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Filella, M

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Hazardous chemical elements in cleaning cloths, a potential source of microfibres



Montserrat Filella^{a,*}, Johanna Brazard^b, Takuji B.M. Adachi^b, Andrew Turner^c

^a Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva, Switzerland

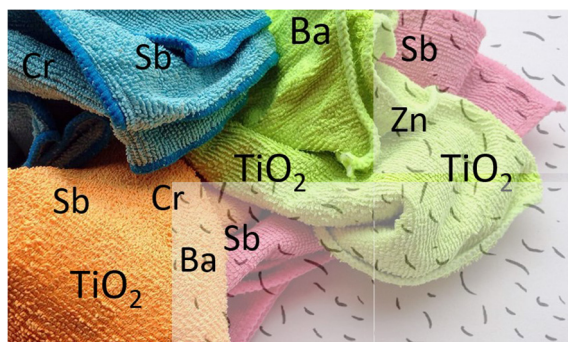
^b Department of Physical Chemistry, University of Geneva, Sciences II, 30 Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

^c School of Geography, Earth and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, UK

HIGHLIGHTS

- First study on potentially hazardous chemical elements in cleaning textiles
- 48 cleaning cloth products (81 samples) purchased in Europe analysed by XRF.
- Element concentration ranges similar to those found in for clothing materials.
- Titanium ubiquitously present; Ba, Br, Cr, Cu, Fe, Sb and Zn frequently detected.
- TiO₂ present as anatase and not rutile.

GRAPHICAL ABSTRACT



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ABSTRACT

Although potentially hazardous chemical elements (e.g., Cu, Cr, Pb, Sb, Ti, Zn) have been studied in clothing textiles, their presence in cleaning textiles is unknown. In this study, 48 cleaning cloth products (consisting of 81 individual samples) purchased in Europe, and consisting of synthetic (petroleum-based), semi-synthetic or natural fibres or combinations of these different types, have been analysed for 16 chemical elements by X-ray fluorescence (XRF) spectrometry. Titanium was detected in most cases (median and maximum concentrations ~3700 and 12,400 mg kg⁻¹, respectively) and Raman microspectroscopy revealed that TiO₂ was present as anatase. Barium, Br, Cr, Cu, Fe and Zn were frequently detected over a range of concentrations, reflecting the presence of various additives, and Sb was present at concentrations up to about 200 mg kg⁻¹ in samples containing polyester as catalytic residue from the polymerisation process. Lead was detected as a contaminant in four samples and at concentrations below 10 mg kg⁻¹. Overall, the range of the chemical element profiles and concentrations was similar to those for clothing materials published in the literature, suggesting that broadly the same additives, materials and processes are employed to manufacture cloths and clothing textiles. The mechanisms by which potentially hazardous chemical elements are released into the environment with microfibres or mobilised into soluble or nano-particulate forms remain to be explored.

1. Introduction

The interest in investigating the chemical composition of textiles has often been driven by toxicological considerations. To this end, the

* Corresponding author.

E-mail address: montserrat.filella@unige.ch (M. Filella).

possible human toxicological effects are essentially studied by mimicking the release of chemical elements in various physiological extractants (Rovira et al., 2017; Herrero et al., 2019; Kawakami et al., 2020; Biver et al., 2021). More recently, research on the possible deleterious effects of textiles in the environment has been fuelled by their potential to form synthetic microfibres. These have been detected in water, sediment, and air (Claessens et al., 2011; Desforges et al., 2014; Lusher et al., 2015; La Daana et al., 2017), and even in human lung tissue samples, where polypropylene and polyethylene terephthalate fibres were most abundant (Jenner et al., 2022). In these studies, attention has focused on textiles and fabrics used in clothing and the generation of microfibres through wearing (Catarino et al., 2018) and laundering (Browne et al., 2011; Hartline et al., 2016; Napper and Thompson, 2016; Hernandez et al., 2017; Cai et al., 2020; Yang et al., 2021). In contrast, cloths, dusters, sheets, pads and mops used for household cleaning and where other processes, such as abrasion (Cai et al., 2021), might also produce microfibres, have thus far received no attention.

Cleaning cloths and mops can have different polymer compositions. Traditional cleaning materials were typically cotton and other natural fibres but nowadays a range of synthetic fibres is used. Contemporary cleaning cloths are usually constructed from split conjugated fibres of polyester and polyamide and contain approximately 200,000 fibres per square inch of fabric. Cloths based on synthetic fibres have many advantages over traditional products, such as higher absorbency, greater ability to pick up dirt, lower weight and greater softness (Nilsen et al., 2002). Consequently, they are ideal for various applications in a variety of settings, including the household, business and commerce (e.g., office spaces, hotels, car cleaning), and industry (e.g., pharmaceuticals, food processing, semiconductor manufacturing, maintenance of production facilities).

Fundamental data on the production or demand of textiles for cleaning purposes is difficult to obtain. According to World Bank statistics by country for 2021 (World Integrated Trade Solution, 2022), gross global exports for product code 630710 (cloths: floor cloths, dish-cloths, dusters and similar cleaning cloths) were 150,000 tonnes t and worth 1.4 billion USD. By comparison, exports for product code 630900 (clothing: worn and other worn articles) were three million tonnes and worth 4.6 billion USD. Although export data are not equivalent to production figures, they suggest that, by mass and, therefore, potentially hazardous chemical element emissions, clothing contributes more than cleaning cloths by more than an order of magnitude.

