UNIVERSITAT ROVIRA I VIRGILI

EXPOSICIÓN A SUSTANCIAS QUÍMICAS A TRAVÉS DE TEXTILES: EVALUACIÓN DE RIESGOS PARA LA SALUD

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Exposición a sustancias químicas a través de textiles: Evaluación de riesgos para la salud

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CERTIFICAN

Que la presente tesis doctoral, titulada "Exposición a sustancias químicas a través de textiles: Evaluación de riesgos para la salud" presentada por Marta Herrero Casado para la obtención del grado de Doctora, ha sido realizada bajo nuestra supervisión en el Departamento de Ciencias Médicas Básicas de la Universidad Rovira i Virgili, y cumple todos los requisitos para optar a la Distinción de Doctor Internacional.

Reus, Septiembre 2023

Dr. Joaquim Rovira Solano

Dr. Martí Nadal Lomas

A mi padre

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ABREVIATURAS

A

Ag: Plata

Al: Aluminio

As: Arsénico

B

B: Boro

Ba: Bario

Be: Berilio

Bi: Bismuto

BPA: Bisfenol A

BPA_{d16}: Bisfenol A deuterado

BPB: Bisfenol B

BPE: Bisfenol E

BPF: Bisfenol F

BPS: Bisfenol S

BPs: Bisfenoles

BW: peso corporal (*body weight*)

C

C: Algodón (*Cotton*)

Ca: Calcio

Cd: Cadmio

CMC: Carboximetilcelulosa

Co: Cobalto

CR: Riesgo de cáncer (*Cancer Risk)*

Cr: Cromo

Cu: Cobre

CV: Coeficiente de variación

D

DBO: Demanda bioquímica de oxígeno

DL: Límite de detección (*Detection Limit*)

dl-PCBs: PCBs con efecto dioxina

DNA: Ácido desoxirribonucleico

DQO: Demanda química de oxígeno

DR: Rango de detección (*Detection Rate*)

E

E: Elastano

ECHA: Agencia química europea (*European Chemical Agency*)

EDC: Disruptor endocrino (*Endocrine Disrupting Chemical*)

EDTA: Disódicoetilendiaminotetraacético

EE.UU: Estados Unidos

EDX: Energy dispersive X-ray

EFSA: Agencia Europea de Seguridad Alimentaria (*European Food Safety Agency*)

EH: 2-etil hexanol

ESEM: Microscopio electrónico de barrido ambiental (*Environmental scanning electron microscope*)

F

Fe: Hierro

G

GC-MS: Cromatografía de gases - espectrometría de masas

GI: Gastrointestinal

GOTS: Global Organic Standard Textiles

H

Hg: Mercurio

H_2O_2: Agua oxigenada

HNO_3: Ácido nítrico

HQ: Cociente de peligrosidad (*hazardous quocient)*

H_2SO_4: Ácido sulfúrico

I

IARC: Agencia Internacional para la Investigación del Cáncer (*International Agency for Research on Cancer*)

ICP-Ms: Espectrometría de Masa con Plasma Acoplado Inductivamente (*Inductively Coupled Plasma Mass Spectrometry*)

IISPV: Institut d'investigació Sanitària Pere Virgili

IUR: Unidad de riesgo de inhalación (*inhalation unit risk*)

L

LOAEL: Efecto más bajo observado (*Low Observed Effect Level*)

LOD: Límite de detección

M

Mg: Magnesio

Mn: Manganeso

Mo: Molibdeno

N

NA: No aplica

NaCl: Cloruro de sodio

NaH_2PO_4: Fosfato sódico

ND: No detectado

ndl-PCBs: PCBs sin efecto dioxina

Ni: Niquel

NPMs: Nanopartículas metálicas

NOAEL: Dosis sin efectos observados (*No Observed Effected Level*)

NTA: Ácido nitrilotriacético

P

P: Poliéster

PA: Poliamida

Pb: Plomo

PCBs: Bifenilos policlorados

PBDE: Éteres difenílicos polibromados

PCDD/Fs: Policlorodibenzo-*p*-dioxinas, policlorodibenzofuranos

PDMS: Amidas de poli dimetil siloxano

PFAS: Sustancias perfluorades y polifluoradas

ppb: Partes por billón

ppm: Partes por millón

PVA: Alcohol polivinílico

R

RAIS: Sistema de información sobre evaluación de riesgos (*Risk Assesment Information System*)

REACH: Registro, evaluación, autorización y restricción de sustancias químicas (*Registration, Evaluation, Authorisation and restriction of CHemicals*)

RfD: Dosis de referencia (*reference dose*)

S

Sb: Antimonio

Sb_2O_3: Trióxido de antimonio

Sc: Escandio

Se: Selenio

SF: Factor de potencia cancerígena (*Slope Factor*)

Sm: Samario

Sn: Estaño

Sr: Estroncio

SVOCs: Compuestos orgánicos semivolátiles (*Semi-volatile Organic Compounds*)

T

TDS: Sólidos disueltos totales

TBP: Fosfato de tributilo

Ti: Titanio

TiO_2: Dióxido de titanio

Tl: Talio

TNK: Nitrógeno total Kjeldahl

U

URV: Universitat Rovira i Virgili

US EPA: Agencia de Protección Ambiental de EE.UU (*United States Environmental Protection Agency)*

UV: ultravioleta

V

V: Vanadio

Z

Zn: Zinc

RESUMEN

La industria textil contribuye en gran medida a la contaminación mundial. Es la responsable del 10% de las de las emisiones totales de dióxido de carbono (CO_2) y de la contaminación de aproximadamente del 20% de la contaminación mundial de agua potable. Las sustancias tóxicas utilizadas durante los procesos de fabricación de los tejidos son las principales fuentes de contaminación asociadas a este tipo de industria.

La presencia de sustancias químicas en la ropa ha sido objeto de estudio en los últimos años. Ésta se debe al uso de las mismas durante las diferentes etapas de fabricación de los tejidos y/o como resultado de la propia fabricación. Además, las prendas de vestir hoy en día no sólo responden a la necesidad básica de cubrir el cuerpo. Actualmente se busca cubrir unas demandas del mercado muy específicas como por ejemplo prendas de fácil planchado, resistentes al calor, impermeables, que protejan contra los rayos UV… incluso ya se está investigando en prendas funcionales. Y todo ello es posible gracias al uso de sustancias químicas. Desgraciadamente, el uso de alguna de estas sustancias químicas resulta tóxico tanto para el medio ambiente como para los seres humanos. Sus efectos negativos en la salud humana abarcan desde pequeñas y puntuales reacciones cutáneas, dermatitis hasta algunos tipos de cáncer.

La evaluación de riesgos permite determinar los posibles efectos adversos sobre un organismo, sistema o población derivados de la exposición a un agente o sustancia química. Sus principales etapas son la identificación del peligro, la caracterización del peligro, la evaluación de la exposición, la caracterización del riesgo, gestión de riesgo y comunicación del riesgo.

Esta tesis se ha realizado con el objetivo de evaluar el riesgo para la salud debido a la exposición dérmica a elementos químicos y otras sustancias presentes en la ropa y utilizadas ampliamente por la industria textil. Debido al contacto directo de la ropa con la piel, en este caso, la evaluación de riesgos se realiza en torno a la exposición dérmica.

En el *Capítulo 1* se ha determinado la presencia de metales y metaloides en 42 prendas vaqueras y 39 bañadores. Los metales y metaloides aportan una mayor impermeabilidad y/o transpirabilidad a la ropa como resultado de su adición voluntaria durante la fabricación de los tejidos. Sin embargo, otros metales son inherentes del tejido, como es el caso del antimonio (Sb) en las fibras de poliéster, o forman parte de los pigmentos utilizados para dar color a los tejidos, como es el caso del cadmio (Cd) y el cromo (Cr). Además, actualmente, se utilizan combinaciones de metales, conocidas como nanopartículas metálicas (NPMs) que aportan propiedades antibacterianas y bloqueo de rayos UV. Los resultados obtenidos muestran como la presencia de metales es dependiente del color y del tipo de fibra con el que están fabricadas las prendas de ropa. Las prendas de color oscuro presentan niveles más altos de Cr, cobre (Co) y plomo (Pb) que la ropa de colores claros. Así como las prendas fabricadas con fibras de poliéster contienen más Sb y las fabricadas con poliamida contienen más titanio (Ti).

Con el objetivo de conocer que metales y metaloides son capaces de liberarse de las prendas con el uso diario, se realizaron dos test de migración con sudor artificial, uno con sudor ácido y otro con sudor básico para obtener unos resultados más representativos. Se observó que hay diferencias entre los dos tipos de sudores, siendo la migración de los metales y metaloides superior en el sudor ácido.

El índigo es el colorante causante de la típica coloración azul tan característica de la ropa vaquera. Se le atribuyen un potencial mutagénico y carcinogénico, además poderse desprender ligeramente del tejido sobre todo cuando las prendas son nuevas. Por ello también se analizó el contenido de índigo en los extractos de sudor. Del mismo modo que en los resultados de metales y metaloides, el extracto de sudor ácido libera más índigo que el sudor básico.

La evaluación de riesgos realizada con datos obtenidos en los estudios realizados concluye que la exposición a metales y metaloides es mayor cuanta más superficie corporal es cubierta por la ropa. El cociente de peligrosidad (HQ) utilizado para evaluar los riesgos no cancerígenos fue inferior a 1 en todos los metales y metaloides evaluados tanto para las prendas vaqueras como para la ropa de baño. Los riesgos cancerígenos para el Cr y Pb fueron admisibles en el caso de las prendas vaqueras al presentar un riesgo de cáncer (CR) inferior a 10^{-6}. Sin embargo, en el caso de los bañadores, el Cr supera el valor aceptable en los grupos de bebés y en niñas con edades comprendidas entre los 3 y 6, y 6 y 11 ambos grupos, cuando utilizan un bañador completo.

En el *Capítulo 2* se determinó y evaluó a los bifenilos policlorados en 10 *bodies*. Los bifenilos policlorados (PCBs) son compuestos organoclorados que están presentes en la ropa debido a que forman parte de algunos tintes o pigmentos, sobre todo en los de coloración amarilla. Su exposición se asocia al desarrollo de melanomas malignos, problemas neurológicos y cardiovasculares y con efectos antiandrogénicos y estrogénicos, entre otros. Los resultados obtenidos muestran que el tipo de congénere que predomina en las prendas analizadas, son los PCBs sin efecto dioxina (ndl-PCBs), además de confirmar que su presencia está relacionada con los pimientos amarillos. Los riesgos asociados a su exposición, HQ y CR, estuvieron por debajo de los límites de peligrosidad, tanto para los PCBS con efecto dioxina (dl-PCBs) como para los ndl-PCBs.

En los siguientes capítulos se evaluaron los riegos de formaldehído y diferentes bisfenoles en las mismas prendas de vestir correspondientes a los grupos de población de mujeres embarazadas, recién nacidos y niños.

Los riegos derivados de la exposición a formaldehído se evaluaron en el *Capítulo 3*. Inicialmente, el formaldehído se introdujo en la industria textil por su efecto antiarrugas pero sus características lo han posicionado como un buen fijador de color, agente blanqueante y endurecedor de fibras. Sus principales efectos adversos son la sensibilización de la zona expuesta, aparición de eczemas y dermatitis. Pero, a pesar de que su absorción dérmica no es muy elevada, se ha relacionado su presencia con una mayor proliferación celular en algunos tipos de melanomas. El porcentaje de detección del formaldehído fue de un 19 %, siendo las prendas de vestir para mujeres embarazadas. De nuevo, la evaluación de riesgos asociada a la exposición al formaldehído muestra como a mayor superficie corporal cubierta, mayor exposición, siendo los bebés con edades inferiores a 12 meses los que presentaban una exposición dérmica más elevada. Los riesgos no cancerígenos se mantuvieron inferiores al límite (1). No es el caso del riesgo de cáncer para los niños/as que combinaran camisetas con pantalones que superarían el límite establecido (10^{-6}).

En el caso de la experimental de bañadores no se detectó formaldehído en ninguna de las 39 prendas analizadas.

Por último, en el *Capítulo 4*, se evaluaron los riesgos asociados a la exposición de diferentes bisfenoles (BPs): bisfenol A (BPA), bisfenol B (BPB), bisfenol F (BPF) y bisfenol S (BPS). Los BPs son uno de los grupos químicos más producidos y utilizados por la industria, incluyendo a la industria textil. Su uso se debe a su efecto protector sobre las fibras, sobre todo en las sintéticas, aportando una mayor resistencia del color en los lavados. El principal riesgo de estas sustancias se debe a su efecto sobre el sistema endocrino, con especial afectación del sistema reproductivo, y su absorción placentaria que provocaría bajo peso al nacer y problemas de neurodesarrollo en recién nacidos. Se detectó la presencia de BPA en la totalidad de las prendas, siendo las prendas de mujeres embarazadas las que más niveles presentaban. Nuevamente la presencia de los diferentes tipos de bisfenoles está asociada al tipo de material, detectando concentraciones más elevadas en las fibras poliéster respecto a las fibras de algodón. También se observó una relación entre los bisfenoles y los diferentes colores. En este caso el BPA y el BPF predominan en la ropa gris, mientras que el BPS predomina en la ropa negra. La evaluación de riesgos mostró el BPA es el análogo del bisfenol que presenta mayor exposición dérmica siendo las mujeres embarazadas el grupo de población con valores de exposicón más altos. Los valores de HQ correspondientes a los riesgos no cancerígenos se mantuvieron por debajo de 1.

En los últimos años, el fenómeno conocido como "eco-friendly" ha experimentado un gran crecimiento. En la industria textil, este movimiento se traduce en mayor calidad de las prendas, reducir la huella de carbono utilizando materiales naturales u orgánicos, reducción del uso de sustancias tóxicas durante el proceso de producción y minimizar el impacto en el medio ambiente. Por ello, en los capítulos 2, 3 y 4 se tuvo especial atención a las prendas fabricadas con algodón orgánico. Los resultados obtenidos muestran como las prendas fabricadas con algodón orgánico contienen niveles más elevados de algunos metales (aluminio (Al), boro (B), bario (Ba), hierro (Fe), magnesio (Mg), manganeso (Mn), Sb y Ti) y también de formaldehído. Por el contrario, éstas contienen niveles más bajos de BPA.

Resumiendo, a pesar de los intentos de la industria textil por reducir el uso de sustancias tóxicas en sus procesos de producción, la presencia de sustancias tóxicas en las prendas de vestir es difícil de ignorar. Además, esta presencia está asociada al tipo de fibra, siendo las fibras de algodón las que más formaldehído contienen, Sb, BPA y BPS serían mayoritarios en las fibras de poliéster y el Ti en las fibras de poliamida. El color también influye en estos niveles siendo las prendas de colores oscuros las que contienen niveles más altos de Mg, Cr, Cu y Pb, BPS. Los PCBs serian mayoritarios en las prendas de tonalidades amarillas y el BPA en las prendas de color gris. Desgraciadamente, las prendas fabricadas con algodón orgánico no están libres de sustancias tóxicas ya que algunas contienen niveles más altos de metales y formaldehído. En términos generales la evaluación de riesgos es positiva, exceptuando a los grupos de población de bebés y niñas con edades comprendidas entre los 3 y 6 años, en los que el CR fue ligeramente superior al umbral para el Cr (VI).

Introducción

1. LA INDUSTRIA TEXTIL Y EL USO DE SUSTANCIAS QUÍMICAS

La ropa es, por definición, el conjunto de prendas de vestir y accesorios confeccionados a partir de tejidos textiles o de tejidos animales cuya finalidad es abrigar, cubrir, proteger y adornar el cuerpo (RAE, 2022). Según algunos indicios arqueológicos, entre los años 35.000 y 10.000 a.C., el ser humano empezó a usar prendas de cuero para cubrir su cuerpo, pero no fue hasta el Neolítico, entre el 9.000 y 4.000 a.C., cuando el ser humano aprende a tejer e hilar fibras vegetales y animales como el cáñamo, el lino y la lana, dando así origen a los tejidos textiles como tal. Poco después, la vestimenta dejó de utilizarse sólo para cubrir el cuerpo y fue usada por muchas civilizaciones como un símbolo de identidad, que se ha mantenido constante en la historia. Además, las técnicas fueron perfeccionándose obteniendo así tejidos mucho más resistentes que permitieron que se utilizaran como recipientes (cestos o sacos), como transporte (camillas) e incluso como materiales de construcción en las jaimas (Andrés y Alcalde, 2020).

La revolución industrial aportó un gran avance en la maquinaria, lo que supuso una fabricación más rápida y a menor coste, naciendo así las cadenas de montaje y dejando en un segundo plano la producción artesanal. En el siglo XX aparecen las primeras fibras sintéticas. En 1935, Wallace Carouthers descubre el Nylon 6.6 y en 1941, John Whinfield y James Dickson descubren el poliéster. La llegada de estas fibras fue una auténtica revolución, no sólo por su bajo coste de producción sino por la multitud de ventajas que presentaban respecto a las fibras naturales existentes, como mayor ligereza, más resistencia, etcétera. A pesar de ello, no las sustituyeron por completo, sino que pasaron a formar parte del amplio abanico de fibras textiles existente (Flory et al., 2016; Xu et al., 2018).

En la última década se ha desarrollado un creciente interés por los tejidos funcionales, textiles con acabados muy específicos, casi a gusto del consumidor. Desde cualquier color o estampado, a textiles antibacterianos, antiácaros, antimanchas, impermeables, destruye olores, antiarrugas, antiestáticos o ignífugos (Grgac et al., 2020; Richards et al., 2018; Roy Choudhury, 2017; Xin y Lu, 2017). De hecho, la innovación en el sector textil no cesa, pues los últimos avances se centran en los llamados textiles inteligentes (de Oliveira et al., 2022; Nikolova et al., 2021).

Todo este progreso ha sido posible gracias a la mejora constante de las técnicas, pero también gracias al uso de aditivos durante los procesos de fabricación. Durante toda la historia, la industria textil y las sustancias químicas han ido de la mano.

1.1. Fases de producción y sustancias químicas

La producción de los tejidos textiles es un proceso relativamente complejo que dependerá del tipo de fibra, pero podría resumirse en las etapas de hilatura, tejeduría, tintura, acabado y, por último, confección del producto final (Figura 1.1). En estas etapas, las sustancias químicas tienen una gran relevancia ya que están presentes en la mayoría de ellas, formando parte de los diferentes procesos por los que pasan las fibras. La Tabla 1.1 resume las principales sustancias utilizadas durante el proceso de producción textil.

1.1.1. Encolado

Es el primer paso en la producción de textiles. Se añaden carboximetilcelulosa (CMC), alcohol polivinílico (PVA), poliacetato y/o ácidos policíclicos a las fibras, independientemente de su origen, para que éstas puedan soportar la tensión y al abrasión de los procesos posteriores (Kishor et al., 2021).

1.1.2. Descrudado/Desengrasado

Procesos para eliminar todas las impurezas que puedan quedar en las fibras y que pueden interferir en los procesos posteriores. Se utilizan compuestos aniónicos (etoxilato de alcohol y etoxilato de alquilfenol), agentes alcalinos (hidróxido de sodio, glicerol), agentes humectantes, quelantes combinados con grandes cantidades agua y diferentes temperaturas. El tipo de sustancias químicas que se utilizarán en este proceso dependerá del origen de la fibra, la cual determina el tipo de impurezas (Hauser, 2015; Kishor et al., 2021).

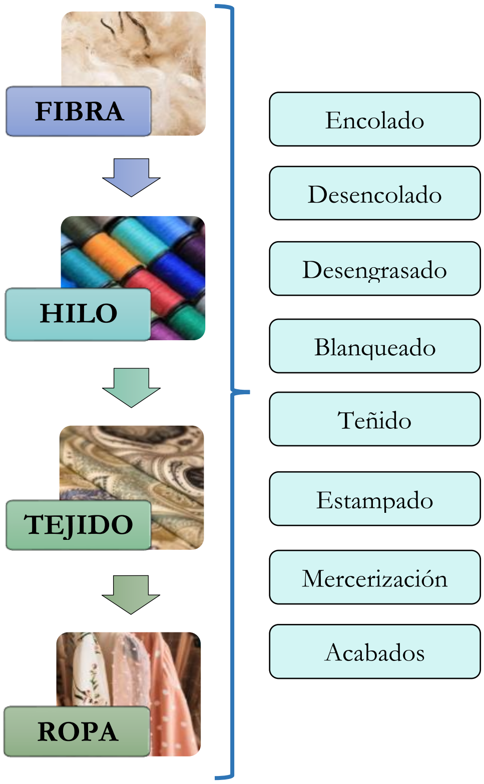

Figura 1.1. Etapas del proceso de manufactura textil.

1.1.3. Blanqueo

Proceso que permite evitar coloraciones no deseadas en las fibras. Los compuestos más utilizados son el hipoclorito o el clorito y el peróxido de hidrógeno junto a compuestos auxiliares como estabilizadores, agentes humectantes, activadores y anticorrosivos. Normalmente este proceso sólo es necesario en las fibras naturales. (Hauser, 2015; Kishor et al., 2021).

Tabla 1.1 Principales productos químicos utilizados en la manufactura de productos textiles (Kant, 2012; Katheresan et al., 2018; Markandeya et al., 2022).

Acetato	Disolventes orgánicos
Ácido acético	Emulsión de poliestileno
Ácido clorhídrico	Hidrosulfatos
Ácido fórmico	Hidrosulfitos
Ácido hiperclórico	Isotiazolinonas
Ácido oxálico	Jabón
Ácido sulfúrico	Organotina
Acrilatos	Parafina y polietileno
Agente de nivelación y dispersión	Peróxido de hidrógeno
Agentes humectantes	Resinas orgánicas
Agentes quelantes	Soda cáustica
Amoníaco	Suavizante
Ciclohexanol	Sulfato de amonio
Clorato de sodio	Sulfatos de alcohol
Clorato sódico	Sulfatos y sulfitos
Colorantes y pigmentos	Tensioactivos aniónicos
Compuestos de Cr	Tensioactivos no iónicos
Diclorofenilo	Triclosano
Disolventes	Urea

1.1.4. Mercerización

Este proceso utiliza la sosa cáustica, sulfatos de alcohol, productos tensioactivos aniónicos y/o ciclohexanos para mejorar las propiedades de las fibras, aportando mayor resistencia y afinidad de éstas por los tintes (Hauser, 2015; Kishor et al., 2021).

1.1.5. Teñido/Tintura

Es el proceso por el cual se le da color al material. Puede realizarse en cualquiera de las etapas del proceso de manufactura, desde el inicio, en la hilatura, hasta incluso una vez terminada la prenda de ropa. Este proceso incluye también las fases de preparación del tinte, teñido, fijación, lavado y secado, hecho que aumenta la cantidad de sustancias químicas utilizadas (Kishor et al., 2021).

Las opciones de clasificación de los tintes textiles son diversas, variando en función de su origen, estructura química o también solubilidad, entre otros parámetros. Según su aplicación industrial, los tintes pueden clasificarse en dispersos, directos, reactivos, de cuba, básicos, de azufre y azoicos.

a) Tintes dispersos: la mayoría de ellos presentan estructuras azoicas, aunque algunos se basan en estructuras derivadas de la antraquinona. Se utilizan sobre fibras sintéticas, poliéster, poliamida, acetato de celulosa y fibras acrílicas principalmente. Son insolubles o poco solubles en agua, además de ser persistentes y no biodegradables (Nikfar y Jaberidoost, 2014).

b) Tintes directos: su estructura incluye azo, estibeno, oxazina y ftalocianina, con algunos tintes azoicos de tiazol y complejos de cobre. Estos tintes tienen gran afinidad por las fibras celulósicas.

c) Tintes reactivos: estos tintes están formados por dos grupos químicos, el primero es un derivado grupo azo, antraquinona o ftalocianina que está conectada a un segundo grupo reactivo (vinilsulfona monoclorotriazina, diclorotriazina, difluoropirimidina o dicloroquinoxalina). Estos tintes se utilizan en fibras de celulosa, seda, lana o poliamidas (Nikfar y Jaberidoost, 2014).

d) Tintes de cuba: se utilizan principalmente para dar color a las fibras de algodón, lino, lana y rayón. Se caracterizan por su resistencia a luz y a la humedad. Son solubles en agua caliente pero insolubles en agua fría.

e) Tintes básicos: Normalmente se aplica en acrílicos, papel y nylon. Pueden tener la carga positiva localizada en un grupo de amonio o la carga deslocalizada que se encuentra en muchos triarilmetanos, xantenos y acridinas. A menudo contienen cloruro de zinc (Sharma et al., 2021).

f) Tintes ácidos: contienen un grupo ácido sulfónico y son solubles en medios alcalinos. Se utilizan para teñir poliamida, algodón y lana (Nikfar y Jaberidoost, 2014).

g) Tintes de azufre: son un tipo de colorante de cuba. Se aplican sólo en fibras celulósicas (Burkinshaw y Salihu, 2019).

h) Tintes azoicos: Se caracterizan por tener el grupo funcional (-N = N-) que une dos radicales alquilo o arilo simétricos y/o asimétricos idénticos o no azoicos (Mittal et al., 2010). Son los más utilizados en la industria textil pero al mismo tiempo la mayoría de ellos son tóxicos, cancerígenos y no biodegradables (Berradi et al., 2019).

En el proceso de tintura, además de los tintes, también intervienen los auxiliares de tintura, productos químicos que permiten que el proceso de tintura se lleve a cabo con una mayor eficacia y eficiencia (Mamun y Koh, 2020).

1.1.6. Estampado e impresión

A diferencia del proceso de tintura, que tiñe todo el material de manera homogénea, en la impresión o estampado la aplicación del color se centra sólo en un área definida, obteniéndose así un patrón muy concreto. Es un proceso que a nivel mecánico y de maquinaria implica grandes diferencias con la etapa anterior, pero a nivel químico, las sustancias utilizadas no se diferencian demasiado. Los tintes, ftalatos, metales, disolventes, formaldehído y urea son las sustancias más utilizadas en esta fase (Kishor et al., 2021). Los principales tipos de auxiliares de tintura y de impresión, así como sus funciones quedan resumidos en la Tabla 1.2.

1.1.7. Acabados

El acabado es la etapa final del proceso textil. En ella se realizan los tratamientos mecánicos o químicos para mejorar la fibra, el hilo o el tejido. La variedad de acabados es muy amplia y algunos de ellos casi a gusto del consumidor. Desde los acabados tradicionales, como por ejemplo antiarrugas (Lou et al., 2022) o impermeables (Siddig et al., 2020), hasta textiles antimosquitos, con protección solar (Singh y Sheikh, 2022) e incluso e-textiles (Avellar et al., 2022).

Tabla 1.2. Principales tipos de auxiliares de tintura e impresión utilizados en los textiles y su función (Mamun y Koh, 2020).

Tipo de auxiliar	Función	Ejemplos
Agentes quelantes	Eliminar la dureza del agua mediante su unión a metales pesados	Ácido glicólico, ácido glucónico, ácido disódicoetilendiaminotetraacético (EDTA) y ácido nitrilotriacético (NTA)
Agentes dispersantes	Romper las partículas de colorante agregadas y dispersar el tinte en el líquido colorante.	Sulfonato de dinaftilmetano y lignosulfonato
Agentes niveladores	Contribuir a la uniformidad del teñido.	Aminas polietoxiladas
Electrolitos	Dirigir el colorante hacia el material, agotar las moléculas de colorante y fijar el colorante en el tejido.	Sulfato de sodio deshidratado, bicarbonato y sal (NaCl)
Agentes antiespumantes	Reducir la formación de micro y macro espumas.	2-etil hexanol (EH), fosfato de tributilo (TBP), amidas de poli dimetil siloxano (PDMS), aceite mineral, ácidos grasos y sus derivados
Agentes reductores	Reducir el tinte, sobre todo en los baños de cuba.	Ditionato de sodio, formaldehído sulfoxilato de sodio, glucosa, fructosa y melaza
Agentes antiarrugas	Reducir la formación de arrugas	N-Hidroxietil acrilamida, derivados de aziridina y precursores de divinil sulfonas

Tabla 1.2 (Continuación)**.** Principales tipos de auxiliares de tintura e impresión utilizados en los textiles y su función (Mamun y Koh, 2020).

Tipo de auxiliar	Función	Ejemplos
Reguladores de pH	Mantener un alto grado de acidez, controlar el pH dentro de tolerancias estrictas y regular el pH en condiciones ácidas.	Sulfato de amonio y ésteres orgánicos
Surfactantes	Disminuir la tensión superficial del agua	Alquilbencenosulfon, laurilsulfato sódico, lauril dimetil betaína y cocamidopropil betaína
Suavizantes	Mejorar la apariencia de las telas, mejoran la resistencia al desgarro y reducen el corte de las agujas cuando se cosen las prendas.	Derivados del óxido de etileno, siliconas, ceras de hidrocarburos a base de parafina o polietileno, sales de amonio cuaternario, aceites ligeramente sulfonados

La Tabla 1.3 resume los principales acabados y las sustancias utilizadas para conseguirlos.

Tabla 1.3. Principales acabados y sustancias químicas (Hakeim et al., 2015; Raj et al., 2022)

Tipo de acabado	Sustancias aplicadas
Desodorizante	Metales y metaloides, nanopartículas, triclosan, aminas cuaternarias, chitosan.
Impermeable	Plasma, ácido perfluorooctanoico, ácido perfluorohexanoico, dendrímero, cera, silicona y poliuretano.
Antimanchas	Compuestos fluorocarbonados.
Ignífugos	Trihidróxido de aluminio, éteres de difenilo, bifenilos policlorados.
Antiestático	Sales orgánicas, glicoles, polietilenglicoles, sales de amonio cuaternario con cadenas de alquilos grasos, polihidroxipoliaminas, copolímeros de polialquileno y poliacrílicos.
Antiarrugas	Compuestos a base de N-metilol, resina de urea-formaldehído, dimetilol dihidroxietileno-urea y resinas modificadas.
Protección UV	Dióxido de titanio, óxido de zinc, acetato de cobre, tratamientos con plasma de nitrógeno, diaminas de etileno y derivados de triazina.

El uso de algunas de estas sustancias es de gran importancia, ya que algunas de ellas pueden ser tóxicas para el ser humano y el medio ambiente.

1.2. Sustancias químicas utilizadas en la industria textil y su riesgo para la salud

La presencia de sustancias tóxicas en la ropa no puede ignorarse. La cantidad y diversidad de sustancias encontradas en los diferentes tipos de prendas es muy amplia. Así, se han detectado trazas de metales pesados (Bielak y Marcinkowska, 2022; Mercan et al., 2015; Rovira et al., 2017a), bisfenoles (Freire et al., 2019; Wang et al., 2019; Xue et al., 2017), biocidas (Munir et al., 2022; Richardson et al., 2022), pesticidas (Attallah et al., 2018; Cai et al., 2016), retardantes de llama (Peng et al., 2022; Yang et al., 2022), ftalatos (Tang et al., 2020) aminas aromáticas (Crettaz et al., 2020; Nguyen et al., 2021; Tölgyesi y Sharma, 2020), hidrocarburos aromáticos policíclicos (Wang et al., 2011), compuestos per- y polifluoralquilados (Mumtaz et al., 2019; Zhu y Kannan, 2020), benzotiazoles y benzotriazoles (Carlsson et al., 2022; Liu et al., 2017), dioxinas y furanos (Klasmeier y McLachlan, 1998; Križanec y Le Marechal, 2006)y formaldehído (Aldag et al., 2017; Monnie et al., 2021), entre otras.

La piel es el órgano más grande que el ser humano posee y también el más expuesto al ambiente (Walker, 2022). Debido al contacto diario y directo entre la piel y la ropa, se debe prestar especial atención al contenido de sustancias químicas que la ropa de vestir y de cama pueden presentar y a sus posibles efectos adversos sobre la salud. La mayoría de los estudios se han centrado en las reacciones alérgicas que las fibras textiles pueden provocar, en su mayoría dermatitis (Balbin et al., 2021; Mobolaji-Lawal y Nedorost, 2015; Svedman et al., 2019). Incluso se ha solicitado la inclusión de una mezcla de textiles en las baterías estándar de las pruebas cutáneas que se realizan en España para el diagnóstico de la dermatitis por contacto (Hernández-Fernández et al., 2021). Otros estudios evidencian sensibilización que las sustancias presentes en la ropa producen al estar contacto con la piel (Ben Salah et al., 2021; Thierse y Luch, 2019).

No obstante, los efectos potenciales de algunas de las sustancias presentes en la ropa pueden incluso ser más graves y peligrosos. Algunos metales pueden afectar al sistema nervioso (Vellingiri et al., 2022), mientras que otras sustancias, como los bisfenoles o los ftalatos, pueden actuar como disruptores endocrinos (Carli et al., 2022; Kassotis et al., 2022; Rubin y Seebacher, 2022). Así mismo, la exposición a tintes azoicos y formaldehído puede conllevar efectos mutagénicos y/o cancerígenos (Brüschweiler y Merlot, 2017; Lin et al., 2022; Rizzi et al., 2016)

Además, las sustancias presentes en las fibras pueden liberarse con la transpiración, el sudor, la fricción diaria y ser absorbidas por la piel, dando lugar a una exposición sistémica que incrementa los riesgos para la salud. Algunos estudios han demostrado que como algunas sustancias como metales o nanopartículas, pueden desprenderse de las fibras tanto con el sudor extremo como con la sudoración normal (Biver et al., 2021; Matoso y Cadore, 2012; Rovira et al., 2017b; Stefaniak et al., 2014). Otras investigaciones se han centrado en estudiar la permeabilidad cutánea de algunas de las sustancias químicas presentes en los tejidos. Iadaresta et al. (2018) observaron como el benzotiazol podía liberarse de los materiales textiles y penetrar a través de la piel, mientras que Abdallah y Harrad (2018) evaluaron la absorción dérmica de los retardantes de llama presentes en telas del mobiliario doméstico. Por el contrario, Alonso et al. (2022) no encontraron evidencias de la absorción cutánea del grafeno presente en las tapicerías fabricadas con fibras de poliéster.

A pesar de las investigaciones realizadas hasta la fecha, son necesarios más estudios sobre el contenido de las sustancias presentes en los tejidos, su comportamiento con el uso normal y sus riesgos para la salud.

1.3. Industria textil y medio ambiente

La importante huella de carbono asociada, la gran cantidad de agua consumida, la falta de reciclaje, la enorme cantidad de residuos generados y el uso de sustancias químicas, hacen de la industria textil una de las más contaminantes del sector, convirtiéndose en la segunda industria más contaminante, por detrás del petróleo (Parlamento Europeo, 2020). El impacto de la industria textil sobre el medio ambiente se produce durante todo del proceso de producción (Figura 1.2), desde la obtención de las materias primas hasta el desecho de la prenda de ropa por parte del consumidor.

La obtención de las materias primas, que serán las bases de las fibras de algodón o de seda, supone la necesidad de disponer de grandes extensiones de cultivo, un gran consumo de agua, así como el uso de fertilizantes y pesticidas (WRAP, 2017). Por otro lado, las fibras sintéticas como el poliéster se fabrican a partir del petróleo, hecho que contribuye a la generación de gases de efecto invernadero (Šajn, 2019). Como se ha explicado anteriormente, durante las diferentes etapas del proceso de manufactura (pretratamiento, teñido, estampado, acabado, costura, lavado, secado) se utilizan una gran variedad de sustancias químicas, muchas de las cuales terminarán formando parte de las aguas residuales. Además, implican el consumo de grandes cantidades de agua y de energía. Este elevado consumo de energía, junto a las emisiones directas de CO_2 derivadas de las cadenas de suministro, son los responsables de que la industria textil genere el 10% de las emisiones de los gases de efecto invernadero (L'Abbate et al., 2018; Okafor et al., 2021).

1.3.1. Sustancias químicas

Uno de los mayores problemas de la industria textil está relacionado con las aguas residuales (Wang et al., 2022)., ya que en su mayoría no se tratan antes de ser vertidas, a pesar de que pueden contener residuos tóxicos, pH no adecuados y temperaturas elevadas, los cuales provocan grandes cambios en los ecosistemas acuáticos (Alderete et al., 2021).

El contenido de los efluentes residuales de una industria textil dependerá del tipo de textil generado y de las sustancias químicas empleadas en su fabricación. En términos generales, estos efluentes suelen tener altos niveles de demanda bioquímica de oxígeno (DBO), demanda química de oxígeno (DQO), sólidos totales, productos químicos, olor y coloración (Mani, Chowdhary y Bharagava, 2018). La Tabla 1.4 presenta las características tipo de las aguas residuales no tratadas de una industria textil.

Otras de las sustancias que se suelen encontrar en las aguas residuales de las industrias textiles, y que también suelen utilizarse durante las fases de tintura y estampado, son los metales pesados (Kant, 2012; Kaur et al., 2021). De un modo similar a los tintes, los metales también pueden provocar cambios en la coloración del agua, afectando a la penetración de la luz y reduciendo por tanto la actividad fotosintética de las plantas y el contenido de oxígeno, lo cual afecta la vida de todo el ecosistema (Chandanshive et al., 2020; Kadam et al., 2018).

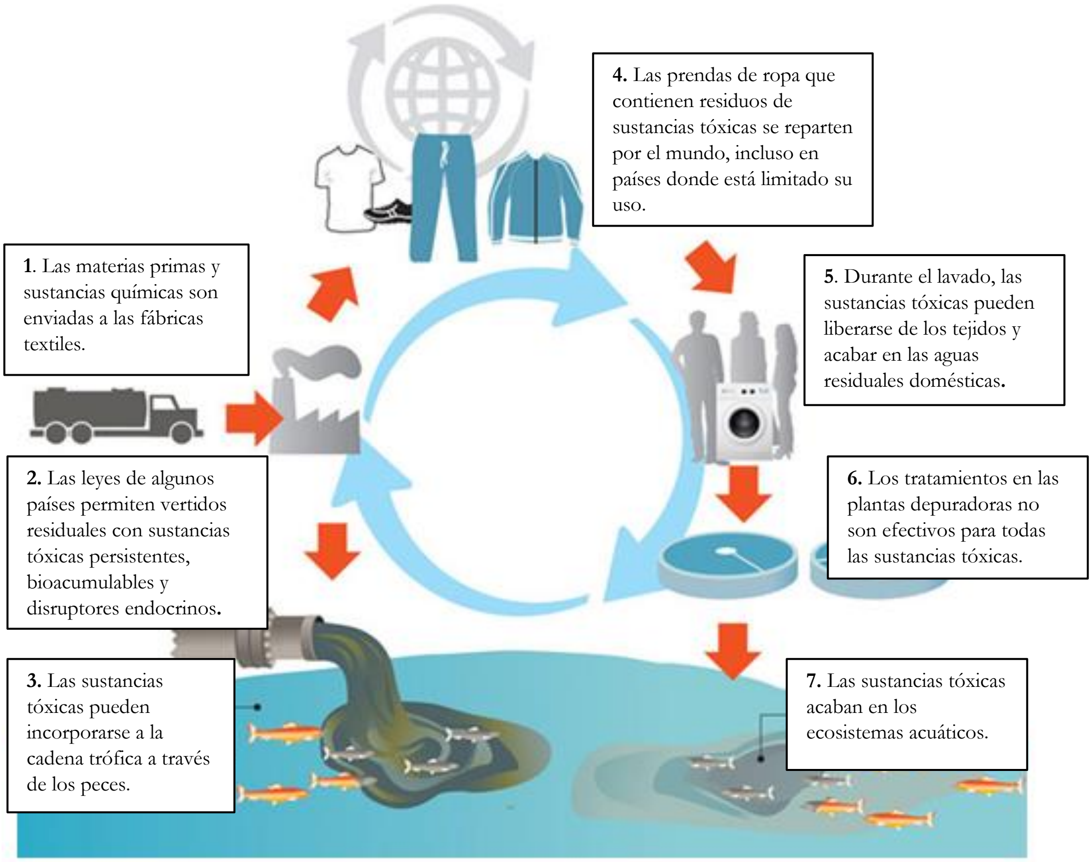

Figura 1.2. El ciclo tóxico de la ropa. Imagen adaptada de Casper et al. (2013)

El abanico de sustancias químicas que estas aguas pueden contener es muy amplio, incluyendo azufre, naftol, nitratos, ácido acético o jabones. Sin embargo, en su mayoría son tintes o productos relacionados con los procesos de tintura y acabados (Jadhav et al., 2015; Kant, 2012). El simple cambio en la coloración del agua provocado por el tinte, por poco que este pueda ser, provoca un cambio en la absorción de la luz. En lugar de penetrar en el agua, la luz solar se refleja en el tinte, modificando la actividad fotosintética de las algas, alterando así toda la cadena alimentaria y la vida acuática (Holkar et al., 2016). Además, estos tintes pueden tener efectos cancerígenos y mutagénicos sobre los organismos que viven en los ecosistemas acuáticos (Garcia et al., 2021).

Tabla 1.4: Características de las típicas aguas residuales textiles no tratadas. Adaptada de Mani, Chowdhary y Bharagava, 2018)

Parámetro	Rango
pH	6-10
Temperatura	35-45
TDS	8.000-12.000
DBO	80-6.000
DQO	150-12.000
Cloro	1.000-6000
Sodio	70%
Oligoelementos (mg/L)	<10
Aceite y grasa (mg/L)	10-30
Amoníaco libre	<10
SO4	600-1.000
Sílice (mg/L)	<15
TNK	10-30
Nitrógeno total (mg/L)	70-80
Color (Pt-Co)	50-2.500

TDS: Sólidos disueltos totales, DBO: demanda bioquímica de oxígeno, DQO: demanda química de oxígeno, TNK: nitrógeno total Kjeldahl.

