

Hazardous chemicals in branded luxury textile products on sale during 2013

Kevin Brigden, Samantha Hetherington, Mengjiao Wang,
David Santillo & Paul Johnston

Greenpeace Research Laboratories Technical Report 01/2014, February 2014

Contents

Executive Summary	2
1. Introduction	4
2. Materials and methods	5
2.1 Nonylphenol ethoxylates (NPEs)	5
2.2 Carcinogenic amines released under reducing conditions	5
2.3 Phthalates in plastisol prints	5
2.4 Organotins	5
2.5 Per- and polyfluorinated chemicals (PFCs)	5
2.6 Antimony in polyester fibre	6
3. Results and discussion	6
3.1 Nonylphenol ethoxylates (NPEs)	6
3.2 Carcinogenic amines released under reducing conditions	10
3.3 Phthalates in plastisol prints	10
3.4 Organotins	13
3.5 Per- and polyfluorinated chemicals (PFCs)	15
3.6 Antimony	19
4. Conclusions	21
5. References	25

Appendix 1. Concentrations of NPEs, carcinogenic amines, phthalates, organotins, ionic PFCs, volatile PFCs and antimony in all articles tested

Appendix 2. Concentrations of individual phthalates in the 5 articles tested

Appendix 3. Concentrations of individual organotins in the 7 articles tested

Appendix 4. Concentrations of individual PFCs in the 5 articles tested

Greenpeace Research Laboratories
School of Biosciences
Innovation Centre Phase 2
University of Exeter
Exeter EX4 4RN, UK

Executive Summary

Greenpeace has recently published a number of investigations showing that a wide range of textile products, manufactured and sold in many countries around the world, can contain residues of hazardous substances, including hormone-disrupting alkylphenols and their ethoxylates, reprotoxic phthalates, highly persistent per- and polyfluorinated chemicals, and – in some cases – azo dye precursors of carcinogenic amines. This study extends this work to include a set of 27 luxury clothing and footwear products, sold by eight major clothing brands and purchased in nine countries/regions around the world between May and June 2013. This set of products included examples reported to have been manufactured in at least seven different countries, although the countries of manufacture of five of the articles could not be determined.

The range of chemical residues investigated in the current study included nonylphenol ethoxylates (in all 27 articles), carcinogenic amines released under reducing conditions (in 11 articles having dark or deeply coloured fabric), phthalates (in five articles with plastisol printed fabric), organotins (in three articles with plastisol printed fabric and four items of footwear), per- and polyfluorinated chemicals (in three items of footwear, a waterproof clothing article, and an article of swimwear), and antimony (in three products containing polyester-based fabrics). Details of the analyses carried out, and information on the various chemicals quantified in this study, are provided within this report.

Nonylphenol ethoxylates (NPEs) were detected in fabric from 12 of the 27 articles (44% of the articles investigated), with concentrations ranging from 1.7 to 760 mg/kg. Of these, six articles (22% of the total sample) contained NPEs at concentrations above 100 mg/kg. NPEs were detected in at least one article from five of the eight brands included in this study, and examples in which NPEs were detected were found for most (seven of nine) countries/regions in which the articles were purchased, and just under half (three of seven) of the countries of manufacture. The detection of NPEs in a substantial percentage of articles tested is consistent with our previous investigations of related textile products, though the percentage of articles in which NPEs were detected was somewhat lower compared to the previous studies (between 61% to 67% of articles tested).

NPE residues within textile products are readily released when the items are washed as part of their normal use (Brigden *et al.* 2012, Greenpeace 2012b). In addition, these results suggest the common use of NPEs during the manufacture of many of the textiles analysed, which would be expected to result in releases of NPEs and nonylphenol to the environment from manufacturing facilities.

The use of NPEs during textile manufacture is regulated in the EU and some other individual countries, though ongoing use is permitted in many others, including countries in which many of the articles investigated in this study were known to have been manufactured. However, no regulations currently exist anywhere in the world that restrict the sale of textile products containing NPE residues, although 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 to cover as wide a range of NPEs as possible.

Phthalates were detected in sections of printed fabric from all five articles investigated, at levels above the detection limit of 3 mg/kg, with total phthalate concentrations ranging from 4.1 to 48 mg/kg. Similarly, phthalates were detected in all, or almost all, such samples from our previous studies, although total phthalate concentrations were found to be above 50 mg/kg for approximately a third of articles tested for each of the previous studies, and far higher concentrations (over 1000 mg/kg, 0.1% by mass) were found for a small number of samples from each study.

The concentrations of phthalates for the five articles illustrates the widespread distribution of these chemicals as ingredients and/or contaminants in industrial processes, though the levels found suggest that these phthalates had not been used as plasticisers within the plastisol formulations used to manufacture the products. The sale of textiles products containing phthalates is not currently regulated in any of the countries where the articles were purchased, though in China draft limits are under consideration concerning the presence of six phthalates at levels above 0.1% by mass in clothes sold for babies and young children (SAC 2012b).

At least one **per- or polyfluorinated chemical (PFC)** was detected in each of the five articles tested. Ionic PFCs were more commonly detected, with examples being found in all of these five articles; total ionic PFC concentrations were in the range 2.52-16.9 mg/kg (by area; 0.589-7.58 $\mu\text{g}/\text{m}^2$). Volatile PFCs were only detected in two of the five articles (a clothing article TX13109 and a footwear article TX13078), though were detected the

concentrations were considerably higher than those of ionic PFCs. Total volatile PFCs concentrations were in the range 31-374 µg/kg (by area; 13.9-26.2 µg/m²).

Differences were seen in the composition of PFCs in different types of articles. For the three items of footwear and the single swimwear article, the predominant ionic PFC was perfluorobutanoic acid (PFBA), composing between 65-100% of the total ionic PFC concentration of PFCs in each of these articles. For the clothing article, a Versace jacket (TX13109), PFBA was not detected, and the ionic PFCs were composed of the long-chain equivalents, perfluorooctanoic acid (PFOA) and perfluorodecanoic acid (PFDA).

