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Enclosed (on line) please find an electronic copy of the manuscript entitled: **"Risk assessment due to dermal exposure of trace elements and indigo dye in jeans: Migration to artificial sweat",** which we are pleased to submit for publication in Environmental Research

Hoping that you will find our manuscript worthy of being published in Environmental Research, we look forward to hearing from you.

Sincerely,

Dr. Joaquim Rovira (on behalf of all authors)

Risk assessment due to dermal exposure of trace elements and indigo dye in jeans: Migration to artificial sweat

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The concentration of a number of trace elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Cr, Co, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sr, Sn, Tl, Ti, V and Zn) were determined in 42 commercialized denim garments (jeans and shirts), being dermal exposure subsequently assessed. Migration experiments with artificial acid and basic sweat were also conducted to determine the release of these elements, as well as indigo dye. In a similar way than for the total content, Mg (124 and 99.4 μg/g) and Mn (27.1 and 7.20 μg/g) showed the highest concentrations in both artificial sweat, acid and basic, respectively. Indigo dye migrated at levels ranged from 3.22 to 7.76 mg/g, being higher in dark than in light blue fabrics. The levels of trace elements and indigo were analysed according to materials of fabric, colour, brand, and eco-labelling. Using total content and migrations rates, dermal exposure to trace elements for adult men, women and teenagers were calculated under the two sweat extractions. Non-carcinogenic and carcinogenic risks due to dermal exposure to the elements here analysed in cloths were assessed. Both risks were in the limits of safe to according to international regulations. However, the maximum exposure to Sb reached a hazard quotient (HQ) of 0.3 in clothes partially made of polyester. Despite some authors have established that indigo is an agonist of the aril receptor, health risks due to exposure to indigo dye were not calculated due the lack of toxicological data.

Key words: trace elements, indigo, sweat migration, dermal exposure, jeans

1. Introduction

The presence of potentially hazardous substances in textiles is known. The process of production of the fabrics is associated with the addition of chemical elements and the presence of others substances resulting from the manufacturing itself. Clothing not only respond to the basic need to cover us, but it goes much further. Current research is working to obtain functional fabrics (Hoefer and Hammer, 2011; Richards et al., 2017), which means adding more compounds to the production.

Chemicals that can be found in the textiles are very diverse, being their presence widely studied. A number of studies have detected bisphenol analogues (Xue et al., 2017), biocides (Windler et al., 2013), pesticides (Cai et al., 2013; Hu et al., 2012), polycyclic aromatic hydrocarbons (Pukale et al., 2017; Wang et al., 2011), formaldehyde (Rizzi et al., 2016), phthalates (Brigden et al., 2012b; Gong et al., 2016; Negev et al., 2018), benzothiazole (Iadaresta et al., 2018; Kloepfer et al., 2004; Luongo et al., 2016), and dioxins and furans (Klasmeier et al., 1999) in textiles. In recent years, research has focused on trace elements such as heavy metals (Lorenz et al., 2012; Matoso and Cadore, 2012; Negev et al., 2018; Rovira et al., 2017a, 2017b, 2015), for the important number of applications they can have, such as antimicrobials, catalysers and flame retardants, among others (Brüschweiler et al., 2014; Bundesinstitut für Risikobewertung, 2012; Kajiwara and Takigami, 2013; Lorenz et al., 2012; Spielman-Sun et al., 2018). However, the use of these elements and compounds in the textile industry can mean a considerable environmental impact (Oliveira et al., 2018; Saxena, S. et al., 2017), which could also mean hazards for human health. Various studies associate the presence of these compounds with dermatitis, reduction of the micro flora of the skin, and allergies, among others (Giménez-Arnau, 2011; Mobolaji-Lawal and Nedorost, 2015; Walter et al., 2014).

Dyes means another concern. While some of them can be harmless, others, as disperse dyes (Hatch and Maibach, 2000), can be the cause of dermatitis (Dawes-Higgs and Freeman, 2004; Mobolaji-Lawal and Nedorost, 2015; Mohamoud and Andersen, 2017) and sensitisation (Heratizadeh et al., 2017). In addition, some studies show that azo dyes, the most used synthetic organic dyes in textiles, can have mutagenic (Brüschweiler and Merlot, 2017) and/or carcinogenic (Lyon, 2010) effects.

Some of the substances or elements that are added to the fibbers can be released during the normal use of the garments. The normal use of clothes lead to skin-cloth contact, and if the substances migrate from clothes to skin, dermal absorption cannot be considered as negligible. In recent years, some studies have shown the migration of some trace elements with sweat,

both extreme and normal sweating (Leme et al., 2014; Matoso and Cadore, 2012; Rovira et al., 2017b, 2015).

Jeans are probably the most popular garments in the world. Their industry has a revenue of more than 6000 million dollars per year (GlobeNewswire; P&S Market Research, 2017). In the manufacture process, take part numerous chemical agents -including dyes- are involved (Rathinamoorthy and Karthik, 2017). Indigo is one of the most used dyes, which gives jeans their characteristic blue colour. It is a dye mainly synthesized from products of fossil fuels, with a potential mutagenicity and carcinogenicity (Rannug et al., 1992), being able to activate a transcription factor that regulates the genes involved in xenobiotic metabolism, cell proliferation and differentiation (Adachi et al., 2001; Denison and Nagy, 2003). However, information on the characterization of the dyes and other products that can be found in commercial jeans is scarce in the scientific literature. Nowadays, studies about the possible presence of hazardous substances in clothes, have tended to focus on the random analysis of clothing sets, without involving a particular type or material (Brigden et al., 2012a). On the other hand, some studies have investigated the relationship between the manufacture of denim with occupational diseases (Akgun et al., 2008; Reinoso-Barbero et al., 2013) or with the environmental impact (Amutha, 2017).