El impacto ambiental de la industria textil no se limita a nivel de producción y distribución. Los ciclos de lavados llevados a cabo por los consumidores y su desecho como destino último tienen un gran impacto ambiental. Luongo et al. (2016) y Windler et al. (2012) han demostrado como, durante los ciclos de lavado, sustancias como el benzotiazol, el benzotriazol, la quinolina y el dióxido de titanio pueden desprenderse de la ropa, llegando así a las aguas residuales. Más recientemente, se han detectado trazas de sustancias perfluoradas y polifluoradas (PFAS) provenientes de los textiles funcionales (Schellenberger et al., 2022; van der Veen et al., 2020) en el agua utilizada para el lavado. A pesar de que las aguas residuales de cualquier población pasan por las plantas de tratamiento de aguas residuales antes de ser devueltas al sistema, éstas no están preparadas para retener este tipo de sustancias, por lo que terminan contaminando los ecosistemas acuáticos (Barisci y Suri, 2021).

1.3.2. Microfibras

Existe una creciente preocupación sobre los fragmentos de fibra que, en los últimos años, se están acumulando en ríos, mares y océanos. Estos fragmentos se liberan principalmente en la colada de ropa sucia (Dreillard et al., 2022). El material con el que están fabricadas las prendas de ropa tiene una gran influencia. Prendas fabricadas con materiales sintéticos, 100% poliéster, 100% poliamida o 100% acrílicos, liberan más fragmentos que prendas fabricas con una combinación de materiales, como por ejemplo poliéster y elastano, o poliamida y poliéster (Belzagui et al., 2019). Del mismo modo que ocurre con algunas de las sustancias químicas, y debido a su tamaño, las plantas de tratamiento de aguas residuales no pueden retener algunas de estas microfibras, por lo que terminan en los ecosistemas acuáticos. En varios países como Suecia (Magnusson y Norén, 2014), EE.UU (Sutton et al., 2016), Finlandia (Talvitie et al., 2017) o Australia (Ziajahromi et al., 2017), se ha detectado la presencia de estas microfibras en los efluentes de las plantas de tratamientos de aguas. Otros estudios apuntan a la notable presencia de microfibras en los ecosistemas acuáticos, siendo encontradas en aguas y playas del mar Mediterráneo, Océano Pacífico, el Mar del Norte, el Océano Atlántico e incluso en el Ártico y en sedimentos de aguas profundas (Expósito et al., 2021; Salvador Cesa et al., 2017).

Lamentablemente, la llegada de las microfibras al medioambiente ha sido y es continua. Además, no son materiales biodegradables. A pesar de ser microfibras naturales, pueden permanecer en el medioambiente durante años debido a los tratamientos recibidos durante la fase de acabados en la que, precisamente, se les añaden sustancias químicas para hacerlas más resistentes (Zhang et al., 2022). Ante la persistencia de las microfibras y su creciente acumulación medioambiental, la comunidad científica ha centrado su interés en las posibles consecuencias de su presencia en los ecosistemas. Una prueba de ello son las investigaciones sobre la ingestión de microfibras por parte de moluscos, así como su posterior distribución por los diferentes tejidos (Cole et al., 2019; Kolandhasamy et al., 2018) y sus efectos tóxicos (Y. Zhao et al., 2021). La acumulación en los tejidos evidencia la bioacumulación y la biomagnificación de las microfibras y su impacto a través de la cadena alimentaria. Aunque de momento no hay estudios que así lo demuestren, Zhang et al. (2022), en su extensa revisión sobre la contaminación ambiental causada por microplásticos de origen textil, evidencian como los microplásticos (incluidas las microfibras) se fijan a las microalgas, que a su vez son ingeridas por el zooplancton, base alimentaria de organismo superiores como el salmón y otras especies acuáticas como el camarón y otros tipos de peces. En última instancia, todas estas especies marinas son consumidas por el ser humano.

1.3.3. Residuos textiles

La aparición del fenómeno conocido como "fast fashion" ha supuesto un gran cambio en la industria textil. Este fenómeno tiene como objetivo aumentar el consumo OMS

inmediato de las prendas, consiguiéndolo mediante una rápida producción. Este tipo de moda va asociada a prendas de bajo coste, hecho que fomenta el desecho, que en 2015 supuso 92 millones de toneladas y que se estima que aumente hasta las 148 toneladas en 2030 (Echeverria et al., 2019). Por otro lado, el tipo de fibras con el que se fabrican las prendas de ropa de este tipo de moda, suelen ser fibras sintéticas, difícilmente reciclables, hecho que implica que el 85% de las prendas acaben en los vertederos (Allary, 2021).

1.4. *Eco-friendly*

En las últimas décadas, ha aumentado la preocupación social por el gran impacto que la industria textil tiene sobre el medio ambiente. Después de algunas publicaciones como las realizadas por Greenpeace en 2011, en las que evidenciaron las presencia de sustancias químicas tóxicas en la ropa que todos llevamos, la visión/preocupación del consumidor está cambiando (Brigden et al., 2012). Actualmente no sólo preocupa el daño que la industria textil puede causar en el medio ambiente, sino también el impacto de la ropa sobre la salud. Día a día, la demanda de prendas fabricadas con fibras naturales, ecológicas y biodegradables ha ido en aumento, naciendo así el fenómeno/moda "eco-friendly" o "slow fashion".

La industria textil ha ido modificando sus métodos de fabricación para adaptarse a los nuevos tiempos. Las nuevas políticas van encaminadas a la reducción del gasto de agua, y del uso de tóxicos, así como al aumento de la sostenibilidad de los productos textiles. Muestra de ello son las investigaciones llevadas a cabo en el campo de la reducción de la contaminación de los efluentes de las industrias textiles. Tecnologías como el tinte electroquímico y el AirDye reducen el consumo de agua y la cantidad de químicos presentes en las aguas residuales (Debs Corporation, 2019; Li et al., 2020). En cuanto al tratamiento de las mismas, se ha demostrado que algunas especies de hongos, bacterias y plantas pueden reducir la contaminación presente en las aguas residuales (El-Sharkawy et al., 2022; Goud et al., 2020; Guo et al., 2019)

Por otro lado, también encontramos avances en el uso de sustancias tóxicas durante los procesos de fabricación. Un claro ejemplo es la introducción de tintes naturales en los procesos de tintura (Fazal-ur-Rehman et al., 2022), la sustitución de sustancias basadas en formaldehído en las fases de acabado (Luo et al., 2021), el uso de residuos vegetales o aceites esenciales como retardantes de llama y repelentes de mosquitos (Basak y Ali, 2021; Vashist et al., 2021), la confección textil con algodón orgánico y/o poliéster reciclado (Moazzem et al., 2021) o el uso de enzimas como amilasas, proteasas en las fases de desencolado y blanqueo (Saxena et al., 2017).

El objetivo de la Unión Europea es que en 2030 todos sus productos textiles sean más duraderos y reciclables, fabricados en su mayoría con fibras recicladas, libres de sustancias tóxicas y respetuosos con el medio ambiente así como con los derechos sociales (Parlamento Europeo, 2018).

2. SUSTANCIAS ESTUDIADAS EN LA PRESENTE TESIS

2.1. Metales pesados

2.1.1. Descripción y aplicaciones

Los metales pesados se definen como un grupo de metales y metaloides que tienen una densidad relativamente alta, superior a 5 g/cm^3. Se liberan al medio mediante fuentes antropogénicas como actividades mineras, combustión de combustibles fósiles y emisiones industriales, pero también de manera natural (Raychaudhuri et al., 2021).

A pesar de que algunos de estos elementos son esenciales para llevar a cabo procesos fundamentales como el crecimiento, el metabolismo y el desarrollo de los diferentes órganos en los seres vivos, incluidos los humanos, otros pueden llegar a ser muy tóxicos. Su peligrosidad recae en el hecho de no ser biológicamente degradables. Así, pueden permanecer durante largo tiempo en los ecosistemas, contaminando suelos, plantas y animales y bioacumulándose a través de la cadena trófica (Yadav et al., 2018).

Las aplicaciones de los metales pesados y metaloides son diversas. La mayoría de ellos se generan como productos de la combustión de materia orgánica y de la incineración de residuos (Wang et al., 2019). Debido a su carácter ignífugo, el antimonio (Sb) forma parte de pinturas, esmaltes, cerámicas y plásticos. Arsénico (As), cadmio (Cd) y cobre (Cu) son utilizados en la agricultura como fertilizantes, pesticidas y alguicidas. A su vez, el Cd, por su resistencia a la oxidación, se utiliza en el chapado y soldaduras de aleaciones de hierro y Cu. El cobalto (Co) se encuentra principalmente en los motores de aviones, prótesis y utensilios cortantes. El cromo (Cr) suele utilizarse en baterías, pigmentos, papeleras y en combinación con otras aleaciones por su resistencia a la corrosión. El mercurio (Hg) se encuentra en compuestos farmacéuticos, pinturas, baterías y amalgamas dentales. El níquel (Ni) forma parte de galvanizados, hierro colado y productos químicos. Uno de los metales más extendidos es el plomo (Pb), utilizado ampliamente en la industria metalúrgica y también en la fabricación de pigmentos, recubrimientos, pilas. Por último, el zinc (Zn) se incluye en procesos químicos, farmacéuticos, de galvanización y como insecticida (Yahaya y Don, 2014).

Los metales y metaloides mencionados anteriormente también son utilizados por la industria textil. Algunos de ellos forman parte del material de las fibras textiles, como por ejemplo el Sb en las fibras de poliéster. Otros son el resultado de la propia fabricación. Así mismo, algunos metales pesados también se añaden durante el proceso de fabricación de las prendas de ropa voluntariamente, ya que aportan nuevas propiedades a los textiles como impermeabilidad, transpirabilidad e incluso acción antimicrobiana (Khan et al., 2018; Spielman-Sun et al., 2018).

En la fabricación de las fibras de poliéster, el Sb se usa como catalizador durante las reacciones de polimerización, por lo que éste podría estar presente en el tejido final (Maerov, 1979). Además, en sinergia con los éteres difenílicos polibromados (PBDE), el trióxido de antimonio (Sb_2O_3) se utiliza por su capacidad ignífuga en los textiles (Derden y Huybrechts, 2013).

Algunos metales forman parte de los pigmentos y tintes utilizados para dar color a los tejidos. El Cd se encuentra en los colores rojo, naranja y verde, mientras que el Cr se encontraría en tonalidades azules, marinas o turquesas, además de utilizarse como oxidante en los procesos de tintura con azufre (Matoso y Cadore, 2012; Sima, 2022).

Debido a sus características fisicoquímicas y biológicas, las nanopartículas metálicas (NPMs) otorgan a los tejidos nuevas funcionalidades, en comparación con los aditivos convencionales. Las combinaciones de metales para la fabricación de NPMs son casi infinitas, pero las más utilizadas son las que contienen plata (Ag), Cu u óxido de cobre (Cu/CuO), titanio (Ti) y dióxido de titanio (TiO_2), Ni o Zn. Las nuevas funcionalidades obtenidas con la aplicación de NPMs a los textiles incluyen características antibacterianas, bloqueo de rayos ultravioleta (UV), hidrofobicidad, incluso de autolimpieza (Saleem y Zaidi, 2020). En la Figura 1.3 se resumen las principales NPMs utilizadas por la industria textil y sus propiedades en los tejidos.

Ag	• Antimicrobiana
Al_2O_3	• Protección UV • Anti-arrugas
Cu	• Antimicrobiana
SiO_2	• Antimicrobiana • Hidrofobicidad • Repelente al agua
TiO_2	• Antimicrobiano • Protección Uv • Hidrofobicidad • Anti-arrugas
ZnO	• Antimicrobiana • Protección Uv • Hidrofobicidad • Ignífuga

Figura 1.3. Propiedades de las principales nanopartículas metálicas (NPMs) utilizadas en los textiles.

2.1.2. Efectos sobre la salud

Los riesgos para la salud asociados a los metales pesados dependen de varios factores, como la vía y duración de la exposición, y también de la concentración. Algunos metales, incluso a bajas concentraciones, son altamente peligrosos, por lo que una exposición crónica puede causar graves problemas de salud. El estilo de vida, el lugar de trabajo o los alimentos que se ingieren son factores que influyen en los riesgos asociados a los metales pesados. La Tabla 1.5 muestra los efectos sobre la salud de algunos metales pesados.

A pesar de que la absorción dérmica no es la principal vía de exposición a metales pesados, su contribución no es insignificante. La piel está en permanente contacto con los tejidos, por lo que los metales y otras sustancias químicas que contienen pueden provocar reacciones alérgicas, irritaciones, dermatitis e incluso la reducción de las microflora (Balbin et al., 2021; Walter et al., 2014). Además, algunos de estos metales pueden liberarse de las fibras con el sudor y fricción diarios, pudiendo ser así absorbidos por la piel (Rovira et al., 2017b).

Tabla 1.5: Metales pesados y su efecto sobre la salud (Mitra et al., 2022; Tchounwou et al., 2012)

Metal pesado	Efectos en la salud
As	Neurotoxicidad Problemas cardiovasculares Daños pulmonares, hepatobiliares y renales Cáncer Muerte
Cd	Daños pulmonares, hepatobiliares y renales Cáncer
Co	Posible carcinógeno Daños cardiovasculares, hematológicos y pulmonares Daños en el desarrollo
Cr	Lesiones cutáneas Daños pulmonares y renales Alergia Asma Cáncer
Cu	Anemia normocítica e hipocrómica Leucopenia Osteoporosis
Hg	Problemas gastrointestinales Daños neurológicos y renales
Pb	Dolor de cabeza, falta de atención, irritabilidad y pérdida de memoria Pérdida de peso al nacer, partos prematuros y abortos espontáneos Problemas de neurodesarrollo Cáncer
Ni	Reacciones alérgicas Disminución de la función pulmonar Cáncer
Zn	Daños hematológicos, respiratorios y gastrointestinales

2.1.3. Legislación

La Unión Europea regula el uso y contenido de sustancias peligrosas en los productos textiles. Para algunos metales, como As, Cd, Cr(VI) o Pb, se ha establecido un límite máximo de 1 mg/kg en los tejidos que entran en contacto con la piel (Comisión Europea, 2018a). Además, desde 2011, la información sobre la composición de las fibras de los tejidos es obligatoria.

Tabla 1.6. Límites de metales pesados extraíbles (mg/kg) marcados por certificaciones no obligatorias (Comisión Europea, 2017a, 2018a; GOTS, 2020; OEKO-TEX Association, 2017)

	Límites legislativos	OEKO TEX® Standard 100	GOTS	Ecolabel
As	< 1	0,2	< 0,1	1
Cd	< 1	0,1	< 0,1	0,1
Co		1	< 1.0	1
Cr		1	< 1,0	1
Cr (VI)	<1	< 0,5	< 0,5	
Cu		50	< 25	25
Hg		0,02	< 0,02	0,02
Mn		90	< 90	
Ni		4	< 1,0	1
Pb	< 1	0,2	< 0,2	0,2
Sb		30	<0,2	30
Zn		750	<750	

Por otro lado, existen también certificaciones no obligatorias, las cuales garantizan no sólo que durante las fases de fabricación no se han utilizado sustancias nocivas, sino también su ausencia en los tejidos finales. Éstas son la certificación OEKO TEX® Standard 100, Eco-label y Global Organic Standard Textiles (GOTS), que restringen aún más los niveles de metales en las prendas de ropa. La Tabla 1.6 muestra los niveles máximos permitidos en una prenda según cada tipo de certificación.

2.1.4. Estudios anteriores

Los múltiples beneficios aportados por los metales pesados a fibras y tejidos, y las consecuencias de éstos en la salud, han derivado en diversas investigaciones que estudian su presencia en los diferentes tipos de tejidos y prendas de vestir.

Cómo se ha comentado anteriormente, las materias primas pueden contener sustancias nocivas por sí mismas. Así lo demostraron Rybicki et al. (2004) cuando analizaron los niveles de Cr, Cu y Zn en algodón cultivado. Rezic et al. (2011) también analizaron el contenido de diferentes elementos trazas en materias primas textiles. La máxima concentración de potasio (K) y magnesio (Mg) se halló en las muestras de algodón (ND – 1.170,2 mg/g) y lino (ND - 86,6 mg/g), respectivamente. Por otro lado, lana y cáñamo presentaron los máximos niveles de calcio (Ca) (ND - 660 mg/g y ND - 540 mg/g, respectivamente). Posteriormente, Sungur y Gülmez (2015) analizaron el contenido en metales en diferentes tejidos (algodón, acrílico, nailon, poliéster, polipropileno y viscosa) obtenidos directamente de las plantas textiles en Turquía. Aluminio y Fe fueron los metales con niveles más altos en todas las fibras (Al: 39,5 - 103 mg/kg y Fe: 43,4 – 80,1 mg/kg). Cabría destacar que los niveles de Cd (6,05 – 11,9 mg/kg) y Pb (18,8 – 24,4 mg/kg) en todas las fibras fueron superiores a los exigidos por OEKO-TEX.

La mayoría de estudios en la literatura se centran en los productos textiles finales, ya sean ropa de vestir, recubrimientos textiles, ropa deportiva o ropa del hogar. La Tabla 7 resume los niveles de metales encontrados en algunos de esos estudios. Tuzen et al. (2008) analizaron 13 muestras de ropa recogidas en Tokat (Turquía), detectando trazas, de Cd, Cu, Hierro (Fe), Manganeso (Mn), Ni y Zn. Por su parte, Matoso y Cadore (2012) determinaron las concentraciones de As, Cd, Cr, Co, Cu, Hg, Ni, Pb y estaño (Sn) en camisetas deportivas. El Cr fue el metal con los niveles más altos en tejidos negros. Rovira et al. (2015) analizaron una extensa lista de metales y metaloides, 31 en total, en diferentes tipos de prendas de vestir, incluyendo camisetas, blusas, ropa interior, pijamas de bebé y bodis, todos ellos de diferentes materiales (algodón, poliamida, poliéster, spandex y viscosa). Estos autores también hallaron niveles de Cr altos en ropa oscura de poliamida, así como elevados valores de Sb en prendas de poliéster y de Cu en algunos tejidos de algodón verde. En una investigación posterior, los mismos autores evaluaron la presencia de 28 metales en 37 prendas en contacto con la piel (camisetas, blusas calcetines, pijamas de bebé y bodis). Nuevamente, los niveles de Cr fueron altos en tejidos de poliamida, mientras que las prendas fabricadas con poliéster contenían niveles altos de Sb. Además también encontraron niveles altos de Zn en las camisetas etiquetadas con piritiona de zinc (Rovira et al., 2017b). En otro estudio, se evaluó el contenido elemental en textiles del hogar (toallas, ropa de cama y pijamas), no evaluados hasta esa fecha. Se analizaron un total de 28 textiles domésticos en los que las concentraciones de metales más elevadas fueron de Cu, Mg y Sb (Rovira et al., 2017a). A su vez, Nguyen y Saleh (2017) se centraron en analizar un total de 120 prendas de ropa interior, de diferentes colores y materiales. Según los resultados, la ropa interior de algodón contenía altos niveles de aluminio (Al), Fe y Zn, mientras que los tejidos de poliéster contenían más Fe y Ni. Por otro lado, los niveles de Al, Cu y Cr eran más elevados en prendas de nailon. Por último, Chen et al. (2022) investigaron la presencia de ocho metales en ropa nueva de niños de preescolar fabricada en países asiáticos. Los niveles de Cd fueron superiores en ropa negra, el Co en prendas que no eran de algodón y el Pb en prendas fabricadas en China.

Si bien es cierto que las principales vías de exposición metales y metaloides son la inhalación y la ingestión, la exposición dérmica puede ser también relativamente importante, ya que el sudor puede provocar la liberación de metales presentes en la ropa y favorecer así su absorción. Doğan et al. (2002) cuantificaron la concentración de As, Cr, Co, Cu, Ni y Pb en extractos de sudor artificial, después de haber estado expuesto a diferentes prendas de vestir. A su vez, Rezić y Steffan (2007) analizaron los extractos de sudor de 16 muestras de ropa, en los que detectaron niveles de Al (0,11 – 1,58 μg/mL), Cd (0,02 – 0,05 μg/mL), Cr (0,01 – 0,32 μg/mL), Cu (0,05 – 1,95 μg/mL) y Ni (0,05 – 0,10 μg/mL). Sungur y Gülmez (2015) determinaron el contenido de metales distintas fibras tras su incubación en una solución de sudor artificial, observando un descenso en los niveles de metales. De modo similar, Rovira et al. (2017b) también incubaron diferentes muestras textiles, previamente analizadas, en una solución de sudor artificial. Zn y Ag fueron los elementos con mayor migración, con rangos de 11% - 55% y 19% - 25%, respectivamente. La tasa de migración del Ti fue de 7,1%, mientras que para el Sb, fue de entre 0,3% y 3,7%. Por último, la migración del Cr fue muy menor (entre 0,1% y 0,2%).

Tabla 1.7. Rango de concentración de metales y metaloides (en mg/kg) en ropa según la literatura científica.

Ref.	Pranaitytė et al., (2007)	Tuzen et al., (2008)	Menezes et al., (2010)	Matoso y Cadore, (2012)	Rovira et al., (2015)
Ag					
Al			17,6 – 117,5		1,37 – 198
As				ND	ND
Ba			2,05 - 102		ND – 9,46
Be					ND
Bi					ND – 1,92
Cd	ND	0,10 – 0,25		ND – 0,2	ND – 0,04
Co				ND	ND – 5,18
Cr	0,10 – 0,31		ND – 2,60	0,3 - 965	0,13 – 605
Cu	0,88 – 23,6	0,76 – 341	ND – 273		ND - 287
Fe		3,55 – 34,3	12,1 – 66,1		3,38 – 35,1
Mg					3,75 – 716
Mn		1,02 – 2,50			0,10 – 13,3
Mo					ND – 0,38
Ni		1,20 – 4,69	ND – 5,10	0,9 – 3,3	ND
Pb		0,09 – 0,47		ND – 1,4	0,03 – 0,32
Sb		0,06 – 0,36			ND - 204
Ti					
Zn		0,63 – 4,84	ND – 10,9		ND - 256

ND: no detectado

Tabla 1.7 (Continuación). Rango de concentración de metales y metaloides (en mg/kg) en ropa según la literatura científica.

Ref.	Rovira et al., (2017a)	Rovira et al., (2017b)	Nguyen y Saleh, (2017)	Nyamukamba et al., (2020)	Chen et al., (2022)
Ag	ND – 0,13	ND – 0,57	1,8 – 7,00		
Al	ND – 108	1,68 – 351	ND - 652		
As	ND	ND	ND – 0,35	0,01 - 0,03	ND – 0,62
Ba	ND – 7,20	ND – 19,1			
Be	ND	ND			
Bi	ND – 0,08	ND – 0,10			
Cd	ND	ND – 0,07	ND – 0,41	0,00 – 0,91	ND – 0,11
Co	ND – 0,04	ND – 20,4	ND – 28,0	0,00 – 1,05	0,02 – 4,64
Cr	ND – 374	ND – 754	ND - 118	0,05 – 6,37	0,4 – 49,9
Cu	ND – 1065	ND – 439	1 - 234		0,37 – 481
Fe	ND – 40,7	1,09 - 194	13 - 163		
Mg	ND – 889	ND – 832			
Mn	ND – 7,68	0,07 – 5,77	0,20 – 59,0		
Mo	ND – 0,16	ND – 0,16			
Ni	ND – 1,20	ND – 1,79	ND – 1,74	0,04 – 36,7	ND – 33,0
Pb	ND – 0,90	ND – 1,90	ND – 2,00	0,02 – 23,7	ND – 4,38
Sb	ND – 202	ND – 152			
Ti	ND – 124	ND – 37,8	<0,03		
Zn	ND – 16,4	ND - 1185	4 - 300		ND - 467

ND: no detectado

2.2. Bifenilos policlorados

2.2.1. Descripción y aplicaciones

Los bifenilos policlorados (PCBs) son un grupo sintético de compuestos organoclorados que se forman mediante la cloración de las diferentes posiciones del bifenilo. Constituyen una familia de 209 congéneres de estructura química similar y que presentan distinta variedad de forma, desde líquida a gas, pasando por sólidos y ceras y con diferentes coloraciones, desde amarillo claro a incoloros.

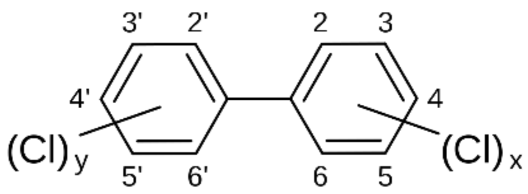

Figura 1.4: Estructura general de los PCBs

La Figura 1.4 muestra la estructura general de los PCBs. Cada uno de los átomos de hidrógeno puede ser sustituido por un átomo de cloro, dividiendo así a los PCBs en coplanares, si las posiciones 2, 2',6 y 6' no tienen ningún cloro, PCBs *mono-orto* sustituidos, si hay un átomo sustituido en cada lado, y PCBs no sustituidos, para el resto. Su fórmula empírica es $C_{12}H_{10-n}Cl_n$, donde n varía entre 2 y 10, siendo mayoritarios los congéneres de entre 2 a 7 cloros sustituidos (IARC, 2016).

Su uso fue muy extendido a mediados del siglo XX por sus propiedades fisicoquímicas. Debido a su resistencia a la inflamabilidad, baja volatilidad o alta estabilidad térmica fueron ampliamente utilizados como aceites lubricantes, plastificantes resinas aislantes, ceras, selladores de juntas, y pinturas (Erickson y Kaley, 2011).

Los PCBs pueden liberarse fácilmente al aire durante los procesos de incineración de productos de consumo tanto en las incineradoras industriales como en las municipales (Nadal et al., 2020). Una vez llegan al medio ambiente se dispersan fácilmente en aire, agua y suelo. Los PCBs no son fácilmente eliminables, por lo que permanecen durante períodos muy extensos en el medio ambiente, hecho que los hace muy persistentes.

Además, se bioacumulan y biomagnifican, acumulándose en los tejidos animales y vegetales e incrementando sus niveles al subir por la cadena alimentaria, de la que el ser humano es el consumidor final. Debido a sus efectos tóxicos y persistentes, su uso ha sido prohibido en la mayoría de los países del mundo. A pesar de ello, actualmente todavía quedan equipos, materiales y productos de consumo que contienen este tipo de sustancias (Liu et al., 2022).

La relación existente entre los PCBs y la industria textil no es directa. A diferencia de otras sustancias que se añaden durante las diferentes etapas del proceso de manufactura por los beneficios que aportan al propio proceso o a las características de las prendas, los PCBs llegan a los productos textiles de manera indirecta. Uno de los motivos por los que se hallan PCBs en prendas de vestir es por el uso de determinados pigmentos o tintes. Concretamente, su presencia, en especial de los congéneres PCB-11 y PCB-52, se relaciona con los pigmentos amarillos (Rodenburg et al., 2015).

Por otro lado, los PCBs se encuentran en el aire, pero también en el interior de las viviendas. Así, los textiles del hogar y las propias prendas de ropa pueden impregnarse de los PCBs ambientales, aumentando la exposición dérmica a los mismos (Kolarik y Morrison, 2022).

2.2.2. Efectos sobre la salud

Las rutas de exposición mayoritarias a los PCBs son la ingesta dietética, principalmente por el consumo de pescado y marisco, y la inhalación de aire contaminado. No obstante, la vía dérmica también puede jugar un papel importante, especialmente para los trabajadores del sector de los residuos (IARC, 2016).

La Agencia Internacional para la Investigación del Cáncer (IARC) define a los PCBs como carcinógenos para los seres humanos (Grupo 1). Concretamente, asocia la exposición a PCB con la aparición de melanomas malignos, con el linfoma de no Hodgkin y el cáncer de mama (IARC, 2016). Así mismo, la exposición provoca importantes efectos adversos para la salud. En el caso del sistema nervioso, los PCBs aumentan los riesgos de deterioro de la función cognitiva y psicomotora en niños, afectando al aprendizaje, atención y a la memoria. En cuanto al sistema endocrino, los efectos que ejercen los PCBs son principalmente antiandrogénicos y estrogénicos, e inhiben la activación de T3, hormona segregada por la glándula tiroides, cuya función es estimular el metabolismo de los hidratos de carbono y de las grasas (Rina et al., 2018; Sethi et al., 2019). Diversos estudios evidencian que los PCBs provocan disfunciones en el sistema inmunitario, como la supresión de la respuesta inmunitaria o la atrofia tímica. Además, también se les relaciona con enfermedades cardiovasculares como la hipertensión o el ictus (Raffetti et al., 2018). Por otro lado, se asocia la exposición a PCBs con unos niveles bajos de testosterona y una baja calidad del semen, concretamente de la motilidad espermática (Meeker y Hauser, 2010). Además, pueden difundir a través de la placenta, por lo que la exposición prenatal a estas sustancias se asocia con bajo peso al nacer y menor desarrollo para la edad gestacional (Lauritzen et al., 2017).

2.2.3. Legislación

El programa de las Naciones Unidas para el Medio Ambiente (PNUMA) considera a los PCBs como uno de los doce contaminantes fabricados por el ser humano más contaminantes del mundo. En 2001, se incluyeron en los anexos A (eliminación) y C (producción no intencional) del Convenio de Estocolmo sobre Contaminantes Orgánicos Persistentes (UNEP, 2001). Su fabricación y comercialización se prohibió en 1976 mediante las Directivas 76/403 y 76/769 (Consejo de la Unión Europea, 1976; Consejo de la Unión Europea, 1976b). Posteriormente se ha regulado la progresiva sustitución y eliminación de equipos y residuos que pudieran contener estas sustancias (BOE, 1999).

Al contrario de lo que ocurre con otro tipo de sustancias, no hay una legislación concreta para los PCBs en los productos textiles. Su uso está prohibido, por lo que los productos textiles tampoco deberían presentar residuos de estas sustancias.

2.2.4. Estudios anteriores

En EE.UU se han realizado varios estudios en productos de consumo buscando la asociando de PCBs con diversos pigmentos. Guo et al. (2014) analizaron concretamente el congénere PCB-11 en material impreso y textiles, así como su lixiviación. Los textiles con diseños impresos presentaban unos niveles de PCB-11 muy superiores a las prendas teñidas (>2 ppb). Además, se hallaron diferencias entre las partes impresas y las no impresas dentro de la misma prenda, concluyendo que la presencia de PCBs está relacionada con el uso de pigmentos durante el proceso de impresión (Guo et al., 2014). En 2016, el Departamento de Ecología de Washington (Estados Unidos) analizó un total de 201 productos de consumo susceptibles de estar contaminados por PCB de manera indirecta (masilla, productos de oficina, envases, colorantes, pinturas, plásticos, cosméticos, plaguicidas, etc.); se incluyeron también 5 muestras de ropa. Se pudieron detectar PCBs en el 89% de las muestras de ropa, con niveles de PCBs en un rango de entre 1,3 y 16,3 ppb (Stone, 2016).

También se ha estudiado la presencia de PCBs en textiles desde la perspectiva que la ropa es un monitor pasivo de contaminación. Estando presentes en una atmósfera contaminada por PCBs, los textiles pueden adsorberlos y aumentar así la exposición humana. En este contexto, se han realizado estudios relacionados con las exposiciones "paraocupacionales", es decir, estudios que relacionan la transferencia de sustancias del lugar del trabajo al hogar mediante la ropa. En varios estudios se ha observado que los familiares de trabajadores de plantas de reciclaje o incineradoras presentaban niveles altos de PCBs en sangre, a pesar de no tener una exposición laboral a dichos contaminantes, asociándose al hecho de llevarse la ropa y calzado del trabajo a casa (Licina et al., 2019; Schettgen et al., 2012).

2.3. Formaldehído

2.3.1. Descripción y aplicaciones

El formaldehído (Figura 1.5) es un aldehído incoloro, inflamable a temperatura ambiente y de fuerte olor. También es conocido como formalina, formol u oximetileno. Es producido por muchos organismos vivos, incluidos los humanos, en sus procesos metabólicos, por lo que está presente de manera natural en el medio ambiente, aunque a concentraciones bajas y no perjudiciales (EFSA, 2014; Nowshad et al., 2018). A nivel industrial, es una de las sustancias químicas más utilizadas en el mundo debido a sus propiedades desinfectantes, fungicidas y germinicidas. Además, se usa en procesos de producción de materiales y en la fabricación artículos de consumo.

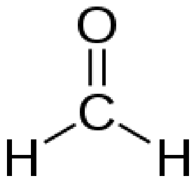

Figura 1.5. Estructura química del formaldehído

La lista de productos en los que podemos encontrar trazas de formaldehído es extensa, estando muy presente sobre todo en artículos del hogar como pinturas, maderas prensadas, pegamentos, productos de higiene, cosméticos y textiles. También es un subproducto de los procesos de combustión, por lo que también está presente en el humo de cigarrillos, estufas de gas o las emisiones de los tubos de escape de los automóviles (CPSC, 2016; Huang et al., 2019).

El formaldehído se produce de manera comercial desde 1889, mediante la oxidación catalítica del metanol. Pero no es hasta mediados de la década de 1920 cuando se introduce en la industria textil debido a su efecto antiarrugas, mediante agentes de prensado y su poder protector frente a (Sanchez, Blanka y Laffleur, 2022). Los agentes de prensado contienen altos niveles de formaldehído debido a su fabricación. A mitad del siglo XX se desarrolló una nueva resina fruto de un proceso de reacción de dos etapas en los que participan glioxal, urea y el propio formaldehído. Con este nuevo método se consiguieron agentes de presando duraderos pero con niveles más bajos de formaldehído (Emmerich et al., 2019; Hazarika y Maji, 2017).

Actualmente su uso está muy extendido, formando parte del proceso de tintura como agente fijador del color, como agente blanqueante y endurecedor de fibras (Grgac et al., 2020; Novick et al., 2013). Además, algunos productos químicos usados en la industria textil, como retardantes de llama o aglutinadores, pueden liberar formaldehído, pudiendo ser finalmente absorbido por los tejidos.

2.3.2. Efectos sobre la salud

La amplia presencia de formaldehído en los productos de consumo incrementa la exposición y sus posibles efectos perjudiciales sobre nuestra salud. A pesar de su gran uso, la IARC clasifica al formaldehído como carcinógeno (Grupo 1), mientras que el Programa Nacional de Toxicología de los EE.UU lo define como carcinógeno humano conocido (HHS, 2021; Lyon, 2010).

La incorporación del formaldehído al organismo se produce principalmente por inhalación o absorción dérmica. En cuanto a la vía inhalatoria, la exposición a formaldehído por las vías respiratorias está asociado al desarrollo de cáncer nasofaríngeo y sinonasal, además de leucemia (IARC, 2012). Los riesgos derivados de una exposición a corto plazo incluyen irritación de nariz, garganta y ojos además de tos, náuseas y dificultad respiratoria. La exposición a largo plazo, a parte de los síntomas anteriores, también puede provocar procesos inflamatorios degenerativos y/o hiperplásicos en las mucosas nasales (ECHA, 2021; Karr et al., 2021).

La absorción del formaldehído a través de la piel se debe al contacto directo con los materiales textiles. Diversas investigaciones asocian la presencia de formaldehído en textiles con reacciones alérgicas, siendo sólo necesarias 30 ppm de formaldehído para causarlas. Las reacciones más comunes provocadas por la exposición a formaldehído son dermatitis, eczema, sensibilización (GAO, 2010; Neale et al., 2021; Prodi et al., 2016;

Tunca et al., 2019) e incluso una mayor proliferación celular en los melanomas (Rizzi et al., 2016).

2.3.3. Legislación

El contenido de formaldehído en productos textiles está regulado en la Unión Europea, Japón y Estados Unidos. En la Unión Europea, el límite actual para textiles que están en contacto con la piel es de 75 mg/kg (ECHA, 2017). Además, existen tres sistemas de etiquetado voluntario que también limitan el uso de formaldehído. La etiqueta ecológica europea fija un límite de 16 mg/kg en prendas con el acabado de fácil y que estén contacto directo con la piel, tanto para adultos como bebés. La certificación OEKO-TEX® Standard 100 mantiene el límite en 75 mg/kg en textiles de adulto. Sin embargo, fija un límite más restrictivo para los textiles de bebés, para los cuales el contenido de formaldehído no puede superar los 20 mg/kg (OEKO-TEX Association, 2017). Por último, la certificación GOTS es la más restrictiva, fijando el límite en 16 mg/kg en todos los textiles (GOTS, 2020).

2.3.4. Estudios anteriores

A pesar de que las concentraciones de formaldehído utilizadas hoy en día en la industria textil son menores que hace un siglo, las prendas de vestir pueden contener residuos. Por este motivo, la presencia de formaldehído en textiles se ha estudiado durante décadas en varios países (Tabla 1.8). En 2007, un estudio realizado en la Unión Europea cuantificó el formaldehído presente en diferentes tipos de textiles y descubrió que el 10% de todas las muestras liberaban más de 30 mg/kg de formaldehído, y el 3% superaba el límite de 75 mg/kg (Piccinini et al., 2007). En 2010, la Oficina de Rendición de Cuentas del Gobierno de los Estados Unidos realizó un estudio sobre un total de 180 muestras, de las cuales 10 superaban los valores estándar, con valores entre 75,4 y 206,1 mg/kg (GAO, 2010). Más recientemente, Aldag et al. (2017) analizaron 24 prendas de ropa del mercado europeo, observando valores de formaldehído máximos de 80 mg/kg. Los valores fueron similares a los hallados en 62 muestras textiles de Colombia (ND – 87 mg/kg) (Caro et al., 2018). Por otro lado, Nyamukamba et al. (2020) no encontraron residuos de formaldehído en 17 calcetines comprados en Sudáfrica.

Tabla 1.8: Concentración de formaldehído en ropa.

País	Número y tipo de ropa	Contenido de formaldehído	Referencias
Sudáfrica (2019)	17 calcetines	100% ND	(Nyamukamba et al., 2020)
Colombia (2018)	62 muestras	ND a 87 mg/kg	(Caro et al., 2018)
Europa (2017)	4 cortinas, 4 pantalones, 14 camisetas y 2 camisas	ND – 80 mg/kg	(Aldag et al., 2017)
Japón (2015)	13 muestras	2 – 89 mg/kg	(Kawakami et al., 2015)
Unión Europea (2007)	221 muestras	ND en 52% 30 – 166 mg/kg en 48%	(Piccinini et al., 2007)
Dinamarca (2003)	10 textiles	ND en 70% 35 – 82 mg/kg en 30%	(Laursen et al., 2003)
EE. UU. (1998)	16 tejidos	ND en 50% <200 ppm en 50%	(De Groot et al., 2010)
Finlandia (1993)	>1400 textiles importados	100 – 300 ppm. en 4,4%; > 300 ppm en 0,3%	
Finlandia (1988)	>1400 textiles importados	100 – 300 ppm. en 8,3%; > 300 ppm. en 3,9%	
Finlandia (1987–1994)	144 tejidos y textiles	100–300 ppm en 8,3% > 300 ppm en 2,7%	
EE. UU (1985)	180 tejidos	117 ± 140 en camisas 58 ± 72 en pantalones 19 ± 17 en punto 31 ± 29 ppm en ropa de cama) 86% tejidos <100 ppm	

ND: no detectado

2.4. Bisfenoles

2.4.1. Descripción y aplicaciones

Los bisfenoles (BPs) son un grupo de compuestos químicos orgánicos formados por un par de fenoles, es decir, dos anillos aromáticos de seis carbonos con un grupo hidroxilo unido directamente a él (Figura 1.6) (Chen et al., 2016). Sus propiedades físicas y químicas, dureza, resistencia a altas temperaturas y a productos químicos, transparencia, ligereza y durabilidad sumados su bajo coste de producción, han propiciado que los BPs sean uno de los grupos químicos más producidos y utilizados por la industria. Principalmente se usan para producir polímeros, resinas y plásticos, por ello los encontramos en numerosos artículos de consumo como botellas de plásticos reutilizable, equipamientos deportivos, CDs, papel térmico o contenedores de alimentos, entre otros (Banaderakhshan et al., 2022; Zhang et al., 2019).

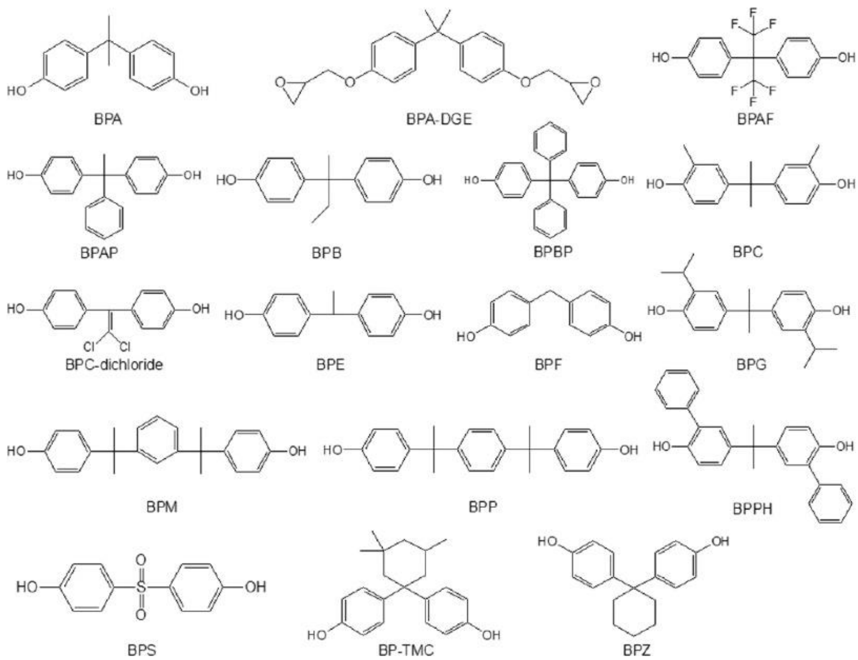

Figura 1.6. Análogos del bisfenol descritos hasta ahora. Fuente: Chen et al. 2016

Se han descrito numerosos análogos del bisfenol, de los cuales el más conocido es el bisfenol A (BPA) (Chen et al., 2016). Aunque se sintetizó por primera vez en 1891, no fue hasta la década de 1960 cuando adquirió un papel importante para la industria al utilizarse como monómero en la producción de, principalmente, policarbonato y resinas epoxi. Ambos materiales son utilizados para recubrir materiales que están en contacto con alimentos como latas, botellas de plástico o vidrio o para fabricar directamente los recipientes que los contendrán, como biberones, vajillas o recipientes de almacenamiento. Hoy en día su uso está mucho más extendido, siendo encontrados en equipos médicos, productos de cuidado personal, juguetes, adhesivos o papel térmico, incrementando así la exposición de los seres humanos al BPA (Xing et al., 2022). Hay estudios que evidencian la presencia de BPA en el medio ambiente, ya sea en la atmosfera por la combustión de productos que contiene BPA (Arp et al., 2017) como en los ecosistemas acuáticos mediante su liberación de los productos plásticos y microplásticos que lo contienen y que se acumulan en ríos y mares (Bouwmeester et al., 2015; Liu et al., 2019). Las fuertes evidencias encontradas sobre sus efectos negativos sobre la salud provocaron su estricta regulación a partir de la década de 2010. Actualmente, en Europa, no se permite la migración de BPA de los recubrimientos de productos destinados a ser utilizados en alimentación por niños con una edad inferior a 3 años (2018/213/EU) (Comisión Europea, 2018).