The Versace jacket (TX13109) was also the only article in which fluorotelomer alcohols (FTOHs), a type of volatile PFC, were detected (8:2 FTOH and 10:2 FTOH). The total concentration of volatile PFCs in this sample was over 40 times higher than the total ionic PFC concentration in the same sample. FTOHs can be transformed into PFCAs, with 8:2 FTOH and 10:2 FTOH giving rise to PFOA and PFDA, respectively. The presence of PFOA and PFDA in this article may originate from the use of 8:2 FTOH and 10:2 FTOH during manufacture.

Previous investigations have shown that concentrations of ionic PFCs can vary widely not only between products but also within different parts of the same product. Such variations are likely to be a characteristic of textile products treated with PFCs in general, and therefore an issue for all brands using PFCs in the manufacture of their products.

Antimony, used as a catalyst during polyester manufacture, was detected in fabrics from three of the articles investigated that were composed either of polyester, or a blend of polyester and other fibres. Antimony concentrations in the fabrics ranged from 54 to 117 mg/kg. The concentrations of antimony within the polyester component of each fabric (calculated from the fabric composition information) were in the range 110-234 mg antimony/kg polyester, consistent with levels commonly reported for commercial polyester fibres (Duh 2002, Lacasse & Baumann 2004). Despite known and suspected toxicity for antimony trioxide, and despite the availability of alternative catalysts for polyester manufacture, no regulations currently exist that prohibit use in textile manufacture.

In addition to the above chemicals, sections of dark or deeply coloured fabric from 11 articles were investigated for carcinogenic amines, which can be released from certain azo dyes, though none showed the presence of such amines at levels above the detection limit of 5 mg/kg. In addition, organotins were quantified in seven articles, consisting of three articles bearing a large plastisol print and four footwear articles, though none of these showed the presence of organotins at levels above the detection limit of 0.1 mg/kg.

In conclusion, this study has highlighted the occurrence of residues for a range of hazardous chemicals in luxury textile products across a number of brands, expanding the range of textile products that have now been investigated. The results from this current study are broadly consistent with the findings from our previous studies of other types of textile products, although these previous studies did include examples of some articles with notably higher concentrations of certain chemicals compared to those found in the current study. The results for the individual articles provide examples from each of the brands included in this study, though too few samples were included to draw any general conclusions on the presence and concentrations of these chemicals in articles from each brand.

The manufacture of textile products using hazardous chemicals can be expected to result in releases from manufacturing facilities, including within wastewaters, in addition to the presence of chemical residues in the products themselves. There is also the potential for losses of hazardous chemicals within the textile products following their sale, either directly or when washed as part of their normal use.

Overall, this study provides additional insight into what appears to be a generic problem for the textile sector, one that is not restricted to any particular brand and is relevant to luxury textile products as well as other types of textile products previously investigated. This aspect deserves further investigation, including from a regulatory and brand policy perspective.

1. Introduction

In recent years, Greenpeace has conducted a number of investigations which identified a range of hazardous chemicals in textile products as a result of their use 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 (Brigden et al. 2012, Greenpeace 2011, Greenpeace 2012, Greenpeace 2013b-d).

Together, these previous studies determined the concentrations of nonylphenol ethoxylates (NPEs) in a broad range of textile clothing products, carcinogenic amines released from azo dyes within dyed fabrics, phthalate esters (commonly referred to as phthalates) in fabrics bearing a plastisol print (a suspension of plastic particles, commonly PVC or EVA, in a plasticiser, used as ink for screen-printing images and logos onto textiles), as well as perfluorinated and polyfluorinated compounds (PFCs) in outdoor clothing. In addition, one study employed a broader qualitative chemical screening method to identify the presence, as far as possible, of other hazardous chemicals present within some of the products.

This study follows on from and extends this recent research, determining hazardous chemicals in a range of luxury textile clothing and footwear products sold by major brands, consisting of 27 products across many countries of manufacture and sale. The chemicals investigated in this current study included those quantified for one or more of the previous reports, and in addition included the determination of the organotins in plastisol printed fabric or footwear articles, as well as antimony in polyester-based fabrics.

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

2. Materials and methods

A total of 27 products were purchased between May and June 2013 at the flagship stores of eight clothing brands, or other stores authorised to sell these branded products. The products were predominantly clothing items, including one swimwear article, but also included four items of footwear. While still in the store, purchased products were immediately sealed in individual, identical, clean polyethylene bags. These sealed bags containing the products were then sent to the Greenpeace Research Laboratories at the University of Exeter in the UK, where subsamples were taken from each article and dispatched to independent accredited laboratories for a range of analyses as detailed below. In addition, three of the articles having fabrics composed of polyester, or a blend of polyester and other fibres, were analysed at the Greenpeace Research Laboratories to determine the concentration of antimony within the polyester fibre. Details of the individual articles are provided in Appendix 1.

2.1 Nonylphenol ethoxylates (NPEs)

The concentrations of NPEs were quantified in a section of fabric from each of the 27 articles investigated. 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, with a detection limit of 1 mg/kg.

2.2 Carcinogenic amines released under reducing conditions

Eleven articles that included dark or deeply coloured fabric were investigated for the concentrations of carcinogenic amines released under certain reducing conditions, related to the presence of certain azo dyes. The samples were tested in accordance with method EN 14362, related to the relevant EU regulations (EU 2002) consistent with equivalent Chinese regulations (SAC 2012a). This 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, and with a detection limit of 5 mg/kg for each amine.

2.3 Phthalates in plastisol prints

For each of the five articles bearing a large plastisol print of an image, logo or text, the concentrations of a range of phthalates were determined within this printed section. Details of the individual phthalates quantified are given in Appendix 2. 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. The concentrations of phthalates in the extracts were subsequently analysed by gas chromatography/mass spectrometry (GC/MS), using an Agilent 5973 single quadrupole mass detector with a programmed temperature vaporising (PTV) injector and a DB5ms column using deuterated (D10)-pyrene as an internal standard, with a detection limit of 3 mg/kg for each individual phthalate.