All textiles also contain inorganic and organic compounds that are residues or impurities from the manufacturing process or that have been deliberately added to modify or improve the product. Lacasse and Baumann (2004) provided an extensive list of compounds added to textiles that encompass bleaching agents, water repellents, dyes and pigments, finishing agents, flame retardants, fillers, biocides, surface modifiers and cross-linking agents. Potentially hazardous chemical elements, including Br, Cr and Sb, are encountered in many of these additives, and the authors also acknowledge that harmful heavy metals, like Cd and Pb, may also be present as impurities. What is lacking from a health and environmental perspective, however, is an indication of which chemical elements are present in contemporary cleaning cloths, and at what concentrations.

The present study is the first to screen widely available cleaning textiles for the presence of potentially hazardous chemical elements. Specifically, cloths bought in six European countries were analysed by energy dispersive X-ray fluorescence (XRF) spectrometry. The possibility of using Raman microspectroscopy to determine the forms in which potentially hazardous compounds occur was also explored. To this end, focus was placed on titanium dioxide (TiO₂) because textiles have been suggested as environmental sources of Ti mineral nanoparticles (Windler et al., 2012; von Goetz et al., 2013).

2. Materials and methods

2.1. Samples and materials

Forty-eight cleaning cloth and mop products were purchased from a variety of homeware stores and supermarkets in Europe (although the products were not necessarily manufactured in Europe), with codes and descriptions, including polymeric composition (where stated), provided in Table 1. The total number of analysed samples was much higher ($n = 81$) because many products either contained more than one cloth (usually of different colour) or were composite objects. Photographs of all products can be found in Table S11.

A polyethylene reference disc, PN 180–619, “Toxic elements in plastic”, was provided by Niton UK. Titania (TiO₂) in anatase form was purchased from Sigma-Aldrich (232033-100G) and annealed at 1050 °C for four hours to convert it to rutile.

2.2. SEM observations

Offcuts of the samples were mounted on aluminium stubs using double-sided conductive carbon tape and sputter-coated with gold (ca. 10 nm). A JEOL JSM-7001F scanning electron microscope operated at an accelerating voltage of 10–15 kV was used to obtain secondary electron images of the samples. As a comparison, samples were analysed new and after being used for cleaning in the household.

2.3. XRF measurements

All samples were analysed for 16 elements (As, Bi, Ba, Br, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, Sn, Ti, Zn) by energy-dispersive field-portable X-ray fluorescence (XRF) spectrometry using a Niton XL3t 950 He GOLDD+ operated in an accessory stand. Material was folded and compressed to a thickness > 13 mm (above the critical thickness for plastics) before being placed over the detector window and counted in a standardless ‘plastics’ mode for 180 s (90 s at 20 kV and 100 μA and 90 s at 50 kV and 40 μA). Spectra were quantified by fundamental parameter coefficients to yield concentrations on a dry weight basis (in mg kg⁻¹) and with a counting error of 2σ (95 % confidence). As a performance check, polyethylene reference disc Niton PN 180–619 was analysed at regular intervals throughout each measurement session. Mean concentrations returned ($n = 8$) were always within 20 %, and for five elements within 5 %, of corresponding reference values (Table 2).

2.4. Raman spectral analysis of TiO₂

Raman spectra were acquired using a home-built microspectroscopy setup that is similar to the setup described previously (Urquidi et al., 2022). A tunable CW laser (Spectra physics 3900) set at 785.54 nm (characterized by a Wavemeter Burleigh WA-10) was used as an excitation source. The laser was first cleaned by a filter (AHF analysentechnik AG, HC Laser Clean-up MaxLine 785/3) and then depolarized using a liquid crystal depolarizer (Thorlabs, DPP25-B). The beam was reflected by a dichroic mirror (AHF analysentechnik AG, Beamsplitter RT 785 rdc) to be focused on a sample by the objective lens (Olympus Plan Achromat, 20×, NA0.4). The laser power was ~15 mW after the objective lens and the spot size was about 1 μm. The collected signal was spatially filtered by a 50 μm pinhole at the conjugate image plane, and the excitation beam was further cleaned by using a long-pass filter (Iridian Spectral Technologies Ltd., 785 Nano Edge). The Raman spectrum was then recorded by a spectrograph (Andor, Kymera 193) with a CCD camera (Andor, iDus 420). Each spectrum was recorded by accumulating ten spectra with the exposure time of 10 s (total 100 s acquisition).

Table 1

Colour, country of purchase and polymeric composition of the samples (where stated). Abbreviations in text.

