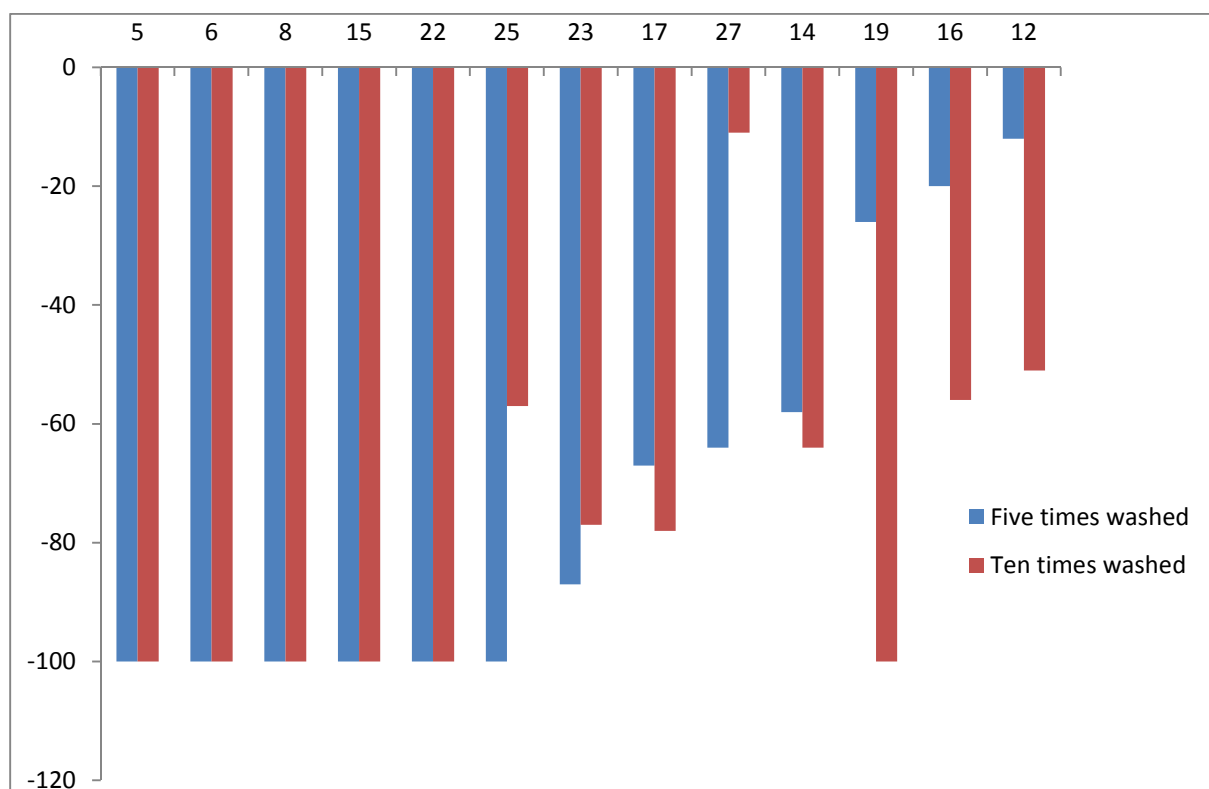
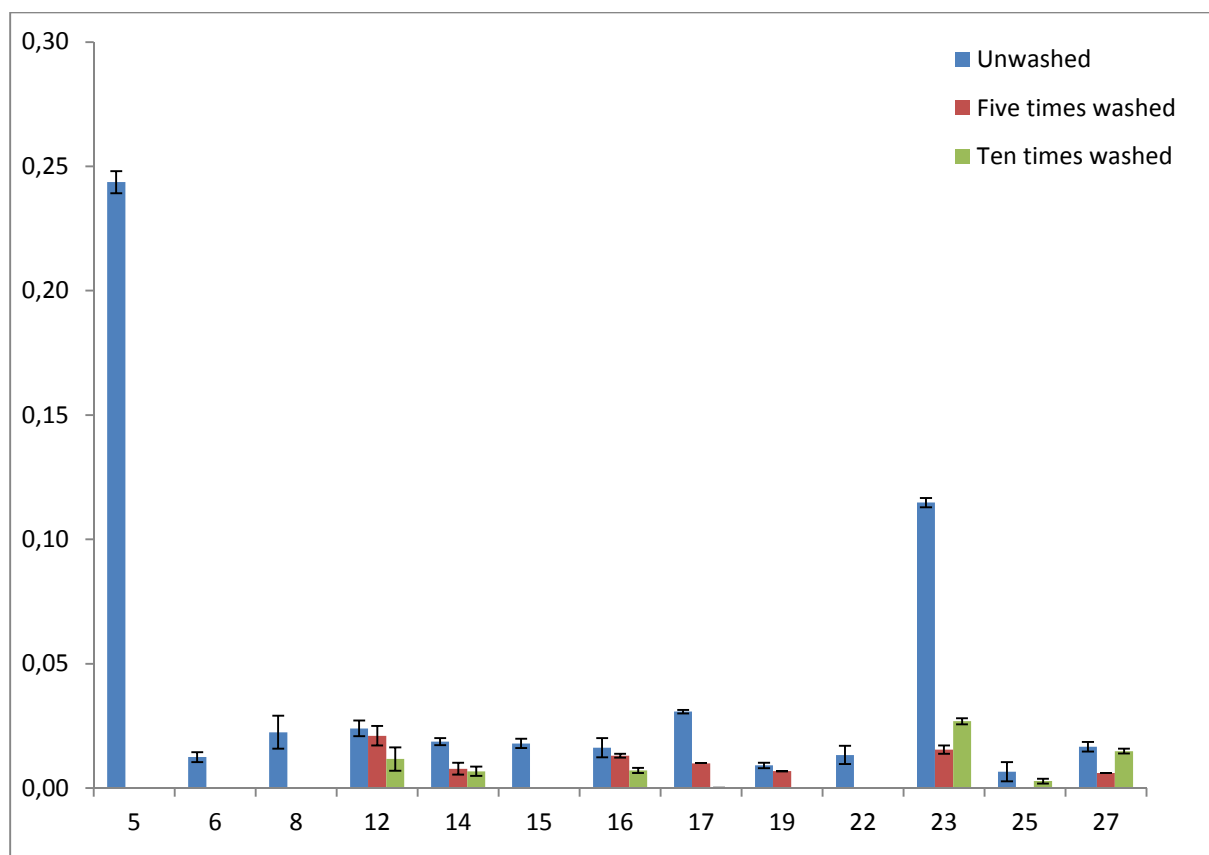


Fig. S3 a) Determined concentrations ($\mu\text{g/g}$) of UV-328 in the clothing textile samples ($n = 2$)
b) Percentage of the concentration decrease after five and ten washing steps