El bisfenol S (BPS) tiene una estructura similar al BPA y se caracteriza por ser más resistente al calor y la luz solar. Aunque fue inicialmente sintetizado como colorante en 1869, no fue hasta los años 2000 que se postuló como el principal sustituto del BPA. El BPS está presente en los mismos productos de consumo en los que se encuentra el BPA (botellas de plástico, contenedores de alimentos, etc.), pero especialmente se encuentra en el papel térmico (Wu et al., 2018). Aunque en un inicio se desconocían sus efectos adversos sobre la salud humana y por ello utilizó como sustituto del BPA, cada vez son más los estudios que afirman sus efectos negativos sobre la salud humana y el medio ambiente (Thoene et al., 2020; Wu et al., 2018).

Otro de los análogos del bisfenol usado como sustituto del BPA es el bisfenol F (BPF). Se utiliza en selladores dentales, barnices, lacas, plásticos adhesivos y también como recubrimiento en envases de alimentos por su menor viscosidad y mayor resistencia a los disolventes. Curiosamente, se puede encontrar de manera natural en plantas (Huang et al., 2018).

Si bien es cierto que la presencia de BPA y/o sus análogos se asocia con la industria alimentaria, su uso en la industria textil también es importante. El BPA se usa como intermediario en la producción de algunos tintes, pero sin duda su papel más importante es a nivel de protección de las fibras. Los BPs y sus derivados se añaden con el objetivo de modificar las características propias de las fibras, sobre todo fibras de sintéticas, en las etapas de acabados, proporcionando así a las fibras mayor protección del color, resistencia del color en los lavados y la creación de tejidos higroscópicos (Guo et al., 2017; Mousavi, 2004).

2.4.2. Efectos sobre la salud

Por su similitud con algunas hormonas humanas, el mayor peligro de los BPs es su potencial de disrupción endocrina, con especial afectación del sistema reproductivo. En el caso de las mujeres, el BPA provoca una disminución de la fecundidad y de la calidad embrionaria (Wang et al., 2018). La fertilidad masculina también se ve comprometida, algunos estudios relacionan los niveles de BPA en orina con daños en el DNA en espermatozoides y aneuploidías espermáticas (Adoamnei et al., 2018).

Diversos estudios relacionan a los BPs con diferentes tipos de cáncer. La exposición a BPA está relacionada con el cáncer de ovario y su posterior metástasis, así como al cáncer de pecho (Guo et al., 2020). El BPS y el BPF también jugarían un rol importante en el desarrollo de cáncer de pecho, incluso a bajas dosis (Huang et al., 2019; Lei et al., 2018).

La exposición a BPs también se ha relacionado con enfermedades crónicas como la diabetes, debido a su influencia sobre el metabolismo de la glucosa. De hecho, diversos estudios asocian la presencia de BPA y BPS en orina y sérum con un mayor riesgo de padecer diabetes mellitus tipo 2 (Duan et al., 2018; Hwang et al., 2018).

Los niños y lactantes son, de entre todos los grupos de población, los más susceptibles a las consecuencias de la exposición a BPs, ya que están en fase de desarrollo. Algunas investigaciones apuntan a la asociación entre exposición al BPA de mujeres embarazadas con diferentes efectos adversos en la salud de recién nacidos, como bajo peso al nacer, asma, anomalías en genitales, incluso en neurodesarrollo y problemas de comportamiento hasta en niños de 2 años de edad (Almeida et al., 2018; Geiger et al., 2023; Ínce et al., 2018).

2.4.3. Legislación

Las evidencias científicas sobre los efectos negativos que tiene sobre la salud la exposición a BPA forzaron la entrada en vigor de una estricta regulación a partir de 2010, sobre todo en lo que alimentación se refiere. Actualmente está prohibida la venta de biberones que contengan BPA así como que éste migre del recubrimiento aplicado en materiales y productos destinados específicamente a ser utilizados en productos alimenticios para niños de hasta 3 años (2018/213/UE) (Comisión Europea, 2018c). Además también se regula el contenido y migración de BPA en policarbonatos, juguetes, el papel térmico (2017/898/UE) (Comisión Europea, 2017b) y en cosmética (2009/1223/UE) (Comisión Europea, 2009).

Actualmente, no existe aún una regulación directa sobre el uso de BPA y su presencia en los productos textiles, con la única excepción de los materiales etiquetados como ecológicos (2017/1392/UE) (Comisión Europea, 2017a).

2.4.4. Estudios anteriores

A pesar de las evidencias claras de la potencial actividad estrogénica y antiandrogénica de los BPs y de uso en la industria textil, existe una falta general de investigación en este campo. Hasta 2020, sólo 4 estudios habían notificado la presencia de BPs en prendas de vestir (Freire et al., 2019; Li et al., 2018; Wang et al., 2018; Xue et al., 2017). En la Tabla 10 se muestra un resumen general de dichos estudios.

Xue et al. (2017) fueron los primeros en analizar la presencia de diferentes BPs en prendas de vestir, en su caso comercializadas en Estados Unidos. Analizaron no sólo los niveles de BPA, sino también de sus análogos (BPS y BPF) en un total de 77 prendas infantiles. La concentración mediana de BPA, BPS y BPF fueron de 10,7, 1,02 y 0,32 ng/g, respectivamente (Xue et al., 2017). Posteriormente, Li et al. (2018) se centraron en analizar los niveles de diferentes BPs en medias y pantis, siendo el BPA el principal contribuyente a la concentración total de BPs (medianas: 14,4 ng/g para BPA, 1,43 ng/g para BPS, 8,80 ng/g para BPF, 1,70 ng/g para bisfenol B (BPB) y 0,9 ng/g para bisfenol Z (BPZ). En España, Freire et al. (2019) evaluaron el contenido de BPA en 32 calcetines infantiles, detectando unos niveles mediana de 20,5 ng/g. También en 2019, el equipo de L. Wang et al. (2019) analizó también el contenido de BPA y BPS en diversas prendas de ropa, cuyos niveles fueron 17,7 y 12,3 ng/g respectivamente. Como factor añadido, Wang y sus colaboradores también realizaron estudios de migración con sudor artificial, concluyendo que la migración de BPA es mayor en materiales diferentes al algodón.

Tabla 1.9. Concentraciones de BPA en ropa según la literatura científica.

Estudio	Adquisición muestras	Nº y tipo de Muestras	Detección (%)	Mediana (ng/g)	Rango (ng/g)
Xue et al. (2017)	EE.UU	77 (Ropa nueva)	82	10,7	<2,21−13.300
Li et al. (2018)	Varios	36 (Medias y pantis)	96	14,3	<1,30−504
Wang et al. (2019)	China	44 (Ropa nueva)	98	17,7	<3,30−1.823
Freire et al. (2019)	España	32 (Calcetines infantiles)	91	20,5	<0,70 – 3.736

3. EVALUACIÓN DEL RIESGO

La toxicología es la ciencia que estudia los efectos adversos resultantes de la interacción de sustancias tóxicas, químicas o agentes físicos con los organismos vivos. La gran diversidad de agentes tóxicos presentes en el medio ambiente y sus posibles efectos dividen a la toxicología en tres grandes áreas de estudio complementarias (toxicología mecanicista, descriptiva y reglamentaria) pero vitales para la evaluación de los riesgos (Patterson y Willis, 2014).

La evaluación de riesgo se define como el proceso designado para determinar los posibles efectos adversos sobre un organismo, sistema o población derivados de la exposición a un agente. En este proceso se valoran las características del propio agente, las del organismo, sistema o población afectados así como las circunstancias en las que ocurre dicha exposición (OECD, 2004). Las seis etapas principales de la evaluación (Figura 1.7) de riesgos son la identificación del peligro, la caracterización del peligro, la evaluación de la exposición, la caracterización del riesgo, gestión de riesgo y comunicación del riesgo.

a) Identificación del peligro: consiste en identificar el tipo de efectos adversos causados por el agente en el receptor (organismo, sistema o población).

b) Caracterización del peligro: descripción cualitativa y, si es posible, también cuantitativa, de la naturaleza de los efectos adversos para la salud asociados a agentes. Esta etapa debe incluir una evaluación de dosis – respuesta que describa la relación entre la dosis de la sustancia en concreto y la incidencia de sus efectos adversos.

c) Evaluación de la exposición: estimación de la concentración, frecuencia y duración que habrá entre un agente y un receptor (organismo, sistema o población).

d) Caracterización del riesgo: determinación cualitativa y, si es posible, también cuantitativa, de la probabilidad de la aparición de efectos adversos de acuerdo con las condiciones de exposición previamente estimadas.

e) Gestión del riesgo: Proceso de toma de decisiones en el que se tienen en cuenta factores políticos, sociales, económicos y técnicos junto con la información pertinente sobre la evaluación de riesgos en relación con un peligro. El objetivo es desarrollar, analizar y comparar opciones reglamentarias y no reglamentarias para aplicar una respuesta adecuada a ese peligro.

f) Comunicación del riesgo: Intercambio de información sobre los riesgos (sanitarios o medioambientales) entre los evaluadores de riesgos, gestores, medios de comunicación, grupos interesados y el público en general.

Figura 1.7: Etapas principales de la evaluación de riesgos. Imagen adaptada de OMS/FAO (2007).

3.1. Evaluación de la exposición

La evaluación de la exposición se describe como la "determinación de las emisiones, vías y tasas de movimiento de una sustancia y su transformación y degradación con el fin de estimar la concentración/dosis a la que están o pueden estar expuestas las poblaciones humanas o los compartimentos medioambientales" (EEA, 2020).

La ruta o vía por la que las sustancias tóxicas entran en contacto con el receptor es uno de los factores más influyentes en su exposición. Las principales rutas de exposición humana a los tóxicos son:

Inhalación: mediante partículas en suspensión, sustancias volátiles, vapores.

Ingestión: mediante la presencia de sustancias tóxicas en alimentos o bebidas, por un lado, o también suelo o polvo, por otro.

Absorción dérmica: mediante el contacto prolongado de la piel con las sustancias tóxicas.

Otro factor importante en la evaluación de la exposición es el escenario en el que se produce esa exposición. El escenario es el contexto, la situación concreta, en el cual la sustancia tóxica entra en contacto con la población. El escenario debe ser lo más realista posible, para ello se deben tener en cuenta los factores siguientes:

- Frecuencia de exposición
- Tiempo de exposición
- Edad, género y peso de los individuos
- Área de contacto (en el caso de que la vía de exposición sea dérmica).

3.2. Caracterización del riesgo

La caracterización del riesgo es la última etapa de la evaluación de riesgos y puede definirse como "la estimación de la incidencia y gravedad de los efectos adversos que pueden producirse en una población humana o en un compartimento medioambiental debido a una exposición real o prevista a una sustancia tóxica" (EEA, 2020).

La caracterización del riesgo se realiza de manera diferente según si la sustancia tóxica tiene efectos cancerígenos o no.

a) Riesgo no cancerígeno

En el caso de las sustancias tóxicas no cancerígenas existe un valor umbral por debajo del cual no se asocian efectos adversos para la salud en la población. Este valor límite se conoce como dosis de referencia (RfD) y se calcula dividiendo la dosis sin efectos observados (No Observed Effected Level, NOAEL) entre varios niveles de incertidumbre. En el caso de no conocerse el NOAEL, se utiliza el nivel con el efecto más bajo observado (Low Observed Effect Level, LOAEL) (US EPA, 2011). Los valores de incertidumbre generalmente tienen valores de 10 y sus principales factores son la variabilidad en la población general (protección de subpoblaciones más sensibles niños y ancianos), variaciones entre especies (extrapolación de animales a humanos), usar LOAEL en lugar NOAEL, uso de NOAEL de estudios subcrónicos y el uso de bases incompletas.

El riesgo no cancerígeno se calcula comparando la exposición de la sustancia tóxica con su correspondiente RfD establecida para cada vía de exposición (Ecuación 1), obteniendo así un cociente de peligro (*hazardous quocient* en inglés, HQ). Un valor de HQ superior a 1 implica la posibilidad de que aparezca algún efecto adverso no cancerígeno asociado a dicha exposición, es decir, existe cierto riesgo. Por otro lado, un HQ inferior a 1 indica que no se ha superado el valor de referencia y por tanto la población se encuentra a expuesta a valores seguros (ATSDR, 2022).

$$\mathbf{HQ} = \frac{\mathbf{Exposición}}{\mathbf{RfD}} \text{ (Ecuación 1)}$$

b) Riesgo cancerígeno

Contrariamente a lo que sucede con las sustancias tóxicas sin efectos cancerígenos, en el caso de las sustancias tóxicas que sí presentan efectos cancerígenos, la Agencia de protección ambiental de EE.UU (US EPA) considera que no hay un valor o dosis umbral por lo que a cualquier dosis existe la posibilidad de sufrir efectos adversos, es decir, de desarrollar cáncer (ATSDR, 2022).

El riesgo cancerígeno (CR) se describe como la probabilidad de desarrollar cáncer en un individuo durante su periodo vital, 6 años en caso de los niños y 70 años para adultos. El riesgo es el resultado de la exposición a la sustancia multiplicado por su propio factor de potencia cancerígena (*Slope Factor* en inglés, SF) siguiendo la ecuación 2 (US EPA, 2021).

$$\mathbf{CR} = \mathbf{Exposición\ x\ SF}$$

(Ecuación 2)

Si el valor resultante es inferior a 10^{-6}, se considera un riesgo aceptable para la población. Si el valor se encuentra en un rango entre 10^{-6} y 10^{-4}, el riesgo seguiría siendo asumible, pero deberían tomarse acciones correctoras para reducir el riesgo. Sin embargo, si el valor es superior a 10^{-4}, la situación de riesgo no es asumible y supondría un aumento del número de cánceres en la población asociados a la exposición a esa sustancia tóxica (ATSDR, 2022).

HIPÓTESIS Y OBJETIVOS

El uso de sustancias tóxicas por parte de la industria textil siempre ha generado preocupación e investigación debido a sus negativas consecuencias medioambientales. En los últimos años, ha crecido el interés por si estas sustancias tóxicas podrían tener también consecuencias negativas sobre la salud de los consumidores.

De las 3 rutas principales de exposición a sustancias tóxicas, la absorción dérmica es la más olvidada. Sin embargo, la piel es el órgano más grande del cuerpo humano y está en contacto directo con las prendas de vestir durante prolongados periodos de tiempo. Por consiguiente, esta ruta tiene un papel importante en el caso de las sustancias tóxicas presentes en materiales textiles.

Se plantea la hipótesis de que algunas sustancias químicas utilizadas durante las diferentes etapas del proceso de manufactura textil pueden estar presentes en los productos finales, por lo que la ropa puede contener sustancias tóxicas que suponen un riesgo para la salud durante el uso de dichos productos, en especial para grupos de población sensibles.

Objetivo general

Evaluar el riesgo para la salud debido a la exposición dérmica a elementos químicos y otras sustancias presentes en la ropa y utilizadas ampliamente por la industria textil.

Objetivos específicos

1) Determinar el contenido de metales, metaloides y sustancias orgánicas (colorante índigo, PCBs, formaldehído y BPs) presentes en ropa en contacto directo con la piel (pantalones vaqueros, bañadores y ropa premamá e infantil) comercializadas en España.
2) Determinar la migración de metales y metaloides presentes en pantalones vaqueros con sudor artificial.
3) Determinar la migración de metales y metaloides presentes en bañadores en distintas condiciones de uso.

4) Determinar la exposición humana a metales, metaloides y sustancias orgánicas (colorante índigo, PCBs, formaldehído y BPs).
5) Evaluar el riesgo para la salud de diferentes grupos de población debido a la exposición dérmica a metales, metaloides y sustancias orgánicas (colorante índigo, PCBs, formaldehído y BPs) presentes en la ropa.

RESULTADOS

RESUMEN DE RESULTADOS

Esta tesis incluye cinco artículos originales ya disponibles en la literatura científica.

Los resultados completos se presentan en los siguientes 4 capítulos. Las diferentes sustancias evaluadas y sus correspondientes publicaciones se muestran en la Tabla 5.1.

Tabla 5.1. Sustancias evaluadas y su correspondientes publicaciones.

Capítulos	Sustancias evaluadas	Publicaciones
Capítulo 1	Metales pesados e índigo	Herrero, M., Rovira, J., Nadal, M., Domingo, J.L. **Risk assessment due to dermal exposure of trace elements and indigo dye in jeans: Migration to artificial sweat.** Environmental Research 172 (2019) 310–318 Herrero, M., Rovira, J., Esplugas, R., Nadal, M., Domingo, J.L. **Human exposure to trace elements, aromatic amines and formaldehyde in swimsuits: Assessment of the health risks**. Environmental Research 181 (2020) 108951
Capítulo 2	PCB	Herrero, M., González, N., Rovira, J., Marquès, M., Domingo, J.L., Abalos, M., Abad, E., Nadal, M. **Health risk assessment of polychlorinated biphenyls (PCBs) in baby clothes. A preliminary study.** Environmental Pollution 307 (2022) 119506
Capítulo 3	Formaldehído	Herrero, M., González, N., Rovira, J., Marquès, M., Domingo, J.L., Nadal, M. **Early-Life Exposure to Formaldehyde through Clothing.** Toxics 2022, 10(7), 361
Capítulo 4	BPs	Herrero, M., Souza, M.C.O., González, N., Marquès, M., Barbosa, F., Domingo, J.L., Nadal, M., Rovira, J. (2023). **Dermal exposure to bisphenols in pregnant women's and baby clothes: Risk characterization.** Science of the Total Environment 878 (2023) 163122

CAPÍTULO 1

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

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Resumen de resultados

En este artículo se determinó la presencia de un total de 28 metales y metaloides (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 y Zn) y la concentración de indigo en 42 prendas de tipo vaquero. También se realizaron experimentos de migración con sudor artificial ácido y básico para determinar la liberación de estos elementos, así como del colorante índigo.

Los niveles medios más elevados correspondieron al Mg (165 µg/g), Al (41,2 µg/g), Mn (37,6 µg/g) y Fe (37,2 µg/g). De forma similar que para el contenido total, el Mg (124 y 99,4 µg/g) y el Mn (27,1 y 7,20 µg/g) mostraron las mayores concentraciones en ambos sudor artificiales, ácido y básico, respectivamente. El colorante índigo migró a niveles que oscilaron entre 3,22 y 7,76 mg/g, siendo mayores en los tejidos azul oscuro que en los azul claro. Además los niveles de metales y metaloides así como de índigo se analizaron en función de los materiales del tejido y el color. Los niveles de Sb fueron significativamente superiores en las muestras con fibras sintéticas con poliéster (35,0 µg/g) que en otras muestras (fibras sintéticas sin poliéster (1,23 µg/g) y algodón 100% (0,21 µg/g)). Con respecto al color, las prendas negras (360 µg/g) presentaban niveles de Mg significativamente más altos de Mg que las grises (156 µg/g), azules (137 µg/g) y muestras blancas (74,7 µg/g).

Por último, se evaluaron los riesgos no cancerígenos y cancerígenos debidos a la exposición cutánea a los elementos aquí analizados en los tejidos. Ambos riesgos se encontraban dentro de los límites de seguridad de acuerdo con la normativa internacional. cociente de peligrosidad (HQ) de 0,3 en las prendas fabricadas parcialmente con poliéster.

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ABSTRACT

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.

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 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

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(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 min 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.

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 × 2 cm) 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 h 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 aluminium (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 $\lambda = 407$ 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

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.

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 Eq. (1), based on the European Chemical Agency (ECHA) (ECHA, 2016).

$$Exp\ derm = \frac{Fcloth \times dcloth \times Askin \times Fmig \times Fcontact \times Fpen \times Tcontactxn}{BW} \quad (1)$$

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, 2018), with the only exception of oral RfD for Pb, which is not defined in the RAIS, being taken from Seiler and Sigel (1988). GI absorption factors were obtained from the U.S. EPA Preliminary Remediation Goals (US EPA, 2016).

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.

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	6820 cm^2	(US EPA, 2011)
	Jeans skin area adult women	5980 cm^2	
	Jeans skin area teenager (10–16 years old)	4380 cm^2	
	Shirt skin area adult man	11,410 cm^2	
	Shirt skin area adult women	8910 cm^2	
	Shirt skin area teenager (10–16 years old)	8570 cm^2	
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	16 h/day	Assumed
n	mean number of events per day	1/24	Assumed
BW	Body weight adult man	70 kg	(Bundesinstitut für Risikobewertung, 2012) (US EPA, 2011) (Boniol et al., 2008)
	Adult woman	60 kg	
	Teenager between 10 and 16 years old	46 kg	

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).

Not all denim clothes are made of the same material. Sungur and Gülmez (2015) (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 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 (Fig. 1). In Fig. 1b, 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.

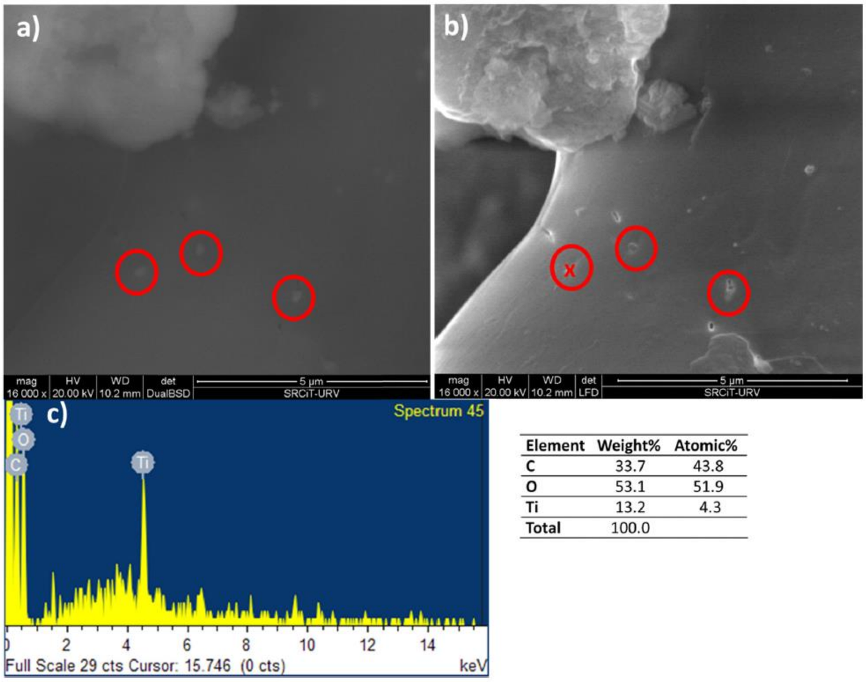
Table 3
Concentrations (μg/g) of trace elements in skin contact clothing samples.

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.

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 fiber, 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



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

Fig. 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.

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).

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.

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.

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).

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).

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

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

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

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

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).

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 and 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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Human exposure to trace elements, aromatic amines and formaldehyde in swimsuits: Assessment of the health risks

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Resumen de resultados

En este artículo se determinó la presencia de 28 metales y metaloides (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 y Zn), aminas aromáticas y formaldehído en un total de 39 prendas de baño cubriendo una amplia gama de materiales, colores y marcas. Se evaluaron la exposición dérmica y los riesgos para la salud de los adultos (hombres y mujeres) maayores de 18 años de edad, bebés de 2 a 3 años, niños y niñas de 3 a 6 años y de 6 a 11 años, y adolescentes de 11 a 16 años. años, y adolescentes (niños y niñas) entre 11 y < 16 años, con bañadores durante 4 h u 8 h.

El formaldehído y las aminas aromáticas estuvieron por debajo de sus respectivos límites de detección en todas las muestras (< 16 y < 1,5 mg/kg, respectivamente). En cuanto a los metales, el Ti mostró los niveles medios más elevados (1844 mg/kg), siendo significativamente más alto en los bañadores de poliamida (3759 mg/kg) que en los de poliéster (24,1 mg/kg). También se observaron concentraciones elevadas de Cr, pero sólo en los tejidos negros de poliamida, con valores que oscilaban entre 624 y 932 mg/kg. Los riesgos no cancerígenos (cocientes de peligrosidad) derivados de la exposición a oligoelementos se encontraban en una zona segura para todos los oligoelementos analizados. Además, se evaluaron los riesgos cancerígenos para el As, el Cr y el Pb, mostrando valores por debajo del umbral de 10^{-5}, con la excepción del Cr en bebés y niños-niñas.

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ABSTRACT

Nowadays, most of the swimsuits are mainly made of artificial fibres, which have interesting properties such as water repellence and fast drying. Swimsuits contain a wide range of additives, which can mean a hazard for the environment and/or human health. In this study, the concentrations of formaldehyde (free and water soluble), 24 aromatic amines, and 28 trace elements (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sr, Sn, Tl, Ti, V and Zn) were analysed in 39 swimsuits covering a wide range of materials, colours and brands. Dermal exposure and health risks were assessed for adults (men and women) aged > 18 years old, babies between 2 and < 3 years old, children (boys and girls) between 3 and < 6 years old and 6 and < 11 years old, and teenagers (boys and girls) between 11 and < 16 years old, wearing swimsuits for 4 h or 8 h. Formaldehyde and aromatic amines were below their respective detection limits in all samples (< 16 and < 1.5 mg/kg, respectively). Regarding trace elements, Ti showed the highest mean levels (1844 mg/kg), being significantly higher in polyamide (3759 mg/kg) than in polyester (24.1 mg/kg) swimsuits. These high Ti levels were confirmed by environmental scanning electron microscope in a single sample made of polyamide. Increased concentrations of Cr were also observed, but only in polyamide black fabrics, with values ranging from 624 to 932 mg/kg. Non-cancer risks (hazard quotients) derived from the exposure to trace elements were in a safe zone for all analysed trace elements. Furthermore, the carcinogenic risks were evaluated for As, Cr and Pb, exhibiting values below the 10^{-5} threshold, with the exception of Cr in babies and children-girls. For Ti, health risks could not be calculated due to the lack of information on toxicological data. However, because Ti was the element with the highest concentrations in swimsuits, and taking into account the potential toxicity of TiO2 nanoparticles, further research is needed to assess the migration of this element from fibres to skin.

1. Introduction

A number of recent studies have demonstrated the presence of toxic substances in clothing (Avagyan et al., 2015; Gong et al., 2016; Lorenz et al., 2012; Luongo et al., 2014; Rovira and Domingo, 2019). In 2012, Greenpeace launched the campaign "Toxic Threads", which was focused on determining the potential levels of nonylphenol ethoxylates, phthalates, and amines, among other toxic substances in clothing (Brigden et al., 2012). Although the definition of clothing wears refers to any type of garment worn in a particular situation ("Clothing. Cambridge Advanced Learner's Dictionary & Thesaurus online," 1993), people do not take into account the bath clothes.

A swimsuit is defined as a piece of clothing whose purpose is to cover a part of the body while people take a bath in beaches, swimming pools, rivers or lakes, among others. In men, swimwear generally covers the part of the genitals and extends to the legs, to a lesser or greater length. In women, the swimsuit usually covers the entire chest and genitals. Initially, swimsuits covered almost completely the body and were made of natural fabrics, either cotton or wool. At that time, swimsuits were heavy and slow to dry when they got wet. In the 1960s, with the generalization of synthetic fibres and because of its resistance, adaptability, elasticity and fast drying, they started to be used for the manufacture of swimwear. Currently, most swimsuits are made of polyester or polyamide, sometimes combined with elastane, due to the multiple advantages that these two synthetic materials offer: lightness, fast drying, perfect fit, and resistance (Niwa et al., 2014). However, synthetic fibres are also associated with some negative aspects such as the environmental impact derived from their manufacture (De Falco

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et al., 2019; Van Der Velden et al., 2014), as well as the presence of hazardous substances for human health (Antal et al., 2016; Jung et al., 2019; Rovira et al., 2015).

Polyester is a plastic material that offers multiple advantages over other fibres, such as cotton. It is more economic, resistant, does not deform, and absorbs less moisture, making more difficult the bacterial development (Martins et al., 2013). However, it gets dirty quickly, owning a high affinity for grease, earth and oil, while only dispersed dyes are used for staining water (Freeman and Mock, 2012). In turn, polyamide is a type of polymer that is characterized by having in the chain recurring amide groups, mostly attached to aliphatic or cyclo-aliphatic groups. These types of fibres stand out for being resistant to abrasions, putrefaction, and even seawater. On the other hand, they dry very rapidly and have low humidity absorption capability, characteristics that make this type of fibres suitable for swimsuits (Mukhopadhyay, 2009).

Chemical additives are used in swimsuits to improve or to add some properties to synthetic fibres (Schindler and Hauser, 2004). For example, catalysts make the production process faster and more efficient (James et al., 2001). Other additives are used to obtain fabrics with different finishes in order to satisfy the consumers' demands or needs (Schindler and Hauser, 2004). These substances include flame retardants (Kajiwara et al., 2009), antimicrobial agents (He et al., 2017), dyes (Ramugade et al., 2019), plasticizers such as phthalates (Negev et al., 2018), pesticides (Cai et al., 2013), as well as a variety of trace elements. Moreover, metals have many uses in the textile industry such as complex dyes, antimicrobials (metallic salts) and water repellents (ZnO) (Derden and Huybrechts, 2013; Morais et al., 2016; Xu et al., 2018; Zhang and Jiang, 2018).

Chemicals used in the textile industry can have a negative impact on the environment and also on human health (Saxena et al., 2017). They can migrate from clothes (Herrero et al., 2019; Leme et al., 2014; Rovira et al., 2017a) and enter in contact with the skin, causing dermatitis, allergies and, microflora alterations, among other adverse effects (Mobolaji-Lawal and Nedorost, 2015; Murayama et al., 2013; Walter et al., 2014). Therefore, it is important to know their contents in clothing, as well as the potential health risks.

The present study was aimed at evaluating the presence of formaldehyde, aromatic amines and a number of trace elements in commercially available swimsuits. Moreover, the dermal exposure to each chemical, and the associated human health risks, were also assessed. To the best of our knowledge, this is the very first time that this kind of textile products are investigated.

2. Materials and methods

2.1. Sampling

Swimsuits characteristics regarding material, colour, manufacture location, and density are shown in Table 1. A total of 39 garments were used for analysis, including man swimwear (n = 16), woman swimwear (n = 16), child swimwear (n = 6), and a T-shirt (n = 1). The range of colours varied from white to black, containing several shades of blue, fluorescent colours (yellow, orange, and pink) and prints. With respect to the materials, 16 were manufactured with a combination of polyamide and elastane, 15 were 100% polyester, 6 combined polyester and elastane, while two were 100% polyamide. All items were randomly purchased in different stores and supermarkets of Reus and Tarragona (Catalonia, Spain). Most of them were made in Asian countries, with only three manufactured in Spain.

2.2. Chemical analysis

2.2.1. Trace elements

Prior to trace element determination, an acidic digestion of each sample was performed. For polyester samples, 0.3 g of each garment was completely digested with 8 mL of HNO_3 (65% Suprapur, E. Merck, Darmstadt, Germany). In turn, polyamide samples were treated differently: 0.2 g of garment was treated with 1.5 mL of H_2SO_4 (96% Suprapur, E. Merck) and 6.5 mL of HNO_3 (65% Suprapur, E. Merck). Irrespective of the material, all samples were digested in a Milestone Start D Microwave Digestion System for 5 min at 105 °C, followed by 15 min at 180 °C, and 20 min at 200 °C. After cooling, extracts were filtered and brought to a volume of 25 mL with ultrapure water. As quality control, blanks were also run during the digestion every 8 samples. Spinach leaves (1570a - National Institute of Standards and Technology, Gaithersburg, MD, USA) were used as reference material every 8 samples (Rovira et al., 2015). All materials in contact with samples and extracts were previously cleaned with a diluted (10%) HNO_3 solution.

The concentrations of aluminium (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, PerkinElmer Elan 6000) in all swimsuits samples, as well as in standards, blanks and replicates (Rovira et al., 2017a). Detection limits were the following: 0.02 mg/kg for Ag, Be, Bi, Cd, Co, Mo, Sc, Sm and Tl; 0.04 mg/kg for As, Ba, Cr, Cu, Mn, Ni, Pb, Sb, Sn, Sr and V; 0.08 mg/kg for Hg and Ti; 0.21 mg/kg for B and 0.42 mg/kg for Al, Se and Zn; 8.33 mg/kg for Fe; and 20.8 for Mg.

2.2.2. Formaldehyde

The content of free and hydrolysed formaldehyde was determined according to the standard UNE-EN ISO 14184-1:2011, Determination of formaldehyde — Part 1: Free and hydrolysed formaldehyde (water extraction method) (AENOR, 2011; Piccinini et al., 2007). Briefly, an amount of the sample (1.0 g) was incubated with water at 40 °C. The total amount of free and hydrolysed formaldehyde was determined by colorimetry with absorbance at 412 nm after adding acetyl-acetone. Blank and standards were used. The detection limit was 16 mg/kg.

2.2.3. Aromatic amines

The analysis of aromatic amines was carried out according to the UNE-EN ISO 14362-1: 2017 method for determination of certain aromatic amines derived from azo (AENOR, 2017; Piccinini et al., 2008). Samples were extracted and the extracts were then added to a reducing media. After that, a liquid –liquid extraction were performed. Quantification of aromatic amines was performed using gas or liquid chromatography coupled to mass spectroscopy (GC-MS or LC-MS). The content of the following aromatic amines was analysed: 4-aminobiphenyl, benzidine, 4-chloro-o-toluidine, 2-naphthylamine, o-aminoazotoluene, 5-nitro-o-toluidine, 4-chloroaniline, 2,4-diaminoanisole, 4,4′-diaminodiphenylmethane, 3,3′-dichlorobenzidine, 3,3′-dimethoxybenzidine, 3,3′-dimethylbenzidine, 4,4′-methylene-di-o-toluidine, p-cresidine, 4,4′-methylene-bis-(2-chloraniline), 4,4′-oxydianiline, 4,4′-thiodianiline, o-toluidine, 2,4-diaminotoluene, 2,4,5-trimethylaniline, o-anisidine, 2,4-xylidine, 2,6-xylidine, and 4-aminoazobenzene. The limit of detection was set at 1.5 mg/kg.

2.3. 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 (Rovira et al., 2017a). ESEM working parameters were the following: low vacuum, 20 kV accelerating voltage, and 10 mm working distance.

Table 1
Main characteristics of the swimsuits.

Nº	Shop place	Material	Colour	Made in	Density
1	Supermarket	81% P; 19% E	Dark blue	Vietnam	193
2	Supermarket	81% PA; 19% E	Black	Vietnam	217
3	Supermarket	85% PA; 15% E	Green (stamping)	China	194
4	Supermarket	82% PA; 18% E	Purple	Cambodia	240
5	Chain Store	80% PA; 20% E	Dark blue	Vietnam	205
6	Supermarket	85% P; 15% E	Pink + white	China	202
7	Chain Store	82% PA; 18% E	Grey	Vietnam	193
8	Supermarket	85% PA; 15% E	Blue (stamping)	China	223
9	Supermarket	82% PA; 18% E	Blue	China	234
10	Chain Store	100% PA	Blue	Albania	107
11	Chain Store	100% PA	Pink	Sri Lanka	101
12	Supermarket	85% PA; 15% E	Green + white	China	198
13	Chain Store	82% PA; 18% E	Grey	Bangladesh	219
14	Chain Store	100% P	Red	Vietnam	131
15	Chain Store	100% P	Fluorescent yellow	Vietnam	122
16	Chain Store	100% P	Fluorescent blue	Vietnam	124
17	Chain Store	80% PA; 20% E	Black	Tunisia	189
18	Supermarket	100% P	Fluorescent yellow	China	116
19	Chain Store	100% P	Dark blue	Vietnam	143
20	Supermarket	100% P	Black	China	99
21	Supermarket	100% P	Fluorescent orange	China	108
22	Supermarket	100% P	Blue	China	107
23	Chain Store	100% P	Black	Spain	127
24	Chain Store	100% P	Fluorescent orange	Vietnam	216
25	Chain Store	100% P	Fluorescent yellow	Bangladesh	88
26	Chain Store	100% P (47% PBT)	Black	Cambodia	145
27	Chain Store	80% P; 20% E	Navy blue	Cambodia	192
28	Chain Store	100% P	Blue	Albania	213
29	Chain Store	100% P (47% PBT)	Black	Cambodia	217
30	Chain Store	80% PA; 20 E	Fluorescent pink	China	203
31	Chain Store	82% PA; 18% E	Black	China	220
32	Chain Store	82% PA; 18% E	Navy blue	China	210
33	Chain Store	72% PA; 28% E	White	Morocco	126
34	Chain Store	95% P; 5% E	Black	Spain	93
35	Chain Store	88% P; 12% E	White	China	145
36	Supermarket	100% P	Red	Bangladesh	206
37	Supermarket	80% P; 20% E	Navy blue + red + white	China	215
38	Chain Store	83% PA, 17% E	Black	Myanmar	349
39	Chain Store	84% PA, 16% E	Cream	Spain	120

[a]Density in g/m^2; E: Elastane; P: Polyester; PA: Polyamide; PBT: polybutylene terephthalate.

2.4. Exposure and risk assessment

The concentration of the analysed trace elements and organic substances in swimsuit samples were used to calculate the dermal exposure and the associated risks. The exposure was estimated for different age groups: adults (men and women) aged > 18 years old, babies between 2 and < 3 years old, child (boy and girl) between 3 and < 6 years old and between 6 and < 11 years old and teenagers (boy and girl) 11 < 16 years old wearing swimsuits for 8 h. We considered swimming briefs and broads shorts in child boys, teenagers' boys and adults' men and also both bikini and swimsuit for teenagers' girls and adults' women in the analyses. Dermal exposure was calculated with the Equation (1) based on the European Chemical Agency (ECHA) (European Chemicals Agency, 2016).

$$\text{Exp derm} = \frac{F_{cloth} \times d_{cloth} \times A_{skin} \times F_{mig} \times F_{contact} \times F_{pen} \times T_{contact} \times n}{BW} \qquad (1)$$

where Exp_{derm} is the dermal exposure (mg/(kg·day)); F_{cloth} is the fraction of element in clothes (dimensionless); d_{cloth} is the density of the clothing (mg/cm^2); A_{skin} is the skin area covered by the clothing (cm^2); F_{mig} is the migration fraction of substance from cloth to skin per day (1/day); $F_{contact}$ is the fraction of contact area for skin (dimensionless); F_{pen} is the penetration rate of the element (dimensionless); $T_{contact}$ is the duration of the clothing skin contact (dimensionless); n is the number of events per day (1/day), and BW is the body weight (kg). A F_{mig} of 0.5% was assumed to calculate dermal exposure (Bundesinstitut für Risikobewertung, 2012). Two scenarios (4 and 8 h) were assumed based on the potential time that swimsuits are worn. The dermal exposure parameters are summarized in Table 2.

Non-carcinogenic risks were determined calculating the hazard quotient (HQ), which is defined as the quotient between exposure and the dermal reference dose (RfD). The carcinogenic risk was calculated multiplying the exposure by the respective dermal slope factor (SF). In turn, as dermal toxicological parameters (RfD and SF) are not available, 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 (US EPA, 1989). RfDs and SFs were obtained from the Risk Assessment Information System (RAIS, 2018). The only exception was the 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 Environmental Protection Agency, 2016).

2.5. Statistics

Data analysis was carried out using the IBM SPSS Statistics software (version 25.0). The Kolmogorov-Smirnov test was used to assess the distribution of the values. Correlations between metal concentrations were performed by applying the Pearson and Spearman correlation coefficients for parametric and non-parametric data, respectively. The student's t-test was used to compare differences of metal levels between polyester and polyamide, as well as elastane and non-elastane fibres. In turn, the ANOVA test for data following a parametric distribution, or

Table 2
Parameters used to assess dermal exposure.