Product #	Colour	Composition/description of fabric stated by the manufacturer ^a	Category ^b	Country of purchase
1	Blue, yellow	80 % viscose, 20 % PP	Felt	Luxembourg
2	Pink	70 % viscose, 30 % PES	Zigzag	Luxembourg
3	Blue	60 % PES, 30 % PU, 10 % PA	Other	Luxembourg
4	Yellow/orange	50 % cotton, 50 % other	Cotton	Spain
5	Yellow	Not stated	<i>Felt</i>	Spain
6	Blue, green, red, yellow	70 % viscose, 30 % PP	Felt	Spain
7	Orange	100 % PES	Microfibre-PES	Luxembourg
8	White	“diverse fibres”	Other	Luxembourg
9	Blue, green, pink, blue	80 % PES, 20 % PA	Microfibre-PES/PA	Luxembourg
10	Blue, green, pink, yellow	88 % PES, 12 % PA	Microfibre-PES/PA	Luxembourg
11	Pink	80 % PES, 20 % PA	Microfibre-PES/PA	Spain
12	Yellow	50 % viscose, 20 % PP, 30 % PES	Felt	Luxembourg
13	Yellow	70 % viscose, 30 % PES	Felt	Spain
14	Green	Not given	–	Switzerland
15	White	Not given	–	Spain
16	Blue stripes	80 % PES, 20 % PA	Microfibre-PES/PA	Spain
17	Orange	80 % viscose, 20 % PP	Felt	Luxembourg
18	Blue, green, yellow	82 % viscose, 18 % PP	Felt	Switzerland
19	Blue	80 % PES, 20 % PA	Microfibre-PES/PA	Spain
20	Blue	100 % viscose	Zigzag	Luxembourg
21	Green	Rayon, acrylic binder, PES	Other	Switzerland
22	Yellow	80 % viscose, 20 % binder	Zigzag	Switzerland
24	Blue, green, yellow	80 % viscose, 20 % PP	Felt	Switzerland
25	Green, yellow	regenerated cellulose, nylon thread	Other	Spain
26	Blue, red	35 % cotton, 35 % viscose, 30 % PES	Other	Luxembourg
27	White with pink flowers	100 % PES	Microfibre-PES	Spain
28	White	90 % viscose, 10 % PES	Felt	Spain
29	White	100 % PES	Microfibre-PES	Spain
30	White	Not stated	–	Switzerland
31	Grey, red	50 % viscose, 50 % PES	Felt	Switzerland
32	Green	80 % PES, 10 % PA, 10 % various fibres	Microfibre-PES/PA	France
33	Grey scrubbing corner	90 % PES, 10 % PA	Microfibre-PES/PA	France
	Blue	88 % PES, 12 % PA		
34	Yellow, orange	80 % viscose, 20 % diverse fibres	Felt	France
35	Orange, pink, yellow	70 % PES, 30 % recycled PES	Microfibre-PES	France
36	Blue, orange, red, yellow	85 % PES, 15 % PA	Microfibre-PES/PA	France
37	Blue	80 % PES, 20 % PA	Microfibre-PES/PA	France
	Pink	85 % PES, 15 % PA		
	Grey, yellow	90 % PES, 10 % PA		
38	Yellow	60 % viscose, 20 % PP, 20 % PES	Felt	Portugal
39	Orange	Not stated	–	Portugal
40	Greenish yellow	85 % PES, 15 % PA	Microfibre-PES/PA	Portugal
41	Green	100 % PES	Microfibre-PES	Portugal
42	White	100 % cotton	Cotton	UK
43	Blue	Viscose	Zigzag	UK
44	Blue, pink, yellow, all with green side	Not stated	–	UK
45	White	100 % cotton	Cotton	UK
46	Yellow/green	65 % viscose, 20 % PP, 15 % “micro-” PES	Felt	UK
47	Yellow, blue, grey, lilac	100 % PES	Microfibre-PES	UK
48a	Grey-white straps	Not stated	–	UK
48b	Grey-white string	Not stated	–	UK

^a PA: polyamide, PES: polyester; PP: polypropylene, PU: polyurethane.^b When italics, based on aspect.**Table 2**Measured and reference concentrations (in mg kg⁻¹) of eight chemical elements in the polyethylene reference disc. Errors are two standard deviations about the mean ($n = 8$).

	Reference	Measured
As	51 ± 7	43 ± 5
Ba	688 ± 45	658 ± 67
Cd	292 ± 20	279 ± 10
Cr	101 ± 10	102 ± 4
Hg	101 ± 10	99 ± 6
Pb	150 ± 12	149 ± 9
Sb	96 ± 10	78 ± 14
Se	200 ± 15	243 ± 7

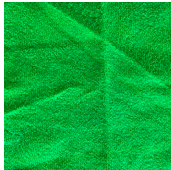
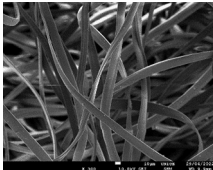

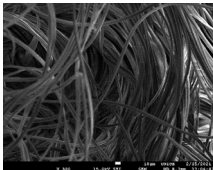

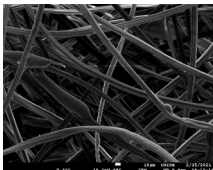
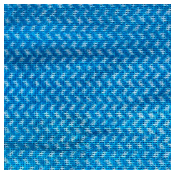
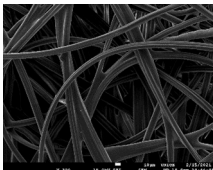

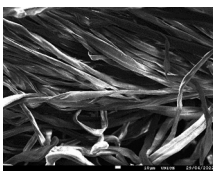
3. Results

3.1. Polymer types based on stated composition

The polymeric compositions of the textile products ($n = 48$) in this study as stated by the manufacturer (composition not always given) are categorised below, with examples of each type shown in Table 3.

