

Hazardous chemicals in branded textile products on sale in 27 countries during 2012

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Executive Summary

Textile manufacturing makes use of a diverse range of process and finishing chemicals, some of which have intrinsic hazardous properties. As a result, finished textile products can contain certain hazardous chemicals used during their manufacture. This may be because of their use as components of the products themselves, or due to residues remaining from their use within the manufacturing processes. Detection of chemical additives and residues in finished textiles can, therefore, provide an indication of chemicals used and potentially released during manufacture.

This report follows on from, and extends, a previous investigation by Greenpeace which found nonyl phenol ethoxylate (NPE) residues to be widespread in a range of sports and recreational textile products. NPEs are used in many countries in the manufacture of textiles, in particular as surfactants and detergents, although such uses have effectively been banned within the EU, with similar restrictions in place in the United States and Canada. Once released, NPEs break down to form nonylphenol isomers. These are persistent, bioaccumulative and toxic chemicals.

The current study, extended the range of chemicals investigated and broadened the range of items analysed for these chemicals. In all, 141 high street fashion textile products were analysed. These included items sold by 20 different major clothing brands, purchased in 27 countries around the world. The range included examples manufactured in at least 18 different countries, although the countries of manufacture of 25 articles were unknown. The investigation included products designed for men, women and children, and covered a variety of articles including t-shirts, jeans/trousers, dresses and underwear, as well as various other types of clothing.

As in the previous investigation, the concentration of NPEs was determined in all items. In addition, all items which included dyed fabric (134 samples) were tested for carcinogenic amines known to be released from azo dyes under certain conditions. In addition, toxic phthalate esters (commonly referred to as phthalates) were quantified in 31 items which featured medium or large plastisol printed areas. Moreover, just under half of the products (63 samples) were investigated using a broader qualitative chemical screening to identify the presence, as far as possible, of any residues of other chemicals present extractable in each product. Information on the hazardous properties of the chemicals quantified in this study, together with those identified through chemical screening, is provided within the report.

Key findings of this study include:-

- **NPEs** were the most commonly detected substances, identified in 89 of the 141 articles (63 % of the total). NPE concentrations ranged from just above 1 mg/kg up to 45 000 mg/kg. One fifth (20%) of the samples contained NPEs at concentrations above 100 mg/kg. Of this 20%, 12 samples (9% of articles tested) showed concentrations over 1 000 mg/kg (0.1% by mass),
- NPEs were detected in one or more product from all of the brands included in this study. NPEs were also found in at least one product from 13 of the 18 identifiable countries of manufacture, and in products sold in 25 out of the 27 countries. Overall, the NPE results were consistent with those from the previous study carried out by Greenpeace in which 78 items of sports and recreational clothing and shoes were analysed.

- **Phthalates** were detected in all 31 samples of fabric bearing a plastisol print. For four of these samples, phthalates were present at high or very high concentrations, indicating their use as plasticisers within the plastisol formulations; Three samples contained total phthalate levels of between 20.0 % to 37.6 % by weight (200000 to 376000 mg/kg) , and a fourth contained 0.52% by weight (5200 mg/kg). The origins of the phthalates detected in the other 27 samples with lower total phthalate levels (4 to 138 mg/kg) are not certain, and sources other than use during manufacture may contribute. Nonetheless, the presence of phthalates within a product at any level is of concern whatever the source,
- The individual phthalates present in the four samples with high or very high levels were DEHP (di-(2-ethylhexyl) phthalate), BBP (butylbenzyl phthalate) or DINP (di-isononyl phthalate),
- A **carcinogenic amine**, *o*-dianisidine, was released from two items under the test conditions, at 7 mg/kg and 9 mg/kg respectively. Any release of such a carcinogenic compound is of concern, though the levels of *o*-dianisidine were below regulatory limits set in certain countries (including the EU and China) designed to prohibit the sale of textile products containing azocolourants that can release carcinogenic amines under the test conditions,
- Numerous other industrial chemicals were identified in various individual items, including many that are hazardous or potentially hazardous, some of which are classified as toxic or very toxic to aquatic life.

Overall, a variety of hazardous chemicals were detected within the broad range of high street fashion textile products analysed. These covered a diverse range of brands and countries of manufacture. These results indicate the ongoing, and in some cases widespread, use of hazardous chemicals in the manufacture of textile products openly marketed to consumers. Specifically, the presence of NPEs within a wide range of items indicates that NPE use is widespread within the international textile industry, including within the supply chains used by many major international clothing brands. The presence of phthalates at high levels in some items shows that the presence of hazardous chemicals within some items is due to their intentional incorporation into certain textile products, and is not only due to residues left over from use in manufacturing processes.

In the case of the NPEs, which are readily water soluble, it should be noted that the concentration in a product cannot be considered indicative of the amount of NPEs used during manufacture. Residue levels will inevitably depend on a range of other factors, including the number of wash cycles employed during product finishing and the efficiency with which these chemicals are removed. For the same reason, the absence of NPE residues from any particular product cannot be taken to confirm absence of use of NPEs at some stage during the manufacturing processes.

The presence of chemicals in textile products indicates both that they are used during manufacture, and that, therefore, there is a potential for their release from manufacturing facilities. It also highlights the potential for releases from the products themselves after they have been sold. An earlier investigation by Greenpeace has shown that NPEs within textiles are readily washed out when they are laundered. Most, if not all, the other hazardous chemicals identified in this study are also likely to be washed out to some degree when the product is laundered. In addition, phthalates in plastisol formulations are not tightly bound to

the plastic, but are present as mobile components within the matrix, and will, therefore, be released from the product over time.

Each individual garment may contain only relatively small quantities of the chemicals identified. Nonetheless, given the overall volumes of textile production and of retail sales, the aggregated quantities of these hazardous chemicals present in textile products could be significant, with total releases representing a significant diffuse source of chemicals in the country of sale.

The range of hazardous or potentially hazardous chemicals identified in the broad screening analysis of 63 items indicates that investigations which focus only on a narrow range of target substances will inevitably underestimate the complexity of chemical residues in finished textiles and, therefore, the overall potential for chemical releases during manufacture and subsequent laundering.

Overall, this study has provided a greater understanding of the presence and, in some cases, concentrations of a broad range of chemicals within high street fashion textile products across a diverse range of brands and of countries of manufacture and sale. The number of articles investigated in this study is inevitably small compared to the vast number of products manufactured and sold per country or per brand. It is, therefore, not possible to draw more general conclusions about the levels or presence of such chemicals which may be expected for all such products. Rather, this study provides a snapshot of what appears to be a generic problem that is not restricted to any particular country, product type or brand. It is one that deserves further investigation. In particular, the current regulatory frameworks need scrutiny and development to improve their effectiveness in regulating this sector of industrial manufacture and marketing. In addition, suppliers and retailers need to develop robust procurement policies designed to force the elimination of such chemicals from manufacturing processes, and hence, in the finished products.

1. Introduction

Finished textile products can contain certain hazardous chemicals used during their manufacture, either because of their use as components of materials incorporated within the product or due to residues remaining from the use within processes employed during manufacture. In either case, textile products can subsequently act as sources of these chemicals to the environment, especially to water during washing. While each individual garment may release only a relatively small quantity of hazardous chemicals through its lifetime, given the overall volumes of textile production and retail, release from textiles as an overall product sector could represent a significant diffuse source of chemicals to water in the country of sale when considered on a national or regional basis. The presence of chemical additives and residues in finished textiles also gives an indication of the nature of chemical use and release during processes by which they are manufactured.

This reports follows on from, and extends, research recent published by Greenpeace International that identified the presence of one group of hazardous chemicals, the hormone-disrupting nonyl phenol ethoxylates (NPEs), in a range of textile products consisting primarily of sports and recreational clothing and shoes (Brigden *et al.* 2012, Greenpeace 2011b).

This current study investigated the presence of hazardous chemicals in a broader range of textile products, consisting of 141 textile products across many countries of manufacture and sale, and for a wide range of major clothing brands. The majority of products were tested quantitatively for NPEs, as well as for carcinogenic amines released from azo dyes within dyed fabric, and phthalate esters (commonly referred to as phthalates) in fabrics bearing a plastisol print¹. In addition, just under half of the products (63 samples) from a selection of the brands included in this study were investigated through a broader qualitative chemical screening to identify the presence, as far as possible, of any other hazardous chemicals present within the products, in order to provide an indication of the extent & nature of other chemical residues within textile products of this type.

As mentioned above, the presence of NPEs has been previously reported in certain textile products (Brigden *et al.* 2012, Greenpeace 2011b, and references within these reports). Similarly, the presence in certain textile products has also been previously reported for carcinogenic amines released under reducing conditions from azo dyes (JRC 2008, Laursen *et al.* 2003) and phthalates in plastisol printed fabric (RAPEX 2012, Greenpeace 2004). The use of a chemical screening approach by Laursen *et al.* (2003) also identified the presence of a wider range of chemicals within a small number of products).

More information on the chemicals investigated in the current study is provided in Boxes A-D.

The 141 products included in this study included items sold by 20 different major clothing brands, and were purchased across 27 countries around the world. According to their labels, the 141 products included examples which were manufactured in at least 18 different countries, with 25 articles being of unknown manufacturing origin. The sample set included products designed for men, women and children and covered a variety of articles including t-shirts, jeans/trousers, dresses and underwear, as well as a various other types of clothing.

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2. Materials and methods

The 141 products were purchased in April 2012 at the flagship stores of the clothing brands, or other stores authorised to sell the branded products. While still in the store, purchased products were immediately sealed in individual identical clean polyethylene bags. Sealed bags containing the products were sent to the Greenpeace Research Laboratories at the University of Exeter in the UK, from where they were dispatched to independent accredited laboratories for analysis of NPEs, phthalates and azo dyes related amines. For just under half of the products, a broader qualitative screening for other chemicals present within the fabric was carried out at the Greenpeace Research Laboratories. Details of the individual articles are provided in Appendix 1.