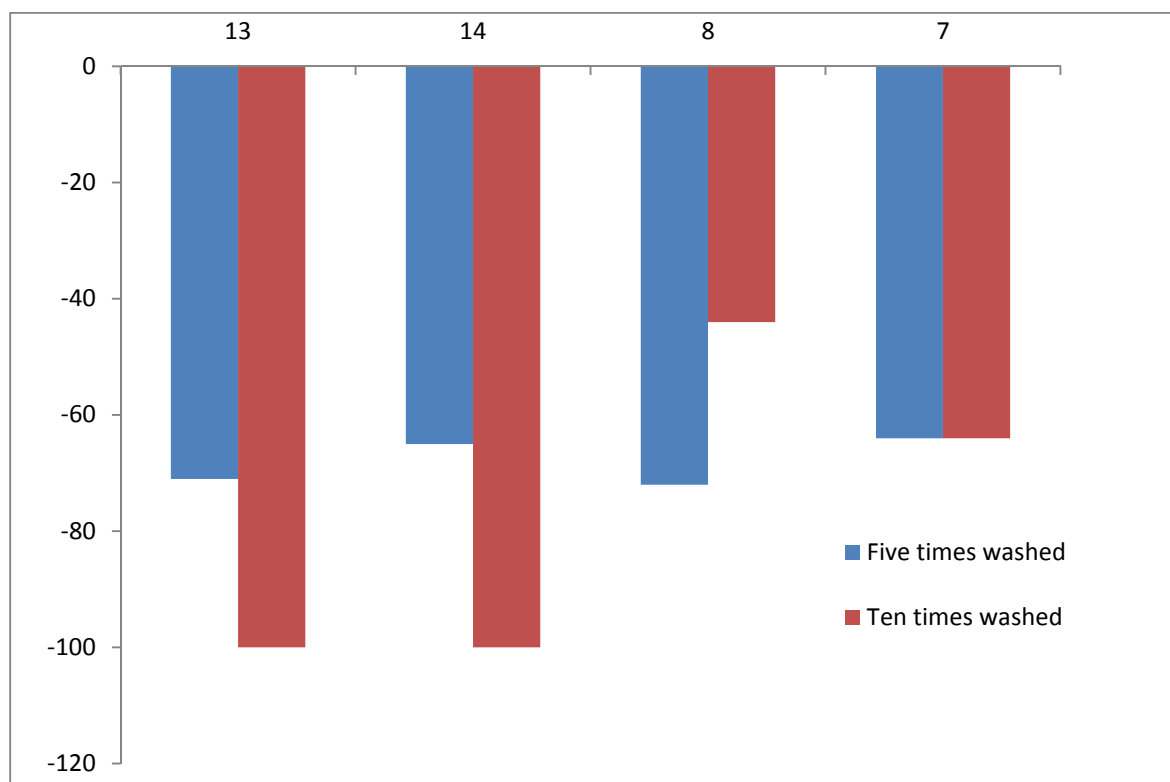
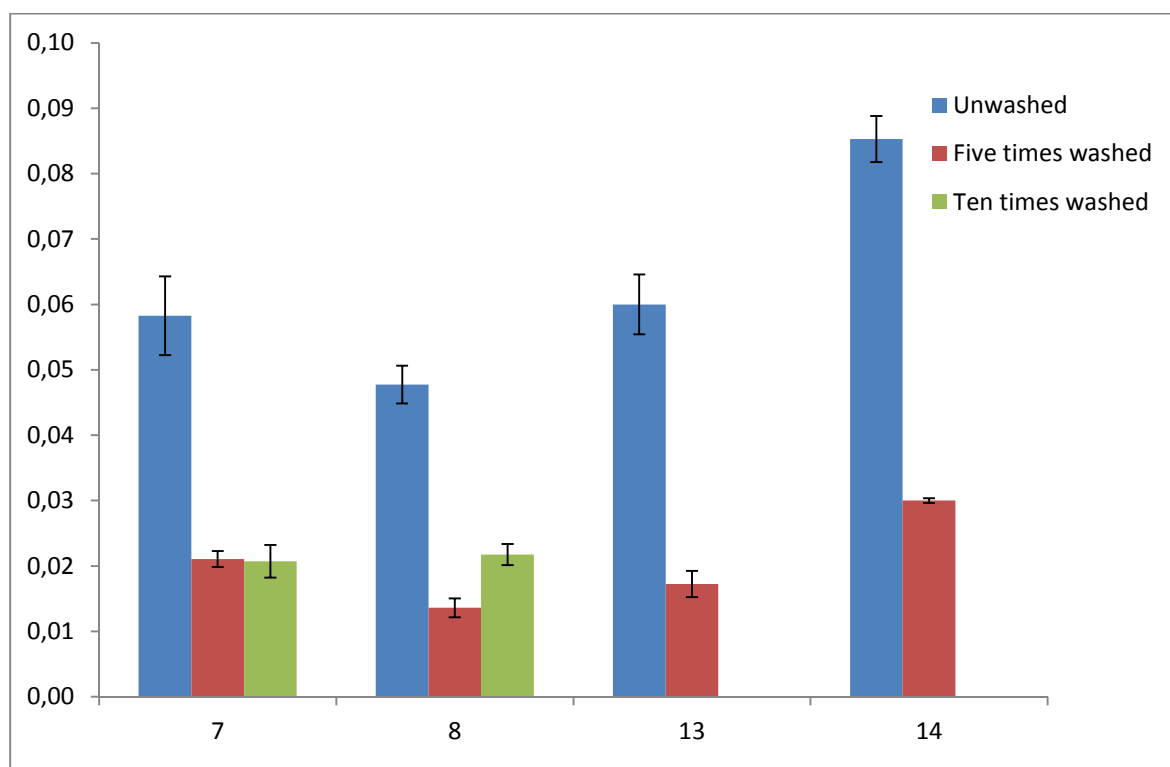


Fig. S4 a) Determined concentrations ($\mu\text{g/g}$) of 5-TTri in the clothing textile samples ($n = 2$)
b) Percentage of the concentration decrease after five and ten washing steps

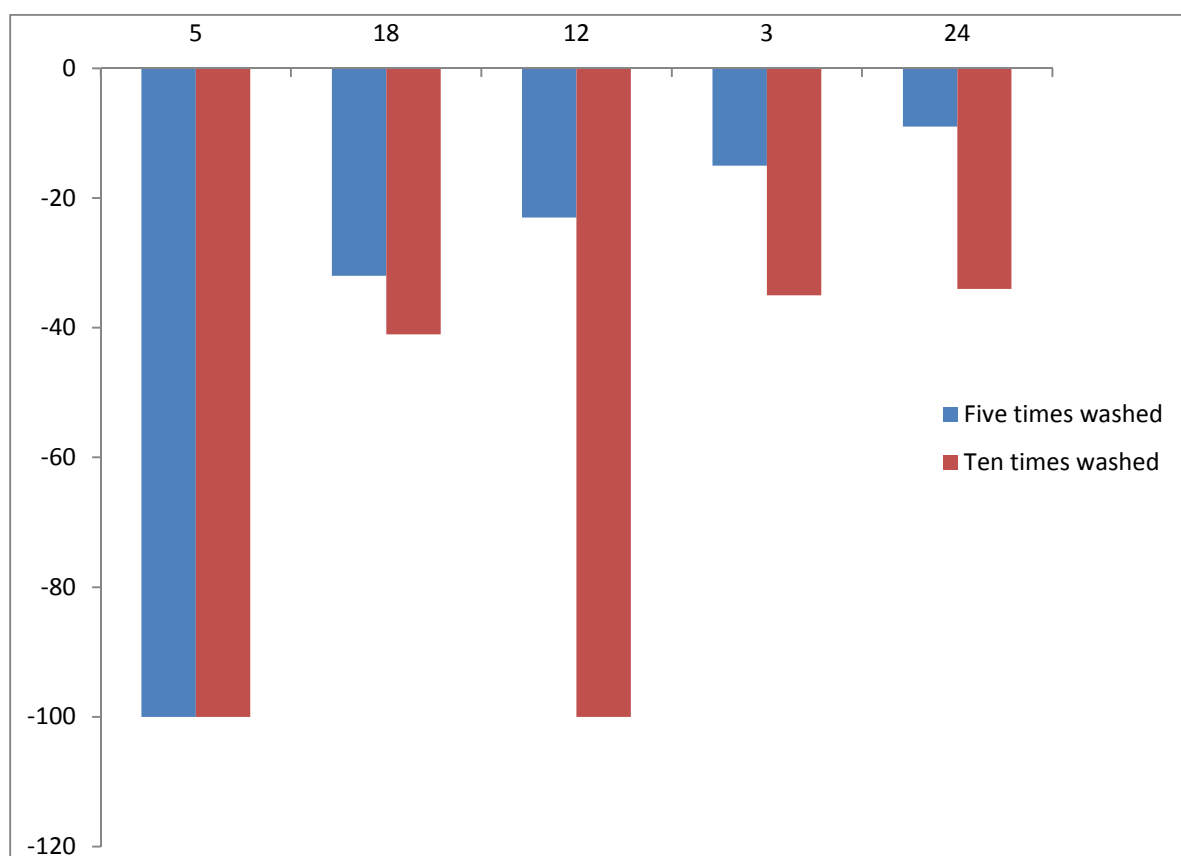
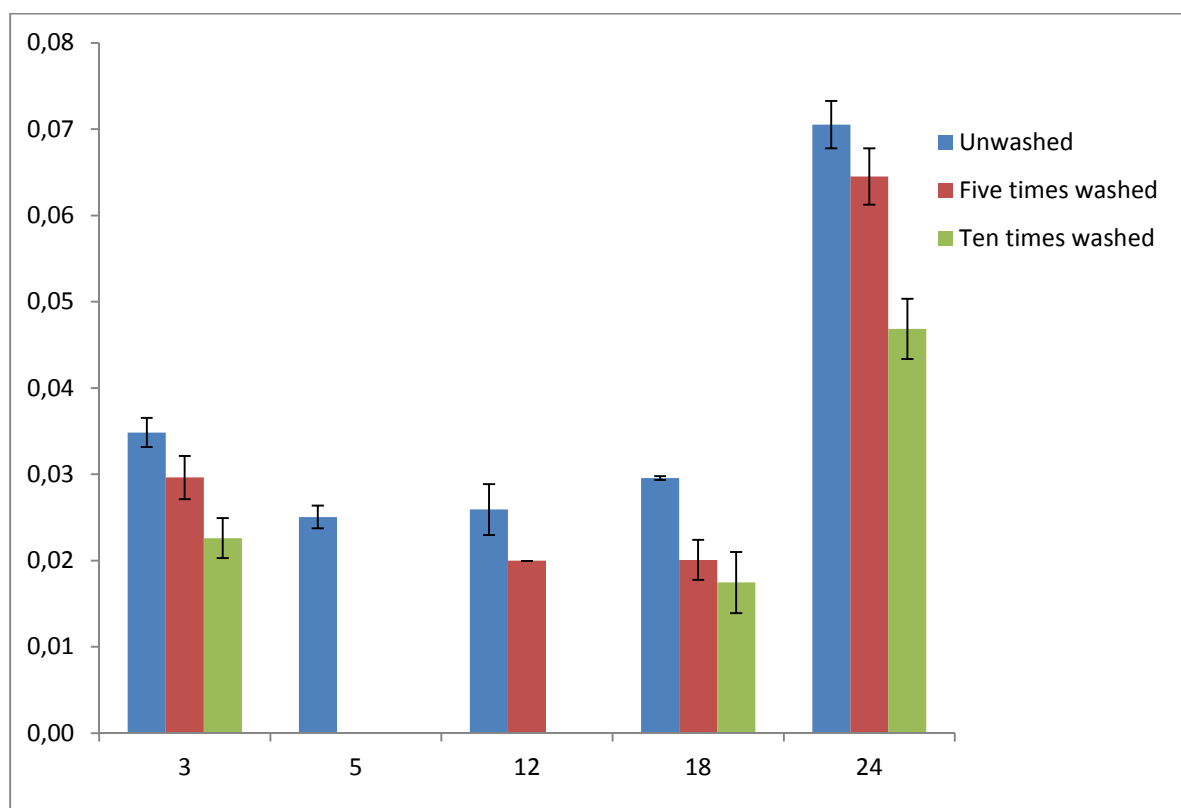