Unfortunately, the available information about the content of trace elements, chemicals or dyes in denim and their behavior during the normal use of jeans is practically non-existent. In addition, risk studies of dermal exposure by skin-contact are also very limited (Avagyan et al., 2015; Luongo et al., 2014). The present investigation was aimed at determining the presence of a number of trace elements in 42 commercialized denim garments (jeans and shirts). Migration experiments with artificial sweat were also conducted to determine the concentrations of the trace elements, and also indigo dye. To the best of our knowledge, this is the first study on denim textiles, analysing such number of trace elements, as well as determining their migration and that of indigo dye to artificial sweat.

2. Materials and methods

2.1. Sampling

A total of 42 denim style clothes were randomly purchased at various stores and supermarkets of two cities (Reus and Tarragona) of Catalonia, Spain. These items included jeans (n=35) and shirts (n=7) of a wide spectrum of colours, from black (n=6) to white (n=4), and different tonalities of blue (n=26) and grey (n=6). Eleven of them were eco-labelled and 13 were

branded items. Details on material, colour, manufacture location, brand, and density are summarized in Table 1.

2.2. Microwave digestion

To analyse the concentrations of trace elements in clothes, a recently reported method was used (Rovira et al., 2017a). Briefly, a piece of each sample (0.3 g) was completely digested with 5 mL of HNO_3 (65% Suprapur, Merck, Germany) and 2 mL of H_2O_2 in a Milestone Start D Microwave Digestion System for 5 min at 105 °C, then 15 min at 180 °C , and finally 20 minutes at 200 °C. After cooling, extracts were filtered and brought to a volume of 25 mL with ultrapure water. As quality control, blanks and replicates were also analysed. Spinach leaves (1570a - National Institute of Standards and Technology, USA) were used as reference material. All materials in contact with samples and extracts were previously cleaned with a diluted (10%) HNO_3 solution.

Table 1. Main characteristics of the denim clothes analysed

Nº	Place	Materials	Colour	Made in	Density[a]	Comments
1	Hypermarket	84% C, 14% P, 2% E	Black	Bangladesh	319	
2	Hypermarket	95% C, 2% E	Grey	Bangladesh	373	Oeko standard 100
3	Hypermarket	95% C, 2% E	Dark blue	Bangladesh	372	Oeko standard 100
4	Hypermarket	82% C, 16% P, 2% E	Dark blue	Bangladesh	383	
5	Hypermarket	82% C, 16% P, 2% E	Blue	Bangladesh	351	Oeko standard 100
6	Hypermarket	100% C	Light blue	Turkey	355	
7	Hypermarket	40% C, 45%P, 15% V	Dark blue	Bangladesh	382	
8	Hypermarket	100% C	Blue	Pakistan	368	
9	Hypermarket	100% C	Dark blue	Spain	389	
10	Hypermarket	80% C, 18% P, 2% E	Black	Bangladesh	349	
11	Hypermarket	98% C, 2% E	Dark blue	Bangladesh	327	Shirt
12	Hypermarket	100% C	Light blue	Bangladesh	163	Shirt
13	Hypermarket	100% C	Blue	India	157	Shirt
14	Hypermarket	100% C	Light blue	India	125	Shirt
15	Chain Store	100% C	Light blue	Bangladesh	185	Shirt
16	Chain Store	100% C	Blue	Bangladesh	193	
17	Chain Store	98% C, 2% E	Grey	Bangladesh	731	
18	Chain Store	65% C, 35%P	Dark blue	Bangladesh	429	
19	Chain Store	98% C, 2% E	Black	Cambodia	391	
20	Chain Store	98% C, 2% E	Blue	Pakistan	396	
21	Chain Store	65% C, 35%P	Blue	Bangladesh	381	
22	Chain Store	98% C, 2% E	Light blue	Pakistan	410	
23	Chain Store	98% C, 2% E	White	Turkey	271	
24	Chain Store	98% C, 2% E	White	Turkey	361	Brand. Organic C
25	Chain Store	98% C, 2% E	Black	Bangladesh	301	Brand
26	Chain Store	100% C	Blue	Bangladesh	272	Brand
27	Chain Store	99% C, 1% E	Grey	Bangladesh	356	Brand
28	Chain Store	76% C, 23% P, 1% E	Blue	Bangladesh	310	Brand
29	Chain Store	75% C, 25% P	Black	NA	347	Bio C (70%)
30	Chain Store	81% C, 17% P, 2% E	Light blue	NA	339	
31	Chain Store	99% C, 1% E	Dark blue	NA	438	Bio C
32	Chain Store	98% C, 2% E	Grey	NA	421	
33	Brand Store	99% C, 1% E	Dark blue	China	504	Brand
34	Brand Store	69% C, 24% V, 6% E	Blue	China	427	Brand
35	Brand Store	93% C, 3% P, 4% E	Black	Tunisia	414	Brand
36	Brand Store	92% C, 6% P, 2% E	Blue	Bangladesh	402	Brand
37	Brand Store	93.5% C, 6% Em, 1.5% E	Dark blue	Bangladesh	467	Brand
38	Brand Store	98.5% C, 1.5% E	Grey	Bangladesh	468	Brand
39	Brand Store	100% C	Grey	Bangladesh	196	Brand. Shirt
40	Brand Store	100% C	Blue	Bangladesh	219	Brand. Shirt
41	Chain Store	100% C	White	China	417	
42	Chain Store	68% C, 30%P, 2% E	White	Bangladesh	341	

[a]Density, in g/m^2 ; C: Cotton; E: Elastane; P: Polyester; V: Viscose; Em: Elastomultiester; NA: Not available