2.1 Nonyl phenol ethoxylates (NPEs)

The concentrations of NPEs were quantified in all 141 articles of clothing. For the majority of articles (110 of 141), a section of fabric that did not bear a plastisol print was tested. For the remaining 31 products, the concentration of NPEs was quantified in a section of fabric bearing a plastisol print of an image, logo or text. These 31 articles were also investigated for the presence of phthalates within the printed fabric (see Section 2.3).

Following isolation of a section of fabric from each article, the sample was extracted with an acetonitrile-water mixture in the ratio 70:30 and then analysed with reversed-phase HPLC liquid chromatography along with Applied Biosystems' API 4000 tandem mass spectrometry (LC-MS/MS). The quantification was carried out for each of 17 individual nonylphenol ethoxylates, consisting of those with between 4 and 20 ethoxylate groups. The quantitative results presented below are the sum of the concentrations of the individual nonylphenol ethoxylates with 4-20 ethoxylate groups. Quality assurance and quality control checks were employed, including the analysis of seven samples in duplicate and the analysis of blank samples and two intra-laboratory textile reference samples with every batch, of between 11 to 52 samples.

2.2 Carcinogenic amines released under reducing conditions

With the exception of 7 articles for which the fabric was white in colour, all articles that were investigated for the presence of NPEs were also investigated for the concentrations of carcinogenic amines released under certain reducing conditions, related to the presence of certain azo dyes (see Box B for detail). The 134 articles were tested in accordance with method EN 14362 related to the relevant European Union (EU) regulations (EU 2002), which involved the determination of certain aromatic amines derived from azo colorants following cleavage of the azo group under reducing conditions, either directly or following extraction from the fabric, depending on the type of fabric in each sample. The analysis included the quantification of two additional amines that are listed under the equivalent Chinese regulation (SAPRC 2012).

2.3 Phthalates in plastisol prints

All articles bearing a medium or large sized plastisol print of an image, logo or text were investigated for the concentrations of a range of phthalates within the printed fabric. These 31 articles, the same ones for which NPEs were quantified within fabric bearing a plastisol print, were quantified for the concentrations of the following phthalates in a section of printed fabric; dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DIBP), butylbenzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-iso-nonyl phthalate (DINP) and di-iso-decyl phthalate (DIDP).

A portion of each sample bearing a plastisol print was extracted with ethyl acetate:cyclohexane (1:1) using deuterated (D8)-naphthalene as a quality control standard to check extraction efficiency. Blanks were also extracted as part of the quality control checks employed. The concentrations of phthalates in the extracts were subsequently analysed by gas chromatography/mass spectrometry (GC/MS) using a LECO time of flight (TOF) instrument with a programmed temperature vaporizing (PTV) injector and a DB5ms column, using deuterated (D10)-pyrene as an internal standard.

2.4 Chemical screening

For each of the 63 samples, a representative portion was extracted using pentane:acetone (3:1) with a Dionex 350 accelerated solvent extractor (ASE), with deuterated (d8)-naphthalene as an internal standard to check extraction efficiency. Concentrated extracts were cleaned through a Florisil column, eluting with pentane: toluene (95:5). Cleaned extracts were concentrated to 0.5 mL and brominated naphthalene added as an internal standard for the analytical procedure.

The final extract was analysed by gas chromatography/mass spectrometry (GC/MS) using an Agilent 6890 Series II GC with a Restek Rtx-XLB column, linked to an Agilent 5973 inert mass selective detector (MSD) operated in electron impact (EI) mode. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides libraries, combined with expert judgment to confirm identification. In addition to the use of internal standards, a range of blank samples were extracted and/or analysed with each batch of five samples. Additional details on the chemical screening method are provided in Appendix 4.

3. Results and Discussion

The results for the various substance groups are presented in the following sections. Details of all results for the individual articles are provided in Appendix 1, along with a breakdown of the concentrations of all individual phthalates in the relevant articles in Appendix 2, and a listing of all substances identified in individual samples that were investigated using the chemical screening method in Appendix 3.

3.1 Nonyl phenol ethoxylates (NPEs)

Of the 141 articles in which NPEs were quantified, 89 articles (63 % of the total) tested positive for the presence of NPEs at concentrations above the limit of detection (1 mg/kg), at levels ranging from just above 1 mg/kg up to 45 000 mg/kg. The highest concentration (45 000 mg/kg) was detected in a sample of fabric bearing a plastisol print from a C&A branded t-shirt manufactured and sold in Mexico (our sample code: TX12041). While some other samples bearing a plastisol print also contained relatively high concentrations of NPEs, this was not always the case, with NPEs not being detected above 1 mg/kg in just under half (14 of 31) of the plastisol printed samples.

One fifth (20%) of the samples contained NPEs at concentrations above 100 mg/kg and, of these, 12 samples (9% of articles tested) had concentrations over 1 000 mg/kg (0.1% by mass). Of the remainder, just over two fifths (43%) of all samples tested contained detectable levels of NPEs at concentrations below 100 mg/kg. A summary of the number of samples containing NPEs within various ranges of concentration is given in Table 1.

NPE concentration range (mg/kg)	Number of samples (of 141)	% of samples
<1	52	37 %
1 – 10	27	19 %
>10 – 100	34	24 %
>100 – 1 000	16	11 %
>1 000	12	9%

Table 1. The number of samples (of the 141 articles tested) within various NPE concentration ranges.

NPEs were detected in one or more product from all of the brands included in this study. Furthermore, NPEs were detected in one or more product from 13 of the 18 countries of manufacture, and in products sold in 25 out of the 27 countries. For the countries of manufacture for which NPEs were not detected in any of the articles tested, only a relatively small number of articles per country were included in the study; Cambodia (2 articles), Jordan (1 article), Romania (1 article), Spain (1 article), Tunisia (3 articles). A summary of the results is presented in Tables 2 to 4, which include a breakdown of the results by brand, by place of sale, and by country of manufacture, respectively. These tables include the median values for all samples in each brand, place of sale or country of manufacture, as well as the median value for only those samples in which NPEs were detected in each case.

Brand	No. of samples	No. tested positive	NPE conc. range, when detected (mg/kg)	Median of detected levels (mg/kg)	Median of all levels (mg/kg)
Armani	9	5	1.2 – 43	8.1	1.2
Benetton	9	3	6.3 - 95	11	<1
Blazek	4	2	47 - 330	190	24
C&A	6	5	1.7 - 45 000	63	35
Calvin Klein	8	7	5.6 - 4 000	20	17
Diesel	9	3	6.6 - 710	16	<1
Esprit	9	6	1.1 - 770	47	17
Gap	9	7	1.3 - 920	43	8.6
H&M	6	2	1.6 - 8.7	5.2	<1
Jack & Jones	5	3	4.6 - 2 100	17	4.6
Levi's	11	7	5.7 - 4 100	80	9.7
Mango	10	6	1.3 - 9 800	690	4.3

Mark & Spencer	6	4	84 - 2 090	590	319
Metersbonwe	4	3	140 - 2 100	1 500	795
Only	4	4	5.5 - 730	35	35
Tommy Hilfiger	9	6	3.9 - 500	24	8.6
Vancl	4	4	7.6 - 150	76	76
Vermoda	5	4	6.3 - 130	38	31
Victoria's Secret	4	2	7.0 - 10	8.5	3.8
Zara	10	6	9.6 - 2 600	27	14

Table 2. The number of samples in which NPEs were identified by product brand, with the NPE concentration ranges, the median NPE concentrations in all samples, and the median values for those samples in which NPEs were detected, for each brand.

Place of sale	No. of samples	No. tested positive	NPE conc. range, when detected (mg/kg)	Median of detected levels (mg/kg)	Median of all levels (mg/kg)
Austria	3	2	7.2 - 8.6	7.9	7.2
Belgium	5	2	27 - 80	54	<1
Canada	4	3	8.6 - 4 000	10	9.3
Mainland China	16	13	5.5 - 2 600	140	32
Hong Kong	2	0	-	-	<1
Taiwan	2	2	9.7 - 79	44	44
Czech Rep.	6	2	47 - 330	190	<1
Denmark	6	3	17 - 730	45	8.8
Finland	2	0	-	-	<1
France	5	4	6.3 - 110	36	8.1
Germany	4	4	9.0 - 770	360	358
Hungary	4	2	1.7 - 29	15	1.1
Indonesia	5	4	3.8 - 550	36	5.6
Israel	4	3	1.3 - 43	8.7	<1
Italy	6	3	3.9 - 95	11	2.2
Lebanon	5	5	1.6 - 130	15	15
Mexico	6	5	56 - 45 000	920	713
Netherlands	5	0	-	-	<1
Norway	1	1	38	38	38
Philippines	4	3	20 - 620	600	311
Russia	6	3	6.6 - 17	17	3.6
South Africa	6	4	1.3 - 700	9.9	3.5
Spain	5	4	8.7 - 9 800	28	25
Sweden	2	1	43	43	22
Switzerland	6	3	1.1 - 64	6.9	<1
Thailand	6	3	32 - 2 090	460	16
Turkey	4	3	18 - 1 500	84	51
UK	5	2	4.8 - 1 400	690	<1
USA	6	5	1.2 - 4 100	26	17

Table 3. The number of samples in which NPEs were identified by the place of sale, with the NPE concentration range, the median NPE concentrations in all samples, and the median values for those samples in which NPEs were detected, for each place.

Country of manufacture	No. of samples	No. tested positive	NPE conc. range, when detected (mg/kg)	Median of detected levels	Median of all levels (mg/kg)
Bangladesh	12	5	1.3 - 1 500	8.6	<1
Cambodia	2	0	-	-	<1

China	34	21	1.3 - 2 600	80	9.9
Egypt	2	2	9.0 - 11	10	10
India	9	6	6.3 - 4 000	27	8.7
Indonesia	8	6	1.2 - 620	12	8.4
Jordan	1	0	-	-	<1
Mexico	6	6	56 - 45 000	2000	2000
Morocco	3	2	7.2 - 710	360	7.2
Pakistan	3	3	3.8 - 29	19	19
Philippines	1	1	26	26	26
Romania	1	0	-	-	<1
Spain	1	0	-	-	<1
Sri Lanka	2	2	3.9 - 7.0	5.5	5.5
Thailand	3	1	14	14	<1
Tunisia	3	0	-	-	<1
Turkey	15	7	17 - 9 800	38	<1
Vietnam	12	8	4.8 - 700	34	5.7
Unknown	23	19	1.1 - 2 100	31	18

Table 4. The number of samples in which NPEs were identified by country of manufacture, with the NPE concentration range, the median NPE concentrations in all samples, and the median values for those samples in which NPEs were detected, for each country.