- Microfibre-PES: 100 % polyester (PES) (#7, #27, #29, #35, #41, #47) ($n = 11$); often referred to as “microfibres” by the manufacturers.
- Microfibre-PES/PA: usually 80 % PES - 20 % polyamide (PA) (#9, #11, #16, #19, #37) ($n = 8$) or similar proportions with 10, 12 or 15 % PA (#10, #32, #33, #36, #37, #40) ($n = 15$); also often referred to as “microfibres” by the manufacturers.
- Felt: viscose and polypropylene (PP) in variable proportions such as 80 % viscose + 20 % PP (#1, #17, #24), 70 % viscose + 30 % PP (#6) or other proportions (#18, #28, #34); they can also contain PES (#12, #38, #46),

Table 3
Examples of the different types of cleaning cloths and mops based on their polymer composition.

Sample type	Example		Picture	SEM image (300×)
	Sample #			
Microfibre-PES	41			
Microfibre-PES/PA	10			
Felt	17			
Zig zag	20			
Cotton	42			

sometimes only viscose and PES mentioned (#13, #31) with a similar aspect, or no composition given (#5); all these viscose-containing cloths have a felt-like touch, total $n = 23$.

- Zigzag (or J-cloth): 100 % viscose (#20, #43), 70 % viscose and 30 % PES (#2) or 80 % viscose and 20 % binder (#22) and all with a distinctive zigzag pattern; a few with similar composition (#13, #28, #31) but showing a completely different aspect are classified in 'felt'.
- Cotton: 100 % cotton (#42, #45) or a mixture of cotton with other (unspecified) polymers (#4).
- Other: mixtures of other polymers, including polyurethane (PU), rayon, nylon and cellulose (#3, #21, #25, #26) ($n = 6$), or no composition stated (#8, #14, #15, #30, #39, #44, #48) ($n = 11$).

Overall, therefore, cleaning cloths consist of synthetic (petroleum-based), semi-synthetic or natural fibres, or combinations of these different types.

Table 4

A summary of the detection frequencies and concentrations (in mg kg^{-1}) of chemical elements in the cloth samples ($n = 81$). DL = indicative (median) detection limit; see text.

	As	Ba	Bi	Br	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	Se	Sn	Ti	Zn
No. detected	0	43	13	29	0	56	22	28	0	13	4	57	0	4	78	42
median		162	7.3	8.8		60.0	97.8	74.9		19.3	5.0	77.1		276	3734	53.8
max		850	64.5	2796		359	846	2246		33.3	7.3	193		305	12,354	215
min		110	4.9	2.5		17.1	12.2	30.0		14.2	3.2	24.0		80.1	25.7	10.3
median DL	2.4	127	5.6	2.8	11.2	4.8	16.6	33.6	8.4	17.9	4.2	20.8	5.8	16.5	34.4	11.2

3.2. SEM observations

Examples of SEM images of new and used cloths at different magnifications are shown in Tables 3 and SI3. All cloths observed were of the non-woven type where fabric is produced by connecting yarn with gummy or bonded materials. This results in a mesh of fibres, with the binder sometimes observed. Individual fibres appear to be mm to cm in length, with bifurcation and grooves often evident that presumably reflect the nature of the extrusion process. Fibre diameter ranges from about 10 to 30 μm , with the cross-section circular or flattened. After cloths had been used, fibres assume a rougher surface and there is evidence of contamination by extraneous particulates and, in some cases, loss or expansion of binder.

3.3. Chemical elements

The frequency of chemical element detection and a summary of their concentrations for the 81 samples is shown in Table 4, with the full data