Fig. S5 a) Determined concentrations ($\mu\text{g/g}$) of Isoquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

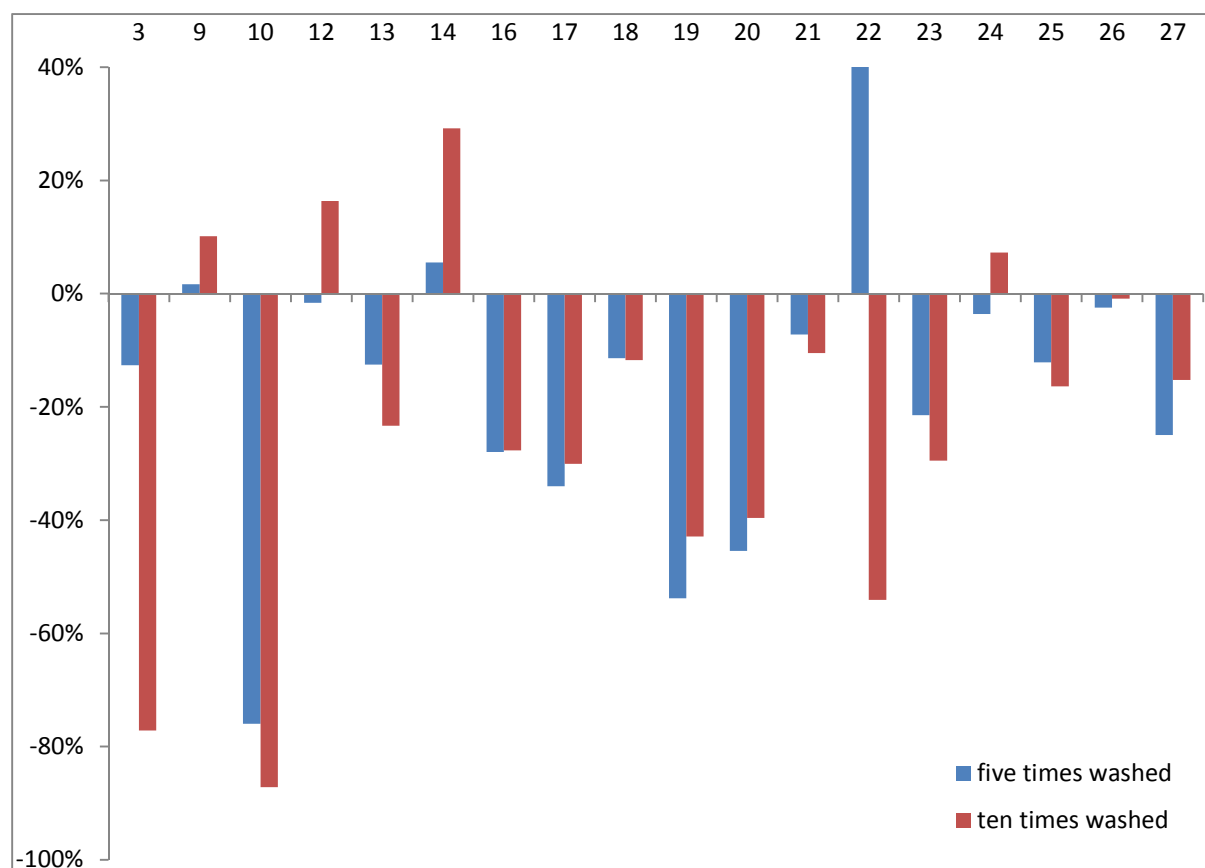
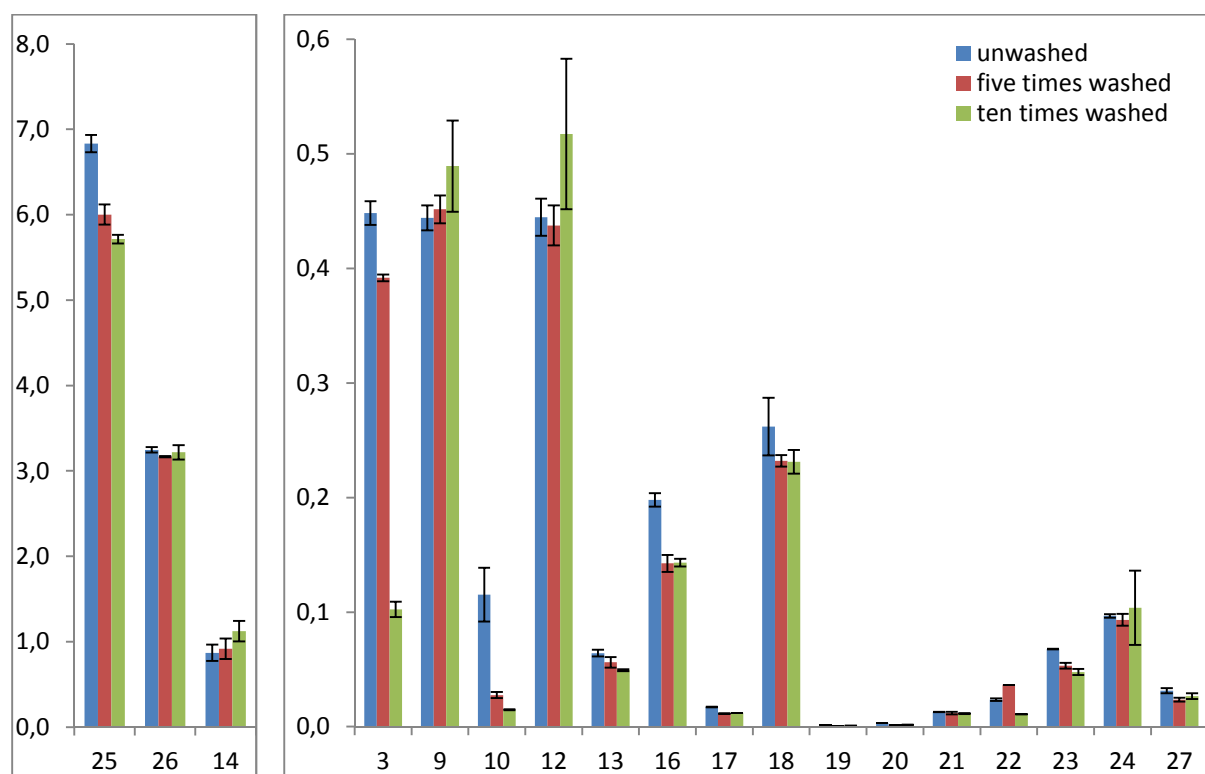


Fig. S6 a) Determined concentrations ($\mu\text{g/g}$) of 2-Methylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