Samples with higher NPE concentrations (above 100 mg/kg) were distributed across a range of countries of sale, countries of manufacture and product brands. However, it is not possible to draw any general conclusions on the variability of NPE concentrations in articles between the country of sale, country of manufacture, or product brand given the relatively small number of products included in this study, compared to the vast number of products manufactured and sold per country or per brand.

Box A. Nonylphenol ethoxylates (NPEs)

Nonylphenol ethoxylates (NPEs) are a group of chemicals used as surfactants, emulsifiers, dispersants and wetting agents in a variety of applications, including the manufacture of textiles. The use of NPEs during the manufacture of textiles can leave residues of NPEs within the final product which are readily released when the items are washed as part of their normal use (Brigden *et al.* 2012, Greenpeace 2012).

Where NPEs are released from manufacture facilities or through the laundering of textile products, either directly into surface waters or via wastewater treatment facilities, they can break down to form nonylphenol, a closely-related group of persistent, bioaccumulative and toxic chemicals (OSPAR 2004, Jobling *et al.* 1996). The manufacture, use and release of NPEs and nonylphenol are regulated in some regions (OSPAR 1998, EU 2003), though uses continue elsewhere. Additional information on nonylphenol and NPEs, including on their hazardous properties, is available in a previous related report (Box C, Greenpeace 2011a).

3.2 Carcinogenic amines released under reducing conditions

Of the 134 articles tested, the presence of one or more carcinogenic amines released under the test conditions was detected in 2 articles, both manufactured in Pakistan. For all other articles, all carcinogenic amines included in the analysis were not detected above the method detection limit (<5 mg/kg).

For the 2 articles in which release of an amine was detected, the same compound was detected for both articles; 3,3'-dimethoxybenzidine (also known as *o*-dianisidine). The other carcinogenic amines included in the analysis were not detected for these 2 articles (<5 mg/kg). Details of the results for these 2 articles are given in Table 5 below, with full results for all articles tested provided in Appendix 1. Additional information on carcinogenic amines that can be released from certain azo dyes under reducing conditions, including the specific amine detected in this study (*o*-dianisidine), is provided in Box B.

Sample code	Brand	Sold in	Made in	Type	Colour	3,3'-dimethoxy benzidine	Other amines
TX12128	Zara	Lebanon	Pakistan	jeans (child)	dark blue	7 mg/kg	<5 mg/kg
TX12130	Zara	Hungary	Pakistan	jeans (child)	dark blue	9 mg/kg	<5 mg/kg

Table 5. Details of articles in which amines were detected under the test conditions.

Although the article sold in Hungary (TX12130) is subject to the EU Directive that regulates the sale of products containing azocolourants that can release carcinogenic amines under specific test conditions (EU 2002), the concentration of *o*-dianisidine recorded was below the regulatory limit set within the EU (30 mg/kg; EU 2002) and, while any detectable presence of such a carcinogenic compound is of concern, would not, therefore, make the sale of the product illegal in the EU. As far as we are aware, there is no relevant legislation covering the presence of these compounds within textiles sold in Lebanon. The concentrations of *o*-dianisidine in this product and in the other in which it was detected (TX12130, on sale in the Lebanon), also fell below the stricter limits set for products sold within China (20 mg/kg, SAPRC 2012). It is not known whether equivalent regulations exist within Pakistan, where both products were manufactured, or in Lebanon, where the second of the two products was on sale.

Box B. Carcinogenic amines released by certain azo dyes

Azo dyes can undergo reduction to release aromatic amines. This reductive release can take place under a number of conditions, including within the body; reduction can occur in many different types of cells, including within intestinal and skin bacteria (Golka *et al.* 2004, Rafi *et al.* 1997, IARC 2008). Some, though not all, aromatic amines that can be released from azo dyes have been shown to be carcinogenic (IARC 1998, 1987).

Azo dyes are manufactured using the same amines that can be later released through reduction, and it is therefore possible for commercial azo dye formulation to contain residues of amines used in their manufacture. Furthermore, certain carcinogenic amines have been detected as residues in other amines that are used for azo dye manufacture, providing an additional route for contamination of commercial azo dye formulations with carcinogenic amines (IARC 2008). These sources could contribute to the presence of carcinogenic amines at trace levels within textile products.

Legislation exists in certain countries, including EU member states and China, which prohibits the sale of products containing dyes that can degrade under specific test conditions

to form carcinogenic amines at concentration above set limits, for textile articles which may come into direct and contact with human skin. The EU regulation lists 22 compounds, with a limit of 30 mg/kg (EU 2002). The regulation in China sets a limit of 20 mg/kg and lists the same compounds as the EU regulation, as well as two additional compounds (SAPRC 2012).

Animal studies have shown that 3,3'-dimethoxybenzidine (also known as *o*-dianisidine), together with certain other benzidine congeners, can have a carcinogenic effect, increasing tumour incidence in many organs (Haley 1975, Morgan *et al.* 1994, IARC 2008). There is clear evidence that exposure to benzidine-based dyes has caused bladder cancer in humans. However, the carcinogenicity of odianisidine alone has not been conclusively demonstrated in humans through epidemiological studies, partly due to the manufacture and use *o*-dianisidine having occurred together with other amines that are known human carcinogens, affecting the ability to demonstrate *o*-dianisidine as a causal compound (DHHS 2011). The International Agency for Research on Cancer (IARC) has classified *o*-dianisidine as possibly carcinogenic to humans (class 2B) (IARC 1998), and similarly the United States Department of Health and Human Service lists *o*-dianisidine and dyes that are metabolized to odianisidine as reasonably anticipated to be human carcinogens (DHHS 2011).

3.3 Phthalates in plastisol prints

Of the 31 articles in which a range of phthalates were quantified in plastisol printed fabric, 4 articles contained one or more individual phthalate at a concentration above 1 000 mg/kg (0.1 % by mass, see Table 6 for details). Of these, three samples contained very high levels, with concentrations of individual phthalates between 200 000 mg/kg (20% by weight) and 320 000 mg/kg (32% by weight). The fourth sample (TX12119) had a lower but still relevant level, 5 200 mg/kg (0.52% by weight). For all other articles, individual phthalates were present at concentrations of 120 mg/kg or less, with a method detection limit of 3 mg/kg. Full details of the individual phthalate concentrations for all 31 articles are presented in Appendices 1 and 2. For the four samples which contained phthalates at levels above 0.1 % by mass, the predominant phthalates identified were di-(2-ethylhexyl) phthalate (DEHP) and di-iso-nonyl phthalate (DINP), with one sample (TX12008) also containing butylbenzyl phthalate (BBP) as a substantial component. The presence of these phthalates at the concentrations found indicate their use as plasticisers within the plastisol formulations used to manufacture these products.

In contrast, the concentrations recorded in the remaining 27 samples would be too low to have any significant plasticising function on their own. For these articles, the identified phthalates may be present due to contamination of another substance used within the plastisol formulation (including other plasticisers, inks or pigments), or through other uses of the phthalates within the facilities that manufactured the products. In addition, it cannot be excluded that the presence of phthalates at these levels could have arisen from sources unrelated to chemical use at the facilities that manufactured the products, such as through contact with phthalate-bearing materials subsequent to manufacture, up until the point at which the products were purchased and separately sealed for analysis. Nonetheless, the presence of phthalates within a product at any level is of concern, whatever the source.

Sample code Brand Sold in Made in Type	TX12008 Armani Italy Turkey t-shirt	TX12110 Tommy Hilfiger USA Philippines t-shirt	TX12115 Tommy Hilfiger Austria Bangladesh t-shirt	TX12119 Victoria's Secret USA Sri Lanka underwear
Phthalate:	mg/kg (% by mass)	mg/kg (% by mass)	mg/kg (% by mass)	mg/kg (% by mass)
Butylbenzyl phthalate (BBP)	23 000 (2.3 %)			
Di-(2-ethylhexyl) phthalate (DEHP)	200 000 (20 %)		56 000 (5.6 %)	5 200 (0.52%)
Di-iso-nonyl phthalate (DINP)		200 000 (20%)	320 000 (32 %)	
NPEs (for comparison)	<1	41	8.6	7.0

Table 6. Concentrations of individual phthalates (mg/kg) where present in articles above 1 000 mg/kg. Also including are the concentrations of NPEs (mg/kg) for comparison.

The phthalates present at high levels in the four articles listed in Table 6 are toxic compounds. DEHP and BBP are known to exert reproductive toxicity, with DEHP being toxic to the developing reproductive system in mammals (Ema & Miyawaki 2002, Mylchreest *et al.* 2002, Aso *et al.* 2005). DEHP and BBP, as well as DnBP and DiBP, have recently been listed as Substances of Very High Concern under the European REACH Regulation (ECHA 2011). DINP, though not among the phthalates of greatest regulatory concern, nonetheless does exhibit toxicity (primarily to the liver and kidney) at high doses. In addition, some hormone-disrupting (anti-androgenic) effects on reproductive development in rats have recently been reported for DiNP (Boberg *et al.* 2011). Further background information on phthalate esters is provided in Box C.

Furthermore, phthalates in plastisol formulations are not tightly bound to the plastic, but are present as mobile components within the matrix, and can therefore be released from the product over time (DoE 1991, Cadogan *et al.* 1993, Jenke *et al.* 2006, Fierens *et al.* 2012, Fasano *et al.* 2012, Latorre *et al.* 2012).