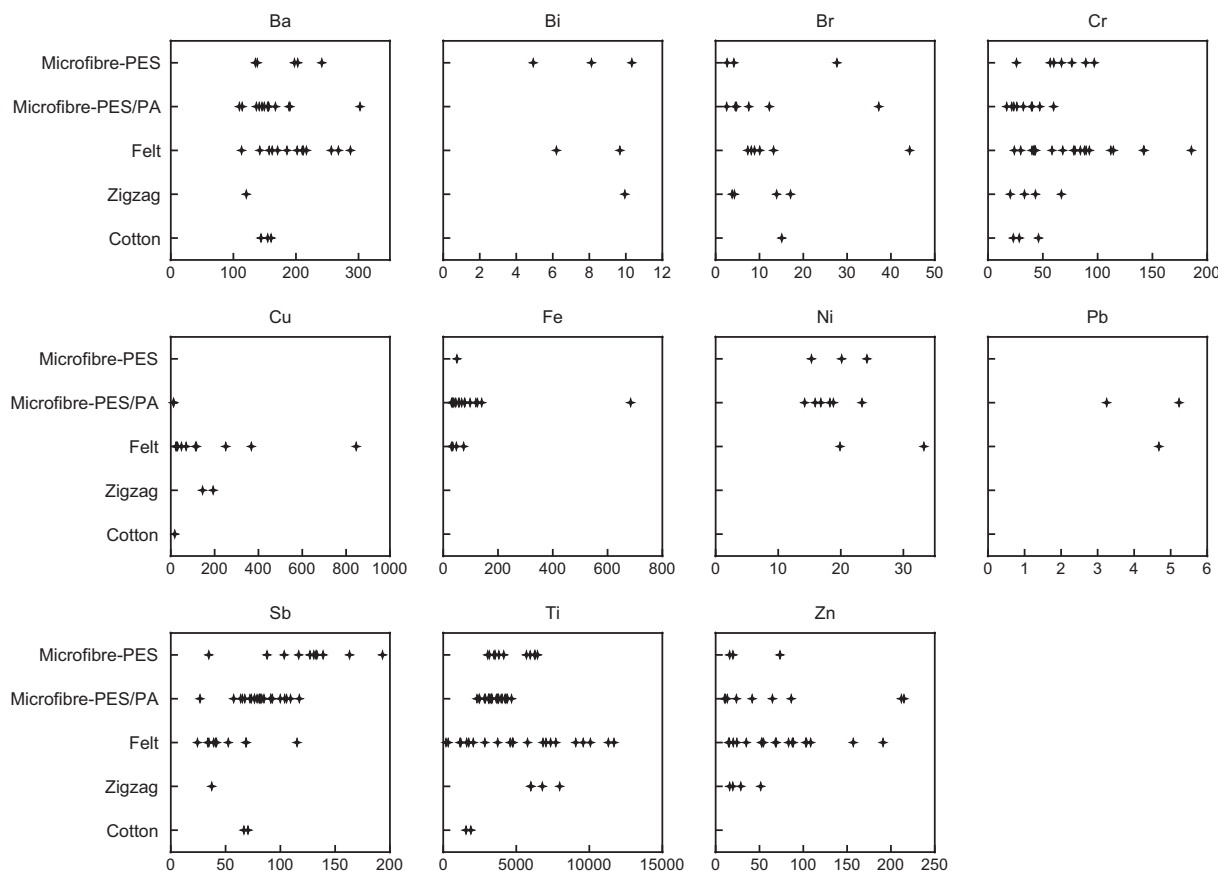


Fig. 1. Graphical comparison of elemental composition of the different types of cloths. Note that samples in category ‘Other’ or whose compositions are not known are not represented. Unit of the x-axis is mg kg^{-1} . Non detected elements (As, Cd, Hg, Se) and Sn, not present in any of these categories, are excluded from this figure.

set provided in the Supporting Information. The detection limit, based on counting error, varies between elements and, for a given element and because of variations in textile composition, amongst the samples. Consequently, indicative detection limits, calculated from the median of three counting errors where non-detects were returned by the instrument, are often greater than the minimum concentrations reported.

Within these constraints, the distributions of elements by composition and by colour are shown in Figs. 1 and 2, respectively. Thus, Ti was detected in all but three samples and across all categories by polymer type and colour, and Ba, Cr, Sb and Zn were detected in more than one-half of all samples and across all categories by polymer type (except Zn in cotton) and colour. Lead and Sn were detected in four samples each, with the latter metal present in four different coloured cloths, and As, Cd, Hg and Se were never detected. Titanium was the element with the greatest median and maximum concentrations (about 3700 and 12,000 mg kg^{-1} , respectively), with other elements exceeding concentrations of 1000 mg kg^{-1} in only four cases (two each for Br and Fe). Conversely, concentrations of Bi, Ni and Pb were always below 100 mg kg^{-1} . All cloth samples contained at least one detectable element, with four samples returning concentrations of eight elements.

3.4. Form of TiO_2 present

Our Raman microspectroscopy setup verified that rutile and anatase crystalline forms of TiO_2 can be clearly distinguished in textile samples based on their distinctive spectra (Fig. 3). However, one confounding factor in some cases, and in particular in products constructed of PES, was fluorescence arising from the presence of certain dyes. Within this constraint, TiO_2 in seven products (and 11 samples) was identified as anatase but rutile was never detected (Table 5). The form of TiO_2 found in synthetic fibres

reported by Puchowicz and Cieslak (2021) was also anatase and attributed to its use as a matting agent.

4. Discussion

This study shows that some potentially hazardous chemical elements are widely but heterogeneously distributed amongst different types and colours of cleaning textiles purchased on the European market. Variability is sometimes also evident amongst different coloured components of the same product, and usually for one or more of the following metals: Cu, Fe, Ni and Zn. Overall, this heterogeneity reflects the sheer number and variety of inorganic-based compounds used as functional additives in textiles (several hundred are listed by Lacasse and Baumann, 2004), making it difficult to identify general usage, trends, co-associations or groupings (by polymer type, for example) of many elements.

The concentrations of potentially hazardous chemical elements reported in the literature for clothing textiles are given in Table 6. Clothing textiles tend to utilise more natural fibres than cleaning cloths (Rovira et al., 2015, 2017; Herrero et al., 2019) and occasionally use specific additives for functionalisation (e.g., appearance and UV protection; von Goetz et al., 2013; Rujido-Santos et al., 2022). Amongst these studies, it is also important to bear in mind that some differences may reflect different analytical approaches employed; specifically, non-destructive XRF (e.g. Kawakami et al., 2020) versus ICP-MS following sample digestion in nitric acid (Rovira et al., 2015) or in three mineral acids plus hydrogen peroxide (Rujido-Santos et al., 2022). Nevertheless, maximum values for many elements used in additives, and in particular those analysed by XRF and including Br, Cr, Cu, Fe, Ti and Zn, are comparable amongst studies and with maximum concentrations we measured in our cleaning cloths and shown in Table 4 (one exception is the high content of Cr reported by Kawakami et al. (2020)) compared with studies undertaken in Europe