2.4 Organotins

Seven articles were quantified for a range of organotins, consisting of three articles bearing a large plastisol print and four items of footwear. For some articles that were composed of a mixture of fabric or print colours, a number of different sub-samples from the article were analysed. Details of the individual organotin quantified in each article are given in Appendix 3. Each sample was extracted with methanol. Organotins in the extract were derivatised using sodium tetraethylborate and extracted into hexane. Analysis of the final extract was carried out using GC/MS, with a detection limit of 0.1 mg/kg for each individual organotin.

2.5 Per- and polyfluorinated chemicals (PFCs)

Analysis for perfluorinated and polyfluorinated compounds (PFCs) was conducted for five articles: 3 items of footwear articles, 1 waterproof clothing article, and 1 swimwear article. Details of the individual PFCs quantified in each article and their detection limits are given in Appendix 4. For each article, a sample was cut where there was no printing or labelling. Two separate analyses were carried out on each sample. One portion was extracted with methanol using Soxhlet extraction, the extract purified using solid phase extraction (SPE), and a range of ionic PFCs were quantified using high performance liquid chromatography (HPLC) combined with tandem mass spectrometry (HPLC-MS/MS). A second portion was extracted with methyl tertiary butyl ether (MTBE) using

ultrasonic extraction, and a range of volatile neutral PFCs were quantified using gas chromatography-mass spectrometry (GC-MS).

2.6 Antimony in polyester fibre

Three articles with fabrics composed of polyester, or a blend of polyester and other fibres, were analysed to determine the concentration of antimony within the polyester fibre. For each sample, a 1g portion was extracted using 20ml of a mixture of nitric acid and hydrochloric acid (4:1). The acidified samples were digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 30 minutes, and then held at 180°C for a further 15 minutes. Cooled digests were filtered, and made up to 50 ml with deionised water. Sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer, with a detection limit of 1 mg/kg.

3. Results and Discussion

Results for the various substance groups are presented in the following sections. The results from all analyses for the individual articles are provided in Appendix 1, along with a breakdown of the concentrations of individual phthalates in the relevant articles in Appendix 2, organotins in Appendix 3, and PFCs in Appendix 4.

3.1 Nonylphenol ethoxylates (NPEs)

Of the 27 articles in which NPEs were quantified, 12 of them (44% of the total number of samples) tested positive for the presence of NPEs at concentrations above the limit of detection (1 mg/kg), with concentrations ranging from just above 1 mg/kg up to 760 mg/kg. The highest concentration was detected in a Louis Vuitton-branded ballerina shoe, manufactured in Italy and sold in Switzerland (TX13078). For six of the articles (22% of the total number of samples) NPE concentrations were above 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 27)	% of samples
<1	15	56%
1 – 10	4	15%
>10 – 100	2	7%
>100 – 1 000	6	22%

Table 1. The number of samples (of the 27 articles tested) within various NPE concentration ranges.

Breakdown of results by brand, place of sale and place of manufacture

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/region of manufacture, respectively. These tables include the median values for all samples in each brand, place of sale, or country/region of manufacture, as well as the median value for only those samples in which NPEs were detected in each case.

NPEs were detected in at least one article from five of the eight brands investigated (see Table 2), with none of the articles tested from Giorgio Armani, Trussardi or Versace (four, three and two articles respectively) containing detectable levels of NPEs. NPEs were detected in one or more products sold in seven of the nine countries/regions concerned (see Table 3). NPEs were not detected in the articles purchased in Denmark or the UK, though only one article was purchased in each country, too few to draw any general conclusions about the absence of NPEs in articles sold in either country.

NPEs were detected in one or more products from three of the seven countries of manufacture (see Table 4). For five articles, the country of manufacture was not specified and could not be determined. NPEs were not detected in articles manufactured in China, Hungary, India or Turkey, although for these only one or two articles were purchased per country, with the exception of China (four articles), too few to draw any general conclusions about the absence of NPEs in articles manufactured in each country.

NPEs are used as in the manufacture of textile products, primarily as surfactants and detergents, which can result in releases from manufacturing facilities, and can leave residues in textile products that are readily released when the items are washed as part of their normal use (Brigden *et al.* 2012, Greenpeace 2012b). Once released to the environment, NPEs can be converted into nonylphenol, a group of persistent, bioaccumulative and toxic compounds. Information on NPEs and nonylphenol is provided in Box A.

Brand	Number of samples	Number tested positive	NPE concentration range, when detected (mg/kg)	Median of detected levels (mg/kg)	Median of all levels (mg/kg)
Dior	7	5	4.0 - 560	400	75
Dolce & Gabbana	3	2	2.1 - 6.1	4.1	2.1
Giorgio Armani	4	0	<1.0	<1.0	<1.0
Hermes	2	1	380	380	190
Louis Vuitton	3	3	100 - 760	370	370
Marc Jacobs	3	1	1.7	1.7	<1.0
Trussardi	3	0	<1.0	<1.0	<1.0
Versace	2	0	<1.0	<1.0	<1.0
Total	27	12	1.7 - 760	240	<1.0

Table 2. The number of samples in which NPEs were identified arranged 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	Number of samples	Number tested positive	NPE concentration range, when detected (mg/kg)	Median of detected levels (mg/kg)	Median of all levels (mg/kg)
China	3	1	560	560	<1.0
Hong Kong	2	2	6.1 - 370	190	190
Taiwan	1	1	460	460	460
Denmark	1	0	<1.0	<1.0	<1.0
France	4	3	75 - 380	100	88
Italy	11	2	1.7 - 2.1	1.9	<1.0
Russia	2	1	4.0	4.0	2.3
Switzerland	2	2	400 - 760	580	580
UK	1	0	<1.0	<1.0	<1.0
Total	27	12	1.7 - 760	240	<1.0

Table 3. The number of samples in which NPEs were identified arranged 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.