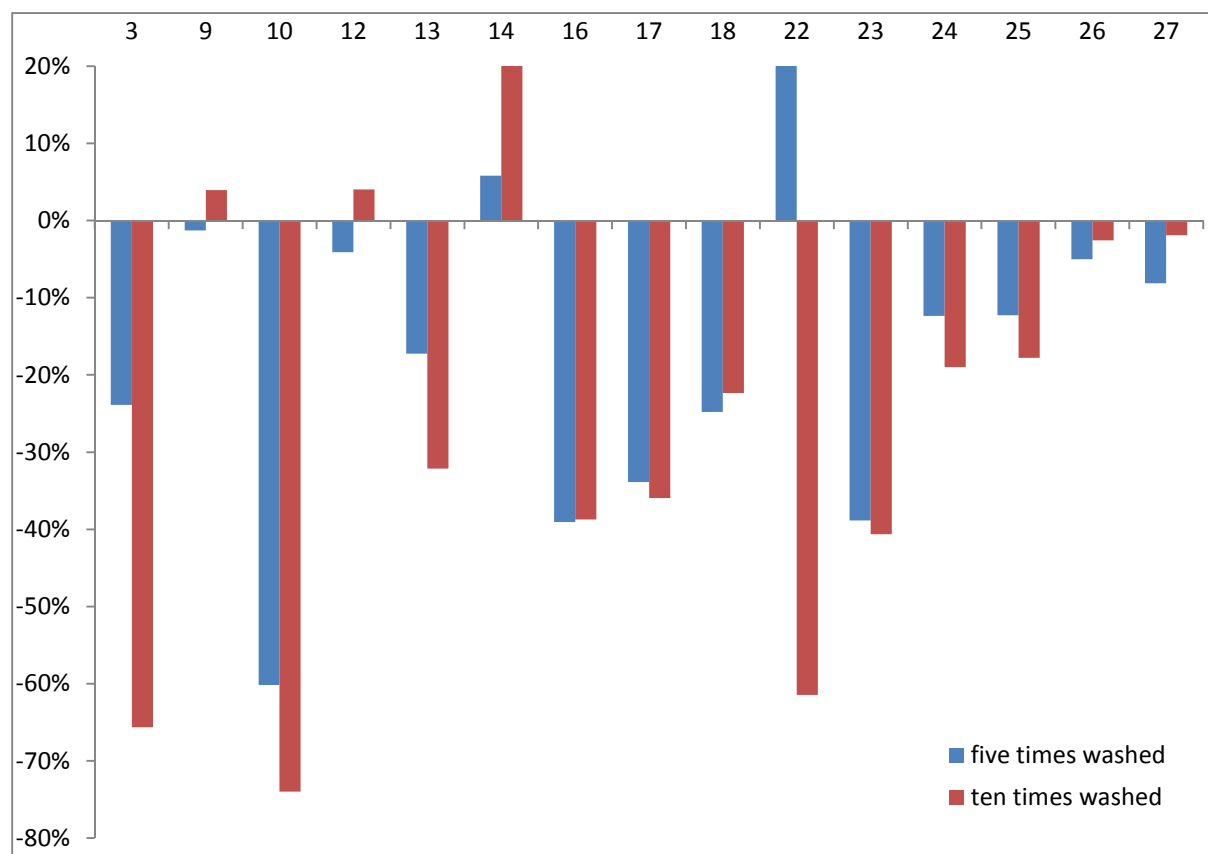
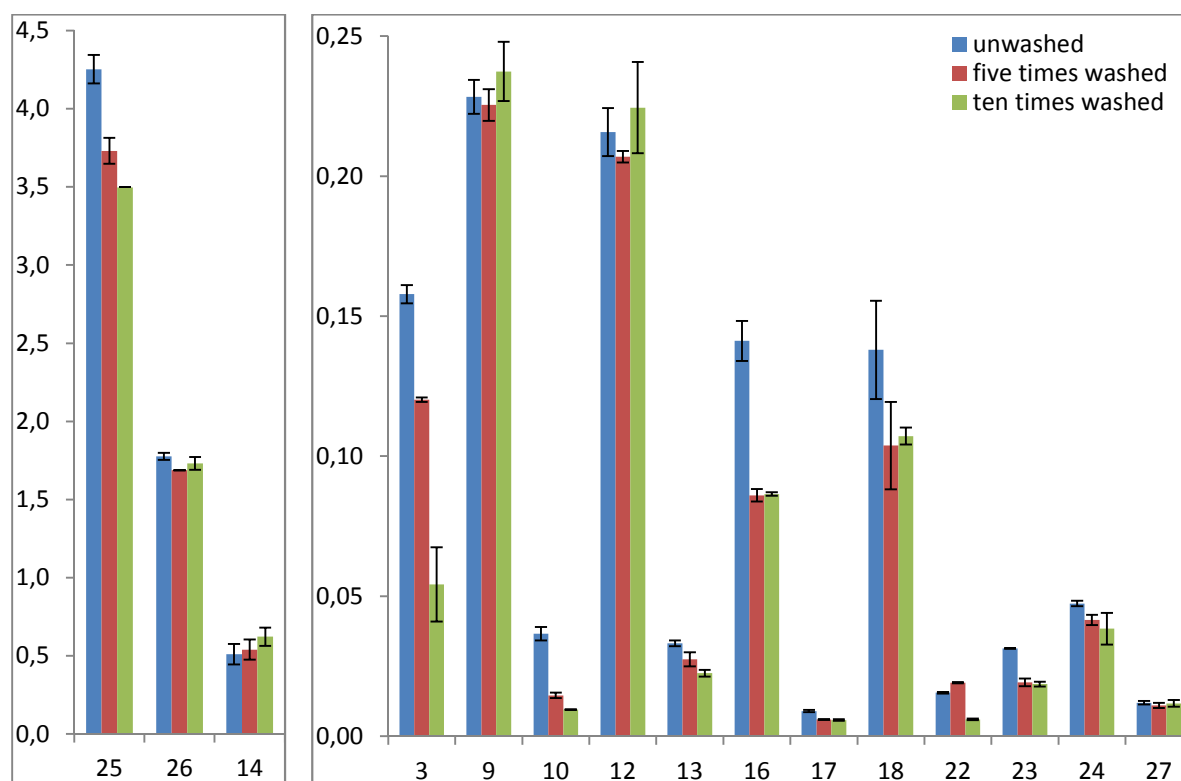


Fig. S7 a) Determined concentrations ($\mu\text{g/g}$) of 8-Methylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

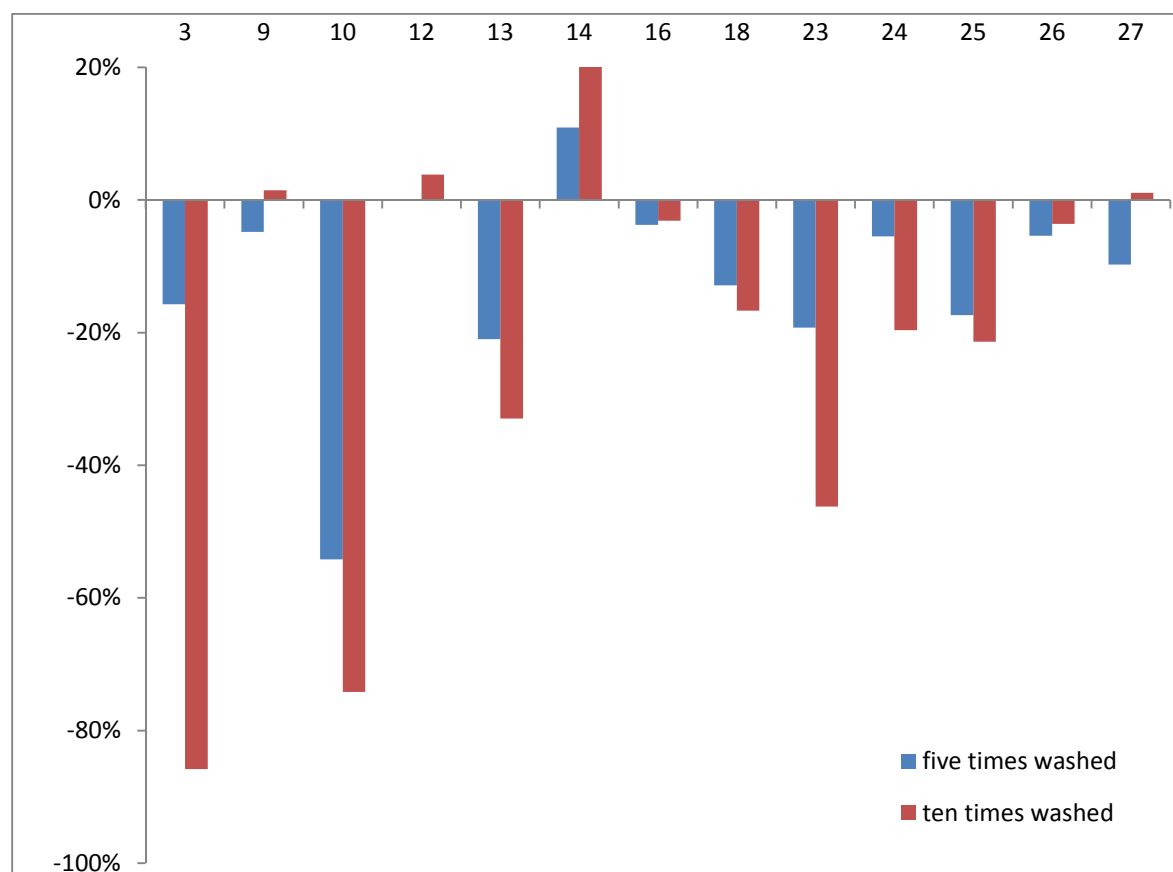
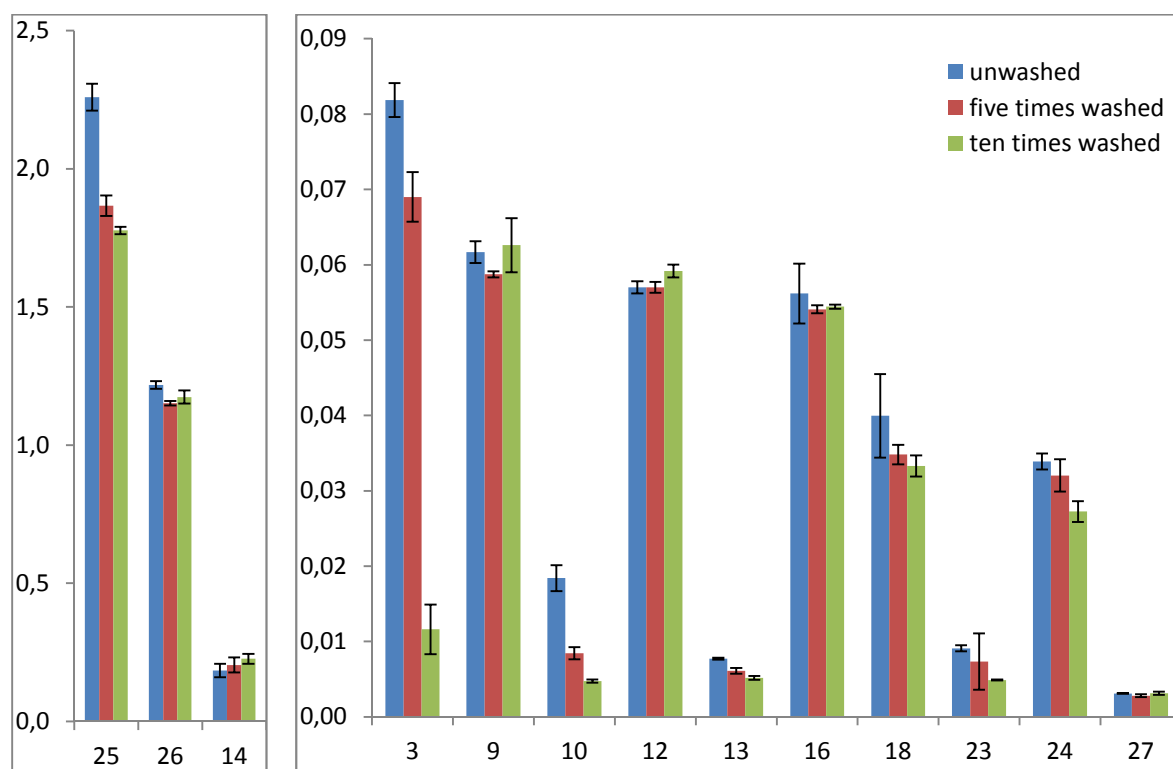