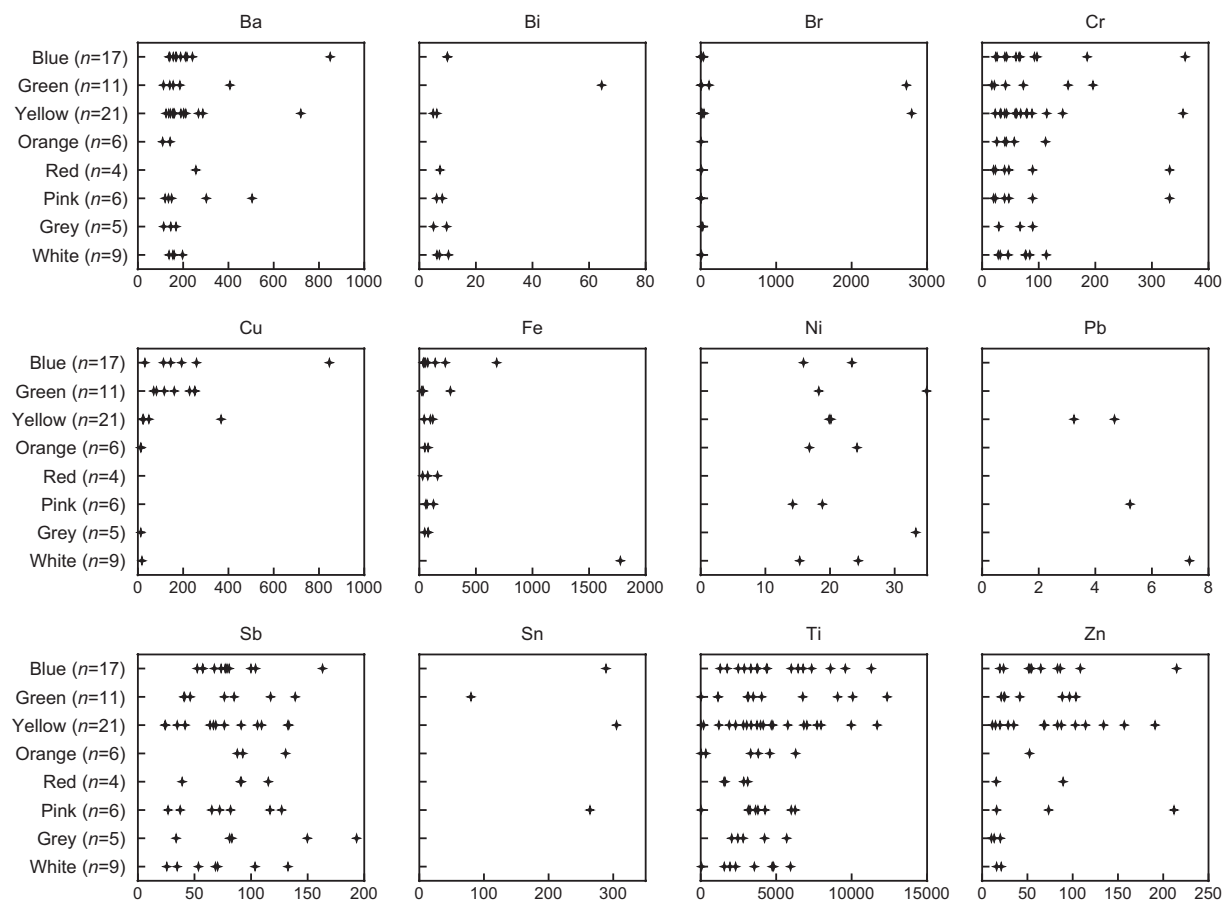


Fig. 2. Graphical comparison of elemental composition as a function of colour (where n is the number of samples in each colour category). Unit of the x-axis is mg kg^{-1} . Non detected elements (As, Cd, Hg, Se) are excluded from this figure.

where chromium-based dyes are restricted). Median concentrations, however, tend to be lower in studies involving ICP-MS reflecting the use of a technique with better detection limits and/or, potentially, incomplete digestion of some metals from the textile matrix.

The most common and abundant element amongst all studies, and regardless of colour or composition, is Ti (present as nano- TiO_2 particles). The addition of titania to textiles because of its flame-retardant properties (Cheng et al., 2017) seems implausible and, while its addition in functionalized clothing textiles is widespread (von Goetz et al., 2013; Rashid et al., 2021), is unlikely in cleaning cloths. Most probably, TiO_2 is ubiquitous in clothing and cleaning textiles because of its properties as a delustering agent in synthetic fibres (Barker, 1975). This assertion is supported by the presence of anatase but not rutile in our samples. Thus, when TiO_2 is used for its photocatalytic activity, the most popular product is Degussa TiO_2 P25, which contains anatase and rutile phases in a ratio of about 3:1 (Rashid et al., 2021), but when used as a delustrant, pure anatase is added (Anstey and Weston, 1997).