Box C. Phthalate esters (Phthalates)

Phthalates (or, more accurately, phthalate diesters) are nonhalogenated chemicals with a diversity of uses, dominated by use as plasticizers (or softeners) in plastics, especially PVC (e.g., in cables and other flexible components). Other applications included uses as components of inks, adhesives, sealants, surface coatings and personal care products. Some phthalates are discrete chemicals, such as the well known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DiNP) and diisodecyl phthalate (DiDP). All uses of phthalates, especially the major use as PVC

plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal, principally because phthalates are not chemically bound but only physically associated to the polymer chains. Phthalates have been found to leach from food packaging materials and contaminate corresponding food products (Fierens *et al.* 2012, Fasano *et al.* 2012); from tubing material used for drug products manufacturing (Jenke *et al.* 2006) and from PVC blood bags which primarily contained DEHP (Ferri *et al.* 2012). Moreover, it has been shown that bacteria, which may grow on PVC plastics in wet conditions (e.g., shower curtains), may enhance DEHP leaching from plastic (Latorre *et al.* 2012). Thus, phthalates are widely found in the indoor environment, including in air and dust (Langer *et al.* 2010, Otake *et al.* 2001, Butte & Heinzow 2002, Fromme *et al.* 2004) at concentrations which commonly reflect the prevalence of plastics and certain textiles within the rooms sampled (Abb *et al.* 2009). Once plastic products are disposed to municipal landfills, phthalates, particularly DiBP and DnBP, may continue to leach, finally reaching groundwater (Liu *et al.* 2010).

Phthalates are commonly found in human tissues, including in blood, breast milk and, as metabolites, in urine (Colon *et al.* 2000, Blount *et al.* 2000, Silva *et al.* 2004, Guerranti *et al.* 2012), with reports of significantly higher levels of intake in children (Koch *et al.* 2006). In humans and other animals, they are relatively rapidly metabolised to their monoester forms, but these are frequently more toxic than the parent compound (Dalgaard *et al.* 2001).

Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. For example, DEHP, one of the most widely used to date, is known to be toxic to reproductive development in mammals, capable (in its monoester form MEHP) of interfering with development of the testes in early life, thought to be mediated through impacts on testosterone synthesis (Howdeshell *et al.* 2008, Lin *et al.* 2008). Even at low doses, exposure to mixtures of phthalates can result in cumulative effects on testicular development in rats (Martino-Andrade *et al.* 2008). In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003, Grande *et al.* 2006, Gray *et al.* 2006).

A more recent study (Abdul-Ghani *et al.* 2012) has shown that both DEHP and DBP can induce gross malformations, damage to DNA and changes in behavioural development when administered to developing chick embryos. The review of Caldwell (2012) highlights recently discovered impacts of DEHP including chromosomal damage, increased cancer progression and changes in gene expression at increasingly lower concentrations. Both DEHP and DBP are classified as “toxic to reproduction” within Europe.

Butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) have also been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Mylchreest *et al.* 2002, Aso *et al.* 2005). Other research has revealed a correlation between phthalate exposure during pregnancy and decreased ano-genital index (distance from the anus to the genitals) in male children (Swan *et al.* 2005). Decreased AGI correlated with concentrations of four phthalate metabolites, namely monoethyl phthalate (MEP), mono-n-butyl phthalate (MBP), monobenzyl phthalate (MBzP), and monoisobutyl phthalate (MiBP). It was also found that DBP can be taken up by crop plants as well impacting on physiology and morphology of some crops during growth

(Liao 2006). Other commonly used phthalates, including the isomeric forms DiNP and DiDP, are of concern because of observed effects on the liver and kidney, albeit at higher doses. DiNP has also been found (Boberg *et al.* 2011) to exhibit anti-androgenic effects on reproductive development of Wistar rats, though less prominent than DEHP, DBP and BBP, however, further safety evaluation of DiNP should be undertaken.

At present, there are relatively few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. Of the controls which do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children's toys and childcare articles, first agreed as an emergency measure in 1999 and finally made permanent in 2005 (EC 2005). While this addresses one important exposure route, exposures through other consumer products have so far largely escaped regulation. Within Europe, three phthalates (DBP, BBP and DEHP) were proposed to be included into the first shortlist of seven substances for which detailed justification and authorization will be required for any proposed continued uses (ECHA 2009). These phthalates, together with recently added di-isobutyl phthalate (DiBP), have been included into the list of candidates as 'substances of very high concern' under the REACH Regulation (ECHA 2010).

Within the EU DEHP is listed as a priority substance under the Water Framework directive, a regulation designed to improve the quality of water within the EU (EU 2008). DEHP and DnBP have also been identified as substances for priority action under the OSPAR convention, under which signatory countries have agreed a target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment of the North-East Atlantic by 2020, the "one generation" cessation target (OSPAR 1998). In August 2012, despite a European Commission ruling from June 2012 (ENDS 2012), the Danish Ministry of Environment announced plan to introduce a wider ban on marketing and use for four hormone-disrupting phthalates; DEHP, DBP, BBP and DiBP (DMOE 2012).

As far as we are aware, legislation does not currently exist in any of the countries where the 31 tested articles were sold that prohibits the sale of textiles products containing phthalates, although this situation may soon change in Denmark (in which six of the products were purchased for this study) as national prohibitions have recently been announced for four phthalates (DMOE 2012). It is already the case, however, that the use of di(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DnBP) and benzyl butyl phthalate (BBP) are prohibited in all toys or childcare articles put on the market within the EU (with a limit of 0.1% by weight, equivalent to 1000 mg/kg), and the use of di-isononyl phthalate (DINP), di-isodecyl phthalate (DIDP) and di-n-octyl phthalate (DNOP) is prohibited in such articles if they can be placed in the mouth by children (EU 2005).

For all plastisol print-bearing fabrics that were analysed for phthalate concentrations, a portion of printed fabric was also analysed for the concentration of NPEs, and therefore the concentration of NPEs in these articles are included in Table 6 for comparison. For these four samples, the concentrations of NPEs in three samples were in the lower end of the range of concentrations found across all samples, with NPEs not detected for one sample (TX12008). However, given the relatively small number of samples, it is not possible to determine any

clear trends between the presence of phthalates at higher concentrations, and the concentrations of NPEs in plastisol printed fabric.

3.4 Chemical screening

As well as the substances identified in the various items (as outlined in Sections 3.1 – 3.3), one or more additional chemicals were identified in almost all of the items that were investigated using the qualitative chemical screening approach (in 61 of 63 items). A summary of the additional chemicals identified using qualitative screening of extractable organic chemicals in 63 items is given in Table 7, below, followed by some background information on the known uses and any intrinsic hazardous properties associated with these substances. Although it has not been possible to determine the concentrations at which these compounds were present in the samples (as the screening method is necessarily qualitative, not quantitative), the results nevertheless provide an indication of the complexity of chemical residues which can remain in finished textile products, perhaps as a consequence of their use in manufacture, and therefore of the potential for discharge of complex chemical mixtures in effluents generated by textile factories and in laundry wash-waters.

A full listing of all substances identified in individual samples is provided in Appendix 3.

Substance	Number of items (of 63 in total)
Linear alkanes	59
Benzenemethanamine, N-(phenylmethyl)-	1
Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	1
Benzophenone	2
Benzyl benzoate	12
1,1'-Biphenyl	2
Benzyl naphthyl ether	1
Bis(2-ethylhexyl) maleate	1
2,6-Di-tert-butyl-4-methyl-phenol (butylated hydroxytoluene, BHT)	2
Ethanol, 2-(2-butoxyethoxy)- / acetate derivative	2
Ethanol, 2-(tetradecyloxy)-	1
Nonyl phenol	1
Hexadecanoic acid & esters	8
Octadecanoic acid & esters	5
Octadecenoic acid & esters	2
Octadecadienoic acid & esters	1
Octyl-diphenylamine	1
Others:	
Amyrin	2
α -Amyrenone	20
Sitosterol	21
Cholesterol	3
Squalene	5

Table 7. Substances & substance groups identified by chemical screening, with the number of items in which the substance/group was identified.

Alkanes. Medium and long chained linear alkanes (from C16 to C36) were commonly identified in the samples investigated, with one or more example being present in 59 of the 63 items tested. These compounds, which are readily biodegradable, are components of petroleum mixtures such as crude oil and refined petroleum products, and some can also

originate from plant sources (Ahad *et al.* 2011, Overton 1994). Longer chained alkanes are used within textile manufacturing, including as part of finishing processes (Lacasse & Baumann 2004). Some medium and long chained linear alkanes can have toxicological effects, though mixtures of longer chain alkanes are used as food additives and these compounds are generally not considered to be of particular toxicological concern in mammals except in high doses (Griffis *et al.* 2010).

Benzyl benzoate. Other than liner alkanes, benzyl benzoate was the most commonly identified compound, being found in 12 items (see Appendix 3 for details). Benzyl benzoate is a readily biodegradable substance that is used in some dye formulation (IPPC 2003). However, this chemical has been classified under the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)² as toxic to aquatic life with long lasting effects (H411) and harmful if swallowed (H302).

A number of other compounds, or groups of compounds, were identified in two or more of the items tested, including;

Benzophenone (in TX12007 & TX12087), widely used as a fragrance chemical and, occasionally, as a flavour ingredient. It is also used in the manufacture of insecticides and other agricultural chemicals, and is used as an additive for certain plastics and adhesives (US DHHS 2000). Benzophenone has been classified under GHS as very toxic to aquatic life with long lasting effects (H410). The liver has been shown to be the primary target organ of benzophenone toxicity in rats and mice, with effects also seen in the kidney for rats (US DHHS 2000).

1,1'-Biphenyl (in TX12015 & TX12121) occurs naturally in petroleum mixtures such as crude oil (Overton 1994), and can also be released through incomplete combustion of petroleum products and coal, including within emissions from vehicles (IPCS 1999). It has been used as a dyestuff carrier for textiles, amongst other uses (IPCS 1999). This chemical has been classified under the GHS as very toxic to aquatic life with long lasting effects (H410) as well as irritating to eyes and skin (H315, H319).