Fig. S8 a) Determined concentrations ($\mu\text{g/g}$) of 1-isomethylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

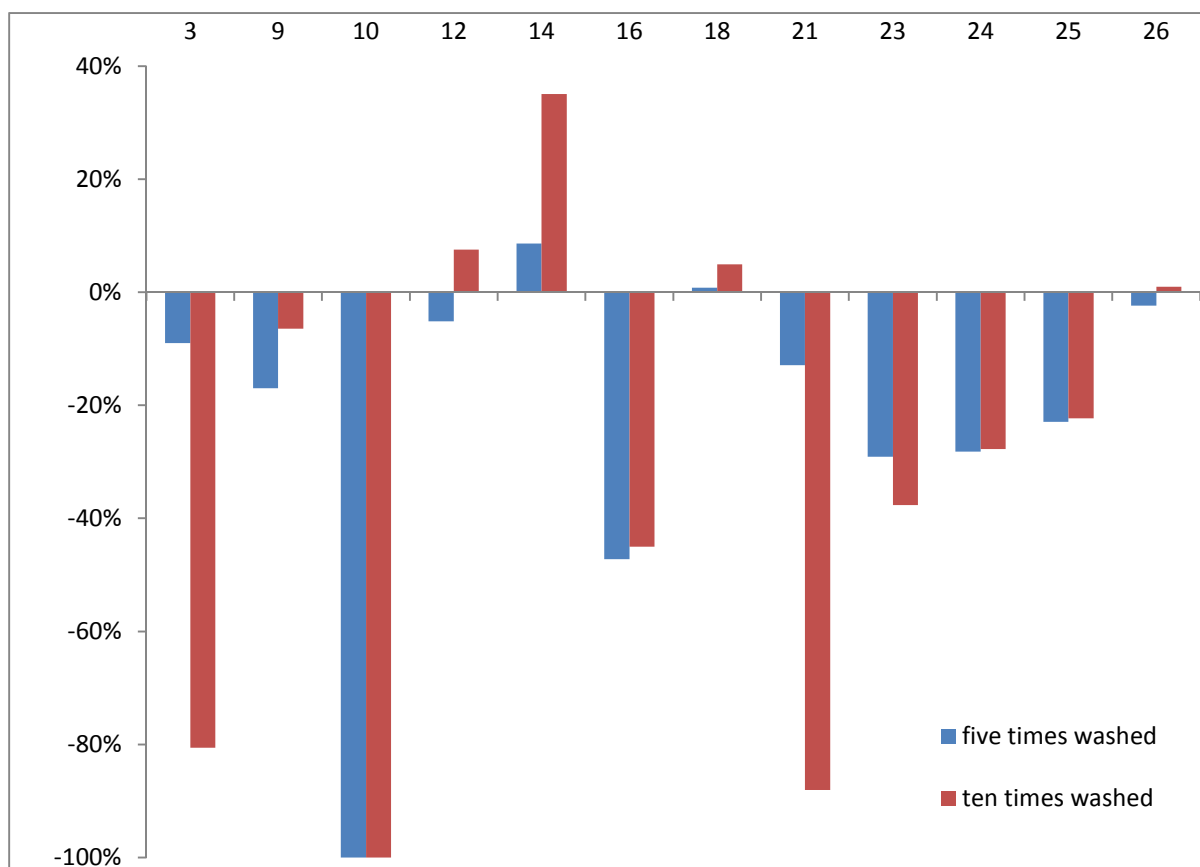
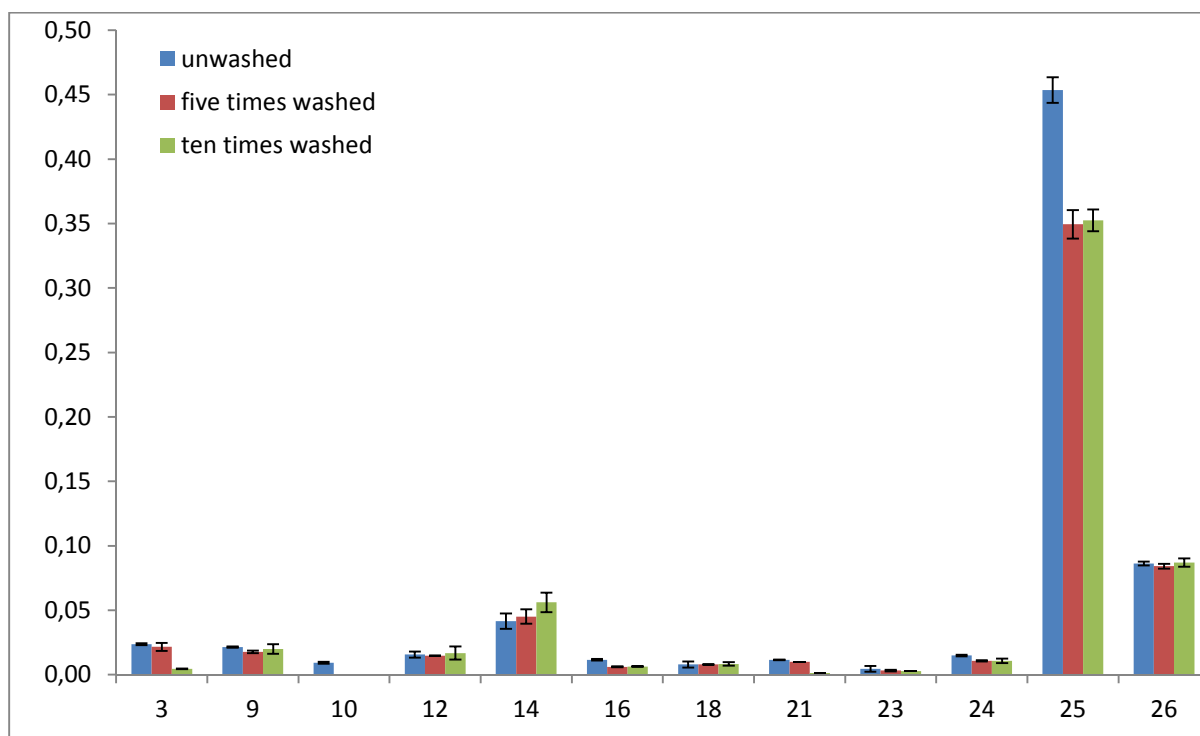