Place of manufacture	Number of samples	Number tested positive	NPE concentration range, when detected (mg/kg)	Median of detected levels (mg/kg)	Median of all levels (mg/kg)
China	4	0	<1.0	<1.0	<1.0
Hungary	1	0	<1.0	<1.0	<1.0
India	1	0	<1.0	<1.0	<1.0
Italy	10	7	2.1 - 760	100	41
Morocco	3	3	4.0 - 560	460	460
Thailand	1	1	1.7	1.7	1.7
Turkey	2	0	<1.0	<1.0	<1.0
Unknown	5	1	380	380	<1.0
Total	27	12	1.7 - 760	240	<1.0

Table 4. The number of samples in which NPEs were identified arranged 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.

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 largest share has been used in industrial and institutional cleaning products (detergents), with smaller amounts used as emulsifiers, textile and leather finishers, and as components of pesticides and other agricultural products and water-based paints (OSPAR 2004, Guenther *et al.* 2002). The use of NPEs during the manufacture of textiles can leave residues of NPEs within the final product that are readily released when the items are washed as part of their normal use (Brigden *et al.* 2012, Greenpeace 2012a).

Where NPEs are released, including from textile 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 (NP), a closely-related group of persistent, bioaccumulative and toxic chemicals (OSPAR 2004, Jobling *et al.* 1996).

Both NPEs and NP are widely distributed in fresh and marine waters and, in particular, sediments, in which these persistent compounds accumulate (Fu *et al.* 2008, Shue *et al.* 2010, David *et al.* 2009). Because of their releases to water, NPEs and NP are also common components of sewage effluents and sludge (Micic & Hofmann 2009, Ying *et al.* 2009, Yu *et al.* 2009), including that applied to land. NP has been detected in rain and snow (Fries & Püttmann 2004, Peters *et al.* 2008), and as contaminants in house dust (Butte & Heinzow 2002, Rudel *et al.* 2003) and indoor air (Rudel *et al.* 2003, Saito *et al.* 2004). Research into levels in wildlife remains limited, although there have been reports of significant levels in both invertebrates and fish in the vicinity of sites of manufacture and/or use of NPEs and close to sewer outfalls (Lye *et al.* 1999, Rice *et al.* 2003, Mayer *et al.* 2008). NP is known to accumulate in the tissues of fish and other organisms (OSPAR 2004), including human tissues (Lopez-Espinosa *et al.* 2009). The most widely recognised hazard associated with NP is estrogenic activity, i.e. the ability to mimic natural estrogen hormones. This can lead to altered sexual development in some organisms, most notably the feminisation of fish (Jobling *et al.* 1995, 1996).

The manufacture, use and release of NPEs and nonylphenol are regulated in some countries (OSPAR 1998, EU 2003, CEPA 2004, USEPA 2010) though no such regulations apply in many others. More than 10 years ago, the Ministerial Meeting under the OSPAR Convention agreed on the target of cessation of discharges, emissions and losses of hazardous substances to the marine environment of the northeast Atlantic by 2020, and included NP/NPEs on the first list of chemicals for priority action towards this target (OSPAR 1998). Since then, NP has been included as a 'priority hazardous substance' under the EU Water Framework Directive, such that action to prevent releases to water will be required throughout Europe within 20 years of adoption of the regulation (EU 2001). Even before the listing under this Directive, however, the widely recognised environmental hazards presented by NP and NPEs have led to some long-standing restrictions on their use in many countries. Among these, a Recommendation agreed by the Paris Commission (now part of the OSPAR Commission) in 1992 required the phase-out of NPEs from domestic cleaning agents by 1995 and industrial cleaning agents by the year 2000 (PARCOM 1992). Furthermore, within the EU, formulations containing greater than 0.1% NP or NPEs may no longer be placed on the market within Europe after January 2005, with some minor exceptions principally for 'closed-loop' industrial systems (EU 2003). Though no regulations addressing manufacture, use and release exist in China, NP and NPEs have recently been included on the 'List of toxic chemicals severely restricted on the import and export in China', which requires prior permission for the import or exports of NP or NPEs (MEP 2011). No regulations currently exist that restrict the sale of textile products containing NPE residues, though such a regulation is currently under development within the EU (KEMI 2012).

3.2 Carcinogenic amines released under reducing conditions

Carcinogenic amines were not released under the test conditions at levels above the method detection limit (<5 mg/kg) in any of the 11 articles tested.

Box B. Carcinogenic amines released by certain azo dyes

Azo dyes can undergo reduction to release aromatic amines. 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 formulations 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 (SAC 2012a).

3.3 Phthalates in plastisol prints

One or more phthalates were detected above the method detection limit (3 mg/kg) in plastisol printed fabric sections from all five articles that were analysed for phthalates. Total phthalate concentrations for these articles were in the range 4.1 to 48 mg/kg. Full details of the individual phthalate concentrations for all five articles are presented in Appendix 2.

For all articles, the phthalate concentrations would be too low to be expected to have any significant plasticising function on their own. For these articles, the identified phthalates are more likely present due to contamination of other substances 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.

Further background information on phthalate esters, including their hazardous properties is provided in Box C, and legislation specific to textile products is discussed in the conclusions.

Box C. Phthalate esters (Phthalates)

Phthalates (or, more accurately, phthalate diesters) are a group of chemicals with a diversity of uses, dominated by use as plasticisers (or softeners) in plastics, especially PVC. 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). Use of phthalates, especially the major use as PVC plasticisers, results 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 that 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 that 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 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), though it is clearly not possible to establish a cause-effect relationship from such studies. 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 to exhibit anti-androgenic effects on reproductive development of Wistar rats (Boberg *et al.* 2011), 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 that 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 (EU 2005). Very similar regulation in China has recently been announced that will address the same phthalates in toys sold in China in the coming year. The use of DEHP, as well as di-n-butyl phthalate (DnBP) and benzyl butyl phthalate (BBP), will be prohibited in all toys with a limit of 0.1% by weight, equivalent to 1000 mg/kg, and the use of DINP, di-iododecyl phthalate (DIDP) and di-n-octyl phthalate (DNOP) will be prohibited in such articles if they can be placed in the mouth (SAC 2013). While these address one important exposure route, exposures through other consumer products have so far largely escaped regulation. In China, draft legislation has been proposed that would prohibit the presence of six phthalates, including DEHP and DINP, at concentrations above 0.1% by weight (1000 mg/kg) for the whole article, in clothes for babies and young children (under 36 months old) (SAC 2012b). It should be noted, however, that this legislation has not entered into force, and should it do so some details in the draft may change. Within the EU, certain phthalates, including DEHP, DBP, DiBP and BBP, have been listed as Substances of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013).