2.3. Artificial sweat extraction test

Migration tests with artificial sweat allow to simulate the release of trace elements and indigo present in textiles, caused by the own normal transpiration of the skin. Approximately 1 g of dried sample was cut in small pieces (2 x 2cm) and introduced in a plastic vessel. Freshly prepared artificial sweat (25 mL) was added to each vessel, being incubated in a water bath for 24 hr at 37°C with a slight agitation. Once the incubation was completed, the sweat extracts were filtered. Two types of artificial sweat were made according to EN ISO 105-E04 standard (EN ISO 105-E04, 1996). Acidic artificial sweat was composed by 0.5 g of L-histidine monohydrochloride monohydrate, 5 g of NaCl and 2.2 g of $NaH_2PO_4 \cdot 2H_2O$ in 1 L of ultrapure water, being adjusted to pH 5.5 with NaOH 0.1 M. In turn, alkaline artificial sweat was prepared as follows: 0.5 g of L-histidine monohydrochloride monohydrate, 5 g of NaCl, and 5 g of $Na_2HPO_4 \cdot 12H_2O$, in 1 L of ultrapure water, being adjusted to pH 8.0 with NaOH 0.1 M. All materials in contact with samples and extracts were previously cleaned with a diluted (10%) HNO_3 solution. Blank and replicate samples were also extracted and analysed.

2.4. Determination of trace elements

In all samples, including standards, blanks and replicates, the concentrations of aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), samarium (Sm), scandium (Sc), selenium (Se), silver (Ag), strontium (Sr), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V) and zinc (Zn) were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan 6000) (Rovira et al., 2017b). Detection limits were the following: 0.02 μg/g for Cd; 0.04 μg/g for Ag, Be, Co, Mo and Sm; 0.08 μg/g for Ba, Bi, Hg, Mn, Ni, Pb, Tl and Sr; 0.21 μg/g for As, Cu and Sn; 0.42 μg/g for Al, B, Sb, Sc and Ti; 0.83 μg/g for Cr and V; 1.25 μg/g for Se and Zn; 4.17 μg/g for Fe, and 20.8 μg/g for Mg.

2.5. Indigo determination

It was based on the measurement of the absorbance of indigo, previous a reduction of the indigo from leuco to soluble form (Buscio et al., 2014). A reduction solution (200 mL/L 1-methyl-2-pyrrolidine, 10 g/L $Na_2S_2O_4$, 13 mL/L NaOH 33%) was used to reduce oxidized indigo. The indigo present in the standards and samples was reduced, being the absorbance read at

λ=407 nm in a spectrophotometer (Perkin Elmer, LAMBDA™ 35 Series UV/Vis Spectrophotometers). Calibration curves, one for each type of sweat, were obtained from five known concentrations. Blank, replicates and standards were analysed. The limit of detection was set at 0.01 mg/g.

2.6. Environmental scanning electron microscope (ESEM)

Environmental scanning electron microscope (ESEM) (FEI Quanta 600) attached to an energy dispersive X-ray (EDX) (Oxford Instruments INCA X-Sight, Abingdon, UK) with a backscattering detector (BSD) contrast by atomic number (Z), was used to evaluate the presence and composition of particles in clothing samples. ESEM working parameters were the following: low vacuum, 20 kV accelerating voltage, and 10 mm working distance.

2.7. Exposure and risk assessment

The concentrations of trace elements in cloth samples and their migration factors to artificial sweat were used to assess dermal exposure and the associated health risks. Exposure was calculated for adults -men and women- as well as for teenagers between 10 and 16 years old, considering jeans and shirts separately. Dermal exposure was calculated with equation 1, based on the European Chemical Agency (ECHA) (ECHA, 2016).

$$\text{Exp derm} = \frac{Fcloth \times dcloth \times Askin \times Fmig \times Fcontact \times Fpen \times Tcontact \times n}{BW} \quad \text{Equation 1}$$

where Expderm is the dermal exposure (mg/(kg·day)); Fcloth is the fraction of element in clothes (dimensionless); dcloth is the density of the clothing (mg/cm^2); Askin is the skin area covered by the clothing (in cm^2); Fmig is the migration fraction of substance from cloth to skin per day (1/day); Fcontact is the fraction of contact area for skin; Fpen is the penetration rate of the element (dimensionless); Tcontact is the duration of the clothing skin contact (d); n is the number of events per day (1/day), and BW is the body weight (kg). Fmig is considered equal to the quotient between levels of the element in artificial sweat extract and the total element level in the clothes. For those elements whose concentrations in artificial sweat were below the detection limit, a Fmig of 0.5% (Bundesinstitut für Risikobewertung, 2012) was assumed. The dermal exposure parameters are shown in Table 2.

The non-carcinogenic risks were assessed calculating the hazard quotient (HQ), which is defined as the quotient between exposure and dermal reference dose (RfD). The cancer risk was calculated multiplying the exposure by the respective dermal slope factor (SF). The dermal RfD was calculated multiplying the respective oral RfD by the gastrointestinal (GI) absorption factor, while dermal SFs were calculated dividing the respective oral SF by the GI absorption factor. RfDs and SFs were obtained from the Risk Assessment Information System (RAIS) (Risk and Information, 2018), with the only exception of oral RfD for Pb, which is not defined in the RAIS, being taken from Seiler et al. (1988). GI absorption factors were obtained from the U.S. EPA Preliminary Remediation Goals (US EPA, 2016).