Fig. S9 a) Determined concentrations ($\mu\text{g/g}$) of 6-Methylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

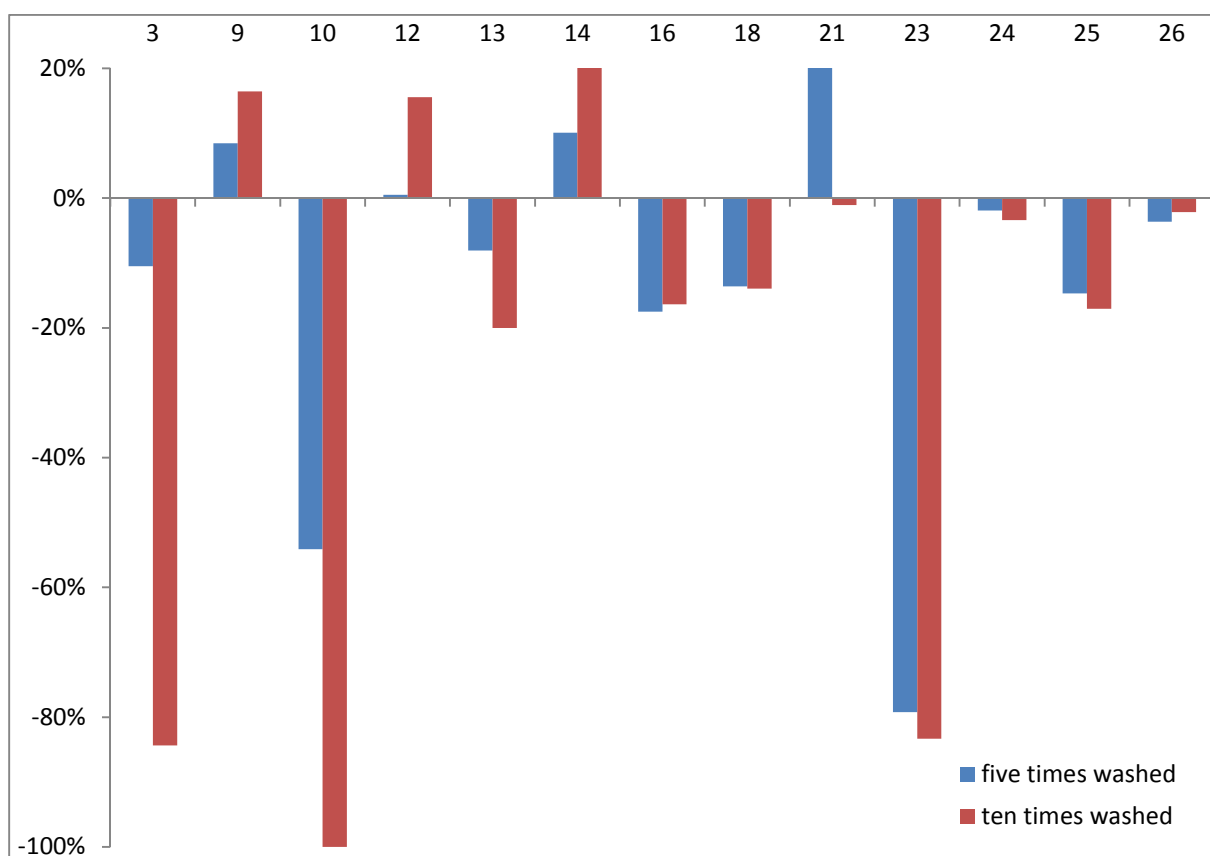
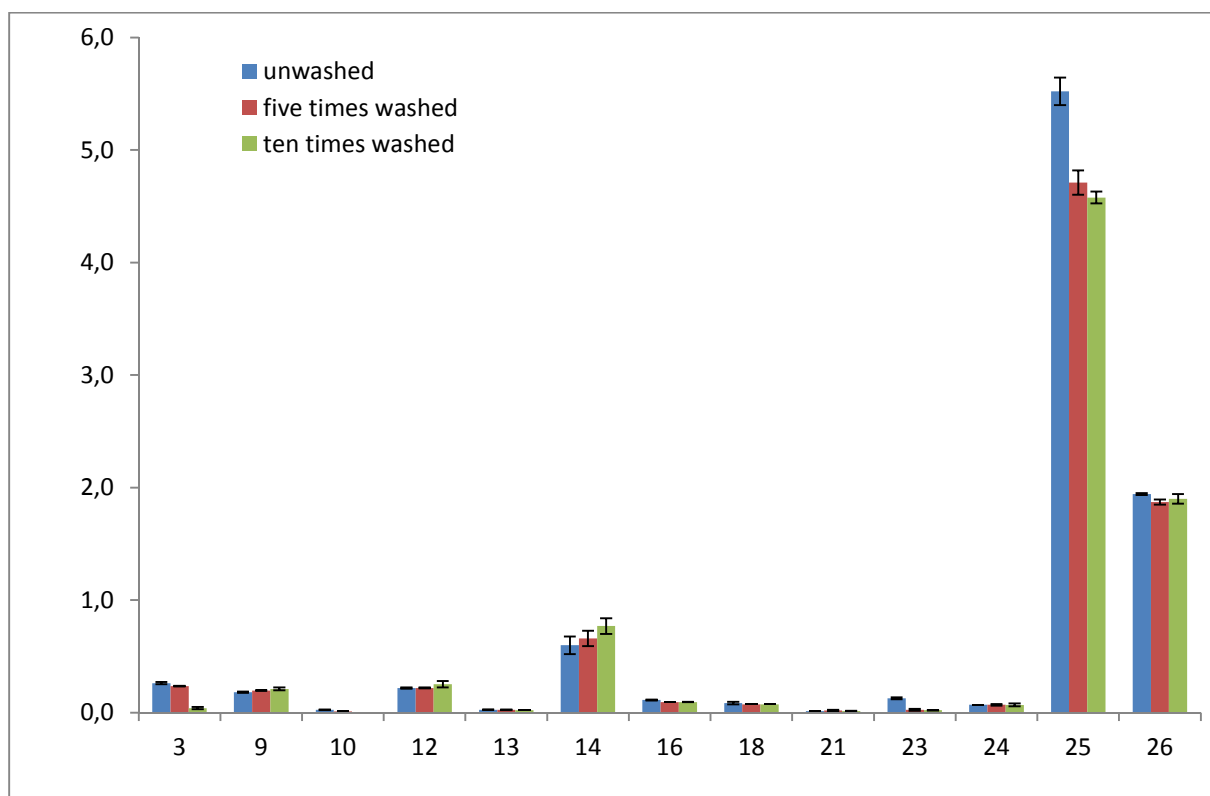


Fig. S10 a) Determined concentrations ($\mu\text{g/g}$) of 3-Methylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