2,6-Di-tert-butyl-4-methyl-phenol, also known as butylated hydroxytoluene (BHT), (in TX12122 & TX12126), has been widely used as an antioxidant in a wide range of products including plastics and other petrochemical products, cosmetics and food products (Jobling *et al.* 1995). BHT has been classified under the GHS as toxic to aquatic life with long lasting effects (H411), and irritating to the skin and eyes (H315, H319).

2-(2-Butoxyethoxy)-ethanol, also known as diethylene glycol monobutyl ether (DEGBE), was identified in TX12088, and the derivative 2-(2-butoxyethoxy)-ethanol acetate was identified in TX12127. DEGBE is widely used as a solvent, especially in the printing ink and paint industries, and diethylene glycol derivatives in general, including acetates, are used in a variety of textile manufacturing processes and formulations (IPPC 2003). The two

2

compounds that were identified are both are classified under the GHS as irritating to the eyes (H319).

Fatty acids. A number of fatty acids and their ester derivatives were identified relatively frequently, with 12 items containing one or more of the chemicals from this group (see Appendix 3 for details). Hexadecanoic acid (also known as palmitic acid) was identified in two items, and various ester derivatives (methyl, butyl, octadecyl or isopropyl esters) were identified in six other items.

A closely related fatty acid, octadecanoic acid (also known as stearic acid), was identified in one item, with either the methyl or isopropyl ester being identified in four others. The methyl esters of octadecenoic acid (or oleic acid) or octadecadienoic acid (or linoleic acid) were each identified in one other item, and octadecenoic acid itself was identified in another item.

Fatty acid esters, which are present in animal or vegetable fats, oils, or waxes, are used in a variety of textile manufacturing processes, including as defoaming and dispersing agents in dye formulations, and as sizing agents. These, and other fatty acid derivatives such as fatty acid ethoxylates which are used as surfactants, can undergo partial degradation to give rise to the fatty acids themselves (IPPC 2003).

Fatty acids and their derivatives are not of particular environmental concern due to their low toxicity and being readily biodegradable, and the compounds identified in this study are generally not categorised as hazardous according to the GHS, with the exception of some being able to cause eye irritation (H319), and for some of these also skin irritation (H315).

Other substances were identified in single items amongst the 63 products tested, these included;

Nonylphenol (in TX12127), which is a persistent, bioaccumulative and toxic substance used to manufacture NPEs, which can degrade in the environment back to nonylphenol. However, NPEs were not detected in this item above the method limit of 1 mg/kg (see Section 3.1). Due to persistence and widespread release, nonylphenol is widely distributed in the environment, having been detected in various media including within surface water environments and in indoor dusts (OSPAR 2004, Butte & Heinzow 2002). See Box A for more information on nonylphenol and NPEs.

Benzenemethanamine, N-(phenylmethyl)-, also known as N,N-dibenzylamine, (in TX12063) is a decomposition product of a compound used in rubber vulcanization processes and has been found in rubber products (Niessner & Klampfl 2000), though it is not clear if the item in which this was identified contained any rubber based materials. N,N-dibenzylamine has been classified under the GHS as harmful if swallowed (H302) and irritating to eyes and skin (H315, H319).

Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-, also known as distyrene, (in TX12121). It was not possible to identify possible origins of this compound, nor any categorisation according to the GHS

Bis(2-ethylhexyl) maleate, also known as dioctyl maleate, (in TX12085) is used as a plasticizer in emulsion-type paints, papers, textile coating, adhesives and oil additives, and is also used in cosmetic skin and hair products, which has resulted in cases of allergic contact dermatitis (Chan & Wakelin 2006, Laguna *et al.* 2009). Bis(2-ethylhexyl) maleate has been classified under the GHS as irritating to eyes and skin (H315, H319).

Ethanol, 2-(tetradecyloxy)-, also known as ethylene glycol monotetradecyl ether or tetradecylglycol, (in TX12083), which can be used as a surfactant (Shinoda *et al.* 1993). As noted above, many glycol derivatives are used in a variety of textile manufacturing processes and formulations (IPPC 2003). It was not possible to identify any categorisation of this glycol derivative according to the GHS, nor other information on its hazardous properties.

Benzyl naphthyl ether, also known as 2-(phenylmethoxy) naphthalene, (in TX12122), the main use of which appears to be in thermal paper and other heat sensitive recording materials (Terasaki *et al.* 2008). Different assessments have classified this ether under the GHS as irritating to the skin and eyes (H315, H319), and as either ‘very toxic to aquatic life with long lasting effects’ (H410) or ‘may cause long lasting harmful effects to aquatic life’ (H413).

Octyl-diphenylamine (in TX12056) which can be used as a lubricant (Thompson *et al.* 2007). It was not possible to identify any categorisation of this compound according to the GHS, nor information on its hazardous properties.

In addition to the industrial chemicals described above, three compounds which belong to a class of naturally occurring terpenoids compounds that can be isolated from plants were commonly identified within the 63 items investigated (Hernández-Vázquez *et al.* 2010, Mallavadhani *et al.* 1998);

- Sitosterol (in 21 items),
- α -Amyrenone (in 20 items),
- Amyrin (in 2 items)

Furthermore, two additional naturally occurring compounds were identified in a number of samples; squalene (in 5 items) and cholesterol (in 3 items). These two compounds have many possible sources, including being part of natural oils that are present on human skin (Lu *et al.* 2009), which could account for their presence in these cases.

4. Conclusions

This study has demonstrated the presence of a number of different hazardous chemicals within a broad range of textile products of the type included in this study, as either components of materials incorporated within the product or residues remaining from use within manufacturing processes.

Amongst these, the most commonly detected substances were NPEs, with residues identified in products across all brands and almost all countries of manufacture and countries of purchase included in the study, indicating that the use of NPEs is widespread within the

international textile industry, including within supply chains used by several major international clothing brands.

The results for the quantification of NPEs are consistent with those from a previous study carried out by Greenpeace for 78 textile articles which consisted primarily of sports and recreational clothing and shoes (Brigden *et al.* 2012, Greenpeace 2011b). In this earlier study, 67 % of the articles tested positive for the presence of NPEs (above 1 mg/kg), with levels ranging from just above 1 mg/kg to 27 000 mg/kg, compared to 63 % of articles in the current study, for which levels ranged from just above 1 mg/kg to 45 000 mg/kg (see Table 8).

NPE concentration range (mg/kg)	Current study: Number of samples (of 141 analysed)	Current study: % of samples (of 141 analysed)	Previous study (a) % of samples (of 78 analysed)
<1	52	37 %	33 %
1 – 10	27	19 %	22 %
>10 – 100	34	24 %	27 %
>100 – 1 000	16	11 %	15 %
>1 000	12	9%	3 %

Table 8. The number and percentage of samples (of the 141 articles tested) within various NPE concentration ranges, compared to a previous study of 78 textile articles. (a) Brigden *et al.* 2012, Greenpeace 2011b.

In the current study, NPEs were detected in one or more product from 13 of the 18 countries of manufacture. For the five countries of manufacture for which NPEs were not detected, only a small number of articles were tested; Cambodia (2 articles), Jordan (1 article), Romania (1 article), Spain (1 article), Tunisia (3 articles). Given the low number of articles for these five countries, and the results of the study as a whole, the fact that NPEs were not identified in products manufactured in these countries cannot be taken to indicate that textile products manufactured in these countries in general do not contain detectable residues of NPEs.

The presence of NPEs in finished products indicates their use during manufacture, which can result in releases of NPEs and nonylphenol from manufacturing facilities within the countries of production as well as residues in the products. In addition, NPE residues within textile products are readily released when the items are washed as part of their normal use (Brigden *et al.* 2012, Greenpeace 2012), resulting in inputs of NPEs and nonylphenol to the environment of the countries in which these products are sold.

The use of NPEs and nonylphenol has effectively been banned within the EU (EU 2003), with similar restrictions in place in the United States and Canada (CEPA 2004, USEPA 2010). The manufacture, use and release of NP and NPEs are not currently regulated in China, though NPEs and nonylphenol have recently been included on the ‘List of toxic chemicals severely restricted for import and export in China’ and their import or export now requires prior permission (MEP 2011). Regulations do not currently exist in EU, or elsewhere, that restrict the sale of textile products containing NPE residues, though such a regulation is currently under development within the EU (KEMI 2012). In order to offer adequate protection, such regulations will need to set any limit for NPEs in products as low as possible and cover as wide a range of NPEs as possible. At the same time, parallel measures to restrict the use of NPEs in manufacture are also needed in countries in which textile products are manufactured.

Some major clothing brands set limits on the presence of certain hazardous substances in their products, as part of their programmes to ensure product safety. However, limits typically set for the presence of NPEs and other alkylphenol ethoxylates (APEs) are currently too high to prevent the continued use of these chemicals during manufacture, and therefore their discharge in the country of manufacture and release through laundering in the country of sale. Details of relevant regulatory measures and the policies of textile brands are discussed in detail in previous reports (Brigden *et al.* 2012, Greenpeace 2012)

In addition to the presence of NPEs, the identification of phthalates at high concentrations in some articles indicates the on-going use of phthalates as plasticisers in formulations used to produce plastisol prints on textile products manufactured in a number of countries around the world. The levels and types of individual phthalates found in the four articles with high concentrations (see Table 6) are consistent with previous investigations of related textile products (RAPEX 2012, Greenpeace 2004).

The presence of phthalates in textiles, such as through the use as plasticisers in plastisol prints, is not currently subject to any regulations in the countries where the items were sold, though further national controls are pending in Denmark. However, regulations do exist within the EU that prohibit phthalates (including those identified in this study) in toys and childcare articles (EU 2005), thereby recognising the hazard associated with products containing phthalates, including plastic parts containing phthalates as plasticisers. Regulations and brand policies are required to address the hazard that the presence of phthalates poses in a broad range of products, including textiles items.

Carcinogenic amines released under reducing conditions were detected in only a small fraction of items tested (2 of 134 items). Previous studies have similarly identified carcinogenic amines for a relatively low fraction of items tested (JRC 2008, Laursen *et al.* 2003), including items for which far higher concentrations of amines were detected compared to levels found in this study.