Variable	Description	Value	Reference
F_{cloth}	Weight fraction of substance in garments	Table 3	Present study
d_{cloth}	Clothing density	Table 1	Present study
A_{skin}	Men slip swimsuit (Genitals and Buttocks)	1498 cm^2	US EPA, 2011
	Men thighs swimsuit (Genitals and Buttocks + thighs)	2765 cm^2	
	Women bikini (Bosom + Genitals and Buttocks)	2032 cm^2	
	Women swimsuit (Trunk)	6540 cm^2	
	Babies 2- < 3 years old t-shirt + swimsuit (Trunk + genitals and buttocks)	2930 cm^2	
	Child boy 3–6 years old slip swimsuit (Genitals and Buttocks)	526.3 cm^2	
	Child boy 3–6 years old thighs swimsuit (Genitals and Buttocks + thighs)	1670 cm^2	
	Child girls 3–6 years old swimsuit (trunk)	3130 cm^2	
	Child boy 6–11 years old slip swimsuit (Genitals and Buttocks)	750 cm^2	
	Child boy 6–11 years old thighs swimsuit (Genitals and Buttocks + thighs)	2575 cm^2	
	Child girls 6–11 years old swimsuit (trunk)	4280 cm^2	
	Teenager boy 11–16 years old slip swimsuit (Genitals and Buttocks)	1117 cm^2	
	Teenager boy 11–16 years old thighs swimsuit (Genitals and Buttocks + thighs)	3957 cm^2	
	Teenager girl 11–16 years old bikini (Bosom + Genitals and Buttocks)	3195 cm^2	
	Teenager girl 11–16 years old swimsuit (Trunk)	6300 cm^2	
F_{mig}	Fraction of substance migrating to skin	0.005	Present study Bundesinstitut für Risikobewertung, 2012
$F_{contact}$	Fraction of contact area for skin	1	Bundesinstitut für Risikobewertung, 2012
F_{pen}	Fraction of penetration inside the body	0.01 0.03 for As	US EPA, 2016
$T_{contact}$	Contact duration between skin-textile	0.33 (8h/24 h)	Assumed
n	Mean number of events per day	1/d	Assumed
BW	Adult male	70	Assumed
	Adult female	60	Assumed
	Baby 2 < 3	13.8	Sobradillo et al. (2000)
	Child boy 3 < 6	19.5	
	Child girl 3 < 6	17.2	
	Child boy 6 < 11 years	27.9	
	Child girl 6 < 11 years	29.0	
	Teenager boy 11 < 16	54.1	
	Teenager girl 11 < 16	48.7	

the Kruskal Wallis tests for non-parametric data, were used to assess differences between groups according to the colour. A difference was considered as statistically significant when the probability was lower than 0.05 ($p < 0.05$).

3. Results and discussion

3.1. Concentrations of formaldehyde, aromatic amines and trace elements

In all samples, the concentrations of formaldehyde and aromatic amines were below the respective detection limits: < 16 mg/kg for free and hydrolysed formaldehyde, and < 1.5 mg/kg for the 24 aromatic amines. Although previous studies have reported the presence of formaldehyde (Novick et al., 2013; Piccinini et al., 2007) and aromatic amines (Brüschweiler et al., 2014) in clothing and their potential health risks (De Groot et al., 2010; Malinauskiene et al., 2012), studies focused on the determination of these chemicals in swimsuits are missing in the scientific literature. For comparative purpose, reported data on the levels of formaldehyde in cloths made with polyester have typically ranged between < 20 and 189.6 mg/kg (United States Government Accountability Office, 2010). In turn, the levels of aromatic amines are between 5 and 65 mg/kg according to a recent study conducted in the Swiss market (Crettaz et al., 2019).

With respect to inorganic chemicals, 28 trace elements were analysed in the current study. The concentrations of Be, Fe, Hg, Sc, Se, Sm and Tl were below their respective detection limits in all the samples. Other elements, such as Ag, As, and Bi, were only detected in a few samples (Table 3). These results are in accordance with those of recent studies conducted in our laboratory (Herrero et al., 2019; Rovira et al., 2017b, 2017a, 2015). Titanium was the element showing the highest mean concentration (1844 mg/kg), followed by Al (249 mg/kg), Cr (122 mg/kg), Sb (45.4 mg/kg) and Cu (27.9 mg/kg). The highest Ti concentration (6603 mg/kg) was found in sample #31 (fluorescent pink girl swimsuit, 80% polyamide and 20% elastane). Furthermore, Ti presented significantly higher levels in all the samples made -totally or partially-of polyamide (range 1382–6603 mg/kg) with respect to those made -totally or partially-of polyester (range 5.21–70.1 mg/kg) ($p < 0.01$).

Chromium also showed high levels in samples #39 (932 mg/kg), #2 (841 mg/kg), #32 (776 mg/kg), and #17 (624 mg/kg), all

Table 3
Concentrations (mg/kg) of trace elements in swimsuits samples.

n = 39	% of detection	Mean	SD	Minimum	Maximum
Ag	3	0.04	0.00	< 0.02	0.04
Al	90	249	286	< 0.42	770
As	8	0.14	0.02	< 0.04	0.16
B	18	10.8	16.2	< 0.21	43.7
Ba	92	0.52	0.54	< 0.04	2.93
Bi	13	0.05	0.02	< 0.02	0.08
Co	41	15.5	31.0	< 0.02	111
Cr	97	122	253	< 0.04	932
Cu	64	27.9	75.7	< 0.15	328
Mg	69	0.87	0.55	< 0.02	1.62
Mn	100	6.42	9.89	0.06	38.9
Mo	21	0.12	0.11	< 0.02	0.40
Ni	44	0.63	0.57	< 0.04	2.02
Pb	31	0.21	0.12	< 0.04	0.47
Sb	97	45.4	42.7	< 0.04	167
Sn	28	1.09	1.38	< 0.04	3.75
Sr	85	0.51	0.74	< 0.04	4.13
Ti	100	1844	2161	5.21	6603
V	28	0.17	0.20	< 0.04	0.79
Zn	62	4.25	4.74	< 0.42	24.6

Be, Cd, Fe, Hg, Sc, Se, Sm and Tl concentrations were below their respective detection limits in all the samples.

corresponding to black swimsuits made of polyamide (PA) and elastane (E) (84%PA and 16%E, 81%PA and 19%E, 82%PA and 18%E, and 80% PA and 20%E, respectively) (Table 1). In fact, high levels of Cr in polyamide black garments were already found in previous studies (Matoso and Cadore, 2012; Rovira et al., 2015). Other trace elements with high individual concentrations were Al (770 mg/kg) in sample #17 (black man swimsuit, 80% polyamide and 20% elastane) and Cu (328 mg/kg) in sample #10 (blue lining of a man swimsuit, 100% polyamide). The presence of some metals, such as Co, Cu, Cr or Ni, in clothing may be due to the use of their salts as mordents to improve the dyeing process, or as metal-complex dyes directly (Chakraborty, 2011; Singh and Bharati, 2014).

Some correlations between trace elements were found, being statistically significant those between Al and Mg ($r = 0.861$, $p < 0.01$), Mn ($r = 0.691$, $p < 0.01$) and Ti ($r = 0.735$, $p < 0.01$), as well as between Mg and Ti ($r = 0.661$, $p < 0.01$), and Ti and Sn ($r = 0.706$, $p < 0.01$)). Interestingly, when analysing the data according to the material, only the correlation between Al and Mg was kept in polyamide fibres ($r = 0.812$, $p < 0.01$); suggesting that these elements could be jointly employed in this material manufacturing. It must be highlighted that the levels of both elements were significantly higher in samples made of polyamide than polyester (Fig. 1). The concentration of Al found in swimsuits - with higher levels ($p < 0.05$) in polyamide (412 mg/kg) than in polyester (54.6 mg/kg)- was even much higher than that found in other garments previously analysed in our lab (Rovira et al., 2015, 2017b) (Table 4). This may be due to the use of Al oxychloride as a water repellent, both in polyester and polyamide (Bundesinstitut für Risikobewertung, 2012; Textor et al., 2001; Waeber et al., 2006), an important feature in a swimsuit. A similar trend was noticed for Co, whose levels were higher in polyamide swimsuits (34.5 mg/kg) than in other garments analysed in previous studies, where mean levels were between 0.05 mg/kg and 0.79 mg/kg (Rovira et al., 2015, 2017b).

Lead, Sr and Ti also showed significantly higher levels according to the textile material (Fig. 1). It is important to highlight the great difference between the mean values of Ti in polyester and polyamide, being much higher in garments made of polyamide (3759 mg/kg) compared to polyester (24.1 mg/kg) swimsuits. Similar results were reported by von Goetz et al. (2013), who analysed pants and long sleeved shirts made with polyamide. The presence of Ti in polyamide fibres is due to the use of TiO_2 particles, which make the material much more hydrophobic, and protects against UV (Bossennec and Charbonneaux, 2007; Salman and Razlan, 2018; Shayestehfar et al., 2018). In addition, Ti is a delustering agent and pigment in synthetic fibres in the textile industry (Vann et al., 2009). TiO_2 is added during the polymerization phase and in the form of particles. The presence of Ti was confirmed using ESEM to analyse sample #31, a pink girl's swimsuit (80% polyamide, 20% Elastane) with high contents of Ti (6603 mg/kg) (Fig. 2). According to the ESEM result, the particles were distributed throughout the fibres, with diameters between 178 and 430 nm.

The levels of Sb in polyester (62.8 mg/kg) were significantly higher than those detected in polyamide (14.5 mg/kg). This was already observed in previous studies conducted in our lab, in which underwear, home textiles (pyjamas or bedclothes) and t-shirts were analysed. The Sb levels of the garments made with polyester, were in the ranges 57.7–152 mg/kg, 0.20–88.4 mg/kg, and 52.4–204 mg/kg, respectively (Rovira et al., 2017a, 2017b, 2015). The differences in Sb levels may be attributed to polyester manufacturing catalysts, in which Sb is added in the condensation phase in order to improve the reaction (James et al., 2001).

When analysing the data according to the elastane content in swimsuits ($n = 22$), significant differences in the concentrations of Al, Mg, Pb, Sr, Sb and Ti were found. Although Ti was the element with the highest mean value in garments containing elastane, our finding is mainly due to fact that most samples containing elastane here analysed, were made of polyamide (17 out of 19) ($p < 0.01$). Swimsuits containing elastane showed higher levels than other samples for Al (408 vs. 10 mg/kg, $p < 0.01$), Mg (1.00 vs. 0.10 mg/kg, $p < 0.01$), Pb (0.12 vs. 0.04 mg/kg, $p < 0.05$) and Sr (0.44 vs. 0.20 mg/kg, $p < 0.05$). In contrast, Sb concentrations were significantly lower in elastane samples (22.0 vs 58.9 mg/kg, $p < 0.01$), because most of the polyester samples -showing higher Sb levels-did not contain elastane (5 out of 20).

With respect to the colour of the samples, dark coloured garments (e.g., dark blue and black) showed higher concentrations of Al, Cr, Cu, Mg and Mn. However, significant differences were only noticed between dark coloured and fluorescent colours for Mg and Mn, being in both cases the highest concentrations found in dark swimsuits: 0.76 vs. 0.20 mg/kg for Mg ($p < 0.05$), and 9.33 vs. 1.62 mg/kg for Mn ($p < 0.05$). As above commented, polyamide dark colours showed higher Cr levels (204–932 mg/kg) than other swimsuits (polyamide with light colour, or polyester with dark or light colour) ($p > 0.05$). The only exception was item #26 corresponding to a black polyester swimsuit with 47% of polybutylene terephthalate (PBT), with 303 mg/kg of Cr. Two out of 15 polyester swimsuits were manufactured with 47% of PBT. This kind of material is characterized by the resistance to chlorine and water repellence, characteristics that are very appropriate for swimming trunks. Chromium compounds can be used as fixing and

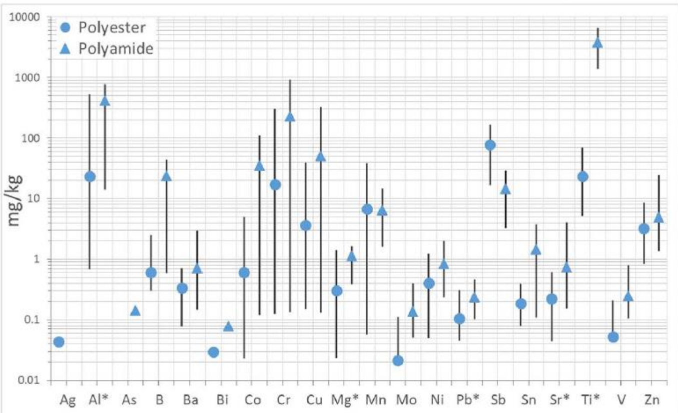

Fig. 1. Concentrations of trace elements (mg/kg) according to the swimsuit material. Blue symbols are mean levels, while black lines are minimum and maximum ranges. Ag in polyamide samples and As in polyester samples were below their respective detection limits. Be, Cd, Fe, Hg, Sc, Se, Sm and Tl levels were below their respective detection limits in all samples. Asterisks (*) indicate significant differences according to the material ($p < 0.05$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4
A summary of concentrations (mean and range) of trace elements in textiles from various studies.

	Menezes et al. (2010)	Matoso and Cadore (2012)	Rovira et al. (2015)	Rovira et al. (2017b)	Rovira et al. (2017a)	Present study	
	Coloured textile	Polyamide	Cotton, polyester, polyamide and viscose	Cotton, polyester and polyamide	Cotton, polyester and polyamide	Polyester	Polyamide
Ag	–	–	–	0.02 (ND - 0.13)	0.05 (< ND - 0.57)	0.04 (0.04–0.04)	ND
Al	38.4 (17.6–118)	–	31.8 (1.37–198)	14.7 (ND - 108)	28.5 (1.68–351)	54.6 (0.68–519)	412 (14.3–770)
As	–	ND	ND	ND	ND	ND	0.14 (0.12–0.16)
B	–	–	0.45 (ND - 2.26)	0.64 (ND - 3.93)	0.30 (ND - 1.27)	1.08 (0.30–2.53)	23.9 (0.59–43.9)
Ba	14.7 (2.05–87.4)	–	1.51 (ND - 9.46)	0.96 (ND - 7.20	2.13 (ND - 19.1)	0.36 (0.08–0.70)	0.71 (0.15–2.9)
Be	–	–	ND	ND	ND	ND	ND
Bi	–	–	0.28 (ND - 1.96)	0.01 (ND - 0.08)	0.02 (ND - 0.10)	0.03 (0.02–0.03)	0.08 (0.08–0.08)
Cd	–	0.2 (ND - 0.2)	0.01 (ND - 0.04)	ND	0.01 (ND - 0.07)	ND	ND
Co	–	ND	0.21 (ND - 5.18)	0.05 (ND - 1.20)	0.79 (ND - 20.4)	0.61 (0.02–5.01)	34.5 (0.12–111)
Cr	6.39 (ND - 1.61)	234.1 (0.3–965)	19.8 (ND - 605)	6.55 (ND - 374)	45.7 (ND - 754)	16.2 (0.12–303)	228 (0.13–932)
Cu	31.1 (ND - 273)	2.77 (2.2–4.0)	20.1 (ND - 287)	32.8 (ND - 1065)	72.8 (ND - 439)	3.67 (0.15–39.8)	50.3 (0.13–328)
Fe	28.5 (12.1–66.1)	–	9.78 (3.38–35.1)	12.9 (ND - 40.7)	18.0 (1.09–194)	ND	ND
Hg	–	ND	ND	0.04 (ND - 0.13)	ND	ND	ND
Mg	–	–	129 (3.75–716)	142 (ND - 889)	114 (ND - 832)	0.41 (0.02–1.41)	1.14 (0.38–1.62)
Mn	–	–	1.82 (0.10–13.3)	0.91 (ND - 7.68)	1.05 (0.07–5.77)	6.42 (0.06–38.9)	6.41 (1.60–14.9)
Mo	–	–	0.03 (ND - 0.38)	0.02 (ND - 0.16)	0.03 (ND - 0.16)	0.07 (0.02–0.11)	0.14 (0.05–0.40)
Ni	0.69 (ND - 5.10)	1.95 (0.9–3.3)	ND	0.19 (ND - 1.20)	0.16 (ND - 1.79)	0.40 (0.05–1.24)	0.83 (0.24–2.02)
Pb	–	0.31 (ND - 1.4)	0.13 (0.03–0.32)	0.13 (ND - 0.90)	0.16 (ND - 1.90)	0.16 (0.04–0.31)	0.23 (0.10–0.47)
Sb	–	ND	22.3 (ND - 204)	26.9 (ND - 202)	26.0 (ND - 152)	76.4 (16.7–167)	14.5 (3.26–29.2)
Sc	–	–	0.18 (ND - 0.72)	ND	0.19 (ND - 0.93)	ND	ND
Se	–	–	0.08 (ND - 0.61)	ND	ND	ND	ND
Sm	–	–	0.01 (ND - 0.04)	ND	ND	ND	ND
Sn	–	–	0.05 (ND - 0.20)	0.05 (ND - 0.35)	0.05 (ND - 0.29)	0.19 (0.08–0.39)	1.43 (0.11–3.75)
Sr	–	–	2.89 (0.05–15.1)	5.37 (ND - 33.8)	2.21 (ND - 10.1)	0.22 (0.04–0.62)	0.74 (0.15–4.13)
Ti	–	–	–	10.9 (ND - 124)	8.34 (ND - 37.8)	24.1 (5.21–70.1)	3759 (1382–6603)
Tl	–	–	ND	ND	0.01 (ND - 0.03)	ND	ND
V	–	–	ND	0.11 (ND - 0.57)	ND	0.08 (0.04–0.21)	0.24 (0.10–0.79)
Zn	3.18 (ND - 10.9)	–	12.1 (ND - 256)	1.57 (ND - 16.4)	36.4 (ND - 1185)	3.48 (0.83–8.52)	4.91 (1.35–24.6)

ND: Not detected.

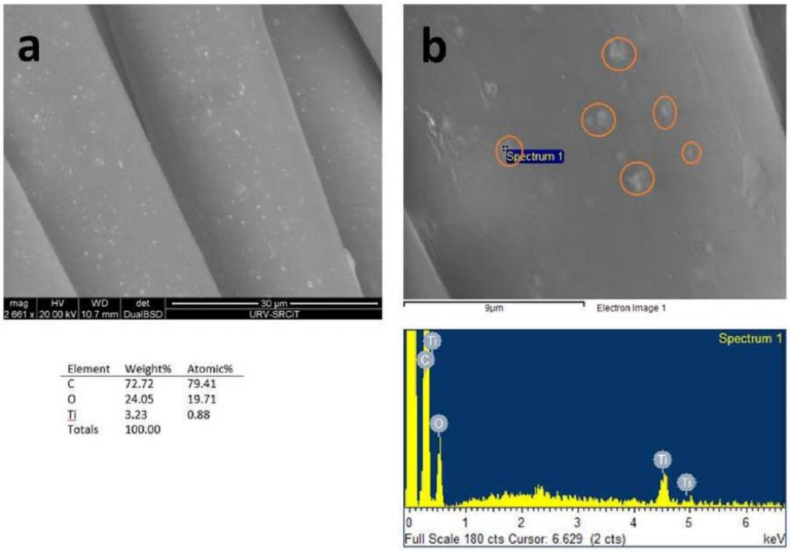

Fig. 2. Backscattering detector (BSD) image (a), and electron microscope image (b) of TiO_2 particles (inside orange circles) found in sample #31. Spectrum 1 indicates where the microanalysis was performed. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

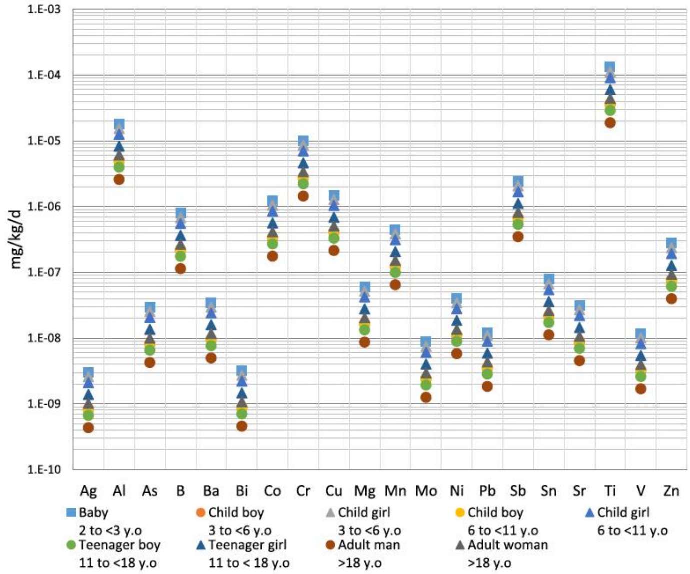

Fig. 3. Dermal exposure (mg/kg/d) due to the use of swimming suits for 8 h a day for the different groups of population. For males (from child, teenager and adult man) mean exposure between board short and briefs swimsuits and for females (teenager and adult woman) mean exposure between bikini and swimsuit were plotted.

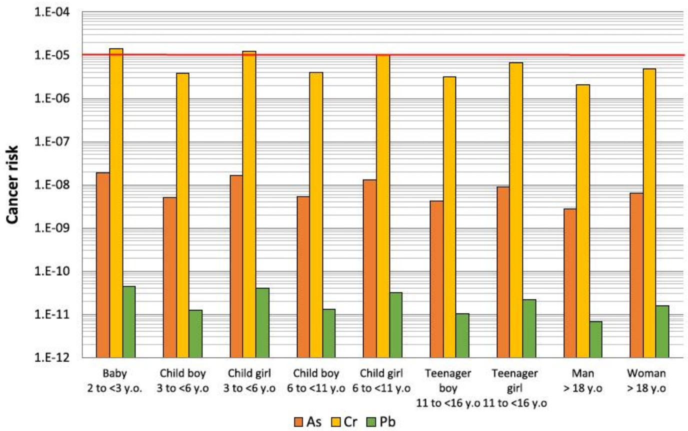

Fig. 4. Cancer risks associated to exposure to trace elements for wearing swimwear.

lighting agents, especially in polyamide fibbers (Matoso and Cadore, 2012). Unlike polyester swimsuits, in polyamide ones some differences between trace elements with respect to coloration were detected. Dark coloured samples showed a significantly higher Mn concentration than light coloured garments (8.44 and 4.05 mg/kg, respectively ($p < 0.05$)). Although polyester garments have higher concentrations of Sb, in the case of polyamide garments there are significant differences between colours, being higher in dark swimsuits (19.5 mg/kg) compared to fluorine colours (11.5 mg/kg, $p < 0.05$) and light colours (8.30 mg/kg, $p < 0.01$). There were also significant differences in the levels of Ti, in which the levels in fluorine garments (6256 mg/kg) were almost twice the values in dark colours (3957 mg/kg, $p < 0.01$), and triple in those of light colours (2763 mg/kg, $p < 0.05$). The fact that Ti levels are so high in fluorescent coloured swimsuits could be due to the fact that these colours are more sensitive to adverse conditions, since titanium is used to protect the fibres of light and heat (Bossennec and Charbonneaux, 2007).

3.2. *Human exposure and risk assessment*

Dermal exposure could not be calculated for formaldehyde and aromatic amines since all levels were below their respective limit of detection. Different population groups were considered, according to the age: babies between 2 and < 3 years old; children (boys and girls) between 3 and < 6 years old, and between 6 and < 11 years old; teenagers (boys and girls) between 11 and < 18 years old; and adults (men and women) above 18 years old. Furthermore, we considered that men/boys wear either swimming briefs or board shorts and women/

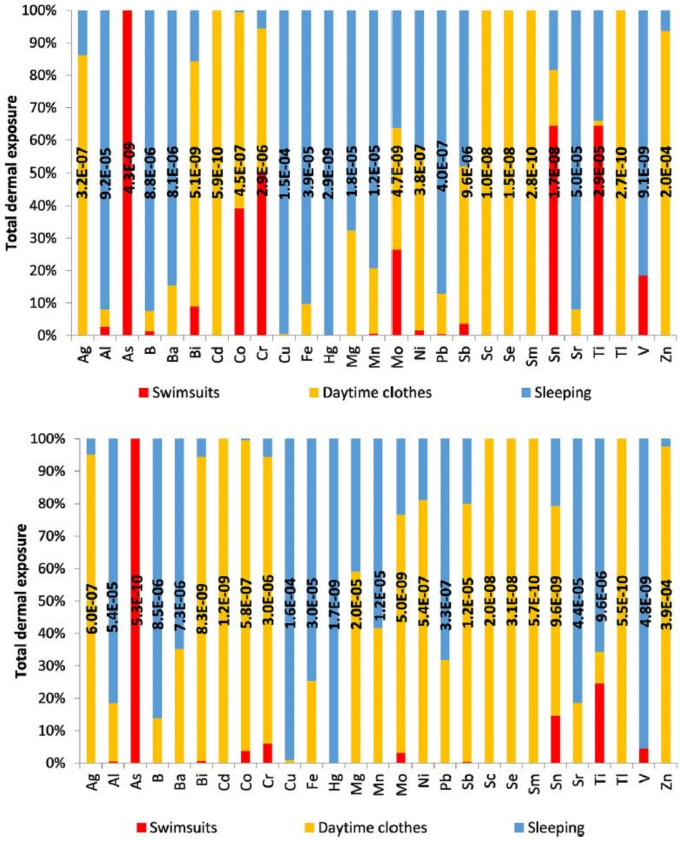

Fig. 5. Contribution (in percentage) of different types of clothes (day time clothes, swimsuits and sleeping wear (pyjamas and bed clothes)) to the total dermal exposure to trace elements during a) summer (8 h/d wearing swimsuits), and b) rest of the year (1 h/d wearing swimsuits). Numbers indicate the total exposure level (mg/kg/day).

girls wear either bikini or swimsuit. For babies we assumed that they wear t-shirts and swimsuits. In terms of exposure time, despite two different scenarios could be considered, half-day (4 h) or the whole day (8 h) using the swimsuit in the beach or pool and as one scenario is a multiple of another, the exposure has only been calculated for the most hazardous situation, wearing a swimsuit during 8 h.

In general, the exposure was higher in women and girls (child or teenager) than in men and boys, as well as higher in younger groups (Fig. 3). Babies between 2 and < 3 years old presented the highest exposure levels for each element, due the higher ratio between surface area (trunk, genitals and buttocks) and body weight, in addition, we assume that babies wear a T-shirt. Exposure levels for all elements for babies were approximately one order of magnitude higher than adult male exposure, which shown the minimum exposure levels in each age group. Obviously, exposure is higher in men or boys (child or teenager) wearing board shorts than those wearing swimming briefs and in women wearing swimsuits than those wearing bikini. In both cases, this difference is related to the area of skin covered by the swimwear, a swimsuit covers more skin than a brief and a swimsuit than a bikini, in the same way that a woman's or girl swimsuit covers more skin than a man or boy's board short. Titanium was the trace element with the highest mean exposure in all population groups, being the group of babies between 2 and < 3 years old the group with highest exposure ($1.31 \cdot 10^{-4}$ mg/kg/d) and adult men the lowest exposure levels ($4.41 \cdot 10^{-5}$ mg/kg/d).

The HQ was used to assess the non-carcinogenic risks derived from dermal exposure. All values were far below the limit value, which is set to 1, indicating that analysed trace elements exhibited non-carcinogenic risks. The highest mean HQ levels were Sb for all groups (HQ = 0.04).

Carcinogenic risks were only calculated for As, Cr and Pb, since they are the only detected elements for which an oral SF is established (RAIS, 2018), (Fig. 4). Babies are the population group with the highest cancer risk for the three elements, with Cr being the element with the highest cancer risk, $1.44 \cdot 10^{-5}$ ($1.91 \cdot 10^{-8}$ for As and $4.38 \cdot 10^{-11}$ for Pb). In the other population groups, Cr is also the element with the highest risk, especially for, child girls from 3 to 6 years old and from 6 to 11 years old, who wear swim suit a ($1.23 \cdot 10^{-5}$ and $1.00 \cdot 10^{-5}$, respectively).

Although Ti has been -by far-the trace element found at the highest concentration, risk assessment could not be carried out due to the lack of toxicological data. Obviously, it does not mean that Ti is not dangerous to health. For example, studies in rat and *in vitro* investigations have demonstrated the negative influence of TiO_2, used in the textile industry, on the reproductive system: spermatogenesis , oogenesis (Hou and Zhu, 2017) and suppression of embryonic bone development (Hong et al., 2017). Therefore, in order to establish the potential risk for reproduction of clothes with an important skin contact with reproductive organs, it is important to characterize accurately all the parameters that can affect human exposure to Ti–TiO_2 such as particle size, migration from the fabric, and skin absorption.

As above commented, in our laboratory we have conducted several studies regarding exposure to trace elements through clothes and textiles (Rovira et al., 2017a, 2017b, 2015). For adult men, a cumulative exposure to trace elements approach due to dermal contact, using previous published data (day time clothes, pyjamas and bedclothes while sleeping), was added to swimsuits for two scenarios: summer (wearing swimsuits for 8 h/d) and rest of the year (wearing swimsuits 1 h/d). In general terms, exposure through swimsuits was negligible (< 10%) with the exceptions of As, Co, Cr, Mo Sn, Ti and V (Fig. 5). In the summer scenario (wearing swimsuit for 8 h/d), As was only detected in swimsuit samples with a contribution of 100%, while the other trace elements contributed between 40 and 65% for Co, Cr, Sn and Ti, and around 20% for Mo and V. However, during rest of the year, assuming only wearing swimsuits 1 h/d, the contribution of swimwear to the total was above 10% only for As (100%), Sn (15%), and Ti (25%).

4. Conclusions

The levels of formaldehyde and aromatic amines were below their respective detection limits for the 39 swimsuits analysed. Regarding trace elements, high levels of Ti were found especially in polyamide fabrics, while high concentrations of Sb were detected in polyester, probably due to its use as catalyst and delustering agent in these fibres. Dark swimsuits had higher levels of Al, Cr, Mg and Mn than other colours, being remarkable the presence of high concentrations of Cr in black polyamide samples. The times of use, and the surface of skin covered, were two important factors influencing dermal exposure. Titanium was the element with the highest exposure. Non-carcinogenic risks for dermal exposure to trace elements through swimwear were at acceptable levels (HQ < 1). Carcinogenic risks for As and Pb were below acceptable limit (10^{-5}), while Cr(VI) levels were close -or even slightly higher-than this threshold. Despite human health risks could not be estimated for Ti due the lack of toxicological data, the human health risks of this element could not be dismissed. Consequently, further investigations are needed in order to assess the ability of Ti in the migration from the fabric to the skin, as well as to test its potential adverse effects.

A recommendation to minimize the exposure to trace elements contained in swimsuits would be the use of clothes made of natural fibres, such as cotton, instead of clothing exclusively made of synthetic fibres. Unfortunately, there is a lack of natural alternatives in the market, while cotton is less attractive in terms of weight gain or drying time when it is wet. In any case, the textile industry is urged to develop alternative materials which reduce the potential exposure to chemical additives, not only to trace elements but also to a wide range of organic compounds.

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CAPÍTULO 2

Health risk assessment of polychlorinated biphenyls (PCBs) in baby clothes. A preliminary study

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Resumen de resultados

Este estudio preliminar tenía por objeto analizar las concentraciones de PCB en diez *bodies*. Las concentraciones de 12 congéneres de PCB similares a dioxinas y 8 no similares a dioxinas se determinaron mediante cromatografía de gases acoplada a espectrometría de masas de alta resolución. Se estimó la absorción dérmica a PCB de niños de distintas edades (6 meses, 1 año y 3 años) y se evaluaron los riesgos no cancerígenos y cancerígenos. Los niveles totales de PCB oscilaron entre 74,2 y 412 pg/g, con una concentración media de EQT de 13,4 pg WHO-TEQ/kg. Los trajes de presentaron una concentración media total de PCB sustancialmente inferior a la de las prendas de algodón normal (11,0 frente a 15,5 pg WHO-TEQ/kg). (11,0 frente a 15,8 pg WHO-TEQ/kg).

La absorción dérmica de PCB para los lactantes se calculó en torno a $3{\cdot}10^{-5}$ pg WHO-TEQ/kg·day. Este valor es > 10.000 veces inferior a la ingesta dietética de PCB, ya sea a través de la lactancia materna o del consumo de alimentos. Además, este valor de exposición no supondría ningún riesgo para la salud de los bebés que lleven esos trajes.

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ABSTRACT

Clothes may contain a large range of chemical additives and other toxic substances, which may eventually pose a significant risk to human health. Since they are associated with pigments, polychlorinated biphenyls (PCBs) may be especially relevant. On the other hand, infants are very sensitive to chemical exposure and they may wear some contact and colored textiles for a prolonged time. Consequently, a specific human health risk assessment is required. This preliminary study was aimed at analyzing the concentrations of PCBs in ten bodysuits purchased in on-line stores and local retailers. The concentrations of 12 dioxin-like and 8 non-dioxin-like PCB congeners were determined by gas chromatography coupled to high resolution mass spectrometry, with detection limits ranging between 0.01 and 0.13 pg/g. The dermal absorption to PCBs of children at different ages (6 months, 1 year and 3 years old) was estimated, and the non-cancer and cancer risks were evaluated. Total levels of PCBs ranged from 74.2 to 412 pg/g, with a mean TEQ concentration of 13.4 pg WHO-TEQ/kg. Bodysuits made of organic cotton presented a total mean PCB concentration substantially lower than clothes made of regular cotton (11.0 vs. 15.8 pg WHO-TEQ/kg). The dermal absorption to PCBs for infants was calculated in around $3 \cdot 10^{-5}$ pg WHO-TEQ/kg·day, regardless the age. This value is > 10,000-fold lower than the dietary intake of PCBs, either through breastfeeding or food consumption. Furthermore, this exposure value would not pose any health risks for the infants wearing those bodysuits. Anyhow, as it is a very preliminary study, this should be confirmed by analyzing larger sets of textile samples. Further investigations should be also focused on the co-occurrence of PCBs and other toxic chemicals (i.e., formaldehyde, bisphenols and aromatic amines) in infant clothes.

1. Introduction

People are permanently exposed to cocktails of environmental and food contaminants. In non-occupationally exposure populations, dietary intake is the most important exposure pathway for many chemicals, including a wide variety of semi-volatile organic compounds (SVOCs), such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), bisphenol A, polybrominated diphenyl ethers (PBDEs) or per- and polyfluoroalkyl substances (PFASs) (Domingo and Nadal, 2017; Trabalón et al., 2017; González et al., 2018; Fan et al., 2021; Martínez et al., 2021; Sun et al., 2021). However, the contribution of other pathways, such as air inhalation and dermal absorption, cannot be disregarded (Melymuk et al., 2016), since they can be potentially significant, especially for some specific vulnerable populations. While the number of scientific studies on health risk assessment of air inhalation of chemical pollutants is very extensive, investigations on the risks associated to dermal absorption are more limited, being only focused to some specific substances.

Recent studies have indicated that dermal absorption to air contaminants, especially indoors, may be also a significant pathway for some SVOCs (Bekö et al., 2013; Weschler and Nazaroff, 2012; Kolarik and Morrison, 2021). Even for non-occupational environments, wearing clothing exposed to indoor air pollution can substantially increase the dermal uptake of SVOCs (Morrison et al., 2016). In addition, the simple

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Table 1
Characteristics of the 10 purchased bodysuits whose PCB levels were determined.

Nº	Place	Materials	Made in	Color	Official certification	Density (mg/cm^2)
1	Chain Store	100% Organic Cotton	China	White		18.9
2	Chain Store	100% Cotton	Bangladesh	Beige and brown		19.1
3	Chain Store	100% Cotton	Bangladesh	Mustard and brown		18.6
4	Chain Store	100% Organic Cotton	Cambodia	Green		19.3
5	Chain Store	100% Organic Cotton	Cambodia	White		19.5
6	Chain Store	100% Organic Cotton	Cambodia	Grey		20.6
7	Chain Store	100% Cotton	Bangladesh	Pink and white	OEKO-TEX® Standard 100	16.1
8	Chain Store	100% Cotton	Bangladesh	Pink	OEKO-TEX® Standard 100	18.5
9	Chain Store	100% Cotton	Bangladesh	White	OEKO-TEX® Standard 100	18.0
10	Shop	100% Organic Cotton	EU	White, black and yellow	GOTS[a]	17.7

[a] GOTS: Global Organic Textile Standard.

act of bringing home clothes of former occupationally exposed employees may become a key pathway for the contamination of the residential environment (Kaifie et al., 2019), ultimately exposing children to air pollutants from outdoors. Unfortunately, the lack of understanding may lead to wrong assumptions, either considering that dermal absorption on body locations covered by clothing could be neglected or that clothing has no influence on dermal exposure (Gong et al., 2016).

In recent years, the occurrence of some specific SVOCs (e.g., phthalates, bisphenol A) in textile materials, including fabrics designed for newborns and infants (Rovira et al., 2015; Freire et al., 2019; Li et al., 2019; Rovira and Domingo, 2019; Tang et al., 2020) and even in diapers (Ishii et al., 2015; Park et al., 2019; Makoś-Chełstowska et al., 2021) has been extensively studied. Other studies have shown that washing clothes before wearing them could reduce the exposure to some of these chemicals, such as SVOCs (Morrison et al., 2016) or formaldehyde (De Groot et al., 2010).

In turn, information about the presence of other SVOCs like PCDD/Fs is more limited (Klasmeier, 1998; Križanec and Le Marechal, 2006). Horstmann and McLachlan (1994) analyzed the levels of PCDD/Fs in several pieces of new clothing from different manufactures, highlighting that these contaminants might be also transferred from textiles to human skin during wearing (Horstmann and McLachlan, 1994; Klasmeier et al., 1999). Despite their potential toxicity, data on other polychlorinated biphenyls (PCBs) are even scarcer, with only very few recent studies focused on the sorption of PCBs from contaminated air to clothing (Morrison et al., 2018; Kolarik and Morrison, 2021).

The early-life stages are critical for the further development of newborns and infants, who are especially vulnerable population groups. Therefore, their exposure to environmental toxicants and food contaminants must be strictly controlled and minimized. The chemical exposure may occur through different pathways whose contribution may vary. In this study, the content of PCBs in several commercial bodysuits was determined. Furthermore, the dermal absorption to PCBs for children aged <3 years old who might wear those clothing was evaluated and compared with other exposure sources. Finally, the health risks associated to that exposure were assessed.

2. Materials and methods

2.1. Chemicals and reagents

All solvents and reagents used were suitable for residue analysis. The standard solutions of dioxin-like PCBs (dl-PCBs) and non-dioxin-like PCBs (ndl-PCBs) in nonane, used for calibration (P48-W-CS1 to CS5 and P48-M-CS0.1 to CS3), quantification (P48–W-ES and MBP-MXE) and analytical recovery (P48-RS), were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada).

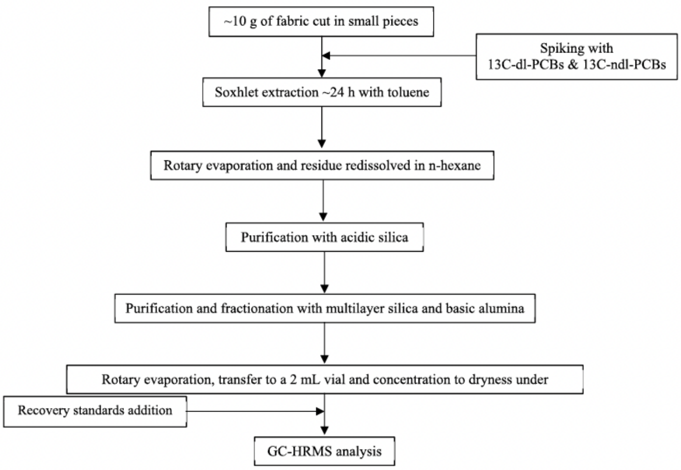

Fig. 1. Schematic representation of the PCB extraction process in clothing.

Table 2
Parameters for exposure assessment and risk evaluation.

Variable	Description	Value	Reference
C_{cloth}	Concentration of each PCB congener	Cloth specific mg/mg	Present study Table 3
d_{cloth}	Cloth density	Cloth specific mg/cm^2	Present study Table 1
F_{mig}	Fraction of substance migrating to skin	0.005	Bundesinstitut für Risikobewertung, 2012
F_{pen}	Fraction of penetration inside the body	0.14	US EPA, 2014
$F_{contact}$	Fraction of contact area for skin	1	Bundesinstitut für Risikobewertung, 2012
$T_{contact}$	Contact duration between skin-textile	1/day	Assumed
BW	Body weight of a 6 months old infant	6 kg	Schuhmacher et al. (2013)
	Body weight of a 1 year old toddler	8.4 kg	ACSA, (2020)
	Body weight of a 3 years old toddler	12.3 kg	ACSA, (2020)
A_{skin}	Skin-cloth contact area for a 6 months old infant	1630 cm^2	US EPA, 2011
	Skin-cloth contact area for a 1 year old toddler	2230 cm^2	
	Skin-cloth contact area for a 3 years old toddler	3380 cm^2	
n	mean number of events per day	1	Assumed
GIABS	Gastrointestinal absorption factor	1	US EPA, 2021

2.2. Sampling

In 2021, ten bodysuits were bought in different Spanish big stores, retailers and on-line shops. The samples were classified according to their labelling: 5 samples were made with organic cotton, while the remaining 5 clothes were made with regular cotton. Additionally, the bodysuits were classified according to the country of manufacture, color and the dyeing/printing. In turn, samples with the OEKO-TEX® Standard 100 label were identified. Table 1 summarizes the characteristics of each item.

2.3. PCB determination

A portion of each unwashed bodysuit was cut in small pieces of approximately 1–2 cm^2 and placed in a glass thimble for Soxhlet extraction. About ¾ of the total volume of the thimble was filled with these pieces (i.e., 8–13 g of textile material depending on the sample). Then, the bodysuits were Soxhlet extracted for ~24 h with toluene after being spiked with known amounts of mixtures of ^{13}C-dl-PCBs (P48–W-ES) and ^{13}C-ndl-PCBs (MBP-MXE) (Fig. 1).