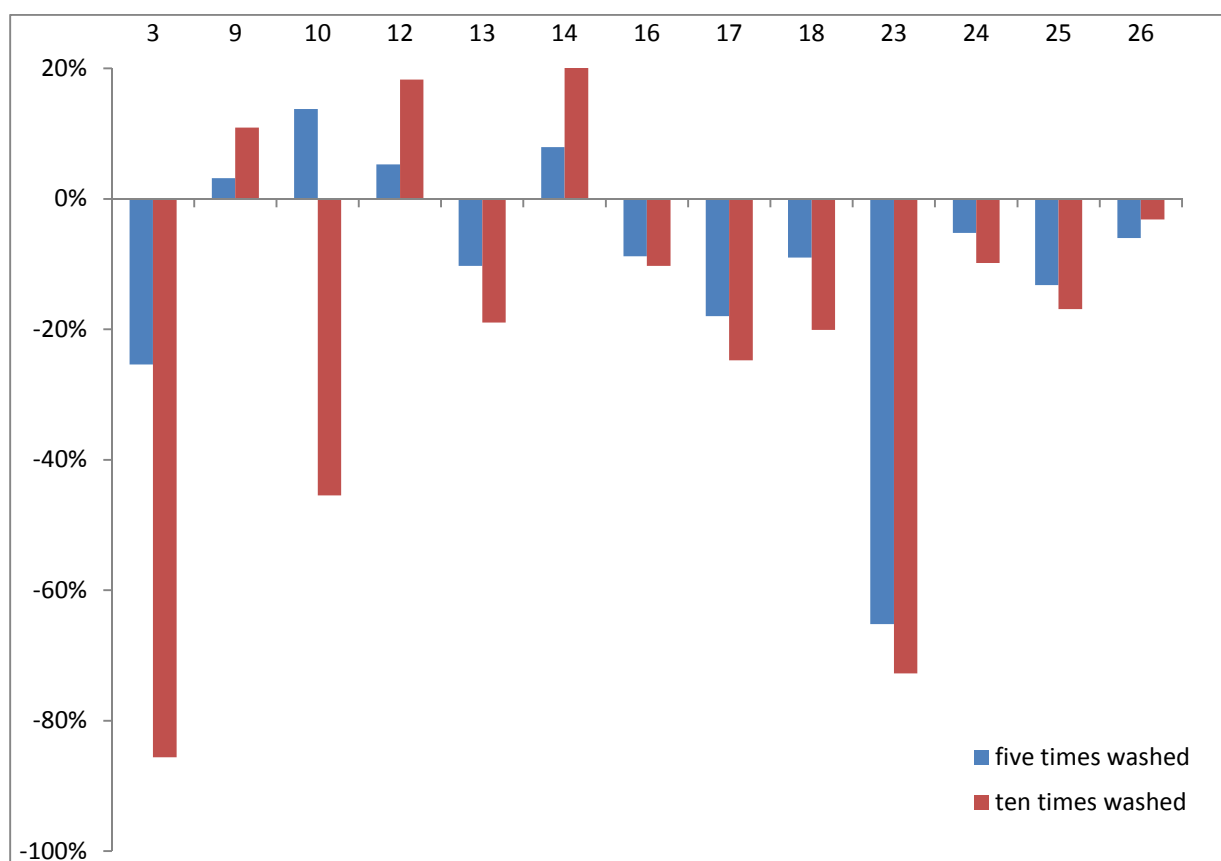
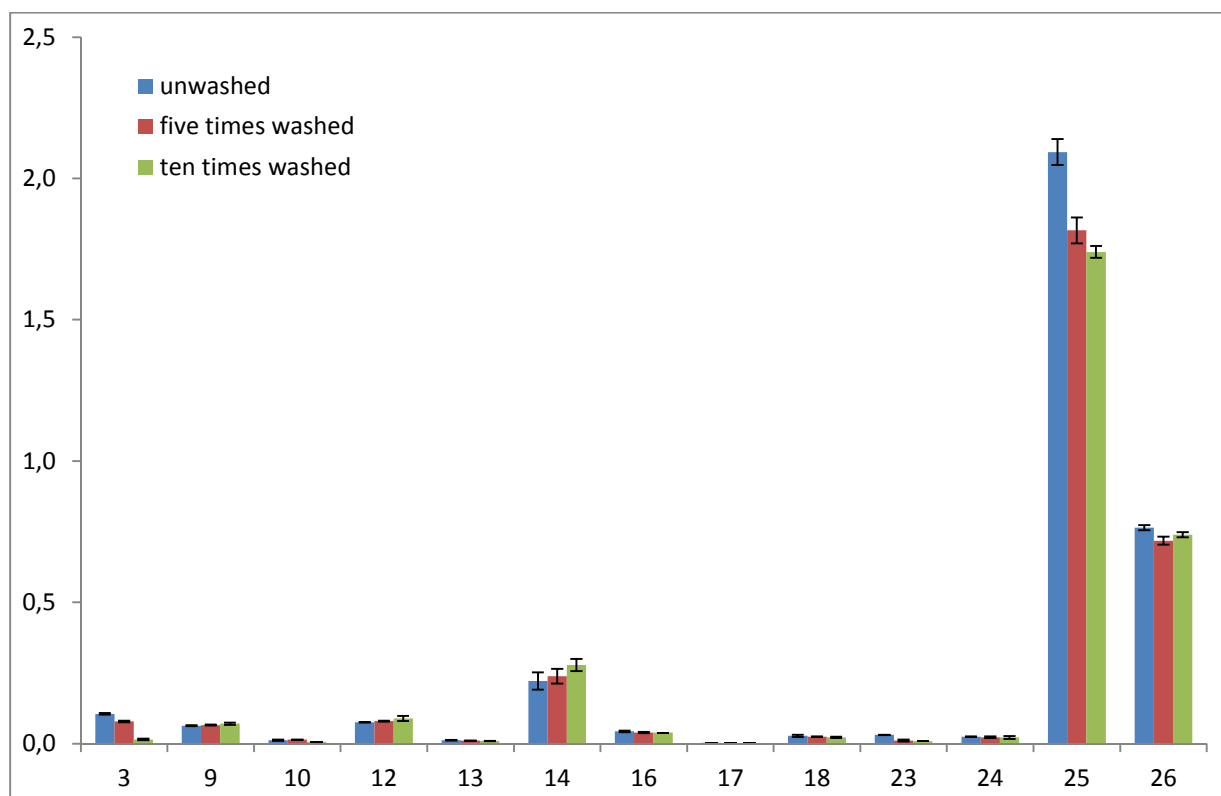


Fig. S11 a) Determined concentrations ($\mu\text{g/g}$) of 4-Methylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

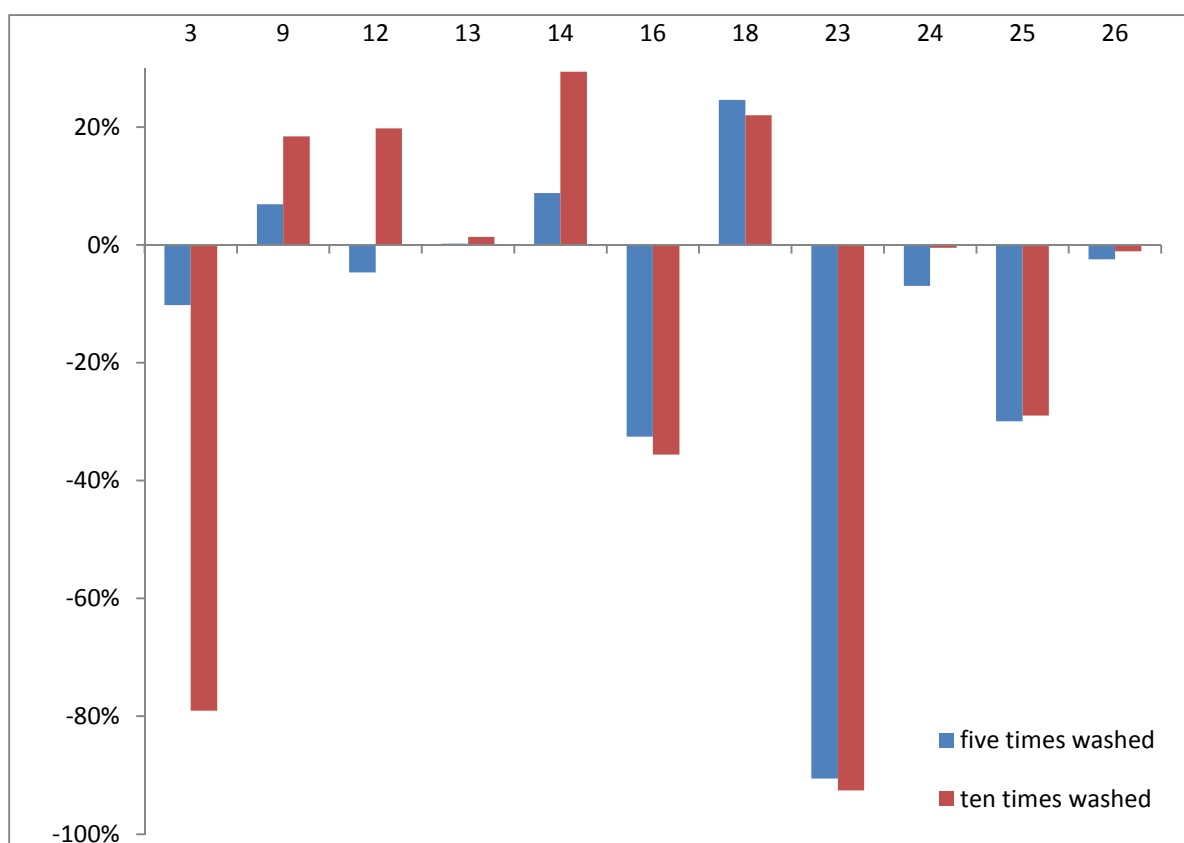
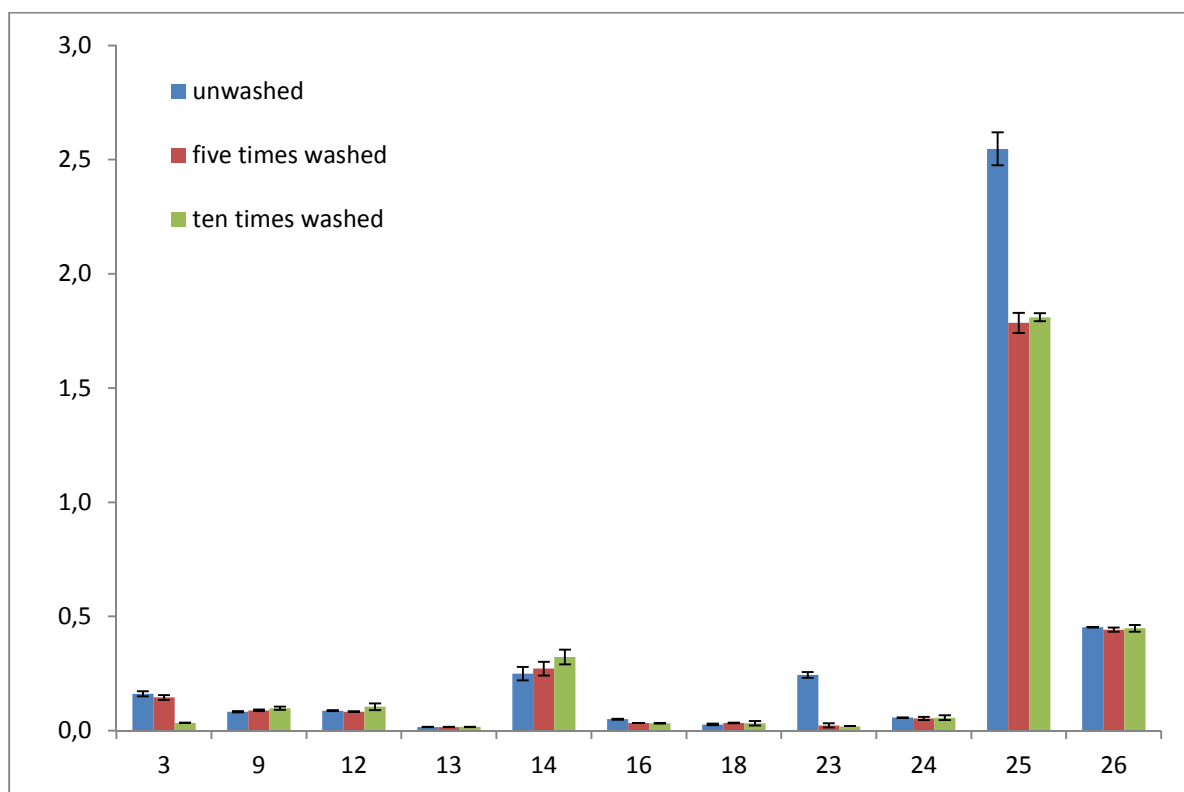