For each of the two items in this study in which amines were detected, the concentration of the amine (*o*-dianisidine) was below limits set by regulations that address the release of carcinogenic amines from textiles treated with azo dyes. For these items, the source of *o*-dianisidine at the levels found may have been the presence of an azo dye manufactured from *o*-dianisidine. However, residues of this amine within other types of azo dye formulations used during manufacture may have contributed to the *o*-dianisidine identified. Whatever the source or level identified, the presence of any substances in textiles capable of releasing a carcinogenic amine following reduction is clearly cause for concern.

In addition to the chemicals that were quantified in the textile products, a wide range of other chemicals were identified in various items through qualitative chemical screening. While not all the chemicals identified are known to have hazardous properties, many have been classified under the GHS as having hazardous properties, including some being classified as being very toxic to aquatic life with long lasting effects (H410). Many of the chemicals that were identified have known uses within textile manufacturing, though some do also have other potential sources unrelated to use during textile manufacture. In addition, three compounds of plant origin and two compounds that can originate from natural oils present on human skin were identified in many of the items investigated.

In most cases, the industrial chemicals identified through screening were found in only one or two of the 63 items investigated in this way, though certain chemicals or chemicals groups

were more commonly found, particularly linear alkanes and benzyl benzoate as well as fatty acids and their derivatives.

For the items investigated, there were no clear associations within individual samples in terms of chemicals identified, other than for fatty acids and their esters to some extent. That is, for each sample, there were no clear patterns in which the presence of one particular chemical was commonly accompanied by the presence of another, with certain exceptions for fatty acids and their esters. For two samples (TX12029 & TX12123), the methyl esters of both hexadecanoic acid and octadecanoic acid were identified in each sample, and similarly both hexadecanoic acid and octadecanoic acid were identified in one other sample (TX12127). These results indicate there may be a common origin for these fatty acids and their methyl esters in some cases.

A number of the compounds identified in this study using a qualitative chemical screening approach have previously been identified in textile items sold in Denmark that were investigated using a similar screening approach, including alkanes, benzyl benzoate, fatty acids, bis(2-ethylhexyl) maleate and squalene (Laursen *et al.* 2003). Also, glycols related to those identified in the current study were identified in this previous Danish study.

The screening aspect of the study highlights the diverse range of chemical residues that can be present within textile products, though from the results of this study do not reveal any associations between the presence of individual chemicals identified through the screening approach and factors such as the type of item, where it was manufactured or sold, or the item brand. However, the qualitative screening data do suggest that analyses which focus only on a narrow range of target substances will underestimate the complexity of chemical residues in finished textiles and, therefore, the potential for chemical releases during manufacture and subsequent laundering.

Overall, this study has provided a greater understanding of the presence and, in some cases, concentrations of a broad range of chemicals within high street fashion textile products, across a diverse range of brands and countries of manufacture and sale. Despite the scale of this study, the number of articles investigated is, of course, inevitably small compared to the vast number of products manufactured and sold per country or per brand. It cannot, therefore, be assumed that the results obtained in this study are representative of levels or presence of the chemicals investigated which may be expected for all such products. Rather, this study provides a snapshot of what appears to be a more generic problem that is not restricted to any particular country, product type or brand, and one that deserves further investigation including from a regulatory and brand policy perspective.

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Appendix 1. Concentrations of NPEs, carcinogenic amines and phthalates in all articles tested

Sample code	Brand	Place of sale	Country of manufacture	Type	Man/Woman/Child	Fabric	NPEs (mg/kg)	amine (mg/kg)	phthalates, total (mg/kg)
TX12001	Armani	Thailand	China	underwear	woman	96% polyamide, 4% elastane	32	<5	-
TX12002	Armani	Sweden	China	shirt	---	unknown	43	<5	-
TX12003	Armani	Switzerland	China	jeans	man	100% cotton excluded decorations	<1	<5	-
TX12004	Armani	UK	Vietnam	polo shirt	man	98% cotton, 2 % elastane	4.8	<5	-
TX12005	Armani	USA	Indonesia	underwear	woman	85% polyamide, 16% elastane	1.2	<5	-
TX12006	Armani	Russia	Thailand	underwear	man	100% cotton	<1	<5	-
TX12007	Armani	Italy	Vietnam	underwear	woman	90% cotton, 10% elastane	<1	<5	-
TX12008	Armani	Italy	Turkey	t-shirt	man	100% cotton	* <1	<5	223440
TX12009	Armani	France	Indonesia	bra	woman	87% nylon, 13% elastane	8.1	<5	-
TX12010	Benetton	Mexico	Romania	t-shirt	child	100% cotton	* <1	<5	128
TX12011	Benetton	Czech Rep.	Tunisia	t-shirt	child	100% organic cotton	* <1	-	33
TX12012	Benetton	Switzerland	Cambodia	hoodie	man	100% cotton	<1	<5	-
TX12013	Benetton	UK	Bangladesh	t-shirt	child	100 % cotton	* <1	-	47
TX12014	Benetton	Russia	Cambodia	t-shirt	child	100% cotton	<1	<5	-
TX12015	Benetton	Italy	China	jacket	child	outside: 70% cotton, 30% polyamide Inside: 100% polyester	95	<5	-
TX12016	Benetton	Italy	Egypt	sweatshirt	child	100% cotton	11	<5	-
TX12017	Benetton	Belgium	Bangladesh	t-shirt	child	100% cotton	<1	<5	-
TX12018	Benetton	France	India	(part of a set) trousers	child	100% cotton	6.3	<5	-
TX12019	Vermoda	Mainland China	unknown	top	woman	61% cotton, 37% polyester, 2% elastane	31	<5	-
TX12020	Vermoda	Mainland China	unknown	top	woman	100% polyester	6.3	<5	-
TX12021	Veromoda	Denmark	India	blouse	woman	unknown	45	<5	-
TX12022	Veromoda	Denmark	India	top	woman	100% cotton	<1	<5	-
TX12023	Veromoda	Lebanon	India	dress	woman	100% polyester	130	<5	-

TX1202 4	Only	Mainland China	unknown	jeans	woman	99% cotton, 1% elastane	5.5	<5	-
TX1202 5	Only	Mainland China	unknown	t-shirt	woman	Fabric 1- 86% viscose rayon, 5% elastane; Fabric 2-62% viscose rayon, 38% polyester	* 32	-	18

Table A1. Details of all articles, including the concentrations of NPEs, carcinogenic amines and phthalates. For NPEs, * indicates the analysis of a section of fabric bearing a plastisol print; for carcinogenic amines '<5 mg/kg' indicates that all quantified amines were below the detection limit (<5 mg/kg) and where a specific amine is listed, all other quantified amines in that sample were below the detection limit (<5 mg/kg); For phthalates, the total concentration of the 9 quantified phthalates is given (mg/kg), with the individual phthalate concentrations provided in Appendix 2; '-' indicates not tested, either due to being undyed fabric (for carcinogenic amines) or article without a medium/large sized plastisol print (for phthalates). TX12066 was not tested as the item was identical to TX12068.

Sample code	Brand		Country of manufacture	Type	Man/ Woman/ Child	Fabric	NPEs (mg/kg)	amine (mg/kg)	phthalates, total (mg/kg)
TX1202 6	Only	Denmark	China	jeans	woman	unknown	730	<5	-
TX1202 7	Only	Norway	Turkey	jeans	woman	unknown	38	<5	-
TX1202 8	Jack & Jones	Mainland China	unknown	t-shirt	man	95% cotton, 5% elastane	* <1	<5	14
TX1202 9	Jack & Jones	Mainland China	unknown	underwear	man	96% cotton, 4% elastane	2 100	<5	-
TX1203 0	Jack & Jones	Netherlands	Bangladesh	polo shirt	man	100% cotton	<1	<5	-
TX1203 1	Jack & Jones	Denmark	Turkey	jeans	woman	unknown	17	<5	-
TX1203 2	Jack & Jones	Lebanon	Bangladesh	t-shirt	man	85% cotton, 15% viscose	* 4.6	<5	17
TX1203 3	Calvin Klein	Germany	Egypt	Underwear	man	82% polyester, 18% elastane	9.0	<5	-
TX1203 4	Calvin Klein	Philippines	China	Underwear	man	95% cotton, 5% elastane	20	<5	-
TX1203 5	Calvin Klein	Mexico	Mexico	jeans	man	100% cotton	56	<5	-
TX1203 6	Calvin Klein	Netherlands	Jordan	underwear	woman	95% cotton, 5% elastane	<1	<5	-
TX1203 7	Calvin Klein	USA	Vietnam	jeans	man	100% cotton exclusive of decoration	73	<5	-
TX1203 8	Calvin Klein	GP Africa	Thailand	underwear	man	100% cotton	14	<5	-
TX1203 9	Calvin Klein	Indonesia	Vietnam	underwear	man	92% cotton; 8% Lycra	5.6	<5	-
TX1204 0	Calvin Klein	Canada	India	t-shirt	man	100% cotton	* 4 000	<5	9
TX1204 1	C&A	Mexico	Mexico	t-shirt	man	100% cotton	* 45 000	<5	61
TX1204 2	C&A	Switzerland	unknown	top	child	100% cotton	6.9	-	-
TX1204 3	C&A	Switzerland	unknown	jacket	child	96% polyester, 4% elastane	64	<5	-
TX1204 4	C&A	Belgium	unknown	t-shirt	man	100% cotton	* <1	<5	33

TX1204 5	C&A	Hungary	unknown	t-shirt	child	100% cotton	* 1.7	<5	18
TX1204 6	C&A	France	unknown	trousers	child	70% cotton, 30% polyester	63	<5	-
TX1204 7	Diesel	Germany	Morocco	jeans	man	98% cotton, 2% polyurethane	710	<5	-
TX1204 8	Diesel	Czech Rep.	Turkey	vest top	woman	100% cotton	<1	<5	-
TX1204 9	Diesel	Spain	China	shorts	man	100% cotton	<1	<5	-
TX1205 0	Diesel	Russia	China	t-shirt	man	100% cotton	* 6.6	<5	56
TX1205 1	Diesel	Italy	Tunisia	jeans	man	100% cotton	<1	<5	-
TX1205 2	Diesel	Austria	Tunisia	denim trousers	woman	76% cotton, 22% polyester, 2% elastane	<1	<5	-
TX1205 3	Diesel	South Africa	India	t-shirt	man	100% cotton	<1	<5	-
TX1205 4	Diesel	Israel	China	t-shirt	man	100% cotton	* 16	<5	83
TX1205 5	Diesel	Hungary	China	t-shirt	man	100% cotton	* <1	<5	57
TX1205 6	Esprit	Mainland China	China	bra	woman	surface 90% cotton, 10% elastane; inside - 100% polyster	<1	<5	-
TX1205 7	Esprit	Hong Kong	China	dress	woman	shell: 96% polyester, 4% elastane; lining: 100% polyester	<1	<5	-
TX1205 8	Esprit	Germany	unknown	t-shirt	youth	100% cotton	* 770	-	14
TX1205 9	Esprit	Thailand	China	jacket	woman	100% cotton	460	<5	-

Table A1. Continued.