3.4 Organotins

Organotins were quantified in seven articles, consisting of three articles bearing a large plastisol print and four items of footwear. For some articles, those consisting of a mixture of fabrics or print colours, a number of different sub-samples were analysed.

None of the quantified organotin compounds were detected in any of the seven articles, with a method detection limit of 0.1 mg/kg for individual organotins. Full details of the individual organotin data for the seven articles are presented in Appendix 3.

Box D. Organotins

In textile products, organotins including mono- and dibutyltin (MBT, DBT) and mono- and dioctyltin (MOT, DOT) are sometimes used as stabilisers in PVC, for example within PVC plastisol prints. Organotins also have also been used as biocides in certain types of textile products, including sportswear, socks and footwear (Matthews 1996, OSPAR 2011). As a result, organotins have been reported in a wide range of textile articles, predominantly MBT/DBT and MOT/DOT (BEUC 2012, Greenpeace 2004, Greenpeace 2012c, Laursen *et al.* 2003, TNO 2003, TNO 2005).

Organotins are known to be toxic to a range of organisms, including mammals, at relatively low levels of exposure, with immunotoxicity, impact on development and neurotoxicity in mammalian systems (Kergosien & Rice 1998, Jenkins *et al.* 2004, Tonk *et al.* 2011a&b).

While consumption of seafood is the predominant source of organotin exposure for humans, exposure to consumer products that contain them or to dusts in the home may also be significant.

At present there is no regulation of organotins in textile products in China, although legislation does exist in some other countries. Within the EU, the presence of certain organotins is prohibited within some consumer products, including certain types of textile products, with maximum permissible levels of 0.1 % by weight (1000 mg/kg) of tin in the product (EU 2010).

3.5 Per- and polyfluorinated chemicals (PFCs)

PFCs were quantified in five articles, consisting of one waterproof clothing article, three items of footwear, and one swimwear article. The articles were analysed for a range of PFCs. Two separate analyses were carried out:

1. analysis for a range of ionic PFC compounds, predominantly perfluorosulfonates (for example, perfluorooctane sulfonate, PFOS) and perfluorinated carboxylic acids (for example, perfluorooctanoic acid, PFOA); and
2. analysis for a range of volatile PFCs that are used as precursors during manufacturing processes, consisting of certain fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs) also known as polyfluorinated acrylates, and N-alkyl perfluorosulfonamides.

One or more PFC were detected in all five articles. Ionic PFCs were more commonly detected, with examples being found in all five articles. For the volatile PFCs, examples were detected in only two of the five articles (the article of waterproof clothing and one item of footwear) although, when detected, these volatile PFCs were found in higher concentrations than the ionic PFCs. A summary of the number of articles in which ionic and volatile PFCs were detected is given in Table 5, together with the total concentrations of ionic PFCs in the various articles, and the same for volatile PFCs. Details of the concentrations of individual PFCs in the articles, both by mass (ng/kg) and by area ($\mu\text{g}/\text{m}^2$), are given in Appendix 4.

Article type	No. of samples	No. in which PFCs were detected	Ionic PFCs		Volatile PFCs	
			No. in which detected	Total conc. range ($\mu\text{g}/\text{kg}$)	No. in which detected	Total conc. range ($\mu\text{g}/\text{kg}$)
Waterproof clothing	1	1	1	8.41	1	374
Footwear	3	3	3	2.52 – 16.9	1	ND - 31
Swimwear	1	1	1	4.5	0	ND
Total	5	5	5	2.52 – 16.9	2	ND - 374

Table 5. Summary of articles in which PFCs were detected, together with a breakdown of the total concentrations for each of the ionic PFC and volatile PFC subgroups. ND = not detected.

The total concentrations of ionic PFCs in the five articles ranged from 2.52 to 16.9 mg/kg, with the highest concentration being for suede ballerina shoes sold by Louis Vuitton (TX13078). However, the lowest total concentration was also found in a Louis Vuitton footwear article (TX13077). There were some notable differences in the composition of ionic PFCs in individual samples. For the three items of footwear and the single swimwear article, the predominant ionic PFC was perfluorobutanoic acid (PFBA), with concentrations in the range 1.65-15.7 mg/kg, composing between 65% and 100% of the total concentration of ionic PFCs in each of these articles.

In contrast, for the clothing article, a Versace jacket (TX13109), PFBA was not detected. The ionic PFCs were composed of the long-chain PFCAs, PFOA (4.75 mg/kg) and perfluorodecanoic acid (PFDA) (3.66 mg/kg). Volatile PFCs were also detected in the Versace jacket (TX13109), predominantly the fluorotelomer alcohols 8:2 FTOH (210 mg/kg) and 10:2 FTOH (130 mg/kg), as well as lesser amounts of a fluorotelomer (8:2 FTA, 34 mg/kg). The total concentration of volatile PFCs in this sample was over 40 times higher than the total ionic PFC concentration in the same sample.

FTOHs can be transformed into PFCAs, with 8:2 FTOH giving rise to C8 compounds including PFOA, and 10:2 FTOH giving rise to C10 compounds including PFDA (Frömel & Knepper 2010, Butt *et al.* 2013, Young & Mabury 2010). The presence of the ionic compounds PFOA and PFDA in this article may originate from the use of 8:2 FTOH and 10:2 FTOH during manufacture. Similarly, 8:2 FTA can be generated during manufacturing processes related to 8:2 FTOH.