Fig. S12 a) Determined concentrations ($\mu\text{g/g}$) of 2,4-Dimethylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

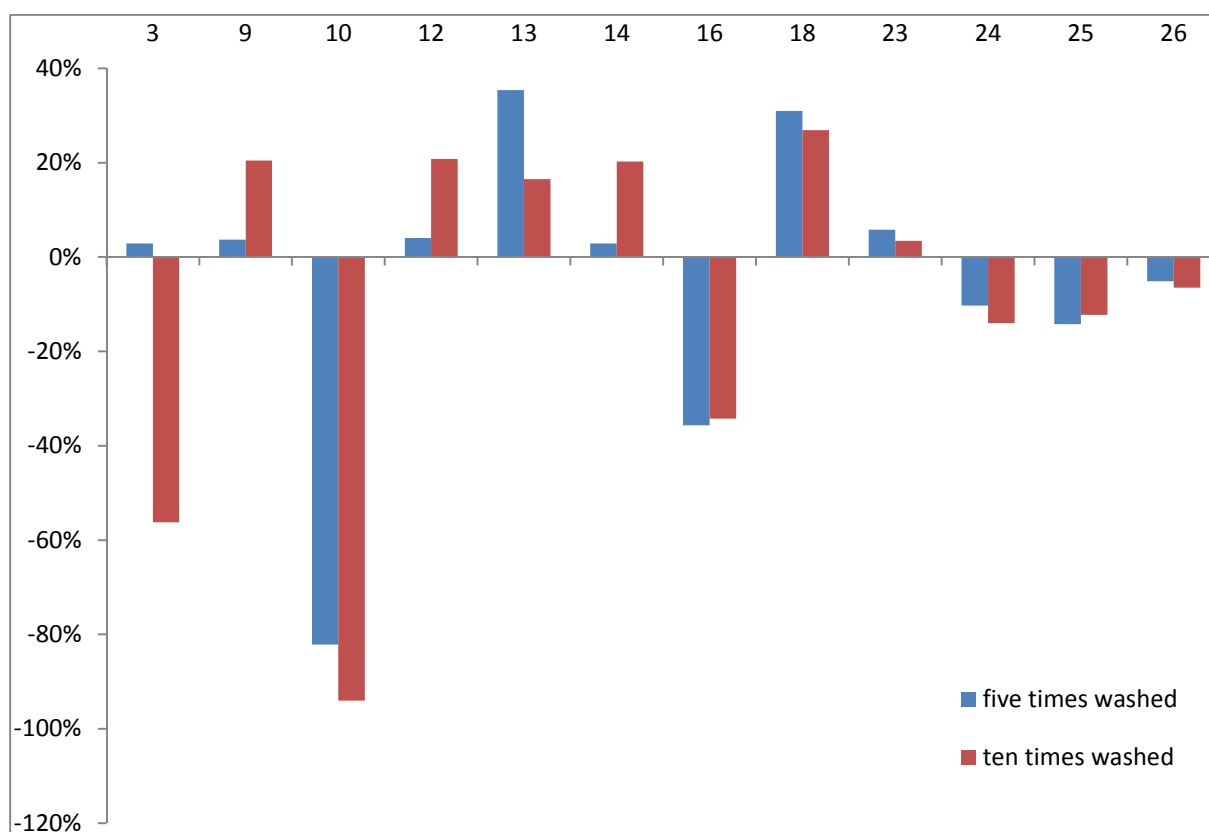
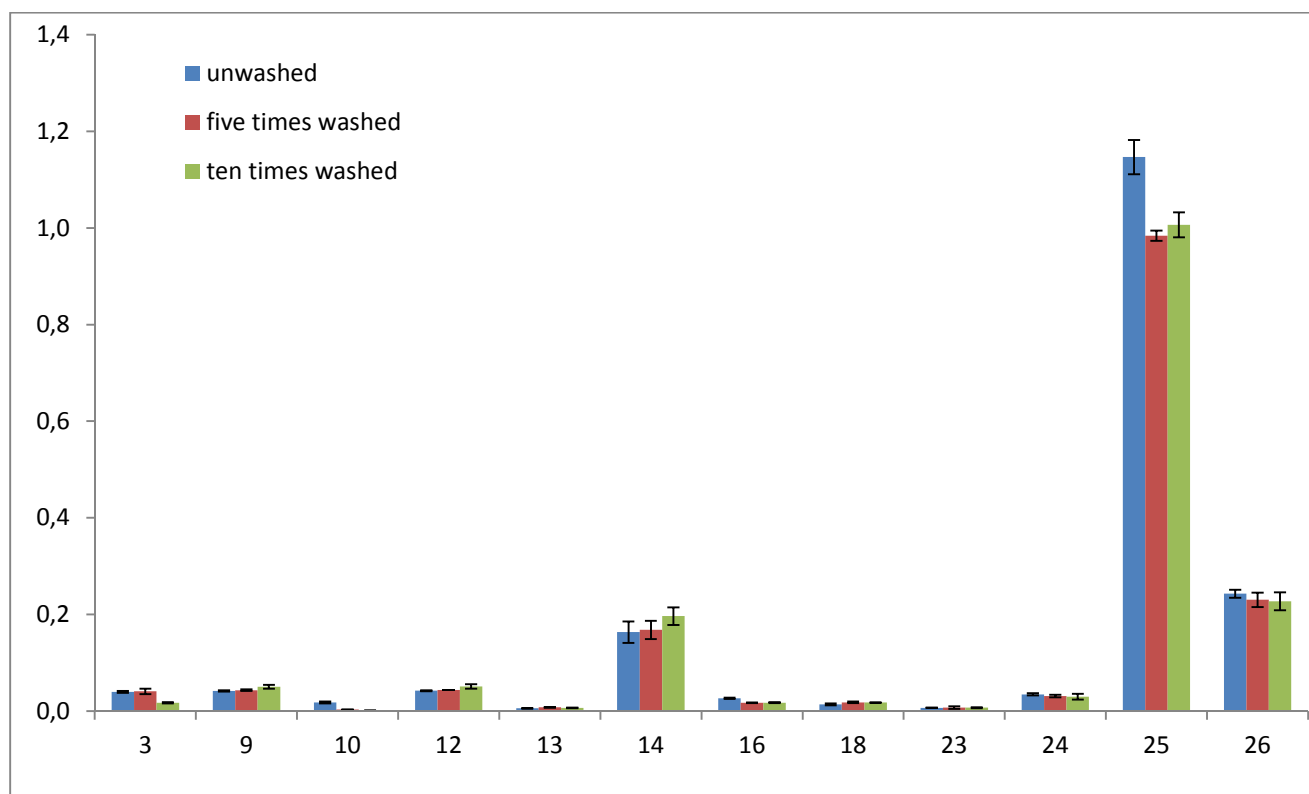


Fig. S13 a) Determined concentrations ($\mu\text{g/g}$) of 2,6-Dimethylquinoline in the clothing textile samples ($n = 2$) **b)** Percentage of the concentration decrease after five and ten washing steps