Afterwards, the extracts were rotary evaporated and the residues were dissolved in 5 mL of *n*-hexane. Then, any organic components and other interfering substances were removed by using a silica gel column modified with sulfuric acid (44%, w/w). Further sample purification and fractionation were carried out by means of multilayer silica and basic alumina. For each sample, all PCBs were collected in a single fraction that was rotary concentrated and transferred into a 2 mL vial. The remaining solvent was subsequently reduced to dryness by a gentle stream of nitrogen. The final extract for instrumental analysis was obtained by adding 50 μL of a nonane solution containing known amounts of the recovery standards.

Samples were analyzed by gas chromatography coupled to high resolution mass spectrometry (GC-HRMS) on an Agilent Technologies 6890N gas chromatograph (Agilent, Palo Alto, CA, USA) coupled to a Micromass AutoSpec Ultima NT (Waters, Manchester, UK) high resolution mass spectrometer (EBE geometry) controlled by a Masslynx data system. All samples, as well as standards, were injected with a CTC combiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) under data control system. Chromatographic separation was achieved with a DB-XLB (Agilent, Folsom, CA, USA) fused-silica capillary column (60 m × 0.25 mm I.D. × 0.25 μm film thickness). Electron ionization (EI) mode was used with an electron energy of 32 eV, trap current of 500 μA and an acceleration voltage of 8000 V, operating in the selected ion monitoring (SIM) mode at a resolving power of 10,000 (10% valley definition).

Separate injections were performed for the analysis of dl-PCBs and ndl-PCBs, using two different chromatographic and MS programs, as well as the appropriate calibration standards. Quantification was carried out by the isotopic dilution method. A procedural blank was also carried out following the same analytical method than for the samples in order to ensure solvents and other reagents do not give a significant contribution to the determined PCB values in the bodysuits.

The laboratory performing the analysis is accredited according to the ISO/IEC 17025 norm for the analysis of dioxins and PCBs in abiotic and abiotic samples (e.g. soils, sediments, ambient air, food and feed). In this sense, the laboratory regularly participates with satisfactory performance in proficiency test for different kind of these matrices. Although the fabric matrix is not included in the accreditation, the same methodology was applied with good performance and optimal analytical recoveries of the labelled compounds added as quantification standards.

2.4. Dermal absorption and human health risk assessment

The exposure to PCBs for children wearing the bodysuits was estimated in a worst-case scenario (unwashed clothes). A typical exposure assessment procedure, previously applied for other chemicals (Rovira et al., 2015), was conducted. The dermal absorption was calculated by applying Eq. (1), which is based on the European Chemical Agency (ECHAEuropean Chemicals Agency,) guidance on information requirements and chemical safety assessment (ECEuropean Commission,).

$$Exp_{derm} = C_{cloth} \cdot 10^{-6} \cdot d_{cloth} \cdot A_{skin} \cdot F_{mig} \cdot F_{contact} \cdot F_{pen} \cdot T_{contact} \cdot n \,/\, BW$$
(Eq.1)

Exp_{derm} is the dermal exposure (in mg/kg·day) and the remaining dermal exposure parameters are summarized in Table 2. As there is no available information regarding PCB migration from textiles to skin, a migration factor of 0.0005 was used, following the criteria of the Bundesinstitut für Risikobewertung (Bundesinstitut für Risikobewertung, 2012). In any case, more studies on the migration of PCBs and other chemical additives are required.

The children exposure to PCBs through dermal contact was compared with data corresponding to the contribution of other potential exposure pathways. For infants <6 months old, the estimated intake of PCBs was considered only through breastfeeding, according to data from a population living in the same area of study (Schuhmacher et al., 2013). In turn, for toddlers aged 1 and 3 years, the dietary intake of PCBs was calculated taking into account the results of a previous total dietary study performed in Catalonia (ACSA, 2020).

The dermal absorption to PCBs through clothing was used to assess the non-cancer and cancer risks. Non-carcinogenic risks were evaluated by calculating the Hazard Quotient (HQ), this is, comparing the dermal exposure with the reference dose (RfD) of each PCB congener, obtained from the Regional Screening Levels (Formerly PRGs) (United States Environmental Protection Agency, 2011). The cancer risk (CR) was assessed by multiplying the dermal absorption with the respective slope factor (SF) (Eq. (2)). Dermal values of RfD (RfD_d) and SF (SF_d) were calculated by using the oral slope factor (SFo) and oral reference dose (RfDo) of PCBs and the gastrointestinal absorption factor (GIABS), which was established as the unity (United States Environmental Protection Agency, 2021). Although no safety values may be applied to carcinogenic substances, CR values below 10^{-6} are considered as

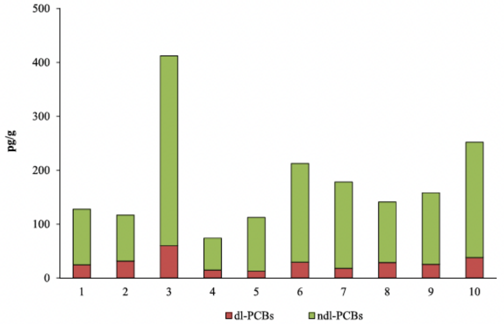

Fig. 2. Concentration of dl- and ndl-PCBs in 10 bodysuits. List of dl-PCB congeners: 81, 77, 123, 118, 114, 105, 126, 167, 156, 157, 169, 189; list of ndl-PCB congeners: 28, 52, 101, 153, 138, 180.

Table 3
Mean concentrations (in pg/g) of 18 PCB congeners in 10 bodysuits.

n = 10	Mean	St. Dev.	MIN	MAX	% detected
dl-PCBs					
PCB-81	0.084	0.06	<0.070	0.241	20
PCB-77	2.18	1.33	0.503	5.02	100
PCB-123	1.12	0.91	<0.098	3.10	90
PCB-118	15.8	7.04	6.93	31.4	100
PCB-114	0.212	0.28	<0.074	0.941	30
PCB-105	6.29	3.22	2.79	13.8	100
PCB-126	0.104	0.05	<0.093	0.203	10
PCB-167	0.646	0.32	0.288	1.15	100
PCB-156	1.47	0.83	0.601	3.10	100
PCB-157	0.318	0.45	<0.047	1.28	20
PCB-169	0.066	0.07	<0.048	0.253	20
PCB-189	0.082	0.03	<0.077	0.128	10
ndl-PCBs					
PCB-28	27.2	19.50	<0.085	71.3	90
PCB-52	42.0	30.17	0.97	106	100
PCB-101	29.1	19.04	9.13	71.3	100
PCB-153	24.0	13.08	11.6	47.3	100
PCB-138	19.8	10.07	10.2	40.5	100
PCB-180	8.14	4.48	4.50	17.3	100
Total dl-PCBs (pg/g)	28.4	13.48	13.0	59.8	
Total ndl-PCBs (pg/g)	150	85.09	59.2	352	
Total PCBs (pg/g)	179	96.95	74.2	412	
Total PCBs (pg WHO-TEQ/kg)	13.4	6.54	2.34	28.8	

acceptable according to international standards (Mahfooz et al., 2020). Data for the exposure assessment and risk evaluation are summarized in Table 2.

$$CR = Exp_{derm} \cdot SF \quad \text{(Eq.2)}$$

2.5. Data treatment

The statistics was performed by means of the statistical software package SPSS 27.0 (IBM Corp. Released, 2020). Samples with PCB values below their respective limit of detection (LODs) were assumed to contain one-half of the LOD (ND = ½ LOD). Total PCB concentrations were also expressed as WHO toxic equivalents (WHO-TEQ) by using the toxicity equivalency factors (WHO-TEF) assigned to the 12 dl-PCBs (Van den Berg et al., 2006).

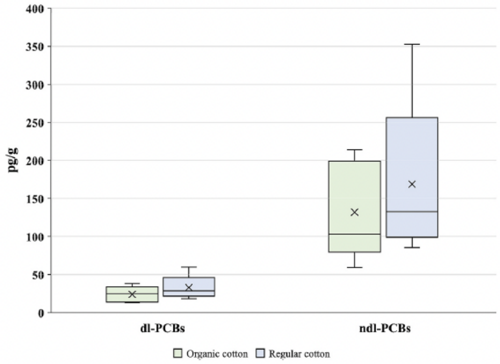

Fig. 3. Boxplots of dl- and ndl-PCB levels in 10 bodysuits, according to the cotton production.

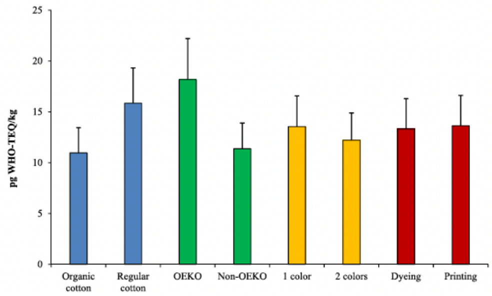

Fig. 4. PCB concentrations in 10 bodysuits according to the (a) cotton production, (d) OEKO-TEX® Standard 100, (c) number of colors, and (d) painting process. Error bars indicate standard deviation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

3.1. PCB levels in clothing

The total concentrations of PCBs in each one of the 10 analyzed bodysuits are depicted in Fig. 2. Total levels of PCBs ranged from 74.2 pg/g, corresponding to a sample with organic cotton, to 412 pg/g, found in bodysuit of regular cotton. The mean concentration of total PCBs was 179 pg/g, with a standard deviation of 96.9 pg/g. When comparing the contribution of both, dl-PCBs and ndl-PCBs, it can be seen that ndl-PCBs were the predominant congeners, with contribution percentages ranging from 73% to 90%. The mean concentration of dl-PCBs in the 10 textile samples was 28.4 pg/g (range: 13.0–59.8 pg/g) or, in terms of toxic equivalents, 13.4 pg WHO-TEQ/kg (range: 2.34–28.8 pg WHO-TEQ/kg). Regarding the individual PCB congeners, maximum and minimum mean concentrations corresponded to PCB-52 and PCB-169, respectively (Table 3).

PCB burdens of each fabric according to a number of factors (e.g., cotton production, colors, dying/painting, OEKO-TEX® Standard 100) were compared. Bodysuits made of organic cotton presented a total mean PCB concentration of 156 pg/g, while those made of conventional cotton showed a mean level of 201 pg/g (Fig. 3). In percentage terms, it means that samples with regular cotton contained 29% more PCBs than

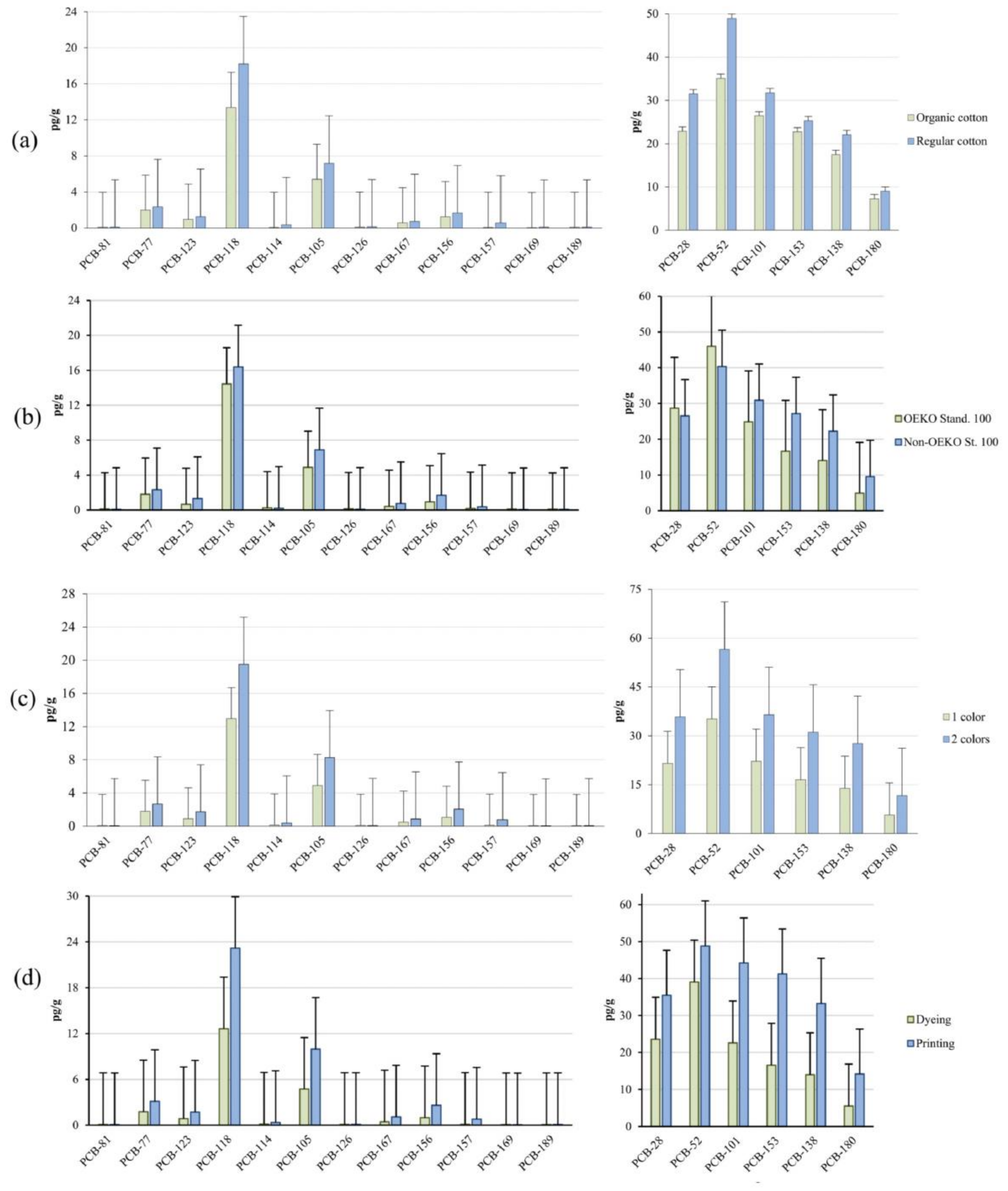

Fig. 5. PCB congener profile according to the (a) cotton production, (b) OEKO-TEX® Standard 100, (b) number of colors, and (d) painting process. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

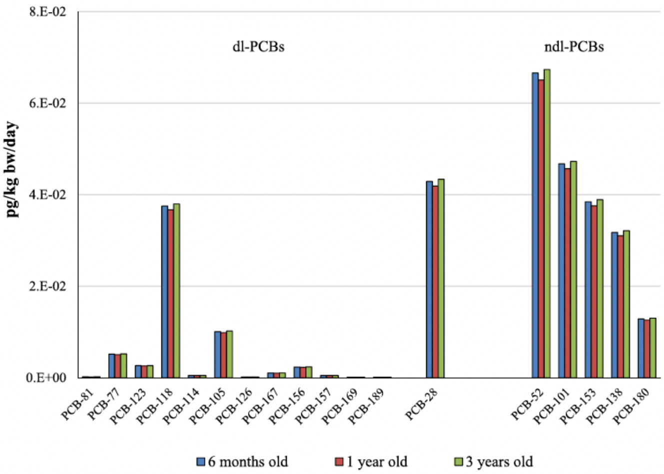

Fig. 6. Mean exposure to dl-PCBs and ndl-PCBs through clothing for children aged 6 months, 1 year and 3 years.

clothes with organic cotton. This difference was especially relevant for dioxin-like congeners, for which samples with regular cotton showed an amount 36% higher than organic cotton fabrics (32.7 vs. 24.0 pg/g). When considering the TEFs, the difference between conventional and organic cotton clothes was even more notorious, of up to 45% (15.8 and 11.0 pg WHO-TEQ/kg, respectively). Similarly, ndl-PCBs were also more abundant in bodysuits of regular cotton with respect to those made of organic cotton (167 and 132 pg/g, respectively).

Eco-labelling in the textile industry entails environmental friendly practices and the promotion of products with a low environmental impact throughout their lifetime (Ţigan et al., 2018) and a low generation of toxic waste (Ranasinghe and Jayasooriya, 2021). It means improving the sustainability of the production process (e.g., use of environmental efficient raw materials and less water, discharge less effluents, etc.), but also minimizing the presence of dangerous chemicals in textile products (Hayat et al., 2020). However, Rovira et al. (2015) reported higher levels of aluminum and strontium in conventional clothes than in eco-labelled and organic cotton items. Unfortunately, although one-half of the samples were made with organic cotton, only one of the 10 analyzed bodysuits (sample No. 10) had an eco-label certification: Global Organic Textile Standard (GOTS). Surprisingly, this sample showed the second highest amount of PCBs (Fig. 2).

Despite bodysuits made of organic cotton showed lower levels of PCBs, they were not toxic-free. In an investigation on the release to water of toxic chemicals from various textiles, including eco-labelled clothes, Dave and Aspegren (2010) stated that eco-labelled products were evenly distributed on a toxicity scale, so eco-labelling in its present form does not necessarily protect users or the environment from exposure to toxic chemicals. Moreover, Herrero et al. (2019) found significantly higher levels of copper in eco-labelled jeans than in conventional items.

In addition to the cotton production, PCB concentrations according to the number of colors, as well as the fact of being labelled with an OEKO-TEX® Standard 100 certificate and the painting process, were compared (Fig. 4). Dyed and painted clothes presented very similar PCB mean concentrations (13.3 and 13.6 pg WHO-TEQ/kg, respectively). Besides, no correlations were found between fabrics concentrations and the number of colors. The presence of PCBs in consumer products may be associated with their color (Anh et al., 2021). In this study, the concentrations of dl-PCBs and ndl-PCBs in white colored bodysuits (21.0 and 111.8 pg/g, respectively) were lower than in colored samples (31.5 and 166.7 pg/g for dl-PCBs and ndl-PCBs, respectively). Sample #53, mustard and brown colored, showed the highest level of PCB-101 (71.3 pg/g), while sample #60, tri-colored (white, black and yellow) presented the greatest value of PCB-153 (47.3 pg/g). Both PCB congeners are directly related to yellow pigments (Anezaki and Nakano, 2014). In turn, very surprisingly the samples certified with the OEKO-TEX® Standard 100 presented higher concentrations of PCBs than non-certified items (18.2 vs. 11.4 pg WHO-TEQ/kg, respectively). PCBs are not currently listed as one of the target chemicals of the OEKO-TEX® Standard 100. In the EC regulation of establishing the ecological criteria for the award of the Community Ecolabel for textile products, it is stated that PCBs and other biocides (i.e., chlorophenols and organotin compounds) shall not be used during transportation or storage of products and semi-manufactured products.

The PCB congener profiles in the 10 textile samples according to the same factors are depicted in Fig. 5. All the analyzed PCB congeners presented higher values in bodysuits made with regular cotton. According to their OEKO-TEX® Standard 100 certification, there was not a homogenous profile, as some PCB congeners (81, 114,126, 169, 189, 28 and 52) showed slightly higher burdens in certified clothes, while the remaining analyzed congeners were more abundant in non-certified textile samples. Regarding the coloring, the levels of most PCB congeners, except for PCBs 81, 169 and 189, were higher in bodysuits with two colors than those single-colored. Finally, printing process had an evident effect on the quantity of PCBs found in textile samples, as samples subject to dyeing presented substantially lower levels of all the PCB congeners than those subject to dyeing (105, 167, 156, and 157).

3.2. Human health risk assessment

The dermal exposure to PCBs through clothing was estimated for children at different stages of development (Fig. 6). Taking into account the total concentrations of PCBs, expressed in terms of WHO-TEQ, the dermal absorption at the age of 6 months, 1 year and 3 years was calculated in $3.19 \cdot 10^{-5}$, $3.11 \cdot 10^{-5}$ and $3.22 \cdot 10^{-5}$ pg WHO-TEQ/kg·day. In conclusion, the exposure to PCBs through clothing was very similar irrespective of the age. The mean exposure to each one of the 12 dl-PCBs and 6 ndl-PCBs here analyzed is summarized in Table 4. Non-dioxin-like PCBs showed a higher contribution to the total exposure to PCBs than dl-

Table 4
Non-cancer and cancer risks of dermal absorption to PCBs through clothing.

	PCB-81	PCB-77	PCB-123	PCB-118	PCB-114	PCB-105	PCB-126	PCB-167	PCB-156	PCB-157	PCB-169	PCB-189	
RfD_o (mg/kg bw/d)	2.30E-06	7.00E-06	2.30E-05	2.30E-05	2.30E-05	2.30E-05	7.00E-09	2.30E-05	2.30E-05	2.30E-05	2.30E-08	2.30E-05	
SF_o (mg/kg bw/d)$^{-1}$	39.0	13.0	3.9	3.9	3.9	3.9	13000	3.9	3.9	3.9	3900	3.9	
RfD_d	2.30E-06	7.00E-06	2.30E-05	2.30E-05	2.30E-05	2.30E-05	7.00E-09	2.30E-05	2.30E-05	2.30E-05	2.30E-08	2.30E-05	
SF_d	3.90E+01	1.30E+01	3.90E+00	3.90E+00	3.90E+00	3.90E+00	1.30E+04	3.90E+00	3.90E+00	3.90E+00	3.90E+03	3.90E+00	
Hazard Quotient (non-cancer risk)													Hazard Index
6 months old	8.63E-08	2.25E-06	1.16E-06	1.63E-05	2.18E-07	4.38E-06	7.29E-08	4.49E-07	1.02E-06	2.14E-07	4.61E-08	5.74E-08	2.63E-05
1 year old	8.44E-08	2.20E-06	1.13E-06	1.59E-05	2.13E-07	4.28E-06	7.12E-08	4.39E-07	9.96E-07	2.09E-07	4.51E-08	5.61E-08	2.57E-05
3 years old	8.73E-08	2.27E-06	1.17E-06	1.65E-05	2.21E-07	4.43E-06	7.37E-08	4.54E-07	1.03E-06	2.17E-07	4.66E-08	5.80E-08	2.66E-05
Cancer risk													Total cancer risk
6 months old	3.32E-12	2.88E-11	4.44E-12	6.27E-11	8.40E-13	1.69E-11	9.34E-10	1.73E-12	3.92E-12	8.24E-13	1.77E-10	2.21E-13	1.24E-09
1 year old	3.24E-12	2.81E-11	4.34E-12	6.13E-11	8.21E-13	1.65E-11	9.13E-10	1.69E-12	3.83E-12	8.05E-13	1.73E-10	2.16E-13	1.21E-09
3 years old	3.36E-12	2.91E-11	4.49E-12	6.35E-11	8.50E-13	1.70E-11	9.45E-10	1.75E-12	3.96E-12	8.34E-13	1.79E-10	2.23E-13	1.25E-09

RfD_o: Oral reference dose; SF_o: Oral slope factor; GIABS: Gastrointestinal absorption factor; RfD_d: Dermal reference dose; SF_d: Dermal slope factor.

PCBs. The congener profile was dominated by PCB-52, with a contribution percentage of up to 22.2% of the total. Regarding dl-PCBs, PCB-118 was the predominant congener (mean percentage: 12.5%). Ingestion and inhalation have been identified as the main routes of exposure to PCBs (Ravenscroft and Schell, 2018; Weitekamp et al., 2021). However, the role of other potential exposure pathways should not be neglected. Zhao et al. (2021) highlighted the importance of the dermal route, especially for waste workers. Other recent studies have pointed out the important role of textiles in the transmission of air pollutants, for which dermal exposure also has a special significance (Morrison et al., 2017; Kolarik and Morrison, 2021; Yu et al., 2022).

Dermal uptake of PCBs was compared with the contribution of other exposure pathways. It has been large reported that food intake, including breastfeeding for newborns, is the main route of exposure to PCBs. For infants aged 6 months living in Tarragona County (Catalonia, Spain), the daily intake of PCBs through breastfeeding has been estimated in 1.58 pg WHO-TEQ/kg·day (Schuhmacher et al., 2013). In turn, the PCB dietary intake by Catalan toddlers of 1 year and 3 years old has been calculated in 0.82 and 1.52 pg WHO-TEQ/kg·day (ACSA, 2020). These values confirm that contact clothes is a negligible exposure pathway in comparison to the intake of PCBs through food and/or breast milk, with contribution percentages of 0.002%–0.004%. The importance of the dietary intake as entrance route of PCBs to the human body, in front of other potential exposure pathways, has been largely reported (Harrad et al., 2006; Linares et al., 2010; Ampleman et al., 2015; Nadal et al., 2020).

Since data on RfD and SF have been derived for dl-PCBs but not for ndl-PCBs, both carcinogenic and non-carcinogenic risks were calculated for the 12 dl-PCBs (Table 4). As the dermal exposure did not differ according to the age, health risks of PCBs through clothing were also very similar in children who are 6 months, 1 year and 3 years old. The HQ associated to the dermal absorption through contact textiles was very low for all the PCB congeners, ranging from $4.59 \cdot 10^{-8}$ to $1.63 \cdot 10^{-5}$ (PCB-169 and PCB-118, respectively). The Hazard Index, calculated as the sum of HQ of the 12 evaluated dl-PCBs, was found to be $2.63 \cdot 10^{-5}$, $2.57 \cdot 10^{-5}$ and $2.66 \cdot 10^{-5}$ for children aged 6 months, 1 year and 3 years, respectively. These levels are far below the threshold, set at the unity. On the other hand, cancer risks were estimated in levels ranging $2.20 \cdot 10^{-13}$ to $9.31 \cdot 10^{-10}$ for PCB-189 and PCB-126, respectively. Some studies suggest that the cancer risk profile in chemical mixtures of PCBs may be dominated by PCB-126 (Besis et al., 2021), due to its relatively higher SF compared with the other dl-PCB congeners. In any case, cancer risks are clearly lower than the value 10^{-6}, an internationally recognized threshold level. In conclusion, the current exposure to PCBs due to the use of bodysuits does not pose any non-cancer and cancer risks to infants, even when they wear clothes not made of organic cotton.

4. Conclusions

Data on the occurrence of some non-regulated chemical additives and environmental pollutants in clothes are very limited. To the best of our knowledge, this is one of the first experimental studies reporting the levels of PCBs in children's clothing and assessing the health risks associated to the dermal absorption to these chemicals through bodysuits, as contact materials. Despite the results are very preliminary, bodysuits made of organic cotton presented a total mean PCB concentration substantially lower than samples made with regular cotton (15.8 and 11.0 pg WHO-TEQ/kg, respectively). Use of organic cotton is an appropriate method to reduce the dermal absorption of PCBs. Nevertheless, traces of PCBs were also found in most bodysuits, so even organic cotton textile samples are not toxic-free, at least in terms of PCB burdens. The PCB congener profile showed a higher contribution of ndl-PCBs, being PCB-52 the most abundant congener. Notwithstanding, the current levels of PCBs do not mean an important health risks for the infants and toddlers, as the dermal absorption to PCBs through clothing was estimated to be more than 4 orders of magnitude lower than their dietary intake. Furthermore, wearing those bodysuits, even for the whole day, was not associated to adverse health effects.

As this is very preliminary investigation, our conclusions should be confirmed by analyzing a larger set of textile samples of different characteristics. Future studies should be also focused on evaluating the co-occurrence of other organic toxic substances, such as formaldehyde, bisphenols or aromatic amines, in children's clothing. Health risks should be eventually assessed by considering an aggregated exposure, this is, estimating the dermal absorption of all the toxicants and not only of a single substance. Moreover, the potential contribution of other exposure pathways, such as dust ingestion and air inhalation, must be considered.

Credit author statement

Marta Herrero: Conceptualization; Formal analysis; Investigation; Methodology; Resources; Writing – original draft, Neus González: Investigation; Resources; Writing – review & editing, Joaquim Rovira: Conceptualization; Supervision; Writing – original draft, Montse Marquès: Conceptualization; Writing – review & editing, José L. Domingo: Supervision; Writing – review & editing, Manuela Abalos: Formal analysis; Investigation; Resources; Writing – review & editing, Esteban Abad: Formal analysis; Investigation; Resources; Writing – review & editing, Martí Nadal: Conceptualization; Funding acquisition; Project administration; Writing – original draft

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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CAPÍTULO 3

Early-Life Exposure to Formaldehyde through Clothing

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Resumen de resultados

Esta investigación tenía como objetivo determinar la presencia de formaldehído en 120 prendas ecológicas y convencionales de mujeres embarazadas, bebés y niños pequeños del mercado catalán (España).

Se detectó formaldehído en el 20% de las muestras, con un nivel medio de 8,96 mg/kg. Los niveles de formaldehído resultaron ser más elevados en las en las prendas ecológicas que en las normales (10,4 frente a 8,23 mg/kg). Sin embargo, estas diferencias sólo fueron significativas ($p < 0,05$) en los sujetadores (11,6 frente a 7,46 mg/kg) y las bragas (27,1 frente a 6,38 mg/kg) de las mujeres embarazadas.

Se evaluaron la exposición dérmica y los riesgos para la salud de tres grupos de población vulnerables: mujeres embarazadas, bebés y niños pequeños. En general, la exposición fue mayor en los bebés (hasta $1,11 \cdot 10^{-3}$ mg/kg/día) que en otros grupos ($2,58 \cdot 10^{-4}$ y $4,50 \cdot 10^{-3}$ mg/kg/día en mujeres embarazadas y niños pequeños, respectivamente). Sin embargo, tanto los riesgos no carcinogénicos como los carcinogénicos estaban por debajo de los límites de seguridad (<1 y <10^{-5}, respectivamente) según la normativa nacional.

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Article

Early-Life Exposure to Formaldehyde through Clothing

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Abstract: Clothes contain a wide range of chemicals, some of them potentially hazardous. Recently, there has been a growing interest in eco-friendly clothing, including the use of organic cotton. However, the process of eco-friendly fabric production does not exclude the use of toxic substances, such as formaldehyde, a known human carcinogen. The present investigation was aimed at determining the presence of formaldehyde in eco-friendly and conventional clothing of pregnant women, babies, and toddlers from the Catalan (Spain) market. The potential effects of washing were also investigated by comparing the reduction of formaldehyde in unwashed and washed clothing. Formaldehyde was detected in 20% of samples, with a mean level of 8.96 mg/kg. Formaldehyde levels were surprisingly higher in eco-friendly than in regular garments (10.4 vs. 8.23 mg/kg). However, these differences were only significant ($p < 0.05$) for bras (11.6 vs. 7.46 mg/kg) and panties (27.1 vs. 6.38 mg/kg) of pregnant women. Dermal exposure and health risks were assessed for three vulnerable population groups: pregnant women, babies, and toddlers. In general, exposure was higher in babies (up to 1.11×10^{-3} mg/kg/day) than in other groups (2.58×10^{-4} and 4.50×10^{-3} mg/kg/day in pregnant women and toddlers, respectively). However, both non-carcinogenic and carcinogenic risks were below the safety limits (<1 and $<10^{-5}$, respectively) according to national regulations. Notwithstanding, although formaldehyde levels were below the legal limits (<75 mg/kg) and health risks were within acceptable ranges, clothing may contain other toxic substances in addition to formaldehyde, thus increasing the risks. Finally, since no formaldehyde was detected in washed textile samples, a safe and simple practice for the consumers is to wash clothing before the first use.

Keywords: formaldehyde; textiles; pregnant women; children; dermal absorption; risk assessment

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1. Introduction

The impact of the textile industry on the environment and the human health is quite important. The large carbon footprint associated with its production, the elevated water consumption, the lack or low recycling rates, the huge amount of waste generated, and the use of chemical substances make the textile industry one of the most polluting productive sectors [1].

Clothes may contain a wide range of chemicals. Although a few substances result from the manufacturing, most chemicals are intentionally added. Skin is constantly in close contact with textiles. Therefore, these substances can be associated with skin adverse effects such as allergies, dermatitis, sensitisation, or reduction of microflora, among others [2–4]. The variety of substances used in the textile industry includes, among others, toxic metals [5–7], flame retardants [8], pesticides [9,10], dyes [6,11], and plasticisers [12]. Some of these substances are used to improve and make the manufacturing process more efficient [13]. Other substances are used to add new properties to fabrics, including antimicrobial activity [14], water repellence [15], flame retardancy [16], colour resistance, or breathability [17]. To date, research has mainly focused on the quantification of chemicals rather than their possible release from textiles. However, once substances are released from textiles, they can be absorbed through the skin, causing potential systemic and/or carcinogenic effects [6,18,19].

Eco-friendly production has rapidly become one of the new trends in the textile industry. New production policies involve a reduction of water and chemicals and the use of organic cotton in order to reduce the environmental impact. However, organic cotton refers only to cotton obtained through organic cultivation, but not to the addition of chemicals during the manufacture of the fibres [20]. Therefore, despite the use of more sustainable raw materials, textiles can accumulate chemicals from their local environment or during their manufacturing process, eventually posing health risks to consumers [21].

Textiles are products used by the entire population. Consequently, all consumers are exposed to their associated chemicals, although some population groups are more vulnerable than others. The early-life stages are critical for the further development of new-borns and infants, hence becoming vulnerable population groups.

Formaldehyde is one of the most widely used chemicals in the world. It is found in a variety of consumer products, such as furniture, glues, adhesives, insulation, paper coatings, disinfectants, tobacco, cosmetics, and textiles [22]. In the mid-1920s, it was introduced into the textile industry to increase the resistance of fabrics (e.g., cotton and polyester) to wrinkling during wear and washing [23]. Nowadays, it is also used as crosslinking, anti-mould, and as a dye-fixing agent [24–26], or for bleaching [27]. Nevertheless, like many other substances added to the fabrics, it is potentially toxic, and it can cause skin and eye irritation, as well as sensitization and toxic effects at the contact site [28]. In addition, formaldehyde is carcinogenic to humans according to the International Agency for Research on Cancer, with sufficient evidence of causing nasopharynx cancer, leukaemia, and sinonasal cancer [29,30]. The health risks of formaldehyde depend not only on its concentration, but also on the exposure route and time. The main risk is associated with inhalation, which may cause discomfort or nausea, stemming from the chemical's pungent odour, irritation of the eyes, nose, and throat, and exacerbation of asthma [31,32]. Clothes are in direct contact with the skin and having formaldehyde in the clothing is associated with dermatitis, eczema, allergies, sensitization [31,33–35], and even increased cell proliferation in melanomas [36]. Unfortunately, although formaldehyde is toxic, nowadays it is still used in the textile industry. Specifically, it is used as a reducing agent during the dyeing step and in the finishing step (urea–formaldehyde resin) to reduce the formation of wrinkles in fabrics [37].

The washout effect during laundry has been studied for different chemicals, such as benzothiazoles [38] and titanium dioxide [39], as well as for microplastics [40]. In most cases, the contents of toxic substances significantly decrease after a few washings, leading to a reduced dermal exposure. However, the release of these pollutants ultimately means that they are a serious source of toxic substances and microplastics to the aquatic habitat [41]. Because of its high volatility, washing clothes may have an important effect on the contents of formaldehyde in clothing. Notwithstanding, it has not been largely proved in the scientific literature.

The present investigation was aimed at determining the presence of formaldehyde in clothes and its associated dermal exposure and human health risks, including "eco-friendly" labelled, used by pregnant women, babies, and toddlers from the Catalan (Spain) market.

2. Materials and Methods

2.1. Sampling

One hundred and twenty first-layer textile items usually worn by pregnant women, babies (<12 months old), or toddlers (12 to 36 months old) were purchased in hypermarkets, chain stores and small retailers of Tarragona County (Catalonia, Spain), and also at online shops. Once at the laboratory, all samples were wrapped in aluminium foil. The characteristics of each clothing item regarding type of fibre, colour, manufacture location, and density, are detailed as Supplementary Information (Table S1). For the three population groups, different clothing types were considered: elastic T-shirts, jeans/trousers/leggings, bras and panties for pregnant women; bodysuits, pyjamas, and socks for infants (<12 months old); and pyjamas, underwear, T-shirts, dresses, and trousers/leggings for toddlers (12–36 months old). Ten items of each one of these categories, covering different characteristics (i.e., colour, origin, material), were sampled. One-half of the samples were organic, either made of organic cotton or free of chemicals.

2.2. Determination of Formaldehyde

Free and extractable formaldehyde analysis was based on the 14184-1:2011 ISO norm. Approximately 2.5 g of sample was cut into small pieces (0.5 cm × 0.5 cm), inserted into an amber vessel with 100 mL of distilled water, and incubated in a water bath for 2.5 h at 40 °C with agitation. Afterwards, the extract was filtered and made up to a volume of 5 mL. Five mL of Nash reagent was then added, and the solution incubated in a water bath for 30 min at 40 °C with agitation. The Nash reagent was prepared by dissolving 150 g of ammonium acetate (≥98% Sigma-Aldrich, Darmstadt, Germany) in distilled water, adding 3.0 mL of glacial acetic acid (99.8%, Labkem, Spain) and 2.0 mL of acetylacetone (≥99% Sigma-Aldrich, Darmstadt, Germany), to a final volume of 1000 mL made up with distilled water. The solution was kept at room temperature for >12 h before its first use. The final extract was cooled at room temperature. The absorbance at 412 nm was read by spectrophotometry, using a UV/Vis Spectrophotometer (Cecil Aurius Series CE 2021, Cecil Instruments Limited, Cambridge, UK). Blanks and two replicates were also analysed every batch of 7 samples to assure the accuracy of the analytical method. The limit of detection was set as 3 times the signal-to-noise ratio set at a concentration of 12.8 mg/kg.

2.3. Washout Effect

Ten samples of jeans/trousers/leggings and 10 samples of panties of pregnant women were washed in a domestic washing machine, and the levels of formaldehyde before and after the washing were compared. The laundering was performed by using an LG F12C3QDP washer, using regular liquid detergent (Jabón de Marsella y Flor de Azahar, Carrefour, Spain; Composition: aqua, ethoxylated alcohol, dodecylbenzene sulphonic acid, sodium laureth sulfate, fatty acids, sodium tallowate, sodium cocoate, polyethyleneimine ethoxylated, sodium chloride, sodium hydroxide, parfum, polypropylene terephthalate, potassium sorbate, phenoxyethanol, modified phosphonate, modified phosphonate, stylbene derivative brightener, styrene/acrylate copolymer, dimethicone) and cleaning vinegar as softener. The clothes were subjected to a quick washing program for 30 min at cold temperature and 1200 rpm, and in the open air. The chemical analyses of formaldehyde were conducted using the same UV/Vis spectrophometer as for unwashed samples.

2.4. Exposure Assessment and Risk Characterization

The concentration of free and extractable formaldehyde in clothes was used to calculate the irritation and sensitization, considering each garment individually. Both were determined by dividing the formaldehyde concentration extracted from the garment by no-observed-adverse effect concentrations (NOAEC) of 0.005% (w/w) [42].

In addition, dermal exposure of formaldehyde through contact textiles was estimated for three different groups: pregnant women, infants (<12 months old), and toddlers (boys and girls, 12–36 months old). A conservative scenario (use of long sleeve tops and long trousers) was considered for calculations, which were based on the following equation, developed by the European Chemical Agency (ECHA) [43].

$$\mathrm{Exp_{derm}} = \frac{\mathrm{F_{cloth}} \times \mathrm{d_{cloth}} \times \mathrm{A_{skin}} \times \mathrm{F_{mig}} \times \mathrm{F_{contact}} \times \mathrm{F_{pen}} \times \mathrm{T_{contact}} \times \mathrm{n}}{\mathrm{BW}}$$

where Exp_{derm} is the dermal exposure (mg/(kg·day)), F_{cloth} is the fraction of element in clothes (dimensionless), d_{cloth} is the density of the clothing (mg/cm^2); A_{skin} is the skin area covered by the clothing (cm^2), F_{mig} (%) is the migration fraction of substance from cloth to skin, $F_{contact}$ is the fraction of contact area for skin (dimensionless) [44], F_{pen} is the penetration rate of the element (dimensionless), $T_{contact}$ is the duration of the clothing skin contact (day), n is the number of events per day (1/day), and BW is the body weight (kg). The dermal exposure parameters are summarized in Table 1.

Non-carcinogenic risks were determined by calculating the hazard quotient (HQ), which is defined as the quotient between exposure and the dermal reference dose (RfD). In turn, the carcinogenic risk was calculated multiplying the exposure by the respective dermal slope factor (SF). RfDs and SFs were obtained from the Regional Screening Level from the U.S. EPA Preliminary Remediation Goals [45].

Table 1. Parameters used to assess dermal exposure.

Variable	Description	Value	Reference
F_{cloth}	Weight fraction of substance in garments	Cloth specific mg/mg	Supplementary Table S1
d_{cloth}	Clothing grammage	Cloth specific mg/cm^2	Supplementary Table S1
A_{skin}	Pregnancy women t-shirt (trunk + arms)	8910 cm^2	[46]
	Pregnancy Troussers_Jeans_Leggings (legs)	5980 cm^2	
	Pregnancy Band of Trouser (trunk/2)	3270 cm^2	
	Pregnancy Troussers_Jeans_Leggings + Band (legs + trunk/2)	9250 cm^2	
	Pregnancy Bra (Bosom)	2594 cm^2	
	Pregnancy underwear without brand (genitals and buttocks)	1469 cm^2	
	Pregnancy underwear with brand (genitals and buttocks +trunk/2)	4739 cm^2	
	Baby Pyjamas (Trunk + Arms + Legs + Feet)	2778 cm^2	
	Baby Bodysuits (trunk + arms)	1795 cm^2	
	Baby socks (Feet)	235 cm^2	
	Toddlers Pyjamas (Trunk + arms + legs)	4355 cm^2	
	Underwear (Genitals)	383 cm^2	
	Dresses (Trunk + arms + 1/2legs)	3665 cm^2	
	T-shirt (trunk + arms)	2975 cm^2	
	Trousser/Jeans/leggings (Legs)	5980 cm^2	
$F_{contact}$	Fraction of contact area for skin	1	[44]
F_{mig}	Migration fraction from cloth to skin	0.5%	[44]
F_{pen}	Fraction of penetration inside the body	0.01	[42]
$T_{contact}$	Contact duration between skin-textile	0.33 (8 h/24 h) 0.67 (16 h/24 h) 1 (24 h)	Assumed
N	Mean number of events per day	1/d	Assumed
BW	Adult Female	76.9 kg	[47]
	Birth to <12 month	7.31 kg	[48]
	1 < 3 years	12.5 kg	

Since formaldehyde is a very volatile compound, the health risk through air inhalation was also evaluated. According to previous studies, inhalation can be considered as the main exposure pathway to this compound, as well as other volatile organic compounds (VOCs) [49], especially in indoor environments [50]. Formaldehyde concentrations in air were obtained from Rovira et al. [51], who analysed the indoor concentration of this chemical in homes of Catalonia. Inhalation exposure levels (Exp_{inh}) were calculated according to the following equation:

$$Exp_{inh} = \frac{(C_i \times IR_i \times F_i) \times EF}{BW \times 365}$$

where C_i is the concentration of formaldehyde in air (in µg/m^3), IR_i is the inhalation rate (in m^3/day), F_i is the daytime fraction spent indoors (unitless), EF is the exposure frequency (in day/year), BW is the body weight (in kg), and 365 is a conversion unit factor (in day/year). Non-carcinogenic risks associated to formaldehyde inhalation were calculated as the relationship between exposure and the inhalation reference dose (RfD_{inh}). On the other hand, carcinogenic risks were also assessed by multiplying the predicted exposure concentration by the inhalation unit risk (IUR). The inhalation exposure parameters are shown in Table 2.