For the second article in which volatile PFCs were detected (TX13078, Luis Vuitton shoes), the only volatile compound was 8:2 FTA (31 mg/kg). The related ionic C8 compound, PFOA (1.19 mg/kg) was also detected in this compound. The reason for the presence of 8:2 FTA and PFOA in this article, despite FTOHs not being detected, is not clear, but may indicate alternative manufacturing processes.

The results for these individual articles provide examples from each of the brands, however, the study included too few samples to draw any general conclusions on the presence and concentrations of PFCs in articles from each brand, or the type of product (waterproof clothing, footwear, swimwear). Information on PFCs, including long-chain PFCAs such as PFOA and PFDA and FTOHs, is given in Box E.

Box E. Per- and polyfluorinated chemicals (PFCs)

Per- and polyfluorinated chemicals (PFCs) are a group of chemicals in which all (perfluorinated), or most (polyfluorinated), of the carbon-hydrogen bonds present in the organic chemical backbone have been replaced by carbon-fluorine bonds, making them highly resistant to chemical, biological and thermal degradation (OECD-UNEP 2013, Buck *et al.* 2011).

PFCs fall into four broad categories; perfluorinated alkyl sulphonates (PFSA), perfluorocarboxylic acids (PFCAs), fluoropolymers (the best known being PTFE, marketed as Teflon and widely used for 'non-stick' cookware) and fluorotelomer alcohols (FTOH) (Dinglasan *et al.* 2004, OECD-UNEP 2013).

In this study, analyses were carried out separately on ionic per-fluorinated chemicals include PFSA (for example perfluorooctane sulfonate, PFOS) and (PFCAs) (for example, perfluorooctanoic acid, PFOA), and for volatile polyfluorinated chemicals that are generally used as precursors during manufacturing processes, including fluorotelomer alcohols (FTOHs) and fluorotelomer acrylates (FTAs) also known as polyfluorinated acrylates.

PFCs are used in many industrial processes and consumer products due to their unique chemical properties, including textile products, primarily due to their stability and ability to repel both water and oil (OECD-UNEP 2013, Herzke *et al.* 2012).

Various PFCs have uses for textile products, including the direct use of PFSA or FTOHs, and the use of fluorinated polymers manufactured from FTOHs. Final products can contain residues of FTOH precursors, or FTAs generated as intermediates in the production of fluorinated polymers from FTOHs. Products can also contain residues of PFCAs or PFSA, including from being unintentional manufacturing by-products or use as process aids in the manufacture of fluorinated polymers (Buck *et al.* 2011, Herzke *et al.* 2012, Poulsen & Jensen 2005).

Despite their widespread use, there is very little information about PFC content in textile products relative to the number of types of products in which PFCs may have been employed during manufacture. Of the few studies that have been reported for textiles, PFCAs, PFSA and FTOHs have frequently been reported in outdoor clothing, swimwear and items of footwear (SSNC FoEN 2006, Greenpeace 2012c, Herzke *et al.* 2012, Schlummer 2013, Greenpeace 2013b, Greenpeace 2013c)

The manufacture and use of PFCs, including for textiles, can result in releases to the environment, either directly from manufacturing facilities, or indirectly when products containing PFCs are used and disposed of. Precursor PFCs, such as FTOHs, are volatile and can be released from products under ambient conditions (Langer *et al.* 2010, Schlummer *et al.* 2013).

Many PFCs, especially longer-chain PFCAs (including PFHxS, PFOS and PFDA) and PFSA (including PFHxS and PFOS), are highly persistent and do not readily break down once released to the environment, which has led to their ubiquitous presence in the environment, even in remote regions (Frömel & Knepper 2010, Ahrens 2011, OECD-UNEP 2013). Furthermore, their ability to bioaccumulate has led to many PFCAs and PFSA being reported in a wide range of both aquatic and terrestrial biota (Giesy *et al.* 2001, Conder *et al.* 2008, Houde *et al.* 2011, Loi *et al.* 2011, Greaves *et al.* 2012). PFSA and PFCAs, particularly PFOS and PFOA, have been reported in human blood (Fromme *et al.* 2009, Olsen *et al.* 2012) and milk (Tao *et al.* 2008, Liu *et al.* 2010, Thomsen *et al.* 2010) for general populations in many countries around the world. Some studies have reported increasing levels of PFHxS in recent years (Kato *et al.* 2011, Glynn *et al.* 2012). For aquatic organisms, take up is generally from water and contaminated food, whereas for terrestrial organisms exposure is primarily via food and air (OECD-UNEP 2013). Precursor PFCs, such as FTOHs, are volatile and have frequently been detected in air samples, even to remote areas (Weinberg *et al.* 2011, OECD-UNEP 2013).

Fluorotelomer alcohol (FTOHs) can be transformed into PFCAs either through biotransformation (Frömel & Knepper 2010, Butt *et al.* 2013), or abiotically in the atmosphere (Young & Mabury 2010). 8:2 FTOH can give rise to C8 compounds including PFOA, while 6:2 FTOH can result in C6 compounds including PFHxA. Humans occupationally exposed to high levels of 8:2 FTOH have been found to have high concentrations of PFOA in their blood (Nilsson *et al.* 2013). In addition, there are indications that biotransformation can form intermediate products in the body that can be more harmful than the PFCA end product (Rand & Mabury 2012).

Studies indicate that PFCs can cause adverse impacts both during development and during adulthood. PFCs, including PFOA, have been shown to act as hormone (endocrine) disruptors (Jensen and Leffers 2008, White *et al.* 2011, Du *et al.* 2013), and studies have suggested that PFOS and PFOA exhibit reproductive toxicity, including for humans (Fei *et al.* 2009, Joensen *et al.* 2009).

Impacts on the immune system have also been reported, (Lau *et al.* 2007, DeWitt *et al.* 2008, Peden-Adams *et al.* 2008), and some are potentially carcinogenic in animal tests (Andersen *et al.* 2008, Lau *et al.* 2007). In addition, it has been reported that epidemiological studies have shown that elevated blood levels of PFOA in humans has possible links with other diseases, including thyroid diseases, elevated blood pressure and certain cancers (Melzer *et al.* 2010, Grandjean *et al.* 2012, OECD-UNEP 2013).