Table 2. Dermal exposure parameters

Variable	Description	Value	Reference
Fcloth	Weight fraction of substance in cloth	Table 3	Present study
dcloth	Clothing density	Table 1	Present study
Askin	Jeans skin area adult man Jeans skin area adult women Jeans skin area teenager (10-16 years old) Shirt skin area adult man Shirt skin area adult women Shirt skin area teenager (10-16 years old)	6820 cm^2 5980 cm^2 4380 cm^2 11410 cm^2 8910 cm^2 8570 cm^2	(US EPA, 2011)
Fmig	Fraction of substance migrating to skin	Table 4 0.005	Present study (Bundesinstitut für Risikobewertung, 2012)
Fcontact	Fraction of contact area for skin	1	(Bundesinstitut für Risikobewertung, 2012)
Fpen	Fraction of penetration inside body	0.01 0.03 for As 0.1 for Indigo	(US EPA, 2016)
Tcontact	Contact duration between skin-textile	16h/day	Assumed
n	mean number of events per day	1/24	Assumed
BW	Body weight adult man Adult woman Teenager between 10-16 years old	70 kg 60 kg 46 kg	(Bundesinstitut für Risikobewertung, 2012) (US EPA, 2011) (Boniol et al., 2008)

2.8. Data analysis

For statistical purposes, results below the respective limit of detection (LD) were assumed to be equal to one-half of that limit (ND = ½ LD). Differences between groups were assessed using the Levine test to establish whether the data showed parametric distribution, or not. Subsequently, the ANOVA test for data following a parametric distribution, or the Kruskal-Wallis for non-parametric data, were used. A difference was considered as statistically significant when the probability was lower than 0.05 ($p<0.05$). The IBM SPSS Statistics software (version 25.0) was used.

3. Results and discussion

3.1. Concentration of trace elements

The concentrations of trace elements in the denim samples are shown in Table 3. Arsenic, Be, Bi, Cd, Hg, Sc, Se, Sm, Tl and V concentrations were below their respective detection limits in all samples, while Ag and Co were detected only in 4 and 7 samples, respectively. These findings are in accordance with the results of previous studies conducted in our laboratory (Rovira et al., 2017a, 2017b, 2015), when not detectable levels of these elements in clothes were also noticed. The highest mean levels corresponded to Mg (165 µg/g), Al (41.2 µg/g), Mn (37.6 µg/g) and Fe (37.2 µg/g). Individually, the highest concentration corresponded to Mg (505 µg/g), found in sample #29 (black, 75% cotton, 25% polyester), Mn (314 µg/g) in sample #15 (100% cotton) and Al (136 µg/g) in sample #4 (82% cotton, 16% polyester, 2% elastane).

Table 3. Concentrations (µg/g) of trace elements in skin contact clothing samples

n=42	% detected[a]	Mean	SD	Minimum	Maximum
Ag	10	0.02	0.01	<0.04	0.05
Al	100	41.2	40.4	4.01	136
B	50	0.77	0.79	<0.42	3.36
Ba	100	3.58	3.49	0.47	20.7
Co	17	0.04	0.04	<0.08	0.21
Cr	24	2.05	4.09	<0.83	16.6
Cu	93	2.23	2.45	<0.21	8.50
Fe	100	37.2	27.6	5.92	126
Mg	100	165	114	28.8	505
Mn	100	37.6	71.7	0.31	313
Mo	10	0.07	0.23	<0.04	1.37
Ni	62	1.92	3.98	<0.08	21.4
Pb	31	0.10	0.12	<0.08	0.49
Sb	40	11.4	19.0	<0.42	60.3
Sn	21	0.22	0.31	<0.21	1.79
Sr	100	8.41	13.0	0.85	65.9
Ti	95	6.19	5.68	<0.42	19.2
Zn	76	4.19	3.83	<1.25	13.9

[a]: percentage of samples with concentrations above the detection limit with respect to the total number of analysed samples (n=42). As, Be, Bi, Cd, Hg, Sc, Se, Sm, Sn, Tl and V concentrations were below their detection limits in all samples.

Not all denim clothes are made of the same material. Sungur and Gülmez (2015) reported that the type of fibre can affect the content of trace elements. For this reason, we divided the samples into 3 groups according to their composition: 100% cotton, cotton and synthetic threads without polyester, and cotton with synthetic threads of polyester. Taking the above into account, significant differences were found for B, Sb, Ti and Zn. Titanium showed

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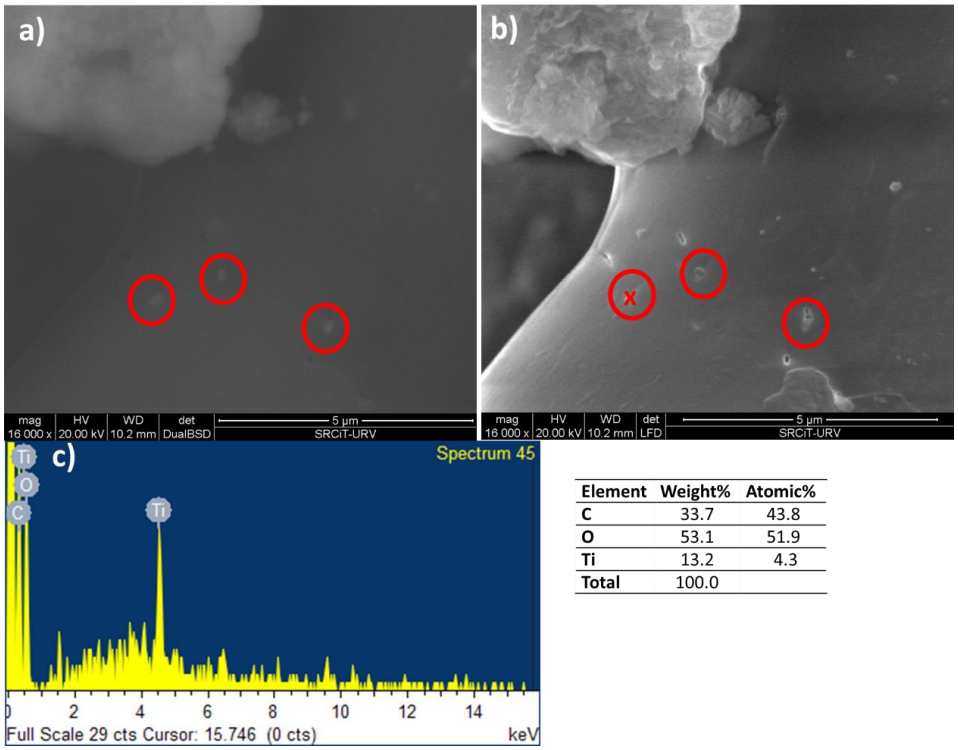
significant differences between all three material groups: clothes made 100% cotton (2.26 µg/g), synthetic fibbers with polyester (5.22 µg/g), and synthetic fibbers without polyester (11.3 µg/g). These results are in agreement with the results of previous studies (Boniol et al., 2008; Rovira et al., 2017b). Titanium oxide is used as delustrant for artificial fibbers such as spandex or nylon (Saxena et al., 2017), and it also provides UV protection to synthetic fibbers (Radetić, 2013). The presence of TiO_2 quasi-nanoparticles (around 220 nm of diameter) was confirmed by ESEM (Figure 1). In Figure 2b, it can be seen that these particles seems to be included inside the fibber, an important result in migration test, as commented in section 3.2.