Table 2. Parameters used to assess inhalation exposure.

Variable	Description	Value	Reference
C_i	Air concentration		
	Bedroom	27.3 μg/m^3	[51]
	Living room	22.5 μg/m^3	
	Outdoor	1.62 μg/m^3	
	Work	21.8 μg/m^3	
IR_i	Inhalation rates		
	Pregnant women	19.2 m^3/day	[52]
	Infants <12 months	5.40 m^3/day	
	Toddlers 12–36 months	8.45 m^3/day	
F_i	Time fraction		
	Bedroom	0.36	[51]
	Indoor (excl. bedroom)	0.37	
	Outdoor	0.10	
	At work	0.14	
EF	Exposure frequency	350 days/year	[51]
BW	Body weight		
	Pregnant women	76.9 kg	[47]
	Infants <12 months	7.31 kg	[48]
	Toddlers 12–36 months	12.5 kg	

2.5. *Statistics*

Data analysis was carried out using the IBM SPSS Statistics software version 27.0 (IBM Corp. Released 2020, Armonk, NY, USA). The Kolmogorov–Smirnov test was used to assess the distribution of the values. In turn, Student's t-test or ANOVA test for data following a parametric distribution, or the Kruskal–Wallis tests for non-parametric data were used to assess differences between groups. A difference was considered statistically significant when the probability was lower than 0.05 ($p < 0.05$). Non-detected (ND) levels were considered as one-half of the detection limit (DL) (ND = 1/2DL).

3. Results

3.1. *Analysis of Formaldehyde*

The concentrations of free and extractable formaldehyde in the clothing of different population groups are shown in Table 3.

Table 3. Free and extractable formaldehyde levels (mg/kg) in the clothing of pregnant women, babies and toddlers purchased from Catalonia (Spain).

		Detection Rate (%)	Mean	SD	Minimum	Maximum
Pregnant women's clothes	T-shirts (n = 10)	20	8.44	4.42	<12.8	18.4
	Jeans/leggings (n = 10)	80	18.2	9.77	<12.8	24.5
	Bras (n = 10)	20	7.94	3.35	<12.8	15.5
	Panties (n = 10)	40	16.7	17.0	<12.8	55.7
Babies clothes (<12 months)	Pyjamas (n = 10)	0	<12.8	0.00	<12.8	<12.8
	Bodysuits (n = 10)	0	<12.8	0.00	<12.8	<12.8
	Socks (n = 10)	10	8.19	5.72	<12.8	24.5
Toddlers clothes (12–36 months)	Pyjamas (n = 10)	0	<12.8	0.00	<12.8	<12.8
	Underwear (n = 10)	0	<12.8	0.00	<12.8	<12.8
	Dresses (n = 10)	10	7.74	4.29	<12.8	20.0
	T-shirts (n = 10)	10	7.48	3.49	<12.8	17.4
	Trousers (n = 10)	40	9.87	4.65	<12.8	16.4

SD: Standard deviation.

Formaldehyde was detected in 20% of the samples, with a mean level of 8.96 mg/kg (range: <12.8 to 55.7 mg/kg). Two pregnancy panties and a sample of baby socks were the garments with the highest burdens of formaldehyde (55.7, 37.3, and 24.5 mg/kg, respectively).

The mean formaldehyde content of each fabric according to several factors (e.g., organic cotton, type of fibre, OEKO certification, dying/painting, number of colours) is depicted in Figure 1. Dyed garments showed significantly ($p < 0.05$) higher levels than printed ones (10.2 vs. 7.07 mg/kg). Considering the type of fibre material, 100% cotton, 100% synthetic, and a combination of both, formaldehyde was detected in 22%, 14%, and 47% of the samples, respectively, proving that synthetic clothes have lower contents of formaldehyde. The garments made of a mixture of cotton and synthetic fibres (12.7 mg/kg) had significant ($p < 0.05$) higher levels than those made of 100% cotton (7.51 mg/kg) or 100% synthetic fibres (6.66 mg/kg). In turn, monochromatic clothing (10.1 mg/kg) had significantly ($p < 0.05$) higher concentrations than garments, with two (8.33 mg/kg) and more than two colours (7.29 mg/kg). Formaldehyde concentrations were also higher in OEKO Standard 100 garments than non-OEKO certified, but this difference was not significant ($p > 0.05$).

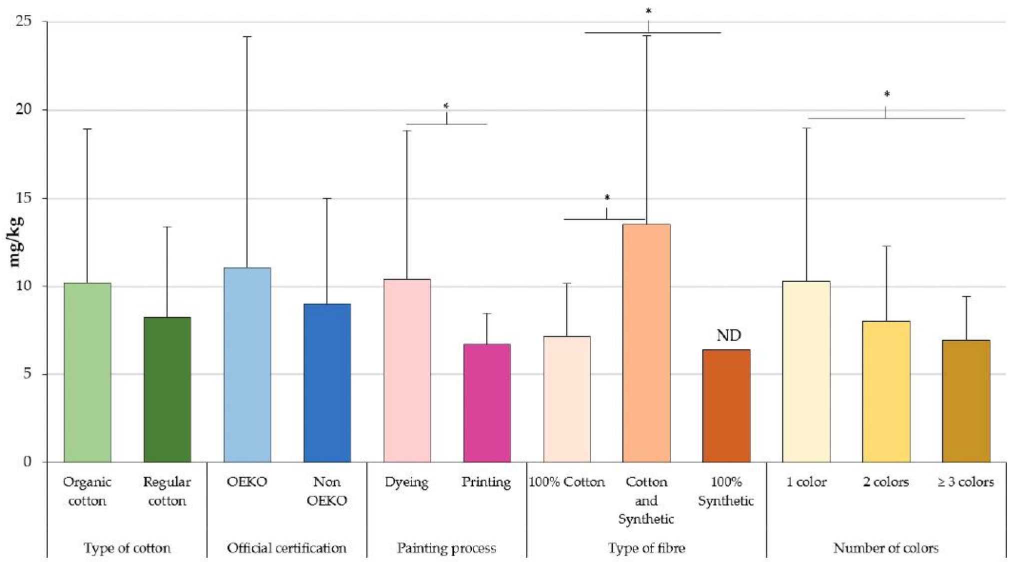

Figure 1. Formaldehyde concentrations according to a number of factors, including cotton production, OEKO-TEX® Standard 100, painting process, type of fibre, and number of colours. * An asterisk indicates significant differences at $p < 0.05$. ND: Not detected.

Up to 40 items of pregnant women's clothing, including T-shirts, trousers/jeans/leggings, bras and panties, were analysed. Among them, trousers and underwear were the items with the highest mean concentrations (18.2 and 12.5 mg/kg, respectively). Particularly, the sample with the greatest amount was #17, corresponding to grey jeans made of 86% cotton (20% recycled cotton from post-consumer textile waste from collected garments) and 12% polyester (Supplementary Information, Table S1), with a value of 24.5 mg/kg. Two black panties (sample #31 and sample #34, showed the highest formaldehyde values of the study (37.3 mg/kg and 55.7 mg/kg), both made of 100% organic cotton.

Pyjamas, bodysuits, and socks are undoubtedly the items of baby clothing with the most direct and prolonged contact with the skin. Ten samples from each category were analysed, formaldehyde residues being detected only in a few socks, sample #63 (24.5 mg/kg), both made of a combination of polyamide, cotton, and elastane.

With respect to toddlers' clothing, pyjamas, underwear, dresses, T-shirts, leggings, and jeans were analysed. Up to 40% of the samples of trousers/jeans, one-half of them made of organic cotton ($n = 2$), presented detectable concentrations of formaldehyde, with levels ranging between 13.1 and 16.4 mg/kg. In turn, only 10% of the T-shirts and dresses ($n = 2$, made of organic cotton) showed traces of formaldehyde. Finally, no traces of formaldehyde were found in the samples of pyjamas and underwear.

T-shirts, bras, and panties of pregnant women, as well as T-shirts and dresses of toddlers, made from organic cotton, showed higher levels of formaldehyde than those made from conventional materials (Figure 2).

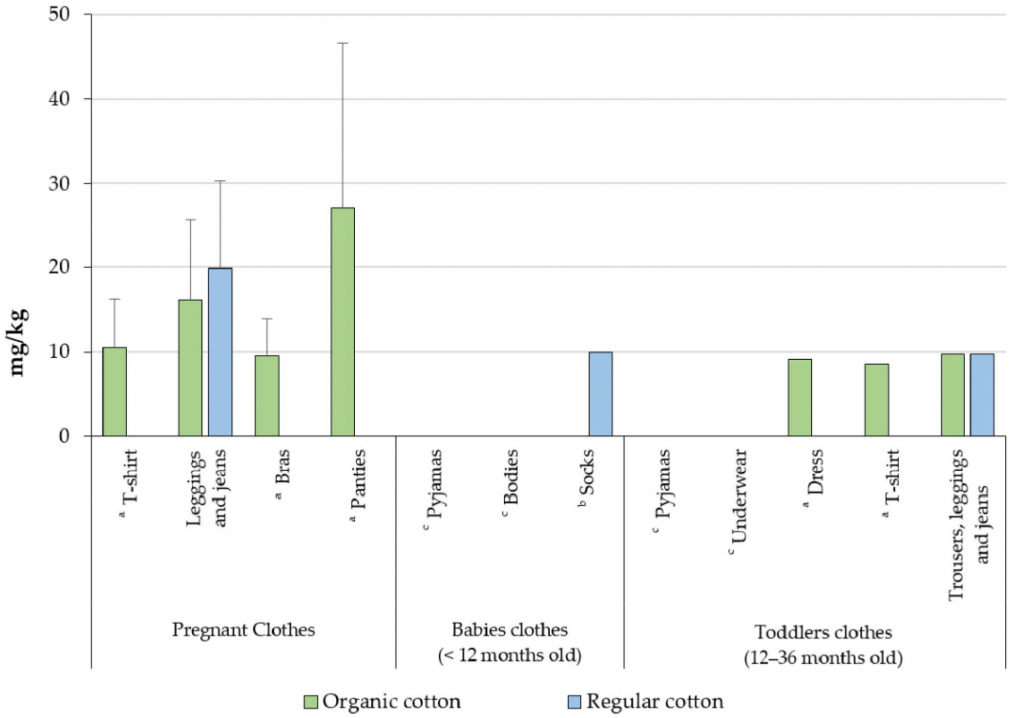

Figure 2. Formaldehyde concentrations according to type of cotton in clothes for pregnant women, babies aged <12 months, and toddlers aged 12–36 months. [a] Not detected in regular cotton. [b] Not detected in organic cotton. [c] Not detected in any types of cotton.

Only 25 samples had an official certification. Twelve of them were certified with the OEKO-TEX® Standard 100 label, while two were OEKO-TEX® Made in Green, and 11 had GOTS certification. The regulation of the OEKO-TEX® Standard 100 and OEKO-TEX® Made in Green labels states a maximum residue level of 75 mg/kg for formaldehyde, which was achieved by all the certified garments. In turn, the GOTS certification is the most restrictive regulation, as certified textile samples must be free of formaldehyde. Despite this, a quantifiable amount of this chemical (20.0 mg/kg) was found in sample #92 (GOTS certified dark blue dress, 100% organic cotton).

The effect of washing clothes, in terms of releasing formaldehyde, was evaluated in some garments with the greatest concentrations of this substance (10 samples of jeans/

trousers/leggings and 10 samples of panties, all of them for pregnant women). For that purpose, formaldehyde levels in unwashed and washed samples were compared. None of the 20 clothing items showed detectable amounts of formaldehyde after washing (<12.8 mg/kg).

3.2. Human Exposure and Risk Assessment

The dermal exposure of formaldehyde, based on the mean concentration of each garment, was assessed for the same population groups: pregnant women, babies of <12 months, and toddlers aged 12–36 months. The individual exposure, considering each textile category, and the total exposure, considering that people wear several clothes at the same time, are summarised in Table 4. Baby socks were identified as the category with the highest exposure (5.13×10^{-4} mg/kg/day), followed by trousers/leggings/jeans (3.30×10^{-4} mg/kg/day). In general terms, total exposure was 2-times higher in babies (1.11×10^{-3} mg/kg/day) than in toddlers (4.50×10^{-4} mg/kg/day), while the lowest exposure to formaldehyde corresponded to pregnant women.

Table 4. Dermal exposure (mg/kg/day) to formaldehyde through clothing.

		Dermal Exposure per Item	Total Exposure (Non-Cancer Risk)
Pregnant women	T-shirts	5.23×10^{-5}	2.58×10^{-4}
	Jeans/leggings	1.48×10^{-4}	
	Bras	1.54×10^{-5}	
	Panties	4.23×10^{-5}	
Babies (<12 months old)	Pyjamas	3.07×10^{-4}	1.11×10^{-3}
	Bodysuits	2.92×10^{-4}	
	Socks	5.13×10^{-4}	
Toddlers (12–36 months old)	Pyjamas	2.68×10^{-4}	4.50×10^{-4} * 1.44×10^{-4} **
	Underwear	2.99×10^{-5}	
	Dresses	1.14×10^{-4}	
	T-shirts	8.96×10^{-5}	
	Trousers	3.30×10^{-4}	

* Dressed with underwear, T-shirt and trousers. ** Dressed with underwear and dress.

Dermatitis or local allergic reactions are probably the most common adverse effects of short-term dermal exposure to formaldehyde [29,34,43]. In the current study, the risk of sensitisation was calculated by using the content of formaldehyde in clothing. Formaldehyde extracted from all garments showed values at least 10 times lower than NOAEC (0.005% *w/w*), being 0.1% the value at which signs of sensitisation could be observed [42].

The hazardous quotient (HQ), estimated from the dermal exposure and the RfD, was far below the limit value, which is set to unity. It is a clear indication that formaldehyde in clothing does not currently mean non-cancer risks for the population. On the other hand, cancer risks ranged from 1.38×10^{-7} to 9.49×10^{-7} for pregnant women, from 4.61×10^{-7} to 2.76×10^{-7} for babies and from 8.13×10^{-7} to 2.97×10^{-6} for toddlers. All values are below the limit of 10^{-5}, the Spanish threshold level. Non-cancer and cancer risks of dermal contact to formaldehyde are shown in Figure 3.

Dermal absorption is not the only pathway of exposure to formaldehyde. Air inhalation is considered as the most serious exposure pathway for this chemical. In 2014, Rovira et al. [51] conducted a study in which formaldehyde air levels were analysed in different spaces, homes, and workplaces (shops, offices, schools). When analysing the total exposure to formaldehyde, the contribution of the inhalation route was found to be much higher than the dermal route, with a percentage of 90% of the total. Therefore, it is evident that clothing is not the most relevant exposure pathway to formaldehyde.

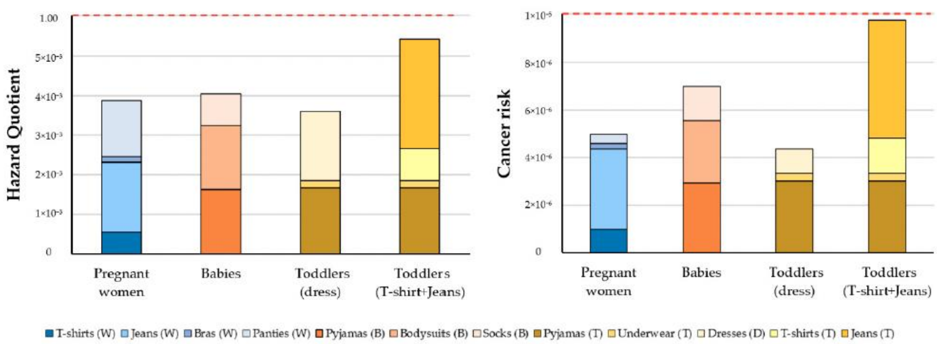

Figure 3. Risk assessment of dermal exposure to formaldehyde in the worst-case scenario, for pregnant women (W), babies (B) aged <12 months, and toddlers (T) aged 12–36 months.

4. Discussion

Because formaldehyde is a usual chemical additive in clothing, its presence in textile materials has been largely studied, especially when assessing the compliance of some certifications, such as OEKO-TEX® Standard 100. However, information on the benefits of using organic cotton before conventional raw materials is scarce. Furthermore, there is a lack of investigations aimed at evaluating the contribution of dermal exposure to formaldehyde through clothing in front of other exposure pathways, such as air inhalation.

Results of previous studies performed worldwide on the contents of formaldehyde in clothes are summarized in Table 5. There is a wide variability in the reported values, possibly due to the use of different analytical methodologies and/or commercial regulations. In 2010, the U.S. Government Accountability Office conducted a study on a representative sample of 180 items. Ten of them exceeded the threshold value of 75 mg/kg, with a maximum of 206.1 mg/kg [30]. In 2018, Caro Zapata et al. [53] found formaldehyde in 74% of the analysed samples in Colombia, reporting a maximum concentration of 87 mg/kg. These levels were similar to those found by Aldag et al. [23], who reported a maximum level 75.9 mg/kg in several T-shirts and pants purchased in Germany. By contrast, formaldehyde levels in 34 textile samples acquired in South Africa were found within the range 0.036–0.090 mg/kg [54].

Table 5. Evolution of the concentration of formaldehyde in clothes.

Country	Year	Number and Type of Clothes	Detection Rate	Formaldehyde Content	Reference
Spain	2022	124 samples	19%	ND–56 mg/kg	This study
South Africa	2019	34 socks samples	0%	100% ND	[54]
Colombia	2018	62 samples	74%	ND–87 mg/kg	[53]
Europe	2017	4 curtains, 4 pants, 14 T-shirts and 2 shirts	71%	ND–76 mg/kg	[23]
European Union	2007	221 samples (48 water extraction)	48%	ND in 52%; 30–166 mg/kg in 48%	[55]
Denmark	2003	10 textiles	30%	ND in 70%; 35–82 mg/kg in 30%	[56]
USA	1998	16 fabrics	50%	ND in 50%; <200 p.p.m in 50%	[57]

ND: not detected.

Focusing on Europe, there is a clear tendency towards a reduction in detection rates and concentrations. In 2007, a study in the European Union quantified the formaldehyde present in different types of textiles, stating that 10% of all samples released more than

30 mg/kg formaldehyde, with 3% even exceeding the limit of 75 mg/kg [58]. In 2017, Aldag et al. [23] carried out a new study that also included curtains, in addition to clothing. The maximum concentrations were substantially lowered from 166 to 80 mg/kg [23]. Our results confirm this decreasing trend.

In recent years, there has been an increasing awareness of eco-friendly fashion with the use of more sustainable textile materials, such as organic cotton. In order to determine whether eco-friendly clothing contains fewer chemical additives, 50% of the garments under study were organic. Surprisingly, in 5 out of the 12 categories, organic cotton clothes showed higher levels of formaldehyde than clothing made of regular cotton. It must be highlighted that regulations of using organic cotton in textile manufacturing refer only to pesticide-free cultivation, but not to the addition or accumulation of toxic substances in clothing [20]. The current results agree with those of other studies, focused on other chemicals [59]. In a previous investigation, significantly higher copper values were found in eco-labelled jeans than in conventional items [6]. However, it should be taken into account that the garments here analysed are brand new. Formaldehyde levels are expected to decrease with exposure to light, and as shown, even a single wash would be sufficient to reduce these concentrations.

By labelling garments, the textile industry informs consumers about the origin of the products, and how taking care of the garment to reduce its environmental impact. The most commonly used terms are “environmentally friendly”, “nature-friendly”, “ethical”, “green”, “responsible”, “ecologically clean”, “ecologically innocuous”, “eco-conscious”, “eco-friendly”, “organic” and “sustainable” [60]. In the present study, samples of the last four were collected. In Europe, there are three voluntary labelling systems for textiles: the European Eco-label [61], the OEKO-TEX® Standard 100 label, and Global Organic Standard Textiles [62], which is the most restrictive. In the European Union, the current limit for formaldehyde in clothing in contact with the skin is 75 mg/kg [63], which is the same threshold set for OEKO-TEX® Standard 100 label. On the other hand, the Eco-label certification establishes a limit of 30 mg/kg, and OEKO-TEX® Standard 100 label sets 75 mg/kg. Moreover, textiles for babies are subjected to more restrictive limits, as they should release less than 20 mg/kg of formaldehyde [64]. Finally, the limit according to the GOTS certification is 16 mg/kg in all the textiles [62]. Despite the value that these labels bring to garments, their use is not yet widespread. In this study, only 21% of the garments had a label of this type. Exceptionally, one of the samples, GOTS certified, did not achieve the specifications in terms of formaldehyde content.

The changes in textile production over the past years, towards an eco-friendlier production with the environment, remain unprecedented. These new production policies are focused on minimising the environmental impact, from production to the life of the clothing [65]. These practices include reduction of water consumption, decrease of waste generation, and recycling of garments, among others. In addition, producers tend to reduce the use of chemicals that are hazardous to both the environment and human health [66,67]. Some studies have shown that eco-garments may contain lower levels of some trace elements, such as aluminium and strontium, than non-eco garments [18]. The concentrations here reported were lower than those reported in the 2007 European survey on the release of formaldehyde from textiles [55], where 11% of samples intended to be in direct contact with skin exceeded 30 mg/kg, and even 3% overpassed the threshold of 75 mg/kg [55]. This decrease could be a consequence of the effectiveness of the new sustainability policies of the textile industry and the commitment of brands to make safer garments for consumers.

Exposure to pollutants does not occur by a single route, but people are exposed to chemicals through different pathways [58]. Food ingestion plays a relevant role, but inhalation, ingestion, and dermal absorption may be also quite contributory. In fact, air inhalation has been identified as the most important exposure pathway for formaldehyde and other VOCs. Formaldehyde is a known indoor pollutant present in many household items. Wood-pressed products, insulation materials, paints, varnishes, household cleaning products, cigarettes, and candle burning, among others, are the main sources of this indoor pollutant [66]. Therefore, most formaldehyde risk assessment studies have focused on the estimation of inhalation risks [51,68–70]. Here, we demonstrated that dermal absorption of formaldehyde contained in clothing is less important than air inhalation (10% vs. 90%).

Washing clothes may be a significant way to reduce the content of formaldehyde and other textile additives. The washout effect is very relevant, as washed samples contained no traces of formaldehyde after only one washing, irrespective of the concentrations in unwashed samples. This is critical information for public health authorities, whose recommendation, especially for early-life population groups, should be to wash all the clothing before the first use. This simple practice is an effective way to substantially reduce the amount of formaldehyde in garments and, consequently, to decrease any potential health risks.

5. Conclusions

Formaldehyde was detected in 20% of the samples analysed with levels ranging from <12.8 mg/kg to 55.7 mg/kg. Formaldehyde levels were below the EU limits (<75 mg/kg) in all the textile samples. The levels in the dyed garments were higher, 10.2 mg/kg, than those found in the printed garments, 7.07 mg/kg. Regarding the material from which the garments are made, clothing made from cotton contained higher concentrations of formaldehyde than clothing made from synthetic fibres (7.51 mg/kg vs. 6.66 mg/kg). Interestingly, eco-friendly clothes contained traces of formaldehyde. In some cases (e.g., underwear of pregnant women, dresses and T-shirts of toddlers) even at higher levels than conventional garments. In spite of this, the dermal contact to formaldehyde through clothing was not significant, being estimated as almost 10-times lower than the air inhalation of formaldehyde, which is the most relevant exposure route to this chemical. Furthermore, both non-carcinogenic and carcinogenic risks were below the safety limits. A simple but very effective practice to reduce these risks would be to wash all the textile items before the first use. Clothing may contain other toxic substances apart from formaldehyde. Therefore, future health risk assessments should be performed under a multi-exposure and multi-chemical scenario, considering also individual susceptibility.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/toxics10070361/s1, Table S1: Main characteristics of the clothes analysed.

Author Contributions: Conceptualization, M.H., J.R., M.M. and M.N.; methodology M.H. and N.G.; formal analysis, M.H. and J.R.; investigation, M.H. and N.G.; writing—original draft preparation, MH.; writing—review and editing N.G., J.R., M.M., M.N. and J.L.D.; supervision, J.R and J.L.D.; project administration, M.N.; funding acquisition, M.N. All authors have read and agreed to the published version of the manuscript.

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CAPÍTULO 4

Dermal exposure to bisphenols in pregnant women's and baby clothes: Risk characterization

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Resumen de resultados

El presente estudio tuvo como objetivo determinar los niveles de bisfenol A (BPA) y algunos análogos del BP (BPB, BPF y BPS) en 120 prendas de ropa nueva comercializada en España para mujeres embarazadas, recién nacidos y niños pequeños. Además, se llevó a cabo una evaluación de la exposición y caracterización de riesgos.

Se encontraron trazas de BPA en todas las muestras, con una concentración mediana de 7,43 ng/g. de 7,43 ng/g. Los valores más altos se detectaron en muestras textiles de poliéster. En cuanto a las fibras naturales, se observaron concentraciones más elevadas de BPA en las prendas de algodón convencional que en las de algodón ecológico con una diferencia significativa en el caso del BPS (1,24 frente a 0,76 ng/g, $p < 0,05$).

A pesar de que los niños pequeños tienen una mayor superficie cutánea en relación con el peso corporal, las mujeres embarazadas mostraron una mayor exposición a los BPS que los niños. En cualquier caso, los riesgos no cancerígenos asociados a la exposición al BPA estaban por debajo de la unidad.

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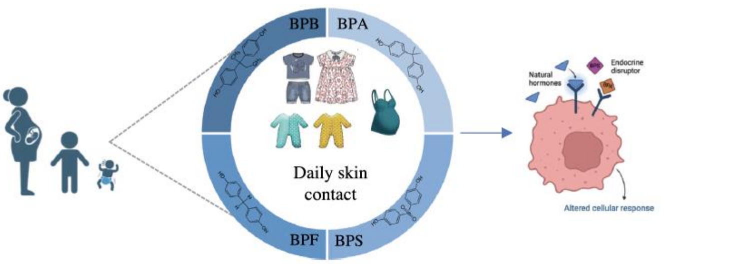
HIGHLIGHTS

- Traces of BPA were found in all clothing samples.
- The highest values of BPA were determined in clothes made with polyester.
- The lower levels of BPs were determined in organic cotton.
- Higher dermal exposure values were observed for BPA in pregnant women.
- Over the years, human exposure to BPs *via* dermal contact may become more relevant.

GRAPHICAL ABSTRACT



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ABSTRACT

Textile manufacturing consists of a multiple-step process in which a wide range of chemicals is used, some of them remaining in the final product. Bisphenols (BPs) are non-intentionally added compounds in textiles, whose prolonged skin contact may mean a significant source of daily human exposure, especially in vulnerable groups of the population. The present study aimed to determine the levels of bisphenol A (BPA) and some BP analogs (BPB, BPF, and BPS) in 120 new clothes commercialized in Spain for pregnant women, newborns, and toddlers. In addition, exposure assessment and risk characterization were also carried out. Traces of BPA were found in all the samples, with a median concentration of 7.43 ng/g. The highest values were detected in textile samples made of polyester. Regarding natural fibers, higher concentrations of BPs were observed in garments made of conventional cotton than in those made of organic cotton, with a significant difference for BPS (1.24 *vs.* 0.76 ng/g, $p < 0.05$). Although toddlers have a larger skin-area-to-body-weight ratio, pregnant women showed higher exposure to BPs than children. Anyhow, the non-carcinogenic risks associated with BPA exposure were below the unity, even under the upper-bound scenario. However, risks could be underestimated because other exposure routes were not considered in this study. The use of BPA has been restricted in some food-related products; therefore, BPA should also be regulated in the textile industry.

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1. Introduction

Clothing should be based on safe materials, as everybody is in daily contact with them. Over the years, the textile industry has been constantly on the rise, using a wide range of chemicals and releasing many residues. Unfortunately, some of these substances, either intentionally added or not, may remain in the final product at relevant concentrations. A wide range of chemicals, such as bisphenol A (BPA), *per*- and poly-fluoroalkyl substances, dyestuffs, trace elements, and brominated flame retardants, have been found in textile products (Iadaresta et al., 2018; Herrero et al., 2019; Rovira and Domingo, 2019; Wang et al., 2019; Herrero et al., 2020; Zhu and Kannan, 2020; Sait et al., 2021; Souza et al., 2023; Undas et al., 2023).

According to the United States Environmental Protection Agency (US EPA), bisphenols (BPs) are one of the most produced chemicals worldwide (US EPA, 2021). BPA (4,4′-(propane-2,2-diyl)diphenol) is the primary compound, but because of its toxicity, increasing use, and regulatory pressure, analog compounds have been introduced to replace it (Ding et al., 2022). Among them, bisphenol F (BPF) and bisphenol S (BPS) are prevalent substances. However, the levels of these compounds and the possible exposure pathways remain still understudied (Chen et al., 2016; Siracusa et al., 2018; Wei et al., 2023).

Traces of BPA can be found in many products, including clothing, especially if made of synthetic fibers. BPA may be used as an intermediate compound to manufacture dyes and antioxidants during textile production. Besides, BPs can be added to the polyester -as an intermediary- to improve its properties and lifespan and be used to create hygroscopic and antistatic material with colorfastness for washing (Xue et al., 2017; Wang et al., 2019; Undas et al., 2023).

Due to its widespread use and well-known endocrine-disrupting chemical (EDC), in recent years, BPA has been extensively studied (Negev et al., 2018; Castro et al., 2021; Martínez et al., 2021; Rovira et al., 2022). Although food intake is considered the most important exposure source to BPs (Karrer et al., 2020), other potential pathways could also play a significant role. Since dermal absorption of BPs may occur through direct skin contact with clothes worn the whole day, this issue needs to be addressed, especially when considering vulnerable groups of the population (Demierre et al., 2012; Xue et al., 2017; Freire et al., 2019; Rovira and Domingo, 2019; Sait et al., 2021; Martínez et al., 2018, 2023; Souza et al., 2023).

A number of studies have reported an association between pre-and postnatal exposure to BPA and the occurrence of adverse health outcomes in children, including behavioral problems, asthma, obesity, alterations in immunity system and hormone levels, as well as changes in puberty timing (Xue et al., 2017; Siracusa et al., 2018; Catenza et al., 2021). Moreover, studies in the laboratory have been reported to cause cytotoxicity and neurotoxicity (Shimabuku et al., 2022). In turn, BPA levels may be linked to various health problems such as breast and prostate cancer, metabolic disorders, and diabetes (Chen et al., 2016; Xue et al., 2017; Siracusa et al., 2018; Freire et al., 2019; Souza et al., 2022). In addition, it has been pointed out that some BPA analogs, such as BPS and BPF, show a similar -or even a higher- endocrine-disrupting activity than BPA (Martínez et al., 2020; Gys et al., 2021). Recently, due to their potential hormonal and toxic reproductive effects, the European Commission and the Scientific Committee on Consumer Safety have modified the regulation concerning the levels of BPs in clothing. For it, the European Chemicals Agency (ECHA) has adopted "Group Restriction" on BPs in the REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) (ECHA/NR/22/08).

Human exposure to BPs is an issue of concern for public health. However, more information is needed regarding the levels of BPs in textile products, as well as the evaluation of dermal exposure. Considering the potential impact on human health, the risk assessment of this EDC in clothing is required in order to ensure consumer safety, mainly for vulnerable groups of the population (Xue et al., 2017; Freire et al., 2019; Rovira and Domingo, 2019; Wang et al., 2019; Herrero et al., 2022a, 2022b). In this context, this study aimed to determine the concentrations of BPA and their analogs (BPS, BPB, and BPF) in pregnant women, newborns, and toddlers clothes, while dermal exposure to these BPs and their associated risks were also assessed.

2. Materials and methods

2.1. Chemicals

Four BPs were included in this study: bisphenol A (BPA, CAS 80-05-7), bisphenol S (BPS, CAS 80-09-1), bisphenol F (BPF, CAS 620-92-8), and bisphenol B (BPB, CAS 77-40-7). Bisphenol A-*d*16 (BPA, CAS 96210-87-6) was used as an internal standard. All native analytical standards and the labeled internal standard were purchased from Sigma-Aldrich® (St Louis, MO, USA). The stock and working solutions were prepared in methanol (HPLC grade from Sigma-Aldrich®) and stored at 4 °C to avoid degradation. Chemicals used in the methodology included acetone, dichloromethane, acetonitrile and methanol, all from Sigma-Aldrich®. High-purity water was obtained from Milli-Q Synergy UV equipment (Millipore).

2.2. Clothes

One hundred and twenty (n = 120) garments for pregnant women (n = 40), newborns (<12 months) (n = 30), and toddlers (12–36 months) (n = 50), which are commercially available in Spain, were analyzed. The following clothing categories were included: T-shirts, trousers/leggings/jeans, dresses, underwear (bra, panties, and socks), pyjamas, and bodysuits. Most clothes (75 %) were purchased from chain stores, hypermarkets, or tiny retailers in Tarragona County (Catalonia, Spain), while the remaining 25 % were purchased online. The detailed list of each sample here analyzed is summarized in Table S1 (*Supplementary Information*).

2.3. BPs chemical analysis

The sample preparation methodology for determining BPs in textiles was adapted from that reported by Freire et al. (2019). Briefly, approximately 0.5 g of each textile sample was accurately cut, weighed, and placed in 15 mL glass centrifuge tubes, where they were spiked with 250 μL of the isotope-labeled surrogate solution (BPA-*d*16, 50 ppb). The extraction was performed by adding 7.5 mL of a mixture of acetone and dichloromethane (1:4, *v*/v). After sonication for 20 min and centrifugation at 5000*g* for 7 min, the solvent was collected and filtered through a 0.2 μm nylon filter and transferred to another glass tube. The solvent was then evaporated to dryness and frozen. Before the instrumental analysis, the residue was reconstituted with 250 μL of acetonitrile.

BPs were quantified using ultra-performance liquid chromatography coupled with mass spectrometry in tandem (UPLC–MS/MS). The used equipment was a 1290 UHPLC system coupled to a QqQ/MS 6490 series from Agilent Technologies® (Santa Clara, CA, USA). The chromatography separation of BP was carried out using a column ACQUITY BEH C18 column (100 × 2.1 mm, 1.7 μm) from Waters Corporation. Details of instrumental analysis and compound-specific analytical parameters are shown in *Supplementary Information* (Tables S2, S3, and S4).

2.4. Quality assurance and quality control

Quality control was performed with procedural blanks and a spiked blank sample containing 5 ng/g of BPA. An isotopically labeled internal standard (d16-BPA) was used to increase the reproducibility of the analysis. All the samples were analyzed in triplicate to evaluate their repeatability. After extraction, the extracts were frozen and then injected into the UPLC-MS/MS in the same order as their preparation. Recoveries for all BPs in the quality-control spiked samples ranged between 78 % and 93 %, with all coefficients of variation (CV) under 20 %. The ranges of the calibration curves were the following: 1.94 ng/g to 500 ng/g for BPA, 0.12 ng/g to 500 ng/g for BPB, 2.29 ng/g to 1000 ng/g for BPF, and 0.38 to 1000 ng/g to BPS. The limits of detection (LOD) were 0.59 ng/g for BPA, 0.04 ng/g for BPB, 0.69 ng/g for BPF, and 0.12 ng/g for BPS.

2.5. Dermal exposure and human health risk assessment

The concentration of BPs in clothes was used to calculate dermal exposure and BPA-associated health risks. Exposure was estimated for pregnant women, infants aged <12 months, and toddlers (12 to 36 months old). Dermal exposure was calculated based on the European Chemical Agency (ECHA) (European Chemicals Agency, 2016) Eq. (1) and already applied elsewhere (Rovira et al., 2015, 2017):

$$\text{Exp derm} = \frac{\text{Fcloth x dcloth x Askin x Fcontact x Fpen x Tcontact x n}}{\text{BW}} \quad (1)$$

where Exp derm corresponds to dermal exposure (mg/(kg·day)), Fcloth is the fraction of element in clothes (mg/mg), dcloth is the density of the clothing (mg/cm^2), Askin is the skin area covered by the clothing (cm^2), Fcontact is the fraction of contact area for skin (dimensionless), Fpen is the penetration rate of the element (dimensionless), Tcontact is the duration of the clothing skin contact (day), n is the number of events per day (1/day), and BW is the body weight (kg). The dermal exposure parameters are summarized in Table 1.

Since BPA is the only bisphenol for which an oral reference dose (RfDo) has been established, the non-carcinogenic risk was evaluated only for this compound. The Hazard Quotient (HQ), defined as the quotient between exposure and the dermal reference dose (RfDd), was calculated by multiplying RfDo with the gastrointestinal absorption factor (GAF), which was set at 1. The RfD of BPA, whose value is 0.05 mg/(kg·day), was obtained from the Regional Screening Level from the US EPA Preliminary Remediation Goals (US EPA, 2021).

2.6. Data analysis

Statistical analysis was conducted using the IBM SPSS Statistics software® version 28.0 (IBM Corp. Released 2020, Armonk, NY, USA). The Kolmogorov–Smirnov test was used to assess the distribution of the values. In turn, the Student's *t*-test or ANOVA test for data, following a parametric distribution, or the Kruskal–Wallis tests for non-parametric data were used to assess any statistical difference between groups. A difference was considered significant when the probability was lower than 0.05 ($p < 0.05$). Non-detected (ND) levels were considered as one-half of the limit of detection (LOD) (ND = 1/2LOD).

3. Results and discussion

3.1. Occurrence of BPs in clothing

The levels of bisphenol in clothes commercialized in Spain are given in Table 2. In agreement with the widespread use of BPA, the highest concentrations corresponded to this EDC. BPA was detected in all the samples, with a median value of 7.43 ng/g (range: 0.69–5872 ng/g). In turn, BPB was detected in only 13 % of the analyzed samples, with a median concentration below the LOD (<0.69 ng/g). BPF and BPS showed similar median values (1.01 ng/g and 1.04 ng/g, respectively), but the range of concentrations was much higher for BPF (0.17–11,333 ng/g for BPF and 0.03–981 ng/g for BPS). Since these compounds can reach the manufacturing processes at different stages, it is not possible to identify a single source of contamination. However, literature data suggest that BPA may originate from textile packaging or, in clothing made of synthetic fibers, it may also come from recycled plastic (Freire et al., 2019). BPs can be used in clothes production to improve their performance and durability and as an intermediate in manufacturing dyes (Xue et al., 2017; Freire et al., 2019).

In the current study, clothes for three vulnerable population groups (pregnant women, newborns, and toddlers) were purchased. The results of the experimental analysis are depicted in Fig. 1. In general terms, higher concentrations (as median values) of BPs were observed in pregnant women's clothes, while the minimum levels were found in newborns' clothes. A significant difference between groups was observed only for BPA ($p = 0.007$ between newborns and pregnant women and $p = 0.001$ between newborns and toddlers). Moreover, BPF was predominant in items of pregnant women (286 ng/g) and BPA in newborns (5.49 ng/g) and toddlers (18.7 ng/g). Higher levels of BPA were observed in underwear/panties clothing of pregnant women and toddlers, with median concentrations of 10.4 and 37.9 ng/g, respectively. This exposure can mean potential risks to women due to the direct contact of this clothing with the vagina mucosa, which presents a greater probability of absorption of compounds in this region because of a large blood flow (Nicole, 2014).

In order to understand the real distribution of BPs in clothing, data were treated according to a number of parameters. Different manufacturing

Table 1
Parameters used to assess dermal exposure.

Variable	Description	Value	Reference
F_{cloth}	Weight fraction of substance in garments	Cloth specific mg/mg	Present Study
d_{cloth}	Clothing density	Cloth specific mg/cm^2	Herrero et al., 2022b
A_{skin}	Pregnancy women t-shirt (trunk + arms)	8910 cm^2	US EPA, 2011
	Pregnancy Troussers_Jeans_Leggings (legs)	5980 cm^2	
	Pregnancy band of trouser (trunk/2)	3270 cm^2	
	Pregnancy Troussers_Jeans_Leggings + band (legs + trunk/2)	9250 cm^2	
	Pregnancy bra (bosom)	2594 cm^2	
	Pregnancy underwear without brand (genitals and buttocks)	1469 cm^2	
	Pregnancy underwear with brand (genitals and buttocks + trunk/2)	4739 cm^2	
	Baby pyjamas (trunk + arms + legs + feet)	2778 cm^2	
	Baby bodysuits (trunk + arms)	1795 cm^2	
	Baby socks (feet)	235 cm^2	
	Child's pyjamas (trunk + arms + legs)	4355 cm^2	
	Underwear (genitals)	383 cm^2	
	Dresses (trunk + arms + 1/2 legs)	3665 cm^2	
	T-shirt (trunk + arms)	2975 cm^2	
	Trouser/jeans/leggings (legs)	5980 cm^2	
$F_{contact}$	Fraction of contact area for skin	1	Bundesinstitut für
F_{pen}	Fraction of penetration inside the body	0.01	Risikobewertung, 2013
Fmig	Fraction of substance migrating to skin	0.005	
$T_{contact}$	Contact duration between skin-textile	0.33 (8 h/24 h) 0.67 (16 h/24 h) 1 (24 h)	Assumed
N	Mean number of events per day	1/d	Assumed
BW	Adult Female	76.9 kg	Martínez et al., 2017
	Birth to <12 month	7.31 kg	Sobradillo et al., 2000

Table 2
Levels of BPs (in ng/g) in clothing commercialized in Spain (n = 120).