Information regarding the toxicology of FTOH is scarce, though some studies indicate that 6:2 FTOH and 8:2 FTOH show endocrine-disrupting activity, including disturbing fish reproduction (Liu 2009, Liu 2010, Rosenmai *et al.* 2013). In addition to direct hazards from FTOH, the potential for FTOHs to transform into other PFCs, including PFCAs, poses an additional hazard.

PFOS have been classified as persistent organic pollutants (POPs) under the Stockholm Convention, a global treaty to protect human health and the environment, requiring contracting parties to take measures to restrict the production and use of PFOS, although a wide range of uses are currently exempted (UNEP 2009). Within the EU, the marketing and use of PFOS has been prohibited for certain uses since 2008, although many similar exemptions exist to those under the Stockholm Convention (EU 2006).

In some countries there are regulations related to textile products. Within the EU a maximum limit of 1 µg/m² is set for PFOS in textiles (EU 2006). Even where regulation of PFOS in textile products is in place, no such limits are currently in place for any other PFCs, despite concerns for their hazardous nature and the fact that they can commonly be found at far higher concentrations in textiles. The one exception is that the sale of textiles containing PFOA above 1 µg/m² will be prohibited in Norway from June 2014 (NME 2013). In addition, PFOA and four other long-chain PFCAs (PFUnA, PFDoA, PFTrA, PFTeA) are also classified as substances of very high concern (SVHCs) within the EU under the REACH regulations (ECHA 2013), and certain long-chain PFCAs (PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA) have recently been added to a list of priority chemicals in Norway, meaning that releases to the environment must be eliminated or substantially reduced by 2020 (NEA 2013).

3.6 Antimony

Antimony was quantified in sub-samples from the three articles that included fabrics composed of polyester or a blend of polyester and other fibres. Where the fabric was reported to be 100% polyester, the antimony concentration was determined directly. Where it was reported that the fabric was composed of a blend of polyester and other fibres, the concentration of antimony was determined within the fabric blend and the concentration in the polyester component was calculated on the basis that all antimony arose from the polyester fibre within the fabric blend. Antimony was detected in all three articles, with concentrations in the fabric blends in the range 54-117 mg/kg. The concentrations of antimony within the polyester component of each fabric (calculated from the fabric composition information) were in the range 110-234 mg antimony/kg polyester. Details of antimony concentrations in individual articles are presented in Table 6 below, and in Appendix 1. The range of concentrations is consistent with reports that commercial polyester fibres typically contain up to 300 mg/kg antimony (Duh 2002, Lacasse & Baumann 2004).

Sample number	Brand	Amount of polyester in fabric blend (%)	Antimony conc. in fabric (mg/kg)	Antimony conc. in polyester (mg/kg)
TX13046	Dolce&Gabbana	50	117	234
TX13061	Giorgio Armani	45	54	120
TX13109	Versace	100	110	110
Total	36	36	14 - 293	120

Table 6. Concentrations of antimony in fabrics containing polyester fibre. The concentration of antimony in the polyester component of the blend was calculated from fabric composition information, on the basis that all antimony arose from the polyester fibre within the fabric blend.

A compound of antimony (antimony trioxide, Sb_2O_3) is commonly used as a catalyst in the manufacture of PET, the predominant polyester polymer (Jaffe & East 2007, Thiele 2004), resulting in polyester fibres containing residues of antimony trioxide (Duh 2002, Lacasse & Baumann 2004). Antimony can also be released in wastewaters from facilities manufacturing textiles from polyester fabrics or fibres (Greenpeace 2013a). More information on antimony, particularly antimony trioxide, is given in Box F.

Box F. Antimony

Antimony trioxide (Sb_2O_3) is commonly used as part of the polymerisation process used to produce polyethylene terephthalate (PET) (Jaffe & East 2007, Thiele 2004). The term 'polyester' refers to a chemical class (group) of polymers rather than a single plastic, and of these PET is of the greatest significance, accounting for the bulk of production. Antimony trioxide has other industrial uses, including as a component of flame retardant formulations, some of which are used in certain textile products, though usually not in clothing products (Lau *et al.* 2003).

Antimony trioxide is the preferred catalyst for PET production due to a balance of cost, catalytic ability and colour of the produced polymer. Alternatives exist, mainly based on titanium compounds, and are reported to be in use, albeit limited compared to antimony trioxide. Certain alternatives exhibit a higher catalytic activity than antimony trioxide, but are generally more expensive and some can produce colour tinted polymer (Thiele 2004, Pang *et al.* 2006). Polyester produced with one titanium-based catalyst has been reported to be able to be dyed at lower temperatures in a shorter time, and with a lower dyestuff concentration compared to that produced with antimony trioxide (Thier-Grebe 2000).

Polyester textile fibres have a very large surface area and are often subjected to harsh conditions during manufacturing processes that can employ wet treatments, high temperatures, and chemical attack. As a result, antimony catalyst within the fibre can leach out into processing water and be released in wastewaters. (Lacasse & Baumann 2004). High levels of antimony were recently reported by Greenpeace in wastewaters discharged from a textile manufacturing facility employing polyester in Indonesia (Greenpeace 2013a).

Polyester fabrics contain residues of antimony trioxide used in their manufacture, with commercial polyester fibres typically containing up to 300 mg/kg antimony (Duh 2002, Lacasse & Baumann 2004). Residues of antimony have also been reported in clothing articles containing polyester fibres, with concentrations in the range 1 - 200 mg/kg (Laursen *et al.* 2003, Greenpeace 2012c, Kemi 2013).

Antimony shows many similarities in its chemistry and toxicity to arsenic (Andrewes *et al.* 2004, Patterson *et al.* 2003). However, unlike arsenic, there are relatively few studies concerning the toxicity and ecotoxicity of antimony and its compounds. Those studies that are available indicate that the toxicity of antimony depends greatly on its particular form (i.e. its oxidation state). Trivalent antimony, such as is present in antimony trioxide, is the more toxic state, whereas its pentavalent form is far less toxic (Patterson *et al.* 2003, De Boeck *et al.* 2003).