Element	Weight%	Atomic%
C	33.7	43.8
O	53.1	51.9
Ti	13.2	4.3
Total	100.0	

Figure 1. Backscattering detector (BSD) image (a) and electron microscope image (b) of TiO_2 particles (inside red circles) found in sample #7 (cotton 40%, polyester 45% and viscose 5% dark blue jean). A red cross indicates where microanalysis were performed. Diameter of TiO_2 particles ranged from 210 to 230 nm.

Regarding Sb, its levels were significantly higher in samples with synthetic fibbers containing polyester (35.0 µg/g) than in other samples (synthetic fibbers without polyester (1.23 µg/g) and 100% cotton (0.21 µg/g)). A maximum level of 60.3 µg/g was found in sample #42, a jean that contained 35% polyester. It is important to remark that none of the analysed samples exceeded the limit value of 260 mg/kg, which is established by the ECOLABEL criteria

(European Commission, 2014). As expected, the garments with the highest polyester content had the highest concentration of Sb, which is due to the fact that antimony oxide is used during the manufacture of the itself polyester fibber, being employed as a catalyser during the polyester polymerization (Maerov, 1979). For boron, significant differences were noted between 100% cotton threads (1.41 μg/g) and synthetic, regardless of whether -or not- it contained polyester (0.49 and 0.48 μg/g, respectively). In garments with synthetic threads containing polyester, Zn levels (6.30 μg/g) were more than double, being significantly higher than in 100% cotton garments (2.46 μg/g). Zinc oxide antibacterial, antifungal and UV protection properties for polyester fibbers have been recently reported (Rimbu et al., 2013; Rode et al., 2015).

With respect to the colour, black garments (360 μg/g) had significant higher Mg levels than grey (156 μg/g), blue (137 μg/g) and white (74.7 μg/g) samples, being almost 5 times higher in the case of white garments. In addition of being used in textiles for its antibacterial properties (Bindhu et al., 2016; Navik et al., 2017), Mg is used in the form of mixtures of magnesium acetate, magnesium citrate and magnesium polyacrylate during the staining process of cotton fibbers (Moore, 1993). Its use as an alternative to the sodium chloride or sulphate salts make this process more respectful with the environment, which is known as ECO-Friendly dying processes (Gunasekar and Ponnusami, 2015). Taking into account the characteristic colour of denim, blue samples (n=26) presented higher levels of Fe than the other colours, 43.9 μg/g and 26.3 μg/g, respectively ($p<0.05$). However, no significant differences were found regarding the different shades of blue.

Samples with ecological label presented significant higher Cu levels, almost doubled, compared with other samples (3.90 vs. 1.77 μg/g). Samples #26 (blue, 100% cotton jean) and #31 (dark blue, 99%cotton and 1% elastane jean) showed the highest Cu levels: 8.11 and 8.50 μg/g, respectively. However, Cu is not considered in the ECO guidelines (European Commission, 2014) (Table 4). Only two elements (Cd and Pb) are considered in Oeko-tex Standard for their total content. In the current study, none of them exceeded this standard (40 and 90 μg/g for Cd and Pb, respectively).

3.2. Migration of trace elements and concentration of indigo in artificial sweat

To establish the amounts of trace elements and indigo dye that could be released wearing denim clothes, two migration tests were performed with acid and basic artificial sweats, in

order to obtain more representative results, taking into account that not all people have the same type of sweat. Results of these migration tests are given in Table 4.

Table 4. Concentrations of trace elements (μg/g) and indigo (mg/g) migrated to acid/basic artificial sweat per weight of sample.