	LOD[a]	DR[b] (%)	Mean	SD[c]	Minimum	Median	95th percentile	Maximum
Bisphenol A	0.59	100	64.2	529	0.69	7.43	76.1	5872
Bisphenol B	0.04	13	0.99	5.27	<LOD	<LOD	5.43	44.1
Bisphenol F	0.69	73	96.0	1022	<LOD	1.01	12.9	11,333
Bisphenol S	0.12	94	15.6	104	<LOD	1.04	14.2	981

[a] LOD: limit of detection.
[b] DR: detection rate (%).
[c] SD: standard deviation.

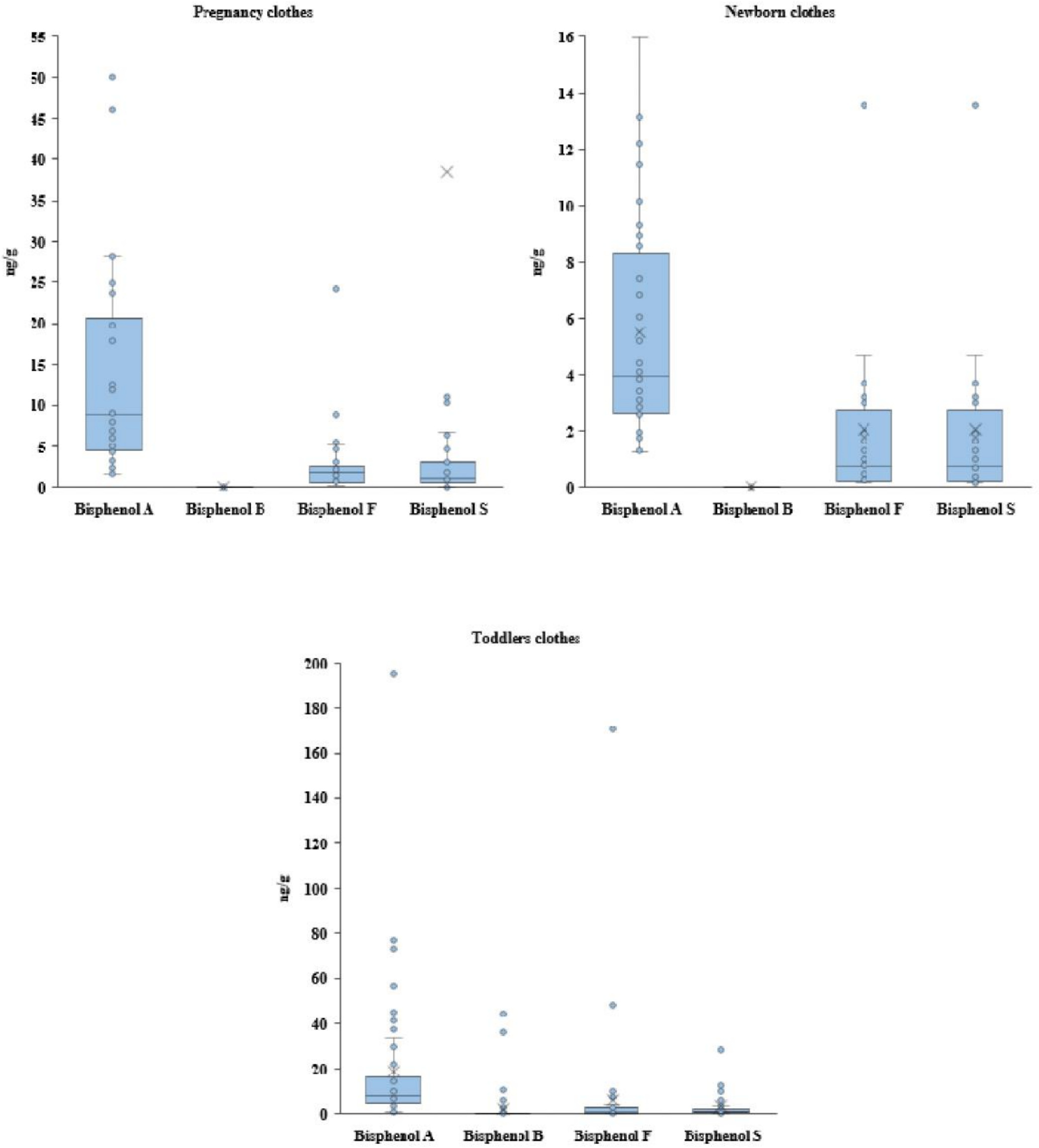

Fig. 1. Concentrations of bisphenols in clothes for pregnant women, newborns and toddlers. Values are expressed as median (ng/g).

fibers were evaluated, including synthetic (elastane, polyester, and polyamine) and natural (cotton) fibers. BPs levels according to the textile material are summarized in Table 3. The highest median levels of the three analyzed BPs, BPA (28.9 ng/g), BPF (1.56 ng/g), and BPS (2.38 ng/g), were observed in polyester fibers. Although the difference was not statistically significant, the observed trend is in agreement with previous data from the scientific literature (Xue et al., 2017). The material composition of clothing is an important factor that influences the levels of BPs in new pieces (Xue et al., 2017; Wang et al., 2019).

Samples made of natural fibers were classified according to the cotton production into organic or conventional cotton. Organic fabrics are a sustainable alternative to textile materials made with synthetic fibers. They are produced with natural and recycled raw materials, offering less environmental impact (Goyal and Parashar, 2023). The present study examined organic cotton as a more sustainable alternative to conventional cotton. Pesticides are not used in plantation management, and there is a preservation of the soil nutrients. Interestingly, higher BPA, BPF, and BPS concentrations were found in clothes made of conventional cotton than in organic garments, with a significant difference for BPS (0.76 *vs.* 1.24 ng/g, $p < 0.05$).

Since BPA may be used as an intermediate compound in the manufacture of dyes in textile production, the evaluation of colors is also important (Xue et al., 2017; Wang et al., 2019; Undas et al., 2023). BPA and BPF were more predominant in grey clothes, while BPS levels were higher in black clothes. When analyzing 77 textiles and infant clothing pieces, Xue et al. (2017) also found higher levels of BPA in grey polyester (97 %) socks for 6–12-month-old infants.

The area of textile manufacture of each item was also considered. Clothes made in the EU showed lower levels of all the compounds than garments made in non-European countries (6.88 *vs.* 7.51 ng/g for BPA, $p < 0.05$; 0.35 *vs.* 1.41 ng/g for BPF, $p < 0.05$; 1.02 *vs.* 1.05 ng/g for BPS). The current results were compared with data found in the scientific literature (Table 4). Higher detection rates (%) for BPA, BPF, and BPS were noted in our study, but concentration values were generally lower than elsewhere. BPS presents similar levels in new clothes commercialized in the United States. Generally, the higher values of BPs were determined in samples from China (Wang et al., 2019).

Table 4
A summary of BPs levels in clothing found in the scientific literature.

Bisphenols	Values	This study New clothes (n = 123)	Freire et al. (2019) Socks (n = 32)	Wang et al. (2019) New clothes (n = 44)	Xue et al. (2017) New clothes (n = 77)
	Marketing country	Spain	Spain	China	USA
BPA	DR (%)	100	91	98	82
	Median	7.43	20.5	17.7	10.7
	Range	0.69–5872	<0.70–3736	<3.30–1823	<2.21–13,300
BPS	DR (%)	94	–	29	53
	Median	1.04	–	12.3	1.02
	Range	<0.12–981	–	<0.53–536	<0.74–394
BPF	DR (%)	73	–	–	5.2
	Median	1.01	–	–	0.32
	Range	<0.69–11,333	–	–	<14.7–194

Concentrations are given in ng/g.
DR: detection rate.

3.2. Exposure assessment and risk characterization

Human exposure was estimated for pregnant women, newborns, and toddlers. Risk assessment considered all the daily worn clothing; hence, the result was reported as the sum of all the analyzed clothing pieces and their contribution percentage. The estimated dermal exposure is summarized in Table 5. Higher dermal exposure values were observed for BPA, since it also showed the highest concentrations in clothing. Furthermore, exposure of pregnant women ($1.24{\cdot}10^{-9}$ mg/kg/day for BPA) was higher than those of the other studied groups ($4.94{\cdot}10^{-10}$ mg/kg/day in newborns and $1.06{\cdot}10^{-9}$ mg/kg/day in toddlers). On the other hand, it is important to remark that toddlers present a larger skin-area-to-body-weight ratio, which might lead to a greater dermal exposure risk to BPA. The use of BPA has been restricted in some food-related products (Huang et al., 2018). Therefore, human exposure to this compound *via* dermal contact with clothes may become more relevant over the years. However, compared with data from different Spanish populations, dermal contact with clothes is 4–5 orders lower than dietary exposure to BPA. Martínez et al. (2021) reconstructed the exposure to BPA during pregnancy and estimated its intake through food consumption in $7.2{\cdot}10^{-5}$, $6.9{\cdot}10^{-5}$, and $3.8{\cdot}10^{-5}$ mg/kg/day in the first, second, and third trimesters, respectively. In turn, González et al. (2020a) performed a biomonitoring study in an adult Spanish cohort population who followed a diet based on high consumption of canned food, which had previously been shown to contain high levels of BPA (González et al., 2020b). After two days, the control group showed a BPA dietary intake of 2.7·10–5 mg/kg bw/day, 4 times lower than the exposed group. Even for participants who did not follow a diet rich in canned food products, the contribution of food consumption is notably larger than dermal exposure to BPA.

The non-carcinogenic risk was evaluated by calculating the HQ. Results are only estimated for BPA, as this is the only analog for which an established RfD value has been established by the US EPA. Fig. 2 depicts the results of the risk assessment under a worst-case scenario, that is to say, considering the maximum concentrations. Because pregnant women's clothes showed higher BPA concentrations, exposure to BPA was estimated to be higher in women than in babies. It must be taken into account that

Table 3
Concentrations of bisphenols (ng/g) determined in different fibers of clothes, including synthetic and natural fibers.

		n	DR[a] (%)	Mean	SD[b]	Minimum	Median	95th	Maximum
Bisphenol A	Cotton	63	100	15.7	28.2	0.69	7.07	55.5	195
	Elastane	41	100	15.5	27.9	0.86	6.95	50.1	146
	Polyester	8	100	772	2062	2.92	28.9	3878	5872
	Polyamide	11	100	9.54	6.76	1.97	8.60	20.4	24.9
Bisphenol F	Cotton	63	81	5.50	22.1	<LOD	0.98	10.2	171
	Elastane	41	73	278	1770	<LOD	1.51	5.45	11,333
	Polyester	8	88	2.28	1.98	<LOD	1.56	5.34	5.47
	Polyamide	11	64	2.37	4.53	<LOD	0.29	11.3	13.6
Bisphenol S	Cotton	63	97	2.51	4.67	<LOD	0.96	12.0	28.4
	Elastane	41	98	2.45	3.25	<LOD	1.10	10.2	14.5
	Polyester	8	100	79.5	217	0.19	2.38	404	618
	Polyamide	11	64	92.9	295	<LOD	0.15	507	981

The median of BPB was lower than LOD.
No significant differences were observed among groups ($p > 0.05$).
[a] DR: detection rate.
[b] SD: standard deviation.

Table 5
Exposure assessment to BPSs through clothing for pregnant women, newborns and toddlers.

		Bisphenol A		Bisphenol B		Bisphenol F		Bisphenol S	
		Dermal exposure per item (%)	Total dermal exposure (mg/kg/day)	Dermal exposure per item (%)	Total dermal exposure (mg/kg/day)	Dermal exposure per item (%)	Total dermal exposure (mg/kg/day)	Dermal exposure per item (%)	Total dermal exposure (mg/kg/day)
Pregnant women	T-shirts	10 %	1.24E−09	22 %	1.39E−12	2 %	2.24E−10	12 %	1.56E−10
	Jeans/leggings	64 %		31 %		30 %		15 %	
	Bras	12 %		22 %		26 %		17 %	
	Panties	14 %		26 %		42 %		56 %	
Newborns (<12 months)	Pyjamas	35 %	4.94E−10	38 %	1.49E−12	68 %	9.93E−11	83 %	1.07E−10
	Bodies	13 %		24 %		22 %		13 %	
	Socks	52 %		38 %		10 %		4 %	
Toddlers (12–36 months)	Pyjamas	27 %	1.06E−09	0.4 %	8.85E−12	33 %	2.05E−10	6 %	1.87E−10
	Underwear	34 %		0.3 %		3 %		12 %	
	Dresses	13 %		98 %		59 %		6 %	
	T-shirt	12 %		0.4 %		3 %		19 %	
	Trousers	13 %		0.5 %		3 %		56 %	

exposure to specific pollutants is hazardous to human health when the HQ value exceeds the unity (HQ > 1).

The EU Scientific Committee on Consumer Safety (SCCS) concluded that there is no risk for systemic health effects due to the use of clothing articles (European Commission, 2021). Notwithstanding, in that Opinion, the SCCS also highlighted that the assessment was based only on one source of BPA (*i.e.*, textiles) and did not consider the contribution of other potential sources. This is a very important issue, as exposure to BPA occurs through different routes: oral, inhalation, and dermal route as leach-out products (Khan et al., 2021). Furthermore, clothes may contain a wide range of chemical additives with the potential to cause adverse health effects. Traces of other toxicants, such as aromatic amines or polychlorinated biphenyls (PCBs), were recently detected in the same textile pieces (Herrero et al., 2022a; Souza et al., 2023). When performing a health risk assessment, it is essential to consider the co-occurrence of chemicals in the sources of exposure, as well as the potential synergetic effects among them. This issue can be tackled by estimating the aggregated exposure to all these chemicals through clothing.

The current study focused on determining BP concentrations in new clothes but not used garments. The availability and levels of BP in used clothes are different. Consequently, human exposure may be altered (Xue et al., 2017; Wang et al., 2019). During laundering, the cross-contamination of BPA may occur due to homogenizing the pollutants together with all used clothes (Wang et al., 2019). However, washing has been pointed out as a safe and simple practice for consumers, as it may be very beneficial to reduce the content of chemicals in clothes (Herrero et al., 2022b).

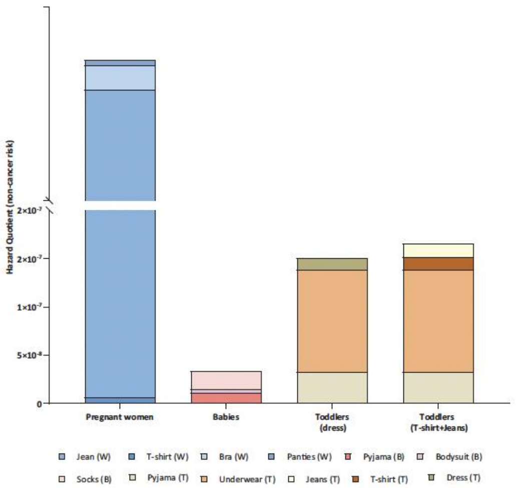

Fig. 2. Hazard quotient (non-carcinogenic risk) of bisphenol A in the upper-bound scenario (maximum concentrations) for pregnant women (W), babies (B) aged <12 months, and toddlers (T) aged 12–36 months.

4. Conclusions

It is well known that early-life exposure to BPA and some analogs are associated with various adverse health effects. However, more data are still necessary to establish the occurrence of these EDCs in clothing, mainly for sensitive groups of populations such as pregnant women, newborns, and toddlers. The current results show significant evidence that clothing is a relevant source of exposure to BPA, with a 100 % of detection rate in all analyzed pieces, mainly those made of synthetic fibers and for pregnant women. Although preliminary calculations suggest that it could be a minor route, dermal exposure to BPA still needs to be addressed compared to other exposure pathways. However, the trend for the coming years is that human exposure to other BPs analogs *via* dermal contact might become more relevant for public health. BPA has already been banned in other sectors, such as in food-related products and baby products. Therefore, as a public health precautionary principle, BPA should also be regulated in the textile industry.

CRediT authorship contribution statement

Marta Herrero: Conceptualization, Formal analysis, Investigation, Methodology, Resources, Writing – original draft. **Marília Cristina Oliveira Souza:** Conceptualization, Writing – original draft. **Neus González:** Conceptualization, Writing – review & editing. **Montse Marquès:** Conceptualization, Writing – review & editing. **Fernando Barbosa:** Writing – review & editing. **José L. Domingo:** Writing – review & editing. **Martí Nadal:** Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **Joaquim Rovira:** Conceptualization, Writing – 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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Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.163122.

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DISCUSIÓN GENERAL

Algunas prácticas de la industria textil se asocian a un uso inadecuado de sustancias químicas tóxicas y contaminantes, con consecuencias negativas tanto para la salud como para el medio ambiente (Wang et al., 2022). Las fábricas textiles utilizan una amplia gama de productos químicos en sus procesos de fabricación a fin de añadir propiedades nuevas a las prendas de ropa, como la resistencia al calor, las arrugas, los olores, etc. (Lacasse y Baumann, 2004). Estas sustancias químicas incluyen retardantes de llama, tintes azoicos, metales pesados, formaldehido, PCBs entre otras, cuya exposición puede ser un riesgo para la salud ya que algunas de ellas pueden provocar dermatitis, alergias, alteraciones endocrinas, problemas inmunitarios y/o cáncer (Balbin et al., 2021; Carli et al., 2022; Rizzi et al., 2016).

La presente tesis doctoral tuvo como objetivo evaluar el riesgo para la salud debido a la exposición dérmica a elementos químicos y otras sustancias presentes en la ropa y utilizadas ampliamente por la industria textil.

1. Niveles de sustancias analizadas

1.1. Metales pesados

Las primeras sustancias evaluadas fueron metales y metaloides (*Capítulo 1*). Los metales y metaloides pueden formar parte del propio material de las fibras textiles o pueden añadirse voluntariamente durante los procesos de fabricación, tal y como se ha explicado anteriormente en *Apartado 2.1.1*. Durante esta tesis, se realizó un primer estudio en 42 prendas de tipo vaquero, incluyendo tanto pantalones como camisas, y en el que se analizaron un total de 28 metales y metaloides (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sn Sr, Ti, Tl, V y Zn) La evidencia disponible acerca del contenido de metales en textiles ha tendido a centrarse en análisis de conjuntos aleatorios de ropa, sin escoger un tipo o material concreto lo que dificulta la comparación de niveles entre estudios, por no analizar exactamente los mismos tipos de ropa y/o materiales. A pesar de ello, los resultados obtenidos fueron parecidos a los encontrados por Rovira et al. (2015, 2017a, 2017b), encontrándose cierta relación entre el color y el contenido de algunos metales. Se observó que las prendas negras presentaban niveles significativamente mayores de Mg que el resto de colores (306 mg/kg), reduciéndose casi a la mitad (156 mg/kg) en prendas de color gris, en el caso de las prendas de color azul los niveles fueron de 137 mg/kg y siendo hasta cuatro veces superior cuando se comparaban prendas de color negro y blanco (306 *vs.* 74.7 mg/kg). Además, se observó que las prendas de colores oscuros presentaban niveles medios más altos de Cr, Cu y Pb que la ropa de colores claros. Esto se debe al uso de estos últimos como oxidantes en las tinturas de azufre (Sima, 2022). En todo caso, ninguno de los metales superó los límites establecidos por las leyes europeas (Comisión Europea, 2018a) ni tampoco por las certificaciones no obligatorias como OEKO® Standard 100 o Ecolabel (Comisión Europea, 2017a; OEKO-TEX Association, 2021).

El tipo de material con el que están fabricadas las prendas puede afectar al contenido de metales y metaloides. Se evaluó su contenido según la composición de las prendas, quedando éstas dividas en 3 grupos: 1) 100% algodón, 2) algodón y fibras sintéticas de poliéster, y 3) algodón con fibras sintéticas sin poliéster. Las prendas con mayor contenido de poliéster presentaban una mayor concentración de Sb (35,0 mg/kg) que las muestras de ropa que no contenían este material. Hay que recordar que el Sb es un elemento catalizador que está presente durante la fabricación de la propia fibra de poliéster (Maerov, 1979). El Ti fue otro de los metales que presentó diferencias en función de la fibra textil, siendo significativamente ($p<0,05$) mayores sus niveles en las prendas que contenían fibras sintéticas que no eran de poliéster (11,3 mg/kg) respecto a las que eran 100% algodón (2,26 mg/kg). Como describió Rovira et al. (2017b), su presencia se debe al uso de este metal como deslustrarte para fibras artificiales y su protección frente a los rayos UV (Saxena et al., 2017).

Estudios previos han señalado la capacidad de migración de los metales de manera que pueden liberarse de las fibras, migrar hasta la piel y ser absorbidos por nuestro cuerpo, incrementando así los riesgos para nuestra salud (Abdallah y Harrad, 2018; Iadaresta et al., 2018). En el marco de este primer estudio, se realizó una segunda prueba experimental para establecer qué cantidad de metales encontrados en las prendas vaqueras analizadas previamente podían liberarse y migrar hacia la piel. Puesto que no todas las personas tienen el mismo tipo de sudor, se llevaron a cabo dos pruebas de migración con sudor artificial: una con sudor ácido y otra con sudor básico. Del mismo modo que ocurre con los estudios previos de contenido de metales, los estudios de migración anteriores no contemplan un tipo de tejido o material concretos, ni realizan las pruebas de migración en las mismas condiciones, ni tienen en cuenta dos tipos de sudores artificiales, por lo que los resultados no son exactamente comparables. Ahora bien, si algo ponen en relieve todos los estudios anteriores es que la extracción de metales por sudor es muy baja y los resultados obtenidos en el presente estudio así lo demuestran, independientemente del tipo de sudor (básico o ácido). De los 28 elementos analizados (Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Sb, Sc, Se, Sm, Sn Sr, Ti, Tl, V y Zn), no se detectaron trazas de 16 de ellos en ninguno de los dos tipos de extractos (As, Ag, Be, Bi, Cd, Co, Cr, Hg, Pb, Sc, Se, Sm, Sn, Ti, Tl and V). Además, los resultados obtenidos apoyan la teoría inicial de que el tipo de sudor afecta a la migración de los metales presentes en la ropa, ya que se observaron diferencias en las ratios de migración de los dos tipos de sudores. En la prueba con sudor ácido, el 50% de los metales y metaloides analizados migraron, sin embargo, en el caso del sudor básico, la ratio fue inferior (39%). Además, el tipo de sudor también afecta al perfil de metales que migran; es decir, los metales que migran en un tipo de sudor y otro no son los mismos ni lo hacen en la misma cantidad. Los metales que tuvieron mayor porcentaje de migración en el sudor ácido fueron Ba, Mn, Sr y Mg, siendo este último también el metal que migró en mayor concentración con respecto a la concentración inicial, 75% (165 *vs.* 124 mg/kg), seguido del Mn, cuya ratio de migración fue del 72% (37,6 *vs.* 27,1 mg/kg). En el caso del Sb, sólo se detectó en 5% de los extractos y además en una concentración media muy baja (0,27 mg/kg). En el caso de los extractos de sudor básico, el Mg también fue el metal que migró en mayor concentración (165 *vs.* 99,6 mg/kg), aunque a niveles inferiores a los detectados en sudor ácido. .

Si por algo destaca la ropa de vaquero es por su característico color azul. El colorante índigo es el responsable de esta coloración. Se trata de un colorante sintetizado principalmente a partir de productos de combustibles fósiles al cual se le atribuye una potencial mutagenicidad y carcinogenicidad, ya que activa factores de transcripción que regulan genes implicados en el metabolismo, proliferación y diferenciación celular (Chia y Musa, 2014; Rannug et al., 1992). El índigo puede desprenderse ligeramente del tejido, especialmente cuando es nuevo. Por ello también se analizó su contenido no sólo en ropa sino también en extractos de sudor artificial. Los resultados obtenidos muestran diferencias entre los dos tipos de sudor, ya detectadas en la migración de metales, detectando una concentración media indigo de 6,04 mg/g en el extracto de sudor básico respecto a 4,90 mg/g en el sudor ácido. No se encontraron diferencias significativas en los niveles de migración en sudor ácido según el material o el tipo de azul. Sin embargo, las prendas de color azul oscuro desprenden más cantidad de índigo que las de tonalidades más claras, en ambos extractos. En sudor ácido y básico se encontraron niveles de índigo de 6,70 y 7,76 mg/g , respectivamente, en prendas azul oscuro, y de 3,22 y 5,25 mg/g, respectivamente, en prendas azul claro. Este es un resultado esperable ya que a más tonalidad más cantidad de tinte. Cabe señalar que una cierta migración del índigo es normal y esperable, especialmente en los vaqueros más oscuros. Sin embargo, una migración excesiva puede ser un signo de mala calidad del tinte o de incorrectos/fraudulentos procesos de fabricación.

Atendiendo a la importancia del material en el contenido de metales y metaloides, se decidió realizar un segundo estudio en que el total de las prendas fueran sintéticas. En este segundo estudio, se escogieron un total de 39 prendas de baño, que abarcaban un amplio espectro de colores. Se analizaron los mismos 28 elementos que en el estudio anterior. En este caso, el Ti fue el metal con mayor concentración media (1844 mg/kg) y máxima (6603 mg/kg). Del mismo modo que en el estudio anterior, se evaluó el contenido en función de los colores, y se observaron también valores superiores en las prendas oscuras para Al, Cr, Cu, Mg y Mn. Los niveles de Cr en bañadores oscuros fueron muy elevados (entre 204 y 932 mg/kg), aunque en este caso las diferencias en función del color no fueron estadísticamente significativas.

Por las múltiples ventajas que ofrecen, como por ejemplo ligereza, rápido secado, resistencia y adaptabilidad, la mayoría de prendas de baño están fabricadas con poliéster y poliamida (Nilsen et al., 2002). En consecuencia, se analizó el contenido de metales en función del tipo de material, diferenciando las prendas de poliamida y poliéster. Los niveles de metales encontrados en cada tipo de fibra fueron diferentes, destacando la gran diferencia significativa entre los niveles medios de Ti encontrados en las fibras de poliamida (3759 mg/kg) en comparación con las de poliéster (24,1 mg/kg). Esto concuerda con los resultados descritos por von Goetz et al. (2013) al comparar otros tejidos con medias fabricadas con poliamida. La presencia de Ti en las prendas de poliamida se debe a la adición de nanopartículas de TiO_2 que aportan más hidrofobicidad y protección contra las radiaciones UV (Khan et al., 2018; Von Goetz et al., 2013). Además, también se observó que los colores fluorescentes presentaban concentraciones 3 veces superiores a las de colores claros (6256 *vs.* 2763 mg/kg, $p<0,01$), con un contenido dos veces superior al de bañadores de color oscuro (3957 mg/kg, $p<0,05$). Esta coloración debilitaría la fibra respecto a la agresión por la UV, por lo que sería más necesaria la adición de protección, hecho que justificaría los niveles más altos de Ti en este tipo de colores. Los niveles de Al, Mg, Pb y Sr fueron también significativamente superiores en las fibras de poliamida. Como ya describieron Matoso y Cadore (2012), este material contiene más Cr y Ni, metales que actúan como fijadores de color sobre todo en las fibras de poliamida.

Por el contrario, al analizar el contenido de los bañadores fabricados con poliéster, el metal encontrado en mayor concentración media fue el Sb (62,8 mg/kg). A su vez, los bañadores fabricados con poliamida presentaron un menor contenido de Sbr (14,5 mg/kg). Esta característica ya fue observada por Rovira et al. (2015, 2017b, 2017a), que detectaron niveles de Sb en un rango de entre 0,20 y 204 mg/kg en diferentes prendas fabricadas de poliésterEn el caso del Sb, su presencia en las prendas se justifica por formar parte de la propia fibra, ya que el Sb se añade durante la fabricación de la fibra de poliéster, y más concretamente durante la fase de polimerización como catalizador (Maerov, 1979). A pesar de haberse encontrado niveles muy altos de algunos metales, como el Ti, el Sb o el Cr, todas las prendas cumplían con la normativa europea (Comisión Europea, 2018a). Hay que recordar que la legislación comunitaria no contempla valores máximos de muchos de estos elementos químicos, así como tampoco de otros contaminantes como por ejemplo las aminas aromáticas.

1.2. PCBs

Los PCBs son unas de las sustancias más contaminantes del planeta y con graves consecuencias para la salud del ser humano (*Apartado 2.2.2*). A pesar de no conocerse una relación directa de uso en la industria textil, algunos estudios los relacionan con algunos pigmentos de tonalidad amarilla (Rodenburg et al., 2015). El estudio presentado en esta tesis (*Capítulo 2*) fue diseñado para demostrar la presencia de PCBs en ropa infantil y realizar su posterior evaluación de riesgos, ya que a pesar de su elevada toxicidad los estudios que analizan el contenido de PCBs en ropa son muy limitados. Se analizaron un total de 10 *bodies* infantiles cuyos niveles totales de PCBs oscilaron entre 74,2 y 412 pg/g. Al analizar los perfiles de los dos tipos de congéneres, dl-PCBs y ndl-PCBs, se observó que los congéneres dominantes eran los PCBs sin efecto dioxina, con una contribución que oscilaba entre 73% y 90%. Además, los resultados confirman la asociación de ciertos PCBs con pigmentos amarillos. En la bibliografía, se han reportado concentraciones más elevadas de PCB-101 y PCB-153 en prendas de tonalidades mostazas y tricolores que incluían el color amarillo (Anezaki y Nakano, 2014).

1.3. Formaldehído

La tercera sustancia química analizada en la presente tesis fue el formaldehído (*Capítulo 3*). Es un producto ampliamente utilizado en productos de consumo. En la industria textil, tiene gran utilidad por su efecto antiarrugas. Tal y como se describe en la introducción con la mejora de las técnicas, las cantidades de formaldehído utilizadas durante la fabricación de las prendas de vestir han disminuido, y así lo demuestran los estudios llevados a cabo durante décadas (*Apartado 2.3.4*). Uno de los objetivos del estudio fue conocer los niveles de formaldehído de las prendas de ropa de mujeres embarazadas, bebés y niños/as pequeños/as. Se analizaron un total de 120 prendas, con un porcentaje de detección del 19% y un rango de concentración media entre 12,8 y 55,7 mg/kg. Estos valores son un 70% menores a los niveles de formaldehído en ropa observados por el Instituto Europeo de Sanidad y Protección de los Consumidores (Piccinini et al., 2007), en el que se detectaron niveles de formaldehído en el 48% de las prendas, con un rango de 30-166 mg/kg. También suponen una reducción del 30% en comparación con otro estudio llevado a cabo también en Europa por Aldag et al., 2017. De esta manera, se confirma que la industria ha reducido el uso de formaldehído, gracias en parte a los modernos acabados químicos de prensado duradero y al cambio de resinas utilizados por la industria textil, incluso llegando no a ser detectado en un estudio llevado a cabo en EE.UU en 2019 (Nikle et al., 2019).

En términos generales, las prendas de vestir para mujeres embarazadas presentaron más contenido en formaldehído (12,0 mg/kg) que las prendas de niños/as inferiores a 3 años (7,88 mg/kg) y bebés (7,57 mg/kg). Respecto al material, del mismo modo que en el estudio de metales, también se encontraron diferencias en las concentraciones de formaldehído según si las prendas estaban fabricadas con fibras de algodón o fibras sintéticas. La ropa de algodón presentaron niveles significativamente más elevados de formaldehído que las prendas sintéticas, siendo unos resultados similares a los encontrados en anteriores estudios (Piccinini et al., 2007). Esto se debe a que las fibras sintéticas no absorben tanta cantidad de agua como a las fibras naturales, por lo que su forma se mantiene más estable, y en consecuencia no sería necesario añadir tanta cantidad de agentes antiarrugas (Rippon y Evans, 2020).

Si bien es cierto que ninguna prenda superó los límites legales establecidos para textiles en contacto directo con la piel (75 mg/kg), sí que se detectaron dos prendas -concretamente 2 bragas premamá- que contenían niveles superiores a los 30 mg/kg, nivel mínimo a partir del cual se conoce que pueden aparecer reacciones alérgicas (Goossens y Aerts, 2022).

Una de las características que presenta el formaldehído es su sensibilidad por la luz UV. Una de las hipótesis del estudio fue que la ropa comprada online podría contener niveles más elevados de formaldehído que la ropa comprada directamente en tienda ya que ésta podría pasarse más tiempo guardada en los almacenes, evitando así el contacto con la luz UV. Sin embargo, los resultados obtenidos demostraron que el contenido en formaldehído no se veía influenciado por el lugar de compra ya que los niveles fueron similares. Este hecho podría explicarse porque algunas de las prendas compradas online no venían directamente de almacenes.

Otro de los factores que pueden afectar a la concentración de formaldehído son los ciclos de lavado (Luongo et al., 2016). Se diseñó un segundo experimento en el que se lavaron las prendas con mayor contenido en formaldehído y se comprobó cómo sus niveles descendían por debajo del límite de detección en todas ellas. Estos resultados coinciden con los de Piccinini et al. (2007), aunque en nuestro caso sólo fue necesario un ciclo de lavado, frente a los 7 del estudio realizado en Ispra (Italia). Ello esto se debe a la concentración de partida, mucho más baja en el estudio presentado en esta tesis (Piccinini et al., 2007).

El formaldehído también se analizó en las 39 muestras de prendas de baño, pero en este caso no se detectaron niveles en ninguna de las prendas. El que no detectara formaldehído en las 39 muestras no se traduce en que esas prendas estén libres de formaldehído, porque aun así pueden contener trazas. Uno de los motivos que pueden explicar la gran diferencia en los resultados es el material con el que están fabricados los bañadores, son prendas totalmente sintéticas. Como se ha explicado anteriormente las fibras sintéticas son más estables, no se arrugan, y por lo tanto no sería necesario añadirles formaldehído a las prendas (Rippon y Evans, 2020).

1.4. BPs

Los BPs fueron el último grupo de sustancias que se analizaron en esta tesis (*Capítulo 4*). Como se ha explicado en la introducción (*Apartado 2.4.1*), por sus favorables propiedades son uno de los grupos de compuestos químicos más utilizados por la industria. El BPA fue el único análogo detectado en la totalidad de las muestras, con una mediana de 7,43 ng/g. Resultados que se ajustan a su amplia aplicación en los productos de consumo (Xing et al., 2022), similares a los hallados por Xue et al. (2017) (10,7 ng/g) e inferiores a los observados por Wang et al. (2019) (mediana de 17,7 ng/g). La concentración mediana de BPS (1,04 ng/g) es también muy similar a la obtenida por Xue et al. (2017) (1,02 ng/g). Sin embargo, el porcentaje de detección es muy superior comparándolo con los estudios anteriores, triplicando su detección si lo comparamos con los resultados de Wang et al. (2019). Por el tipo de mercado, el estudio más parecido al que nos ocupa es el publicado por Freire et al. (2017), quienes analizaron un total de 32 calcetines comprados en España y observaron niveles muy superiores de BPA, tanto en términos de mediana como de rango.

La composición del material también influye en la presencia de BPS en los textiles. Estudios anteriores advierten de la presencia de disruptores endocrinos en los tejidos principalmente en los fabricados con fibras sintéticas y los resultados obtenidos en este estudio así lo demuestran. Concretamente, en las fibras de poliéster se detectó la concentración mediana más elevada de BPA (28,9 ng/g), BPF (1,56 ng/g), y BPS (2,38 ng/g).

Los BPs pueden utilizarse como intermediaros en la fabricación de tintes, por lo que es interesante analizar los resultados desde esta perspectiva. El BPA y el BPF fueron los análogos más predominantes en la ropa gris, mientras que los niveles de BPS fueron más elevados en la ropa negra. Xue et al. (2017) también encontraron diferencias entre los diferentes colores; en su caso, el color gris contenía también niveles más altos de BPA que otros colores

El presente estudio analizó el contenido de BPs y formaldehído en las mismas muestras de ropa, todas ellas pertenecientes a tres grupos de población: mujeres embarazadas, recién nacidos y niños/as pequeños. La ropa premamá contenía, en términos generales, concentraciones más elevadas de BPA, mientras que el nivel mínimo se observó en la ropa de bebés. La ropa interior, tanto de mujer como de niños/as pequeños, presentó las concentraciones más elevadas de BPA (10,4 y 37,9 ng/g). Es importante destacar que las bragas que mayor concentración de BPA presentan son las mismas en las que se detectaron los niveles máximos de formaldehído. No debemos olvidar que la presencia de sustancias tóxicas en este tipo de prendas supone un riesgo elevado, principalmente para las mujeres, por estar ésta en contacto directo con la mucosa vaginal, hecho que provoca una mayor probabilidad de absorción (Marcelis et al., 2022; Nicole, 2014).

2. Niveles de sustancias analizadas en ropa ecologica vs ropa tradicional

En la actualidad, la ropa ecológica cobra cada vez más importancia en una industria altamente contaminante como es la industria de la moda. Los tejidos ecológicos son una alternativa sostenible a los materiales textiles fabricados con fibras sintéticas. A lo largo de todos los estudios realizados en esta tesis se ha tenido especial interés en conocer si las prendas fabricadas precisamente con estos tejidos (básicamente algodón orgánico) presentaban un mayor contenido de sustancias químicas que las que estaban fabricadas con tejidos convencionales.

Análogamente a los resultados previamente hallados por Rovira et al. (2015), los niveles detectados en las prendas etiquetadas como ecológicas fueron superiores a las muestras textiles fabricadas con fibras convencionales. Sin embargo, la diferencia no fue estadísticamente significativa. En el estudio de prendas vaqueras, los niveles de Ni detectados en tejanos ecológicos fueron más de dos veces superiores a los de los textiles convencionales (2,74 *vs.* 1,18 mg/kg). Aun así, los valores se encontraban por debajo de los límites establecidos.

En el caso de los PCBs, los *bodies* fabricados con algodón orgánico contenían un 71% menos de PCBs que los fabricados con algodón convencional (156 *vs.* 201 pg/g). Esta diferencia es especialmente notable en los congéneres similares a las dioxinas, los más peligrosos, en los que las muestras de algodón normal superaban en un 36% a las muestras fabricadas en algodón ecológico (32,7 *vs.* 24,0 pg/g).

A diferencia de otros contaminantes, se hallaron concentraciones más elevadas de formaldehído en prendas fabricadas con algodón orgánico respecto a aquellas fabricadas con algodón convencional (10,4 *vs.* 8,23 mg/kg). Sorprendentemente, las prendas con certificación oficial contenían también más formaldehído que las no certificadas (11,6 *vs.* 8,93 mg/kg). Un hallazgo inesperado fue que las dos muestras que contenían los niveles más altos de todo el estudio (37,3 y 55,7 mg/kg), dos bragas premamá negras, estuvieran ambas fabricas con algodón orgánico, aunque no en su totalidad. Además, la muestra con una mayor concentración de formaldehído estaba etiquetada con la certificación OEKO-TEX® Standard 100. En todo caso, no se incurría en incumplimiento alguno ya que este tipo de certificación fija el límite en 75 mg/kg (OEKO-TEX Association, 2021). Además, otra prenda, un vestido fabricado con algodón orgánico 100% y con certificación GOTS, también contenía residuos de formaldehído (20,0 mg/kg). En este caso, el vestido sí superaría el valor límite establecido por su certificación, fijado en 16 mg/kg (GOTS, 2020).

Por el contrario, los resultados de bisfenoles evidenciaron que las prendas fabricadas con algodón orgánico contenían niveles más bajos de BPA, BPF y BPS que las prendas de algodón convencional, siendo esta diferencia significativa en el caso del BPS (0,76 *vs.* 1,24 ng/g, $p<0,05$). Los niveles de BPA de las prendas etiquetadas con la certificación OEKO-TEX® Standard 100 estaban muy por debajo de los 100 ng/g que marca como límite dicha certificación. La certificación GOTS prohíbe explícitamente el uso de BPA en sus prendas; sin embargo, en todas las prendas etiquetadas con esta certificación se detectaron niveles de BPA. En dos de ellas, ropa interior de color rosa, las concentraciones fueron excepcionalmente elevadas (150 y 96,5 ng/g).

La mitad (n=60) de las prendas en las que se analizó formaldehído y BPs se categorizaron como "ecológicas" por estar fabricadas con algodón orgánico, pero sólo 25 de ellas llevaban una etiqueta con certificación oficial. Las 35 prendas restantes llevan otro tipo de etiquetas, generalmente de color verde, en las que se destacaba que estaban fabricadas con algodón orgánico. Esta mezcla de etiquetas puede confundir al consumidor. Diversos estudios afirman que el consumidor medio no es consciente ni es capaz de diferenciar las mejoras implantadas por la industria y las empresas de ropa para mejorar la sostenibilidad. En 2020, Byrd y Su (2020) investigaron el comportamiento de los consumidores ante diferentes prendas de vestir ecológicas, concluyendo que, en general, los consumidores muestran un interés por el etiquetado medioambiental pero no tienen conocimientos sobre las prendas sostenibles y sociales ni sobre su significado.