Antimony (as the trioxide, Sb_2O_3) is used as a catalyst in the polymerisation of polyethylene terephthalate (PET) ester and commonly contaminates the final product, including polyester (PES) fibres usually employed in textiles. Although Sb was most commonly (but not always) detected in cloth samples theoretically containing PES, its concentration was not proportional to the percentage of PES stated by the manufacturer, with about 70 mg kg^{-1} found in a sample of 10 % PES and values ranging from about 40 to 200 mg kg^{-1} in “pure” PES. By comparison, maximum values ranging from 152 to 472 mg kg^{-1} have been reported in clothing textiles of, presumably, PES construction throughout the literature (Rovira et al., 2015, 2017; Turner, 2019; Biver et al., 2021; Rujido-Santos et al., 2022), and Sb is present in PET bottles with concentrations in the range

200 – 400 mg kg^{-1} (Filella, 2020). Antimony is also used as a synergist for brominated flame retardants. However, the metalloid was not detected where Br concentrations were highest (above 1000 mg kg^{-1} in two samples of one product) and we suspect that Br was present in the form of azo dyes (Turner, 2019).

Amongst the remaining chemical elements that we considered are contaminants arising from the manufacturing process (As, Bi, Cd, Hg, Pb; Lacasse and Baumann, 2004). Arsenic, Cd and Pb are restricted in textile products in Europe, with maximum legal concentrations of the elements or their compounds of 1 mg kg^{-1} (European Union, 2011) and impregnation with Hg compounds is not permitted (European Union, 2006). Our results for As, Bi, Cd, Hg and Pb are qualitatively consistent with those given by Rovira et al. (2015, 2017), Herrero et al. (2019), and Rujido-Santos et al. (2022) involving more sensitive means of textile analysis and reflecting the general but limited contamination of textile materials. Thus, in these studies contaminant elements were occasionally detected but usually at concentrations below the regulatory limit of 1 mg kg^{-1} . However, four of our cloth samples contained traces of Pb above this limit.

Overall, therefore, these observations suggest that broadly the same additives, materials and processes are employed to manufacture cloths and clothing textiles. However, unlike clothing, cloths are not woven and their texture and microstructure are designed for strength, absorbency and chemical resistance rather than comfort and extended wear, with products often intended for single or limited use with aggressive cleaning agents and contact with contaminated surfaces (Gibson et al., 2012). Nevertheless, the mechanisms by which potentially hazardous chemical elements may be released into the wider environment will bear some similarities with those for clothing textiles but are not well understood. These include discharge with microfibres into the atmosphere and greywater, mobilisation from

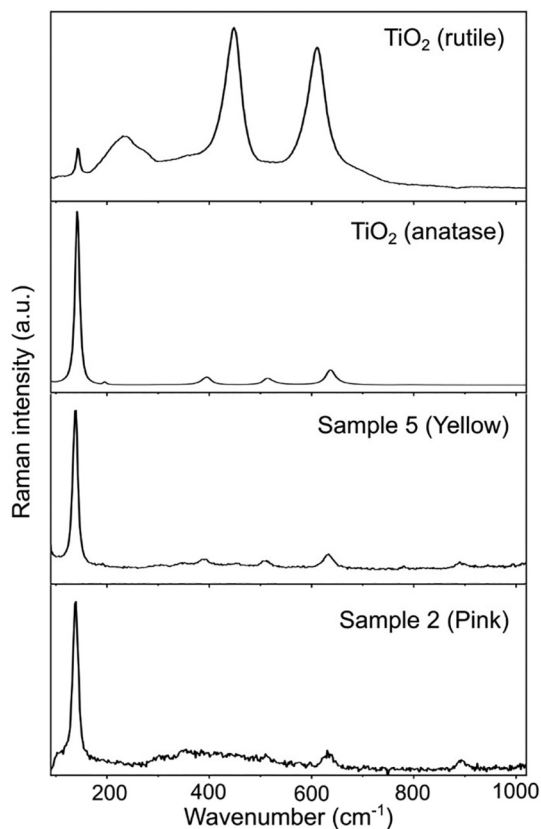


Fig. 3. Raman spectrum of TiO_2 reference spectrum (rutile and anatase form) and representative clothes samples that contained Ti. The spectra of clothes samples match the anatase form of TiO_2 .

the textile material into a soluble form (a process that may be accentuated when using chemical cleaning agents), and release as mineral nanoparticles. Regarding the latter, TiO_2 nanoparticles have gained attention because of their potential health impacts on humans through dermal exposure when wearing certain types of clothing (Windler et al., 2012; von Goetz et al., 2013) and their presence in other types of consumer products (Lorenz et al., 2011). Traditionally, ingestion and inhalation have not been considered significant vectors of external exposure to substances in textiles for adults because of the need for transport from the textile to the intake organ (Licina et al., 2019). This picture is changing now, however, with the detection of micro- and nanofibres in human lungs (Jenner et al., 2022) and their means of providing a new and, unfortunately, efficient intake path for chemicals (including those in nanoparticle form). The

dissolution and transformation of nanoparticles has been clearly demonstrated (Cho et al., 2012; Keller et al., 2020) and are of concern to not only end-users but also producers, transformers and packagers (Borm et al., 2006).