	Acidic artificial sweat					Basic artificial sweat				
Element	%detected[a]	Mean	SD	Min	Max	%detected[a]	Mean	SD	Min	Max
Al	40	0.89	1.38	<0.50	7.89	19	0.48	0.64	<0.50	3.73
B	33	0.55	0.50	<0.50	2.01	19	0.44	0.51	<0.50	2.37
Ba	100	1.00	0.99	0.27	4.97	57	0.26	0.32	<0.10	1.92
Cu	43	0.60	1.04	<0.25	5.22	67	1.10	1.58	<0.25	7.22
Fe	10	2.98	1.59	<0.50	10.2	0	<0.50	-	-	-
Mg	95	124	103	<25.0	425	100	99.6	91.9	13.5	398
Mn	100	27.1	53.9	0.20	256	81	7.20	14.2	<0.10	52.6
Mo	5	0.03	0.01	<0.05	0.06	5	0.03	0.01	<0.05	0.08
Ni	26	0.11	0.13	<0.10	0.70	38	0.16	0.21	<0.10	1.04
Sb	5	0.27	0.08	<0.50	0.62	0	<0.50	-	-	-
Sr	100	4.94	6.96	0.80	31.6	90	2.99	2.99	<0.10	16.0
Zn	40	1.67	1.39	<1.50	5.49	31	1.79	1.72	<1.50	8.39
Indigo[b]	100	4.90	4.00	0.30	17.1	100	6.02	3.94	1.04	15.9

[a]: percentage of samples with concentrations above the detection limit with respect to the total number of analysed samples (n=42). As, Ag, Be, Bi, Cd, Co, Cr, Hg, Pb, Sc, Se, Sm, Sn, Ti, Tl and V concentrations were below their detection limits in all samples.
[b]: only the blue samples (n=26) were analysed.

There are differences between the trace elements found in the kinds of sweat. In the acid sweat extracts, the 50% of the total elements analysed migrated. However, in basic sweat this ratio was lower (39%). Moreover, these differences appear in the migration percentages of each element. The elements migrate more easily in acid sweat (ranging between 0.6% for Sb and 75.0% for Mg), where the two elements with the highest migration were Mg and Mn, 75.0% and 70.4%, respectively, followed by Ni (33.9%). The average migration range in basic sweat was 6.40% for B and 74.8% for Mg. Magnesium was the element showing a greater migration, 74.8%, followed by Ni (55.0%). The differences in the migration ratio were not statistically significant ($p>0.05$). Although the number of detected elements was lower, it should be noted that in the case of Al and Mg, the values were much higher in the basic sweat. It is also important to note that Sb only migrated in acid sweat and in two samples of jeans: #7 (0.58 μg/g) and #18 (0.62 μg/g), which had the highest polyester content, 45% and 35% respectively. In addition, as commented previously, Ti was not detected in sweat extracts which is due to the fact that TiO_2 particles were integrated inside the synthetic fibbers, preventing from migration (Windler et al., 2012).

Similarly than for the elemental total content, samples were grouped according to different characteristics to know if they influenced -or not- the levels of the migrated elements. Regarding the type of material from which the clothes are made, only B in the acid sweat

showed significant differences between clothes made 100% cotton (0.42 µg/g) and synthetic cloth without polyester (0.81 µg/g).

Based on the colour (black, grey, blue or white), in the extracts of acid sweat, similarly as in the digestion, significant differences were found for Mg, specifically between the black (292.2 µg/g) and the rest of colours (117.89, 97.5 and 47.7 µg/g for grey, blue and white samples, respectively). In the same line, similar differences ($p<0.05$) were found in Mg levels in basic sweat, being 244, 95.2, 75.8 and 36 µg/g for black, grey, blue and white respectively. Depending on they are blue garments or not, in acid sweat the differences between Ni levels were significant (0.14 and 0.06 µg/g in blue and other colours, respectively). However, no significant differences significant were observed in any element for the blue tonality. In contrast, in the basic sweat significant differences were found in the levels of Cu and Ni in the blue (1.5 and 0.2 µg/g for Cu and Ni, respectively) and non-blue (0.5 and 0.1 µg/g for Cu and Ni, respectively) garments. The concentrations of Ni extracted by the two sweats were well below the allowed values (4 mg/kg) (OEKO-TEX Association, 2017). Aluminium was the only element in which significant differences were found between the different shades of blue: dark and medium, and dark and light. With respect to the brand, only Al and B showed significant differences in acid sweat. There were no differences regarding the ECO garments.

In 2011, Greenpeace, started a Detox Campaign (Greenpeace International, 2011), whose objective was that the textile industry assumes responsibilities for the environmental impact that their activity produce, as well as to achieve the goal of zero dumping of hazardous chemicals by 2020. Within the framework of this campaign, the OEKO -TEX® Association also elaborated more restrictive limit values (OEKO-TEX Association, 2017) for some trace elements (Table 5).

Table 5. Trace elements limit (mg/kg) suggested to accomplish with different standards certification (OEKO-TEX Association, 2017)

	Oeko-tex Standard 100	Oeko-tex Standard 100 "Detox Campaign"
Extractable heavy metals		
As	1.0	0.2
Cd	0.1	0.1
Co	4	1
Cr	2	1
Cr (VI)	<0.5	<0.5
Cu	50	50
Hg	0.02	0.02
Mn	-	90
Ni	4	1
Pb	1.0	0.2
Sb	30	30
Zn	-	750
Heavy metals (digested sample)		
Cd	40	40
Pb	90	90

Comment [MH2]: Falta ref

The comparison of the current results with the limits summarized in Table 5, shows higher levels of Mg in 4 jeans and one shirt, being in some of them more than double (sample #2, for the Oeko-Standard 100 certification and sample #15). Although it is generally assumed that the dermal absorption of Mn is rather negligible (WHO, 1979), there are reports of cases of dermatitis or dermal irritation (Shallcross et al., 2014). Based on these new limit values, the maximum levels of Ni found in the current study, 0.70 and 1.04 μg/g, would not far below the limit value (1 mg/kg). It is well known that Ni may be the cause of dermatitis (Ahlström et al., 2018; Uter et al., 2018).