3. Evaluación de riesgos de las sustancias analizadas

Una vez determinadas las concentraciones en las que se encuentran las sustancias analizadas en las diferentes prendas de ropa, se realizó la correspondiente evaluación de riesgos. Las prendas de vestir están en contacto directo con la piel a diario, por lo que la principal vía de exposición de estas sustancias es la dérmica. Siguiendo las etapas ya comentadas en la introducción (*Apartado 3*), primero se evaluó la exposición dérmica.

En el caso-estudio de la ropa vaquera y ante un escenario más realista, las concentraciones de metales y metaloides utilizadas para realizar el cálculo de la exposición dérmica fueron las obtenidas en los extractos de sudor. A pesar de no encontrarse trazas de Cd, Cr ni Pb en los extractos de sudor, sí se detectó su presencia en las prenda, por lo que igualmente se evaluaron los riesgos de estos metales. Sin embargo, por falta de información científica, no se tuvieron en cuenta otros factores que pueden facilitar la liberación de los metales, como el fregamiento de las prendas con la piel o el desgaste de éstas. Para las muestras vaqueras, se evaluó la exposición dérmica de adultos, hombres y mujeres, y adolescentes de entre 10 y 16 años en tres escenarios diferentes: vistiendo solo pantalón vaquero, vistiendo solo camisa vaquera y vistiendo las dos prendas juntas.

Respecto a los bañadores, se evaluó la exposición dérmica a metales en los siguientes grupos de población: bebés de entre 2 y 3 años, niños/as (de ambos sexos) entre 3 y 6 años, y entre 6 y 11 años; adolescentes (niños y niñas) entre 11 y 18 años; y adultos (hombres y mujeres) mayores de 18 años. Además, se tuvieron en cuenta los diferentes escenarios según el tipo de prenda de baño que pueden vestir los diferentes grupos de población: bañador tipo bermuda o slip, en el caso de los hombres y niños; bikini o bañador para las mujeres y niñas; y camiseta o bañador, en el caso de los niños de entre 2 y 3 años. Fue precisamente este último grupo de población, el que presentó una mayor exposición dérmica para todos los metales. Esto se debe a la mayor relación entre superficie (tronco, genitales y nalgas) y ropa, así como a su menor peso corporal. También se asumió que los niños de esa edad podrían llevar camiseta, a parte del bañador, por lo que la superficie de piel cubierta es mayor.

La exposición dérmica a los PCBs a través de la ropa se evaluó para niños/as en diferentes etapas de desarrollo, 6 meses, 1 año y 3 años, siendo ésta similar en las 3 etapas ($3{,}19 \cdot 10^{-5}$, $3{,}11 \cdot 10^{-5}$ y $3{,}22 \cdot 10^{-5}$ pg OMS-TEQ/kg·día, respectivamente). Estos niveles son mucho menores a los de otras vías de exposición a PCBs, dado que la inhalación y la ingestión son las vías principales. Según datos de la bibliografía científica, en la provincia de Tarragona, lugar de compra de las prendas adquiridas físicamente, se ha estimado una ingesta diaria de PCBs a través de la lactancia materna de 1,58 pg OMS-TEQ/kg·día (Schuhmacher et al., 2013), y de 0,82 y 1,52 pg OMS-TEQ/kg·día a través de alimentos en niños/as pequeños de 1 y 3 años (ACSA, 2020). Aun así, algunos investigadores destacan la importancia de la vía dérmica para trabajadores del sector residuos (Zhao et al., 2021) y de manera indirecta por la transmisión de contaminantes ambientales a través de los textiles (Kolarik y Morrison, 2022).

El formaldehído se analizó en prendas premamá, de bebés menores de 12 meses, y niños/as de 12 a 36 meses. Las prendas que contribuían más a la exposición a formaldehído fueron los pantalones, en el caso de las mujeres embarazadas y niños/as con edades comprendidas entre los 12 y 36 meses, y los *bodies* y los pijamas, para los bebés menores de 12 meses. Estos resultados eran esperables, ya que son las prendas que más parte del cuerpo cubren. En términos generales, en cuanto a grupos de población se refiere, los bebés con edades inferiores a 12 meses presentan una exposición dérmica al formaldehído más elevada ($1,11 \cdot 10^{-3}$ mg/kg/día), mientras que la menor exposición al formaldehído correspondió a las mujeres embarazadas ($4,50 \cdot 10^{-4}$ mg/kg/día). Los niños/as tienen una mayor relación superficie cutánea/peso corporal, de ahí que su exposición a formaldehído sea más elevada. De los posibles efectos adversos al formaldehído, los más comunes son las dermatitis o reacciones alérgicas. Por ello, se calculó, además, el riesgo de sensibilización. Este resultó ser 10 veces inferior al NOAEC (0,005% p/p), por lo que los niveles de formaldehído encontrados en las prendas no causarían sensibilización alguna (NIOSH, 2011).

De igual manera que con el formaldehído, se evaluó la exposición dérmica de BPA y sus análogos en mujeres embarazadas, recién nacidos y niños/as menores de tres años. En este caso el escenario evaluado tuvo en cuenta la ropa de uso diario, es decir, se sumaron las prendas utilizadas en un día teniendo en cuenta su porcentaje de contribución. El BPA fue el bisfenol con mayor exposición dérmica, por el hecho de hallarse a mayor cantidad en las muestras textiles. Las mujeres embarazadas fueron el grupo que presentó una mayor exposición, aunque no se debe olvidar que la mayor relación entre superficie cutánea/peso corporal que presentan los niños/as puede aumentar los riesgos derivados de la exposición a BPA. Al igual que en otros contaminantes, la ingesta dietética es la vía principal de exposición del BPA (González et al., 2020). Si se comparan los resultados obtenidos en la presente tesis con las estimaciones de exposición por ingesta de alimentos en mujeres embarazadas llevados a cabo por Martínez et al. (2021), se observa como la exposición dérmica es 4-5 órdenes inferior a la dietética.

Por último, se realizó la caracterización del riesgo, por lo que no deben considerarse del mismo modo los efectos adversos de sustancias cancerígenas con el efecto sistémico de contaminantes no cancerígenos. Primeramente, se calculó el riesgo no cancerígeno para todas las sustancias anteriormente analizadas. Para evaluar los riesgos no carcinogénicos derivados de la exposición dérmica, se utilizó el coeficiente de peligro (HQ), cuyo cálculo aparece explicado en el apartado 3.2 de la introducción.

Afortunadamente, el valor de HQ correspondiente a cada metal y metaloide estuvo por debajo del valor umbral, fijado en 1 (ATSDR, 2022) tanto en las prendas vaqueras como en los bañadores, incluso para los metales con los niveles más elevados y para todos los escenarios. Lo mismo ocurre con los PCBs (tanto dl-PCBs como ndl-PCBs) y el formaldehído para todos los grupos de población estimados. En el caso de los bisfenoles, sólo se estimó el HQ para el BPA, ya que es el único análogo que tiene establecido un valor de RfD (US EPA, 2021). A pesar de ello, sus valores en todos los grupos de población también estuvieron por debajo de la unidad. Es importante tener en cuenta de que estos niveles de seguridad existirán siempre y cuando la persona esté sana, es decir, no presente ningún tipo de alergia a alguna de estas sustancias.

Finalmente, se calcularon los riesgos cancerígenos para aquellas sustancias que pueden presentar tales efectos. Como se explicó en la introducción (*Apartado 3.2*), el CR de una sustancia se estima multiplicando la exposición por su propio SF. En el caso de metales y metaloides en textiles vaqueros, el CR se estimó para Cr y Pb, al ser éstos los únicos metales detectados con un SF definido. Para ambos elementos, los CR fueron admisibles al estar por debajo de 10^{-6}, valor considerado aceptable para la población. En cambio, en el caso de la ropa de baño, los resultados no fueron tan esperanzadores. El Cr supera el valor aceptable (10^{-6}) en los grupos de bebés ($1{,}44 \cdot 10^{-5}$) y en niñas con edades comprendidas entre los 3 y 6, y 6 y 11 ambos grupos, cuando utilizan un bañador completo ($1{,}23 \cdot 10^{-5}$ y $1{,}00 \cdot 10^{-5}$, respectivamente). En este caso, el riesgo seguiría siendo asumible por la población, pero deberían tomarse algún tipo de acción para poder reducirlo (US EPA, 2005).

Por lo que respecta a los PCBs, los valores de CR son muy inferiores al valor de 10^{-6}, de manera que el uso de *bodies* no supone un riesgo para los niños/as con edad inferior a 12 meses. Por último, en el caso de formaldehído, los CR de los grupos de población de mujeres embarazadas, bebés y niños/as que vistan vestidos estarían por debajo del umbral considerado aceptable (10^{-6}). Sin embargo, los niños/as que combinaran camisetas con pantalones, superarían el límite ($2{,}97 \cdot 10^{-6}$).

En la presente tesis se han evaluado los riesgos derivados del uso diario de las prendas de vestir debido al uso de sustancias tóxicas utilizadas por la industria textil. Los resultados confirman la presencia de algunos metales y metaloides en prendas de tipo vaquero y bañadores. Algunos están más presentes en algunos tipos de fibras, como el Sb en poliéster o el Ti en la poliamida, y otros se asocian a colores oscuros, como el Cr. En el caso de los PCBs, concretamente el PCB-101 y el PCB-153 se asociaron con prendas de tonalidad amarilla. El formaldehído está más presente en las prendas fabricados con algodón por su poder antiarrugas, al contrario que el BPA, que se encontraba en más concentración en las fibras sintéticas. Afortunadamente, las prendas se encontraban dentro de los valores establecidos por la Unión Europea. Sin embargo, y de forma inesperada, se observó que las prendas fabricadas con algodón orgánico presentaban unos niveles más elevados de formaldehído. Si bien es cierto que la mayoría de las prendas no superaban los niveles marcados por las certificaciones legales, sí que en el caso del formaldehído y el BP algunas prendas no cumplieron con los requisitos. A pesar de ello, y afortunadamente, la evaluación de riesgos estimó que no existe riesgo para la exposición a las sustancias estudiadas.

Las evaluaciones de riesgo llevadas a cabo en la presente tesis se han realizado a nivel individual, de manera que la pregunta de cuál es el riesgo real del uso diario de las prendas de vestir quedaría aún sin respuesta. Son necesarias investigaciones futuras que deberían centrarse en evaluaciones de riesgo de exposición múltiple, incluyendo posibles efectos sinérgicos entre las diferentes sustancias, teniendo en cuenta la susceptibilidad individual, ya que la presencia de diversas sustancias en las prendas de vestir ha quedado demostrada, tanto en la literatura científica como en la presente tesis.

CONCLUSIONES

A partir de los resultados experimentales obtenidos en la presente tesis doctoral, se puede concluir que:

1. Los niveles detectados de metales y metaloides, así como de PCBs, formaldehído y BPs, estuvieron por debajo de los límites establecidos por la legislación en la Unión Europea.
2. El tipo de material con el que está fabricado la fibra textil está relacionado con el tipo de sustancias que contiene, de manera que:
    a. En fibras de algodón se encuentra más formaldehído.
    b. En fibras de poliéster se encuentra más Sb, BPA y BPS.
    c. En fibras de poliamida se encuentra más Ti.
3. El color está relacionado con la concentración de algunas de las sustancias analizadas. Por un lado, las prendas de colores oscuros contienen más Mg, Cr, Cu y Pb, debido a su presencia en los propios tintes y/o a su utilización durante los procesos de tintura al azufre. Por otro lado, las prendas grises contienen más BPA y BPF que las prendas negras, en las que el BPS es más abundante.
4. Los metales y metaloides presentes en las prendas vaqueras pueden liberarse de las fibras con el simple sudor diario, migrar hacia la piel y ser absorbidos por nuestro cuerpo, aumentando así los riesgos para la salud.
5. A pesar de que el estudio de PCBs es un estudio preliminar, éste ya demuestra la presencia de estos compuestos en prendas infantiles (*bodies*) fabricadas con algodón convencional. Su presencia se asocia a colores con tonalidades amarillas.
6. El BPA es el análogo del bisfenol más utilizado en la industria textil, de la misma manera que en otros productos de consumo. Preocupa su presencia en la ropa interior de mujeres embarazadas por su contacto directo con la mucosa vaginal, hecho que aumentaría su probabilidad de absorción.
7. El etiquetaje ecológico no garantiza que las prendas estén libres de sustancias tóxicas. Las prendas fabricas con algodón orgánico contienen niveles más altos

de metales (Al, B, Ba, Fe, Mg, Mn, Sb y Ti) y formaldehído que las fabricadas con algodón convencional.

8. Un lavado inicial tras la compra de la ropa puede disminuir los riesgos asociados a las posibles sustancias tóxicas presentes en la ropa, al menos en el caso del formaldehído.
9. Los riesgos no cancerígenos de las sustancias analizadas están por debajo del valor umbral de la unidad para todos los grupos de población evaluados.
10. En términos generales, los riesgos cancerígenos de las sustancias analizadas estuvieron dentro del límite aceptable ($<10^{-6}$), exceptuando el Cr (VI) en los grupos de población de bebés y niñas con edades comprendidas entre los 3 y 6 años, en los que el riesgo fue ligeramente superior a este umbral.
11. En el futuro es necesario llevar a cabo evaluaciones de riesgo por exposición múltiple que incluyan diferentes sustancias, potenciales efectos sinérgicos y más de una ruta de exposición.

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ANEXO

ANEXO 1 – Publicaciones, congresos y otros

Publicaciones incluidas en la presente tesis

Herrero, M., Souza, M.C.O., González, N., Marquès, M., Barbosa, F., Domingo, J.L., Nadal, M., Rovira, J. (2023). Dermal exposure to bisphenols in pregnant women's and baby clothes: Risk characterization. *Science of the Total Environment* 878, 163122. https://doi.org/10.1016/j.scitotenv.2023.163122 **Quartile 1. Impact factor: 10.754 SJR: 2.11**

Herrero, M., González, N., Rovira, J., Marquès, M., Domingo, J.L., Abalos, M., Abad, E., Nadal, M. (2022). Health risk assessment of polychlorinated biphenyls (PCBs) in baby clothes. A preliminary study. *Environmental Pollution* 307. https://doi.org/10.1016/j.envpol.2022.119506 **Quartile 1. Impact factor: 8.9. SJR: 2.11**

Herrero, M., González, N., Rovira, J., Marquès, M., Domingo, J.L., Nadal, M. (2022). Early-Life Exposure to Formaldehyde through Clothing. *Toxics* 10, 361. https://doi.org/10.3390/toxics10070361 **Quartile 2. Impact factor: 4.472. SJR: 0.761**

Herrero, M., Rovira, J., Esplugas, R., Nadal, M., Domingo, J.L. (2020). Human exposure to trace elements, aromatic amines and formaldehyde in swimsuits: Assessment of the health risks. *Environmental Research* 181. https://doi.org/10.1016/j.envres.2019.108951
Quartile 1. Impact factor: 6.498. SJR: 1.46

Herrero, M., Rovira, J., Nadal, M., Domingo, J.L. (2019). Risk assessment due to dermal exposure of trace elements and indigo dye in jeans: Migration to artificial sweat. *Environmental Research* 172, 310-318. https://doi.org/10.1016/j.envres.2019.02.030 **Quartile 1. Impact factor: 5.715. SJR: 1.52**

Publicaciones NO incluidas en la presente tesis

Herrero, M., Rovira, J., González, N., Marquès, M., Barbosa, F., Sierra, J., Domingo, J. L., Nadal, M., y Souza, M. (2023). Clothing as a potential exposure source of trace elements during early life. *Environmental Research* 233, 116479. https://doi.org/10.1016/j.envres.2023.116479 **Quartile 1. Impact factor: 8.431. SJR: 1.63**

Souza, M., González, N., **Herrero, M.**, Marquès, M., Rovira, J., Nadal, M., Barbosa, F., y Domingo, J. L. (2023). Screening of regulated aromatic amines in clothing marketed in Brazil and Spain: Assessment of human health risks. *Environmental Research* 221 (January). https://doi.org/10.1016/j.envres.2023.115264 **Quartile 1. Impact factor: 8.431. SJR: 1.63**

Souza, M., González, N., **Herrero, M.**, Marquès, M., Rovira, J., Domingo, J. L., Barbosa, F., y Nadal, M. (2023). Non-regulated aromatic amines in clothing purchased in Spain and Brazil: Screening-level exposure and health impact assessment. Journal of Environmental Management, 339 (January). https://doi.org/10.1016/j.jenvman.2023.117905136, 110992 **Quartile 1. Impact factor: 8.910. SJR: 1.68**

Herrero, M., Rovira, J., Marquès, M., Nadal, M., y Domingo, J. L. (2020). Human exposure to trace elements and PCDD/Fs around a hazardous waste landfill in Catalonia (Spain). Science of The Total Environment, 710, 136313. https://doi.org/10.1016/j.scitotenv.2019.136313 **Quartile 1. Impact factor: 10.754 SJR: 1.95**

Asistencia a congresos

SETAC Europe 32th Annual Meeting. Herrero, M., González N., Rovira, J., Marquès, M., Nadal, M., y Domingo, J. L.. Early-life exposure to formaldehyde through textile materials

Participación en otros proyectos

EarlyCLOTHES: Early-life exposure to chemical substances through textile materials: Health risk assessment. Financiado por el Ministerio de Ciencia e Inovación, subvención nº PID2019-104443GB-I00.

ANEXO 2 – Información complementaria del capítulo 3

Table S1. Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
1	Pregnant women Clothes	T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	White		16.0	
2		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Black		15.6	
3		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Beige		15.1	
4		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Black and white		14.7	
5		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Pink		20.5	
6		T-shirt	Supermarket	100% C		Bangladesh	Blue and white	OEKO-TEX® Standard 100	14.6	
7		T-shirt	Supermarket	95% C, 5% E		Bangladesh	Mustard and white	OEKO-TEX® Made in Green	16.0	
8		T-shirt	Supermarket	95% C, 5% E		Bangladesh	Dark Blue	OEKO-TEX® Made in Green	16.6	
9		T-shirt	Chain Store	95% C, 5% E		Pakistan	Yellow		18.2	
10		T-shirt	Chain Store	95% C, 5% E		Bangladesh	Blue and stamp		18.1	
11a		Rib	Chain Store	95% C, 5% E	*	Bangladesh	Grey		20.4	
11b		Jogger	Chain Store	65% P, 35% V		Bangladesh	Grey		19.5	
12a		Rib	Chain Store	95% C, 5% E		Pakistan	Blue		19.5	
12b		Jean	Chain Store	71% C, 27% P, 3% E		Pakistan	Blue		19.0	
13a		Jean	Supermarket	98% C, 2% E		Pakistan	Blue		23.8	
13b		Rib	Supermarket	96% C, 4% E		Pakistan	Blue		38.1	
14		Legging	Chain Store	92% C, 8% E		Sri Lanka	Black		27.6	
15		Trouser	Chain Store	62% P, 31% V, 7% E		Turkey	Cream		24.3	
16		Legging	Supermarket	95% C, 5% E	*	Bangladesh	Navy Blue	OEKO-TEX® Standard 100	16.5	
17a		Rib	Chain Store	95% C, 5% E	*	Bangladesh	Black		21.5	20% recycled
17b		Jean	Chain Store	86% C, 12% P		Bangladesh	Grey		37.9	
18		Legging	Chain Store	94% V, 6% E	*	Turkey	Black		23.1	
19		Legging	Chain Store	96% C, 4% E	*	India	Blue		18.1	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
20		Jean	Chain Store	99% C, 1% E	*	Cambodia	Blue		42.9	
21		Bra	Chain Store	100% P		China	Black		24.4	Lining
22		Bra	Chain Store	100% P		China	Grey		27.7	Lining
23		Bra	Chain Store	95% C, 5% E		China	White		12.2	
24		Bra	Chain Store	95% C, 5% E		China	Grey		16.2	
25		Bra	Chain Store	90% C, 10% E		China	Grey and flowers		19.3	
26		Bra	Chain Store	95% C, 5% E	*	Bangladesh	Grey		14.1	Lining
27		Bra	Chain Store	95% C, 5% E	*	Bangladesh	White		11.7	Lining
28		Bra	Chain Store	95% C, 5% E	*	China	Grey	OEKO-TEX® Standard 100	15.2	
29	Pregnant women Clothes	Bra	Chain Store	95% C, 5% E	*	Myanmar	Grey		17.0	
30		Bra	Chain Store	95% C, 5% E	*	Myanmar	White		14.4	
31		Panties	Chain Store	95% C, 5% E	*	Bangladesh	Black		16.1	
32		Panties	Chain Store	95% C, 5% E	*	Bangladesh	Pink		15.6	
33		Panties	Chain Store	95% C, 5% E	*	Bangladesh	Grey		16.3	
34		Panties	Chain Store	79% C, 15% PA, 6% E	*	Turkey	Black	OEKO-TEX® Standard 100	25.0	
35		Panties	Chain Store	95% C, 5% E	*	China	Grey		17.3	
36		Panties	Chain Store	95% C, 5% E		Turkey	Grey		16.1	
37		Panties	Chain Store	95% C, 5% E		Turkey	Black		18.2	
38		Panties	Chain Store	86% PA, 14% E		Italy	White		14.5	
39		Panties	Chain Store	86% PA, 14% E		Italy	Black		14.5	
40		Panties	Chain Store	95% C, 5% E		China	Grey		19.2	
41	Babies clothes (<12 months old)	Pyjamas	Chain Store	100% C	*	Bangladesh	Beige and stamp		18.8	
42		Pyjamas	Chain Store	100% C	*	Bangladesh	Pink and white		19.0	
43		Pyjamas	Chain Store	100% C	*	Bangladesh	Pink		20.0	
44		Pyjamas	Supermarket	100% C	*	India	Stamp white and grey	OEKO-TEX® Standard 100	18.7	
45		Pyjamas	Shop	100% C	*	Turkey	White and green	GOTS*	19.9	
46		Pyjamas	Supermarket	100% C		China	Pink and black		18.9	
47		Pyjamas	Chain Store	100% C		Sri Lanka	Mustard and white	OEKO-TEX® Standard 100	17.9	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
48	Babies clothes (<12 months old)	Pyjamas	Chain Store	100% C		Sri Lanka	Beige	OEKO-TEX® Standard 100	18.3	
49		Pyjamas	Chain Store	100% C		Sri Lanka	Stamp Green	OEKO-TEX® Standard 100	18.7	
50		Pyjamas	Chain Store	100% C		China	White, green and yellow		18.5	
51		Bodysuit	Chain Store	100% C	*	China	White		18.9	
52		Bodysuit	Chain Store	100% C		Bangladesh	Beige and brown		19.1	
53		Bodysuit	Chain Store	100% C		Bangladesh	Mustard and brown		18.6	
54		Bodysuit	Chain Store	100% C	*	Cambodia	Green		19.3	
55	Toddlers clothes (12-36 months old)	Bodysuit	Chain Store	100% C	*	Cambodia	White		19.5	
56		Bodysuit	Chain Store	100% C	*	Cambodia	Grey		20.6	
57		Bodysuit	Chain Store	100% C		Bangladesh	Pink and white	OEKO-TEX® Standard 100	16.1	
58		Bodysuit	Chain Store	100% C		Bangladesh	Pink	OEKO-TEX® Standard 100	18.5	
59		Bodysuit	Chain Store	100% C		Bangladesh	White	OEKO-TEX® Standard 100	18.0	
60		Bodysuit	Shop	100% C	*	EU	White, black and yellow	GOTS*	17.7	
61		Socks	Chain Store	63% C, 33 PA, 4 E		China	White, camel and blue		31.4	
62		Socks	Chain Store	75% C, 23% PA, 2% E		Pakistan	Grey and pink		30.4	
63		Socks	Chain Store	78% C, 20% PA, 2% E		China	Violet		30.1	
64		Socks	Chain Store	72% C, 26% P, 2% E		China	Dark grey		28.1	
65		Socks	Supermarket	80% C, 20% PA		Spain	Dark blue		26.0	
66		Socks	Shop	98% C, 2% E	*	Germany	Red and white		27.3	
67		Socks	Shop	98% C, 2% E	*	Germany	Blue and white		19.7	
68		Socks	Chain Store	76% C, 22% PA, 2% E	*	Turkey	Light Brown		29.4	
69		Socks	Chain Store	76% C, 22% PA, 2% E	*	Turkey	Cream		32.0	
70		Socks	Chain Store	76% C, 22% PA, 2% E	*	Turkey	White		33.2	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
71	Toddlers clothes (12-36 months old)	Pyjamas	Chain Store	100% C	*	China	Green		18.0	
72		Pyjamas	Supermarket	100% C	*	Bangladesh	Red	OEKO-TEX® Standard 100	17.6	
73		Pyjamas	Chain Store	100% C	*	Bangladesh	Green		22.4	
74		Pyjamas	Chain Store	100% C	*	Bangladesh	Mustard and white		19.5	
75		Pyjamas	Shop	100% C	*	Germany	Blue and white		19.0	
76		Pyjamas	Chain Store	100% C		India	White, red and yellow		19.8	
77		Pyjamas	Chain Store	100% C		India	Fluor		14.7	
78		Pyjamas	Chain Store	100% C		India	Black		15.7	
79		Pyjamas	Chain Store	100% C		Bangladesh	Blue and green		19.1	
80		Pyjamas	Supermarket	100% C		India	Blue and black		13.4	
81		Underwear	Supermarket	100% C	*	EU	White		18.4	
82		Underwear	Shop	100% C	*	Germany	White		17.8	
83		Underwear	Shop	100% C	*	Germany	Dark blue		17.9	
84		Underwear	Shop	100% C	*	Germany	Pink		18.4	
85		Underwear	Shop	100% C	*	Germany	Pink		14.1	
86		Underwear	Chain Store	100% C		India	Yellow		13.0	
87		Underwear	Chain Store	100% C		India	White		13.2	
88		Underwear	Chain Store	100% C		Bangladesh	Rosa		13.0	
89		Underwear	Chain Store	100% C		Bangladesh	Green		12.6	
90		Underwear	Chain Store	100% C		China	Red		13.9	
91		Dress	Chain Store	100% C	*	Bangladesh	White and blue		15.1	
92		Dress	Shop	100% C	*	Germany	Dark blue		18.1	
93		Dress	Chain Store	100% C	*	Bangladesh	White and blue		14.4	
94		Dress	Shop	100% C	*	India	Stamp		18.6	
95		Dress	Shop	100% C	*	India	Stamp		14.1	
96		Dress	Chain Store	100% P		China	White		5.07	Lining
97		Dress	Chain Store	100% C		Bangladesh	Pink		15.4	
98		Dress	Chain Store	100% C		Bangladesh	Pink, green and white		16.6	
99		Dress	Chain Store	69% C, 28% P, 3% E		Portugal	Pink		22.5	
100		Dress	Supermarket	100% C		India	Blue and pink		5.44	Lining

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº	Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
101	T-shirt	Chain Store	100% C	*	Bangladesh	Pink		14.1	
102	T-shirt	Shop	100% C	*	Germany	Pink		16.8	
103	T-shirt	Chain Store	100% C	*	Bangladesh	Blue and white		15.0	
104	T-shirt	Chain Store	100% C	*	Turkey	Blue and red		14.6	
105	T-shirt	Chain Store	100% C	*	Bangladesh	Green and white		14.6	
106	T-shirt	Chain Store	100% C		Spain	Violet		18.8	
107	T-shirt	Chain Store	100% C		Portugal	Grey		17.6	
108	T-shirt	Chain Store	100% C		India	Pink		15.9	
109	T-shirt	Chain Store	100% C		India	Cream, pink and blue		17.1	
110	T-shirt	Supermarket	100% C		Bangladesh	White		16.0	
111	Legging	Chain Store	95% C, 5% E	*	Bangladesh	White and black		17.5	
112	Legging	Chain Store	95% C, 5% E	*	Bangladesh	Blue		18.7	
113	Jean	Chain Store	100% C	*	Bangladesh	Blue		25.1	
114	Legging	Chain Store	100% C	*	Bangladesh	Dark grey		17.4	
115	Jean	Chain Store	100% C	*	Bangladesh	Black		22.7	
116	Jean	Chain Store	98% C, 2% E		Morocco	Blue		34,4	
117	Legging	Chain Store	95% C, 5% E		India	Green and Pink		18,7	
118	Trouser	Supermarket	98% C, 2% E		Bangladesh	Camel		23,6	
119	Trouser	Chain Store	69% C, 28% P, 3% E		Bangladesh	Brown		16,9	
120	Trouser	Chain Store	100% C		Bangladesh	Green		26,2	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

ANEXO 3 – Información complementaria del capítulo 4

Supplementary Information

Table S1. Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
1		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	White		16.0	
2		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Black		15.6	
3		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Beige		15.1	
4		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Black and white		14.7	
5		T-shirt	Chain Store	95% C, 5% E	*	Bangladesh	Pink		20.5	
6		T-shirt	Supermarket	100% C		Bangladesh	Blue and white	OEKO-TEX® Standard 100	14.6	
7		T-shirt	Supermarket	95% C, 5% E		Bangladesh	Mustard and white	OEKO-TEX® Made in Green	16.0	
8		T-shirt	Supermarket	95% C, 5% E		Bangladesh	Dark Blue	OEKO-TEX® Made in Green	16.6	
9		T-shirt	Chain Store	95% C, 5% E		Pakistan	Yellow		18.2	
10	Pregnant women Clothes	T-shirt	Chain Store	95% C, 5% E		Bangladesh	Blue and stamp		18.1	
11a		Rib	Chain Store	95% C, 5% E	*	Bangladesh	Grey		20.4	
11b		Jogger	Chain Store	65% P, 35% V		Bangladesh	Grey		19.5	
12a		Rib	Chain Store	95% C, 5% E		Pakistan	Blue		19.5	
12b		Jean	Chain Store	71% C, 27% P, 3% E		Pakistan	Blue		19.0	
13a		Jean	Supermarket	98% C, 2% E		Pakistan	Blue		23.8	
13b		Rib	Supermarket	96% C, 4% E		Pakistan	Blue		38.1	
14		Legging	Chain Store	92% C, 8% E		Sri Lanka	Black		27.6	
15		Trouser	Chain Store	62% P, 31% V, 7% E		Turkey	Cream		24.3	
16		Legging	Supermarket	95% C, 5% E	*	Bangladesh	Navy Blue	OEKO-TEX® Standard 100	16.5	
17a		Rib	Chain Store	95% C, 5% E	*	Bangladesh	Black		21.5	20% recycled
17b		Jean	Chain Store	86% C, 12% P		Bangladesh	Grey		37.9	
18		Legging	Chain Store	94% V, 6% E	*	Turkey	Black		23.1	
19		Legging	Chain Store	96% C, 4% E	*	India	Blue		18.1	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
20		Jean	Chain Store	99% C, 1% E	*	Cambodia	Blue		42.9	
21		Bra	Chain Store	100% P		China	Black		24.4	Lining
22		Bra	Chain Store	100% P		China	Grey		27.7	Lining
23		Bra	Chain Store	95% C, 5% E		China	White		12.2	
24		Bra	Chain Store	95% C, 5% E		China	Grey		16.2	
25		Bra	Chain Store	90% C, 10% E		China	Grey and flowers		19.3	
26		Bra	Chain Store	95% C, 5% E	*	Bangladesh	Grey		14.1	Lining
27		Bra	Chain Store	95% C, 5% E	*	Bangladesh	White		11.7	Lining
28		Bra	Chain Store	95% C, 5% E	*	China	Grey	OEKO-TEX® Standard 100	15.2	
29	Pregnant women Clothes	Bra	Chain Store	95% C, 5% E	*	Myanmar	Grey		17.0	
30		Bra	Chain Store	95% C, 5% E	*	Myanmar	White		14.4	
31		Panties	Chain Store	95% C, 5% E	*	Bangladesh	Black		16.1	
32		Panties	Chain Store	95% C, 5% E	*	Bangladesh	Pink		15.6	
33		Panties	Chain Store	95% C, 5% E	*	Bangladesh	Grey		16.3	
34		Panties	Chain Store	79% C, 15% PA, 6% E	*	Turkey	Black	OEKO-TEX® Standard 100	25.0	
35		Panties	Chain Store	95% C, 5% E	*	China	Grey		17.3	
36		Panties	Chain Store	95% C, 5% E		Turkey	Grey		16.1	
37		Panties	Chain Store	95% C, 5% E		Turkey	Black		18.2	
38		Panties	Chain Store	86% PA, 14% E		Italy	White		14.5	
39		Panties	Chain Store	86% PA, 14% E		Italy	Black		14.5	
40		Panties	Chain Store	95% C, 5% E		China	Grey		19.2	
41	Babies clothes (<12 months old)	Pyjamas	Chain Store	100% C	*	Bangladesh	Beige and stamp		18.8	
42		Pyjamas	Chain Store	100% C	*	Bangladesh	Pink and white		19.0	
43		Pyjamas	Chain Store	100% C	*	Bangladesh	Pink		20.0	
44		Pyjamas	Supermarket	100% C	*	India	Stamp white and grey	OEKO-TEX® Standard 100	18.7	
45		Pyjamas	Shop	100% C	*	Turkey	White and green	GOTS*	19.9	
46		Pyjamas	Supermarket	100% C		China	Pink and black		18.9	
47		Pyjamas	Chain Store	100% C		Sri Lanka	Mustard and white	OEKO-TEX® Standard 100	17.9	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
48	Babies clothes (<12 months old)	Pyjamas	Chain Store	100% C		Sri Lanka	Beige	OEKO-TEX® Standard 100	18.3	
49		Pyjamas	Chain Store	100% C		Sri Lanka	Stamp Green	OEKO-TEX® Standard 100	18.7	
50		Pyjamas	Chain Store	100% C		China	White, green and yellow		18.5	
51		Bodysuit	Chain Store	100% C	*	China	White		18.9	
52		Bodysuit	Chain Store	100% C		Bangladesh	Beige and brown		19.1	
53		Bodysuit	Chain Store	100% C		Bangladesh	Mustard and brown		18.6	
54		Bodysuit	Chain Store	100% C	*	Cambodia	Green		19.3	
55	Toddlers clothes (12-36 months old)	Bodysuit	Chain Store	100% C	*	Cambodia	White		19.5	
56		Bodysuit	Chain Store	100% C	*	Cambodia	Grey		20.6	
57		Bodysuit	Chain Store	100% C		Bangladesh	Pink and white	OEKO-TEX® Standard 100	16.1	
58		Bodysuit	Chain Store	100% C		Bangladesh	Pink	OEKO-TEX® Standard 100	18.5	
59		Bodysuit	Chain Store	100% C		Bangladesh	White	OEKO-TEX® Standard 100	18.0	
60		Bodysuit	Shop	100% C	*	EU	White, black and yellow	GOTS*	17.7	
61		Socks	Chain Store	63% C, 33 PA, 4 E		China	White, camel and blue		31.4	
62		Socks	Chain Store	75% C, 23% PA, 2% E		Pakistan	Grey and pink		30.4	
63		Socks	Chain Store	78% C, 20% PA, 2% E		China	Violet		30.1	
64		Socks	Chain Store	72% C, 26% P, 2% E		China	Dark grey		28.1	
65		Socks	Supermarket	80% C, 20% PA		Spain	Dark blue		26.0	
66		Socks	Shop	98% C, 2% E	*	Germany	Red and white		27.3	
67		Socks	Shop	98% C, 2% E	*	Germany	Blue and white		19.7	
68		Socks	Chain Store	76% C, 22% PA, 2% E	*	Turkey	Light Brown		29.4	
69		Socks	Chain Store	76% C, 22% PA, 2% E	*	Turkey	Cream		32.0	
70		Socks	Chain Store	76% C, 22% PA, 2% E	*	Turkey	White		33.2	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº		Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
71	Toddlers clothes (12-36 months old)	Pyjamas	Chain Store	100% C	*	China	Green		18.0	
72		Pyjamas	Supermarket	100% C	*	Bangladesh	Red	OEKO-TEX® Standard 100	17.6	
73		Pyjamas	Chain Store	100% C	*	Bangladesh	Green		22.4	
74		Pyjamas	Chain Store	100% C	*	Bangladesh	Mustard and white		19.5	
75		Pyjamas	Shop	100% C	*	Germany	Blue and white		19.0	
76		Pyjamas	Chain Store	100% C		India	White, red and yellow		19.8	
77		Pyjamas	Chain Store	100% C		India	Fluor		14.7	
78		Pyjamas	Chain Store	100% C		India	Black		15.7	
79		Pyjamas	Chain Store	100% C		Bangladesh	Blue and green		19.1	
80		Pyjamas	Supermarket	100% C		India	Blue and black		13.4	
81		Underwear	Supermarket	100% C	*	EU	White		18.4	
82		Underwear	Shop	100% C	*	Germany	White		17.8	
83		Underwear	Shop	100% C	*	Germany	Dark blue		17.9	
84		Underwear	Shop	100% C	*	Germany	Pink		18.4	
85		Underwear	Shop	100% C	*	Germany	Pink		14.1	
86		Underwear	Chain Store	100% C		India	Yellow		13.0	
87		Underwear	Chain Store	100% C		India	White		13.2	
88		Underwear	Chain Store	100% C		Bangladesh	Rosa		13.0	
89		Underwear	Chain Store	100% C		Bangladesh	Green		12.6	
90		Underwear	Chain Store	100% C		China	Red		13.9	
91		Dress	Chain Store	100% C	*	Bangladesh	White and blue		15.1	
92		Dress	Shop	100% C	*	Germany	Dark blue		18.1	
93		Dress	Chain Store	100% C	*	Bangladesh	White and blue		14.4	
94		Dress	Shop	100% C	*	India	Stamp		18.6	
95		Dress	Shop	100% C	*	India	Stamp		14.1	
96		Dress	Chain Store	100% P		China	White		5.07	Lining
97		Dress	Chain Store	100% C		Bangladesh	Pink		15.4	
98		Dress	Chain Store	100% C		Bangladesh	Pink, green and white		16.6	
99		Dress	Chain Store	69% C, 28% P, 3% E		Portugal	Pink		22.5	
100		Dress	Supermarket	100% C		India	Blue and pink		5.44	Lining

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

Table S1 (Continued). Main characteristics of the analyzed clothes

Nº	Type of clothes	Place	Materials[1]	Regular Cotton	Made in	Colour	Official certification	Density	Comments
101	T-shirt	Chain Store	100% C	*	Bangladesh	Pink		14.1	
102	T-shirt	Shop	100% C	*	Germany	Pink		16.8	
103	T-shirt	Chain Store	100% C	*	Bangladesh	Blue and white		15.0	
104	T-shirt	Chain Store	100% C	*	Turkey	Blue and red		14.6	
105	T-shirt	Chain Store	100% C	*	Bangladesh	Green and white		14.6	
106	T-shirt	Chain Store	100% C		Spain	Violet		18.8	
107	T-shirt	Chain Store	100% C		Portugal	Grey		17.6	
108	T-shirt	Chain Store	100% C		India	Pink		15.9	
109	T-shirt	Chain Store	100% C		India	Cream, pink and blue		17.1	
110	T-shirt	Supermarket	100% C		Bangladesh	White		16.0	
111	Legging	Chain Store	95% C, 5% E	*	Bangladesh	White and black		17.5	
112	Legging	Chain Store	95% C, 5% E	*	Bangladesh	Blue		18.7	
113	Jean	Chain Store	100% C	*	Bangladesh	Blue		25.1	
114	Legging	Chain Store	100% C	*	Bangladesh	Dark grey		17.4	
115	Jean	Chain Store	100% C	*	Bangladesh	Black		22.7	
116	Jean	Chain Store	98% C, 2% E		Morocco	Blue		34,4	
117	Legging	Chain Store	95% C, 5% E		India	Green and Pink		18,7	
118	Trouser	Supermarket	98% C, 2% E		Bangladesh	Camel		23,6	
119	Trouser	Chain Store	69% C, 28% P, 3% E		Bangladesh	Brown		16,9	
120	Trouser	Chain Store	100% C		Bangladesh	Green		26,2	

[1]Materials: C: cotton; E: elastane; V: viscose; PA: polyamide; P: polyester.

DETAILS OF INSTRUMENTAL ANALYSIS – UPLC-MS/MS

(Material and methods section – 2.3 Methodology)

The chromatographic separation was performed with a gradient detailed in Table S2. The mobile phase comprised water (A) and methanol (B). The column temperature was set at 50 ºC, being the injection volume 2 µl.

Table S2. UHPLC gradient.

Time (min)	%B	Flow (mL/min)
1.50	0	0.55
3.00	60	0.55
10.5	75	0.55
11.0	95	0.55
14.0	95	0.55

The source parameters applied operating in negative electrospray ionization (ESI) are shown in Table S3.

Table S3. Source parameters.

Parameter	**ESI (-)**
Gas Temperature (ºC)	260
Gas Flow (L/min)	15
Sheath Gas Temperature (ºC)	400
Sheath Gas Flow (L/min)	12
Nebulizer (psi)	15
Capillary Voltage (V)	3000
Nozzle Voltage (V)	1000

Results from the MRM optimization and the retention time are summarized in Table S4.

CE: Collision energy

Table S4. Details of the optimized MRM transition for each analyte

Analyte	Ret Time (min)	Prec Ion. (*m/z*)	Prod Ion. (*m/z*)	CE (V)
Bisphenol A	5.19	227.11	212.2	17
Bisphenol A	5.19	227.11	133.2	29
Bisphenol A *d*16	5.14	241.19	223.2	21
Bisphenol A *d*16	5.14	241.19	142.2	29
Bisphenol A-isomer	5.03	227.11	212.2	17
Bisphenol A-isomer	5.03	227.11	133.2	29
Bisphenol B	5.77	241.12	226.1	17
Bisphenol B	5.77	241.12	212	17
Bisphenol F	4.62	199.07	105	21
Bisphenol F	4.62	199.07	93.1	25
Bisphenol S	4.11	249.02	108.1	25
Bisphenol S	4.11	249.02	92	41

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