Sample code	Brand	Place of sale	Country of manufacture	Type	Man/ Woman/ Child	Fabric	NPEs (mg/kg)	amine (mg/kg)	phthalates, total (mg/kg)
TX1206 0	Esprit	Finland	Turkey	t-shirt	woman	unknown	<1	<5	-
TX1206 1	Esprit	Switzerland	unknown	dress	woman	100% cotton	1.1	-	-
TX1206 2	Esprit	Russia	China	coat	woman	unknown	17	<5	-
TX1206 3	Esprit	Belgium	unknown	t-shirt	child	100% cotton	27	<5	-
TX1206 4	Esprit	Indonesia	Indonesia	dress	woman	outer 100% polyester; inside 100% nylon	66	<5	-
TX1206 5	Gap	Thailand	Indonesia	jeans	child	99% cotton, 1% elastane	<1	<5	-
TX1206 6	Gap	Philippines	Indonesia	beach shirt	child	body: 80% polyester, 20% elastane. sleeve: 80% nylon, 20% elastane	-	-	-
TX1206 7	Gap	Mexico	Mexico	jeans	man	70% cotton, 27% polyester, 3% elastane	920	<5	-

TX1206 8	Gap	USA	Indonesia	beach shirt	child	body: 80% polyester, 20% elastane. sleeve: 80% nylon, 20% elastane	* <1	<5	14
TX1206 9	Gap	South Africa	Bangladesh	trousers	man	100% cotton	1.3	<5	-
TX1207 0	Gap	South Africa	Vietnam	raincoat	child	100% cotton	* 700	<5	14
TX1207 1	Gap	Israel	Vietnam	dress	woman	100% polyester	43	<5	-
TX1207 2	Gap	France	Vietnam	t-shirt	child	100% cotton	* 110	<5	25
TX1207 3	Gap	Indonesia	Pakistan	jeans	child	100% cotton	3.8	<5	-
TX1207 4	Gap	Canada	Indonesia	t-shirt	child	80% nylon 20% elastane	* 8.6	<5	26
TX1207 5	H&M	Denmark	Turkey	t-shirt	child	unknown	* <1	<5	23
TX1207 6	H&M	Spain	India	dress	woman	100% polyester	8.7	<5	-
TX1207 7	H&M	Belgium	China	sweater	man	100% cotton	<1	<5	-
TX1207 8	H&M	Lebanon	China	top	woman	100% polyester	1.6	<5	-
TX1207 9	H&M	Hungary	Bangladesh	underwear	woman	86% polyamide, 14% elastane	<1	<5	-
TX1208 0	H&M	France	China	trousers	child	85% cotton, 14% polyester, 1% elastane	<1	<5	-
TX1208 1	Levi's	Hong Kong	Vietnam	jeans	man	100% cotton	<1	<5	-
TX1208 2	Levi's	Taiwan	China	t-shirt	man	100% cotton	* 9.7	<5	-
TX1208 3	Levi's	Thailand	Thailand	denim shirt	woman	100% cotton	<1	<5	-
TX1208 4	Levi's	Philippines	China	jeans	man	100% cotton	600	<5	-
TX1208 5	Levi's	Mexico	Mexico	jeans	woman	99% cotton, 1% elastane	3 100	<5	-
TX1208 6	Levi's	Switzerland	Turkey	t-shirt	man	100% Cotton	* <1	<5	12
TX1208 7	Levi's	USA	Mexico	jeans	man	100% cotton	4 100	<5	-
TX1208 8	Levi's	South Africa	Vietnam	jeans	woman	100% Cotton	5.7	<5	-
TX1208 9	Levi's	Belgium	China	t-shirt	man	100% cotton	80	<5	-
TX1209 0	Levi's	Turkey	Unknown	hoodie	man	unknown	18	<5	-
TX1209 1	Levi's	Indonesia	China	t-shirt	man	100% cotton	* <1	<5	138
TX1209 2	Mango	Philippines	Bangladesh	t-shirt	woman	100% cotton	<1	<5	-

Table A1. Continued.

Sample code	Brand	Place of sale	Country of manufacture	Type	Man/Woman/Child	Fabric	NPEs (mg/kg)	amine (mg/kg)	phthalates, total (mg/kg)
TX12093	Mango	Netherlands	Vietnam	jacket	woman	98% cotton, 2% elastane. lining: 100% polyester	<1	<5	-
TX12094	Mango	Finland	China	t-shirt	woman	unknown	<1	<5	-
TX12095	Mango	UK	China	jeans	woman	100% cotton	1 400	<5	-
TX12096	Mango	Spain	Turkey	t-shirt	woman	100% cotton	9 800	<5	-
TX12097	Mango	Austria	Morocco	trousers	woman	100% polyester	7.2	<5	-
TX12098	Mango	South Africa	Turkey	t-shirt	woman	100% cotton	* <1	<5	13
TX12099	Mango	Turkey	Bangladesh	rumper suit	woman	55% linen, 45% cotton	1 500	<5	-
TX12100	Mango	Lebanon	Indonesia	coat	woman	100% polyester	15	<5	-
TX12101	Mango	Israel	China	dress	woman	100% polyester	1.3	<5	-
TX12102	Mark & Spencer	Thailand	China	underwear	woman	80% silk, 13% polyamide, 7% elastane	2 100	<5	-
TX12103	Mark & Spencer	Philippines	Indonesia	shorts	man	68% cotton, 32% polyamide	620	<5	-
TX12104	Mark & Spencer	UK	India	underwear	woman	95 % cotton, 5% elastane	<1	<5	-
TX12105	Mark & Spencer	UK	Turkey	pyjama top (part of a set)	child	100% cotton	* <1	<5	15
TX12106	Mark & Spencer	Turkey	Turkey	t-shirt	woman	100% linen	84	<5	-
TX12107	Mark & Spencer	Indonesia	Turkey	top	woman	100% polyester	550	<5	-
TX12108	Tommy Hilfiger	Mexico	Mexico	jeans	man	100% cotton	500	<5	-
TX12109	Tommy Hilfiger	Sweden	Vietnam	polo shirt	---	unknown	<1	<5	-
TX12110	Tommy Hilfiger	USA	Philippines	t-shirt	man	100% cotton exclusive of decoration	* 26	<5	200013
TX12111	Tommy Hilfiger	Spain	Turkey	top	woman	80% polyester, 20% viscose excluding decoration	30	<5	-
TX12112	Tommy Hilfiger	Russia	Turkey	jeans	man	100% cotton	17	<5	-
TX12113	Tommy Hilfiger	Russia	China	shirt	man	100% cotton	<1	<5	-
TX12114	Tommy Hilfiger	Italy	Sri Lanka	t-shirt	woman	96% cotton, 4% elastane excluding decoration	3.9	<5	-
TX12115	Tommy Hilfiger	Austria	Bangladesh	t-shirt	man	100% cotton	* 8.6	<5	660079
TX12116	Tommy Hilfiger	Canada	Bangladesh	shorts	man	100% cotton exclusive of decoration	<1	<5	-
TX12117	Victoria's Secret	Netherlands	China	bra	woman	65% nylon, 35% elastane	<1	<5	-

TX1214 1	Blazek	Czech Rep.	unknown	t-shirt	man	50% cotton, 45% modal, 5% elastane	<1	<5	-
TX1214 2	Blazek	Czech	unknown	underwear	man	50% cotton/45% modal, 5% elastane	<1	<5	-
Number of articles tested							141	134	31

Table A1. Continued.