On the other hand, indigo was determined only in blue samples (n = 26). Indigo was released and detected in all blue samples extracts for both, acid and basic sweat (Table 4). Non-significant differences were found between acid (4.90 mg/g) and basic (6.04 mg/g) sweats. The highest concentration, 17.1 mg/g, was found in sample #31 (dark blue, 99% cotton - 1% elastane) in artificial acidic sweat, and in sample #21 (blue, 65% cotton - 35 polyester), 16.0 mg/g in basic sweat. No significant differences were noticed in migration levels in acid or basic sweat, according to the material, type of blue, brand and ecolabel. Despite that the differences did not reach the level of significance, higher concentrations were found in dark blue (6.70 and 7.76 mg/g in acid and basic sweat, respectively) than in blue (4.35 and 5.23 in acid and basic sweat, respectively) and light blue (3.22 and 5.25 in acid and basic sweat, respectively).

3.3 Human exposure and risk assessment

Dermal exposure was evaluated for adults, men and women, and teenagers between 10 and 16 years old under three different scenarios: wearing jeans, wearing denim shirts, and wearing the two garments, all in acid and basic sweat. For jeans, we assumed exposed surfaces of the legs and for shirts the surface of the trunk and the arms.

The exposure of these three scenarios is summarized in Table 6. Exposure would be slightly higher when the two items, jean and shirt, are combined with respect to wearing only jeans or only shirts. Manganese was the element with the highest mean exposure in all scenarios in men ($5.40 \cdot 10^{-3}$ and $4.92 \cdot 10^{-3}$ mg/(kg·day) for acid and basic sweat, respectively), women ($5.26 \cdot 10^{-3}$ and $4.83 \cdot 10^{-3}$ mg/(kg·day) for acid and basic sweat, respectively), and teenagers ($5.64 \cdot 10^{-3}$ and $5.08 \cdot 10^{-3}$ mg/(kg·day) for acid and basic sweat, respectively). For indigo, depending on the type of sweat, mean exposure was between 2.22 and 2.64 mg/(kg·day) for men, 2.16 and 2.59 mg/(kg·day) for women, and 2.32 and 2.74 mg/(kg·day) for teenagers (10 and 16 years). The maximum exposure was around 7 mg/(kg·day) for all the scenarios.

The hazardous quotient (HQ) was used to assess the non-carcinogenic risks derived from dermal exposure. In all scenarios, all HQs were below the threshold value, which is set at 1. The element with the highest HQ mean values was Sb, regardless of being a man, woman, or teenager. The maximum Sb values were higher than 0.1; between 0.1 and 0.3 in samples #7, #18, #21 and #42, whose fibbers contained between 30 and 45% of polyester.

Carcinogenic risks were only calculated for Cr and Pb, since they were the only detected elements for which an oral SF is established. The carcinogenic risk of Cr was in a range between 5.15×10^{-8} and 6.43×10^{-8}, with maximum values one order of magnitude higher (10^{-7}). In turn, the carcinogenic risk of Pb was in a range between 9.97×10^{-11} and 8.66×10^{-10}. For both elements, the carcinogenic risks were in an acceptable range.

Risk assessment of indigo was not calculated due the lack of toxicological data. There is an absence of knowledge regarding this substance, which is noticeable taking into account that indigo shows affinity for aryl receptor (AhR) (Rannug et al., 1992). Denison and Nagy (2003) stated that indigo is an AhR agonist (equipotent or 50 fold higher) than 2,3,7,8-tetrachlorodibenzo-p-dioxin in yeast, but between 50,000 and 100,000 fold less potent in mammal cells (Denison and Nagy, 2003).

Table 6. Human exposure to trace elements and indigo (mg/(kg·day)) due to contact with denim clothes[a].