5. Conclusion

Cleaning textiles are used across a range of sectors, with artificial polymers, and in particular polyester, having largely replaced traditional natural fibre-based products. This study has shown that potentially hazardous chemical elements are widely but heterogeneously distributed amongst cleaning textiles purchased in Europe, with concentration ranges for many elements, including Cr, Cu, Sb, Ti and Zn, that are similar to those reported for textiles used in clothing. Although any hazardous effects derived from skin-contact are likely to be less significant than those arising from clothes, their potential to form microfibres containing hazardous elements and nanoparticles that can be dispersed in water and inhaled by humans is a matter of concern.

CRediT authorship contribution statement

Montserrat Filella (conceptualization, investigation, analysis, writing – original draft, review & editing) Johanna Brazard and Takuji B. M. Adachi (analysis, writing review & editing) Andrew Turner (investigation, review & editing).

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.157419>.

Table 5

Summary of the Raman spectroscopy measurement to identify the phase of TiO_2 .

Sample type	Sample #	Colour	TiO_2 phase	Comment
Microfibre-PES/PA (80 % PES - 20 % PA)	9, 10, 11, 16, 19, 37	9 (Blue, green), 10 (Blue, green), 11 (Pink), 16 (Blue stripes), 19 (Blue), 37 (Pink, blue, grey, yellow)	Unidentified	Highly fluorescent
		9 (Pink, yellow), 10 (Pink)	Unidentified	Fluorescent
		10 (Yellow), 11 (Pink)	Anatase	
Microfibre-PES/PA (Other proportions)	32, 33, 36, 37, 40	32 (Green), 33 (Blue), 36 (Blue, red), 37 (Blue), 40 (Yellow)	Unidentified	Fluorescent
		33 (Grey), 36 (orange, yellow), 37 (pink, blue, grey, yellow)	Unidentified	No TiO_2 peaks
Felt	1	Blue, yellow	Anatase	
Felt	5	Yellow	Anatase	
Felt	6	Yellow	Unidentified	
Felt	18	Blue, green, yellow	Anatase	
Zigzag	2	Pink	Anatase	
Zigzag	20	Blue	Anatase	
Zigzag	22	Yellow	Anatase	

Table 6
Published concentrations of potentially hazardous elements in clothing textiles. ND = not detected.

		As	Ba	Bi	Br	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Sb	Se	Sn	Ti	Zn	Reference
31 textiles, Spain	HNO ₃ digestion	ND	1.51	0.28	-	0.01	19.8	20.1	9.78	ND	ND	0.13	22.3	0.08	0.05	-	12.1	Rovira et al., 2015
	ICP-MS	max	9.46	1.92	-	0.04	605	287	35.1	ND	ND	0.32	204	0.61	0.20	-	256	Rovira et al., 2017
37 textiles, Spain	HNO ₃ digestion	ND	0.73	0.01	-	0.01	0.13	0.21	9.54	ND	0.05	0.01	0.05	ND	0.03	-	1.44	Rovira et al., 2017
	ICP-MS	max	19.1	0.10	-	0.07	754	439	194	ND	1.79	1.90	152	0.29	0.22	-	1185	Herrero et al., 2019
42 denim clothes, Spain	HNO ₃ digestion	-	3.58	-	-	-	2.05	2.23	37.2	-	1.92	0.10	11.4	-	0.22	6.19	4.19	Herrero et al., 2019
	ICP-MS	max	20.7	-	-	-	16.6	8.50	126	-	21.4	0.49	60.3	-	1.79	19.2	13.9	Turner, 2019
72 textiles, UK	XRF	ND	-	-	6.3	-	-	39.0	89.2	-	ND	ND	146	-	-	1210 ^a	33.4	Turner, 2019
	max	-	-	-	13 ^a 400	-	-	67.2	1150	-	ND	0.63	476	ND	-	5500 ^a	33,100	Herrero et al., 2020
39 swimsuits, Spain	HNO ₃ digestion	mean	0.14	0.05	-	-	1.22	27.9	ND	ND	2.02	0.21	45.4	ND	1.09	1844	4.25	Herrero et al., 2020
	ICP-MS	max	0.16	0.08	-	-	932	328	ND	ND	2.02	0.47	167	ND	3.75	6603	24.6	Biver et al., 2021
8 textiles, Lux/UK	XRF	median	1794 ^a	-	143 ^a	-	52.3 ^a	-	-	-	-	-	298 ^a	-	-	1841 ^a	-	Biver et al., 2021
	max	-	2628 ^a	-	754 ^a	-	60.2 ^a	-	-	-	-	-	471 ^a	-	-	8393 ^a	-	Kawakami et al., 2020
78 textiles, Japan	XRF	range	1000–10,000	-	-	<100–10,000	<100–10,000	100–1000	<100–10,000	-	-	-	100–1000	-	-	100–10,000	<100–10,000	Rujido-Santos et al., 2022
	mineral acids + H ₂ O ₂ digestion	median	0.62	4.4	-	0.24	0.37	0.832	18.7	0.16	0.19	0.77	63.5	-	0.10	1593	5.68	Kawakami et al., 2020
14 textiles, EU, some enriched in ZnO	ICP-MS	max	15.8	53.9	-	0.32	1.03	41.1	57.1	0.38	0.34	1.39	218	-	0.16	6223	873	Rujido-Santos et al., 2022

^a Unpublished data.

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