Appendix 2. Concentrations of individual phthalates in the 31 articles tested

S a m pl e	B ra n d	Pl a c e of	C o u n t r y of m a n u f a c t u r e	Concentration of phthalate (mg/kg)								
				D M P	D E P	D n B P	B B P	D E H P	D N O P	D I N P	D I D P	D I B P
T X 12 00 8	A r m i t	It al y	T ur ke y R	< 3. 0	13	17	23 00 0	20 0 0	< 3. 0	< 3. 0	< 3. 0	41 0
T X 12 01 0	B e n e t t o n	M e x i c o C	m a n i a	< 3. 0	29	11	55	9. 6	3. 0	3. 0	3. 0	23
T X 12 01 1	B e n e t t o n	ch R ep .	T un i s i a B a n g l a d e s h M a i n l a n d	< 3. 0	9. 4	5. 2	7	4. 8	3. 0	3. 0	3. 0	6. 3
T X 12 01 3	B e n e t t o n	U K	gl a d e s h M a i n l a n d	< 3. 0	11	20	9. 1	3. 0	3. 0	3. 0	3. 0	7. 3
T X 12 02 5	O n l i n e	h i n a n a	o w n u n k n	< 3. 0	3	4	< 3. 0	5. 9	3. 0	3. 0	3. 0	4. 8
T X 12 02 8	J a c k & J o h n s	M a i n l a n d	u n k n	< 3. 0	< 3. 0	3. 7	< 3. 0	5. 8	< 3. 0	< 3. 0	< 3. 0	4. 4

T X 07 00	G A P	S. A fri ca	Vi et na m	< 3. 0	< 3. 0	4. 5	< 3. 0	6. 3 0	< 3. 0	< 3. 0	< 3. 0	3
T X 07 2	G ap	Fr an ce	Vi et na m	< 3. 0	5. 8	13	< 3. 0	< 3. 0	< 3. 0	< 3. 0	< 3. 0	6. 5
T X 07 4	G ap	C an ad a	In do ne si a	< 3. 0	18	2	< 3. 0	< 3. 0	< 3. 0	< 3. 0	< 3. 0	4. 5
T X 07 5	H & M	D en m ar k	T ur ke y	< 3. 0	16	0	< 3. 0	< 3. 0	8	0	< 3. 0	3
T X 08 2	L ev i's	Ta iw an S wi	C hi na	< 3. 0	23	5	< 3. 0	4.	3. 4	3. 0	< 3. 0	< 3. 0
T X 08 6	L ev i's	er la nd	T ur ke y	< 3. 0	3	0	< 3. 0	5.	3. 1	3. 0	< 3. 0	3. 5
T X 09 1	L ev i's	ne si a	C hi na	< 3. 0	5. 8	4	< 3. 0	12	3. 0	3. 0	< 3. 0	7. 9
T X 09 8	M an go	S. A fri ca	T ur ke y	< 3. 0	< 3. 0	9. 8	< 3. 0	< 3. 0	0	< 3. 0	< 3. 0	3. 4
T X 12 10 5	M ar ks an d S pe nc er	U r K	T ur ke y	< 3. 0	< 3. 0	< 3. 0	< 3. 0	15	< 3. 0	< 3. 0	< 3. 0	< 3. 0
T X 12	T o m	U S A	P hi li	< 3. 0	3. 6	4. 7	< 3. 0	< 3. 0	< 3. 0	20 00	< 3. 0	4. 6

110	my Hifiger	ppines								0		
TX12115	Trommy Hifiger	Atrigadesh	Ban	< 3.0	4.9	21	23	56.00	11	32.00	< 3.0	19
TX12119	Trommy Hifiger	UAS	Sri Lanka	< 3.0	6.2	3.1	4	52.00	< 3.0	< 3.0	< 3.0	3.4
TX12125	Trommy Hifiger	Denmark	Turkey	< 3.0	< 3.0	< 3.0	< 3.0	3.8	< 3.0	< 3.0	< 3.0	< 3.0
TX132	Trommy Hifiger	China	China	< 3.0	< 3.0	< 3.0	< 3.0	3.4	< 3.0	< 3.0	< 3.0	6.1
TX136	Trommy Hifiger	Canada	USA	< 3.0	3.3	22	0	58	< 3.0	< 3.0	< 3.0	3.9

Table A2. Concentrations (mg/kg), in plastisol printed fabric, of the following phthalates; dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DIBP), butylbenzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-iso-nonyl phthalate (DINP) and di-iso-decyl phthalate (DIDP).

Appendix 3. Additional substances identified using qualitative chemical screening

Sample code	Brand	No. of chemicals isolated	No. of chemicals reliably identified	Linear alkanes	Benzophenone	Benzyl benzoate	1,1'-Biphenyl	2,6-Di-tert-butyl-4-methyl-phenol	derivatives* Ethanol, 2-(2-butoxyethoxy)- &	Nonyl phenol	(& esters*) Hexadecanoic acid	(& esters*) Octadecanoic acid	(& esters*) Octadecenoic acid	Octadecadienoic acid, ester*	Amyrin	α -Amyrenone	Sitosterol	Cholesterol	Squalene	Others
TX120 01	Armani	12	8	6	Y														Y	
TX120 02	Armani	13	5	4	Y															
TX120 03	Armani	26	13	1	Y															
TX120 04	Armani	17	9	9																
TX120 05	Armani	26	5	5																
TX120 06	Armani	19	7	7																
TX120 07	Armani	6	5	3	Y	Y														
TX120 08	Armani	9	7	7																
TX120 09	Armani	13	1	0									Y							
TX120 10	Benetton	15	10	1																
TX120 11	Benetton	33	14	1	Y										Y	Y				
TX120 12	Benetton	18	12	0	Y												Y			
TX120 13	Benetton	11	6	5													Y			
TX120 14	Benetton	19	11	9						butyl*										
TX120 15	Benetton	21	13	1	Y	Y														
TX120 16	Benetton	17	10	8											Y	Y				
TX120 17	Benetton	22	10	7						methyl*				methyl*				Y		

34	Klein										yl*								
TX120 35	Calvin Klein	46	14	13												Y			
TX120 56	Esprit	11	1	0															octyl-diphenylamine
TX120 57	Esprit	7	7	7															
TX120 58	Esprit	19	6	6															
TX120 59	Esprit	13	7	7															
TX120 60	Esprit	27	9	7		Y												Y	
TX120 61	Esprit	17	8	6												Y	Y		
TX120 62	Esprit	14	3	2														Y	
TX120 63	Esprit	35	14	11		Y												Y	Benzenemethanamine, N-(phenylmethyl)-
TX120 64	Esprit	14	5	4								methyl *							
TX120 81	Levis	24	11	8											Y	Y	Y		

Table A3. Continued.

Sample code	Brand	No. of chemicals isolated	No. of chemicals reliably identified	Linear alkanes	Benzophenone	Benzyl benzoate	1,1'-Biphenyl	2,6-Di-tert-butyl-4-methyl-phenol	derivatives*Ethanol, 2-(2-butoxyethoxy)- &	Nonyl phenol	(& esters*)Hexadecanoic acid	(& esters*)Octadecanoic acid	(& esters*)Octadecenoic acid	Octadecadienoic acid, ester*	Amyrin	α -Amyrenone	Sitosterol	Cholesterol	Squalene	Others
TX120 82	Levi's	15	9	7							Y									
TX120 83	Levi's	61	14	11		Y										Y				Ethanol, 2-(tetradecyloxy)-
TX120 84	Levi's	38	17	11		Y								Y	Y	Y	Y	Y		
TX120 85	Levis	32	11	9							isopropyl*									Bis(2-ethylhexyl) maleate
TX120 86	Levis	24	10	7											Y	Y	Y			
TX120	Levis	38	14	10	Y						isoprop				Y	Y				

87												yl*							
TX120 88	Levis	31	13	9				Y								Y	Y	Y	
TX120 89	Levis	32	10	9													Y		
TX120 90	Levis	15	10	10															
TX120 91	Levis	22	5	5															
TX121 21	Zara	56	15	13			Y												Benzene, 1,1'-(3-methyl-1-propene-1,3-diy)bis-
TX121 22	Zara	58	13	9				Y								Y	Y		Benzyl naphthyl ether
TX121 23	Zara	18	5	3						methyl*	methyl*								
TX121 24	Zara	60	11	11															
TX121 25	Zara	44	13	11												Y	Y		
TX121 26	Zara	30	9	8			Y												
TX121 27	Zara	35	13	7				acetate*	Y	Y	Y					Y	Y		
TX121 28	Zara	28	4	3												Y			

Table A3. Continued.

Appendix 4. Detailed method for the chemical screening analysis

Sample Preparation

Extraction was performed using a Dionex 350 accelerated solvent extractor (ASE)(Dionex, UK). 34 mL stainless steel cells were lined with a cellulose filter and packed with 2 g Florisil (activated at 200°C overnight before use) and c.a. 8 g diatomaceous earth, separated by a second cellulose filter. Cells were loaded into the ASE and cleaned with pentane:acetone in a ratio of 3:1 under the following conditions: temperature 105°C, heat time 6 min, static time 3 min, 1-2 cycles, 0% rinsing volume, purge time 60 s. Following cleaning, around half of the diatomaceous earth was emptied from each cell into a pentane cleaned glass beaker.

0.5-3.0 g of textile was weighed, cut into pieces of approximately 2-3 cm² and loaded into the cell. An internal standard of 10 µg of deuterated naphthalene in 50 µL toluene was added to the textile sample in cell. Cells were then refilled with the cleaned diatomaceous earth, sealed and loaded into the ASE for extraction.

ASE parameters for extraction were: pentane:acetone in a ratio of 3:1, temperature 100°C, heat time 5 min, static time 5 min, 3 cycles, 20% rinse volume, purge time 60 s. Solvent lines were rinsed between cells. Extracts were collected in 60 mL glass vials and were c.a. 25 mL in volume. In preparation for clean-up, extracts were concentrated to 5 mL under nitrogen using a TurboVap II (Zymark).

Concentrated extracts were cleaned by elution through a Florisil column with 95:5 pentane:toluene. The c.a. 15 mL elutes were collected in 30 mL glass vials. If an eluent remained strongly coloured, was not clear or contained precipitate, it was re-concentrated to 5 mL and the clean-up procedure repeated. Cleaned-up extracts were concentrated to 0.5 mL under nitrogen using a TurboVap II and transferred to 2 mL glass vials, to which a second internal standard of 10 µg brominated naphthalene in 50 µL toluene had been added. The TurboVap vessel was rinsed twice with pentane, the solvent from each rinse being added to the extract to make a final volume of 1.0 mL, which was subsequently used for gas chromatography/mass spectrometry (GC/MS) analysis.

GC/MS analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rtx-XLB column (30 m, 0.25 mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert mass selective detector (MSD) operated in electron impact (EI) mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 35°C, held for 2 minutes, raised to 260°C at 10°C/min, then to 320°C at 6°C/min (held for 8 min). The carrier gas was helium, supplied at 1 ml/min.

Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary to confirm identification. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of phthalates and aliphatic hydrocarbons in order to provide further verification of the identities of chemicals within these compound groups.

Quality control

One extraction blank, one clean up blank and one solvent blank were analysed with every five textile samples to ensure the detection of any possible contamination resulting from sample handling in the laboratory. Background contaminants detected in blanks were

excluded when interpreting mass spectra from the textile samples. Peaks corresponding to the internal standards were observed in all spectra, indicating adequate recovery.