	Men				Women				Teenagers (10-16 years old)			
	Acid sweat		Basic sweat		Acid sweat		Basic sweat		Acid sweat		Basic sweat	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
Ag	5.66×10^{-9}	6.21×10^{-9}	5.66×10^{-9}	6.21×10^{-9}	5.79×10^{-9}	6.35×10^{-9}	5.79×10^{-9}	6.35×10^{-9}	5.51×10^{-9}	6.05×10^{-9}	5.51×10^{-9}	6.05×10^{-9}
Al	3.43×10^{-5}	3.08×10^{-4}	9.73×10^{-5}	2.93×10^{-3}	3.12×10^{-5}	2.94×10^{-4}	9.94×10^{-5}	2.99×10^{-3}	3.50×10^{-5}	3.09×10^{-4}	9.51×10^{-5}	2.85×10^{-3}
B	6.47×10^{-6}	3.64×10^{-5}	3.88×10^{-6}	4.84×10^{-5}	6.61×10^{-6}	3.72×10^{-5}	3.95×10^{-6}	4.95×10^{-5}	6.33×10^{-6}	3.55×10^{-5}	3.80×10^{-6}	4.72×10^{-5}
Ba	4.11×10^{-5}	1.48×10^{-4}	1.02×10^{-5}	4.96×10^{-5}	4.04×10^{-5}	1.47×10^{-4}	1.01×10^{-5}	4.97×10^{-5}	4.25×10^{-5}	1.51×10^{-4}	1.05×10^{-5}	4.99×10^{-5}
Co	3.10×10^{-8}	4.04×10^{-8}	3.10×10^{-8}	4.04×10^{-8}	3.00×10^{-8}	3.96×10^{-8}	3.00×10^{-8}	3.96×10^{-8}	3.26×10^{-8}	4.18×10^{-8}	3.26×10^{-8}	4.18×10^{-8}
Cr	5.19×10^{-7}	3.61×10^{-6}	5.19×10^{-7}	3.61×10^{-6}	5.02×10^{-7}	3.51×10^{-6}	5.02×10^{-7}	3.51×10^{-6}	5.49×10^{-7}	3.78×10^{-6}	5.49×10^{-7}	3.78×10^{-6}
Cu	1.81×10^{-5}	1.24×10^{-4}	4.39×10^{-5}	2.24×10^{-4}	1.79×10^{-5}	1.25×10^{-4}	4.29×10^{-5}	2.23×10^{-4}	1.84×10^{-5}	1.23×10^{-4}	4.58×10^{-5}	2.26×10^{-4}
Fe	2.55×10^{-5}	2.05×10^{-4}	8.02×10^{-6}	2.48×10^{-5}	2.52×10^{-5}	2.06×10^{-4}	7.82×10^{-6}	2.42×10^{-5}	3.87×10^{-6}	1.15×10^{-5}	8.36×10^{-6}	2.57×10^{-5}
Mg	5.40×10^{-3}	1.75×10^{-2}	4.92×10^{-3}	2.94×10^{-2}	5.26×10^{-3}	1.71×10^{-2}	4.83×10^{-3}	2.94×10^{-2}	5.64×10^{-3}	1.84×10^{-2}	5.08×10^{-3}	2.95×10^{-2}
Mn	1.45×10^{-3}	1.01×10^{-2}	3.22×10^{-4}	2.32×10^{-3}	1.39×10^{-3}	9.73×10^{-3}	3.13×10^{-4}	2.27×10^{-3}	1.55×10^{-3}	1.07×10^{-2}	3.37×10^{-4}	2.40×10^{-3}
Mo	7.63×10^{-7}	1.48×10^{-6}	1.04×10^{-6}	2.18×10^{-6}	7.80×10^{-7}	1.51×10^{-6}	1.06×10^{-6}	2.23×10^{-6}	7.43×10^{-7}	1.44×10^{-6}	1.01×10^{-6}	2.12×10^{-6}
Ni	3.52×10^{-6}	2.31×10^{-5}	7.67×10^{-6}	3.62×10^{-5}	3.47×10^{-6}	2.29×10^{-5}	7.47×10^{-6}	3.57×10^{-5}	3.62×10^{-6}	2.36×10^{-5}	8.02×10^{-6}	3.72×10^{-5}
Pb	4.26×10^{-8}	7.48×10^{-8}	5.35×10^{-8}	5.92×10^{-8}	5.18×10^{-8}	8.44×10^{-8}	5.18×10^{-8}	6.06×10^{-8}	5.63×10^{-8}	8.74×10^{-8}	4.91×10^{-8}	7.66×10^{-8}
Sb	4.30×10^{-6}	1.73×10^{-5}	3.30×10^{-6}	7.40×10^{-6}	4.40×10^{-6}	1.77×10^{-5}	3.38×10^{-6}	7.57×10^{-6}	4.19×10^{-6}	1.68×10^{-5}	3.22×10^{-6}	7.20×10^{-6}
Sn	1.17×10^{-7}	2.54×10^{-7}	1.47×10^{-7}	2.84×10^{-7}	1.42×10^{-7}	2.82×10^{-7}	1.42×10^{-7}	2.82×10^{-7}	1.56×10^{-7}	2.89×10^{-7}	1.56×10^{-7}	2.89×10^{-7}
Sr	2.00×10^{-4}	9.17×10^{-4}	7.76×10^{-5}	4.45×10^{-4}	1.96×10^{-4}	9.21×10^{-4}	7.67×10^{-5}	4.49×10^{-4}	2.06×10^{-4}	9.19×10^{-4}	7.95×10^{-5}	4.43×10^{-4}
Ti	1.01×10^{-6}	2.75×10^{-6}	1.07×10^{-6}	2.88×10^{-6}	1.08×10^{-6}	2.91×10^{-6}	1.08×10^{-6}	2.91×10^{-6}	1.07×10^{-6}	2.85×10^{-6}	1.07×10^{-6}	2.85×10^{-6}
Zn	4.74×10^{-5}	1.85×10^{-4}	3.23×10^{-5}	2.53×10^{-4}	5.69×10^{-5}	2.15×10^{-4}	3.23×10^{-5}	2.54×10^{-4}	6.17×10^{-5}	2.27×10^{-4}	3.26×10^{-5}	2.54×10^{-4}
Indigo	2.22	7.03	2.64	6.46	2.16	6.95	2.59	6.33	2.32	7.19	2.74	6.70

[a] Jeans (n=35) and shirts (n=7).

Total content of As, Be, Bi, Cd, Hg Sc, Se, Sm, Tl and V were below the respective detection limit and were not considered to assess human exposure.

4. Conclusions

In this study, we determined the concentrations of a number of trace elements, which are present in denim cloth, and the migration to artificial sweat (acid and basic) of these elements and indigo dye. These levels were studied according to the materials of fabric, colour, brand, and eco-labelling. Antimony and Zn showed higher levels in fabrics containging polyester than in other fabrics. In relation to the colour, Mg and Fe presented higher contents in black and blue colour, respectively. Copper showed higher levels in eco-labelled samples. Taking into account the migration with artificial sweat of trace elements and indigo, significant differences were not found.

Manganese was the element with the highest mean exposure in all scenarios in men ($5.40 \cdot 10^{-3}$ and $4.92 \cdot 10^{-3}$ mg/(kg·day) for acid and basic sweat, respectively), women ($5.26 \cdot 10^{-3}$ and $4.83 \cdot 10^{-3}$ mg/(kg·day) for acid and basic sweat, respectively) and teenagers ($5.64 \cdot 10^{-3}$ and $5.08 \cdot 10^{-3}$ mg/(kg·day) for acid and basic sweat, respectively). Carcinogenic and non-carcinogenic risks for element dermal exposure to denim cloths were in acceptable ranges (HQ<1 and CR<10^{-6}), being between 0.1-0.3 the highest HQ due to Sb exposure. No health risks were estimated for indigo due the lack of toxicological values.

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