One trivalent compound, antimony chloride, has been reported to have high estrogenicity *in vitro* (Choe *et al.* 2003), suggesting that trivalent antimony may have the potential to be disruptive to the estrogenic system. Antimony compounds have been associated with dermatitis and irritation of the respiratory tract, as well as interfering with normal function of the immune system (Kim *et al.* 1999). Where released to the aquatic environment, toxicity has been reported for a range of aquatic organisms (Nam *et al.* 2009 and references therein). Some organic antimony compounds (including trimethylstibine) are very toxic (Andrewes *et al.* 2004). There is evidence for the formation of organic antimony compounds following the disposal of antimony containing wastes to landfill (Andrewes *et al.* 2004, Filella *et al.* 2002). Also, there is some evidence that inorganic antimony compounds, if ingested, can be converted to organic compounds or reduced to the more toxic trivalent forms in the body (Andrewes *et al.* 2004).

In addition, antimony trioxide is listed by the International Agency for Research on Cancer (IARC) as 'possibly carcinogenic to humans' (group 2B), with inhalation of dusts and vapours the critical route of exposure (IARC 1989). The assessment found sufficient evidence for the carcinogenicity of antimony trioxide in experimental animals, though there is inadequate evidence in humans due to human carcinogenicity data being difficult to evaluate given the frequent co-exposure to both antimony and arsenic. Subsequent epidemiological studies have investigated increased cancer incidence in humans through occupational exposure (smelter workers), though again observed increase in cancer mortality may have been influenced by co-exposure to arsenic (Schnorr *et al.* 1995). Antimony trioxide has been classified under the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) as suspected of causing cancer (H351). Inhalation exposure to antimony is more common in occupational settings, whereas the general population is exposed to antimony mainly through ingestion of food and water. A previous study that found similar levels of antimony in polyester as those in the current study made the assessment that antimony at the levels found did not pose a direct risk to the wearer, due to leaching of antimony compounds into saliva or sweat (Laursen *et al.* 2003)

No regulations currently exist that prohibit use in textile manufacture, despite the availability of alternative catalysts for polyester manufacture. Within the EU, the Ecolabel Regulation, which aims to promote products with a reduced environmental impact compared with other products in the same product group, requires that the antimony content in polyester fibres does not exceed 260 mg/kg for articles bearing the Ecolabel (EC 2009).

4. Conclusions

This study has demonstrated the presence of a number of different hazardous chemicals within a range of luxury textile clothing and footwear products sold by major brands, as either components of materials incorporated within the product, or residues remaining from use within manufacturing processes.

Among these, NPEs were commonly detected substances, with residues identified in products sold by most brands (five of the eight brands). Examples in which NPEs were detected were found for most (seven out of nine) countries/regions countries in which the articles were purchased, and just under half (three out of seven) of the countries of manufacture. These results indicate that the use of NPEs is reasonably widespread within the manufacture of textile products of the type investigated in this study, including within supply chains used by several major brands.

The percentage of articles in which NPEs were detected (44% of 27 articles) was broadly consistent with previous studies, though NPEs were detected for a somewhat higher percentage of samples for these (between 61% to 67% of articles tested) (Brigden *et al.* 2012, Greenpeace 2011a, Greenpeace 2012a, Greenpeace 2014). The highest concentration of NPEs in the current study was 760 mg/kg, while a small number of samples (between 3% and 9% of articles analysed) in each of the previous studies contained NPE concentrations above 1000 mg/kg, with considerably higher levels in certain example. However, the current study consisted of fewer articles (27 in total) compared to the number tested in each of the previous studies (78, 141 and 82 articles, respectively), and this smaller number of samples may have contributed to the differences in the range of NPEs concentrations in this study.

The presence of NPEs in finished products indicates their use during manufacture, which can result in releases of NPEs and nonylphenol from manufacturing facilities. 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 2012b).

The use of NPEs and nonylphenol during textile manufacture has effectively been banned within the EU (EU 2003), with similar restrictions in place in the US and Canada (CEPA 2004, USEPA 2010). No regulations currently exist 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.

In addition to NPEs, one or more phthalates were detected in each of the five articles from which a section of plastisol printed fabric was analysed, with total concentration in the range 4.1 to 48 mg/kg, illustrating the widespread distribution of these chemicals as ingredients and/or contaminants in industrial processes. Previous studies similarly detected phthalates in all, or almost all, such samples (Greenpeace 2012a, Greenpeace 2014). However, for each of the previous studies, total phthalate concentrations were found to be above 50 mg/kg for approximately a third of the articles tested, and for a small number of samples from each study (four or two articles, respectively) the total phthalate concentration was over 1000 mg/kg (0.1% by mass).

As for NPEs, the current study investigated phthalates for considerably fewer samples (five in total) compared to the number tested in each of the previous studies (31 and 35 articles, respectively), which may have contributed to the differences in the concentrations found in this study, and in particular to the fact that a concentration above 1000 mg/kg was not identified in any of the five samples.

The sale of textiles products containing phthalates, including as components of plastisol prints, is not currently regulated in the countries where the items were sold. However, draft legislation has been proposed in China that would prohibit the presence of six phthalates, including DEHP and DINP, at concentrations above 0.1% by weight (1000 mg/kg) in the whole article, in clothes for babies and young children (under 36 months old) (SAC 2012b). It should be noted, however, that this legislation has not entered into force, and should it do so, some details in the draft may change. The phthalate data presented in the current study are for sections of printed fabric rather than the whole article.

Regulations do exist in some countries that prohibit certain phthalates (including those identified in this study) in other consumer products, primarily toys, including within the EU (EU 2005) and China (SAC 2013). While such regulations and initiatives do not relate directly to clothing articles, they do recognise the hazard associated with products containing phthalates, including plastic parts containing phthalates as plasticisers. The concentrations found for the articles tested in this study did not exceed the levels in the draft Chinese legislation for certain textiles, nor those in the regulations relevant to toys.

The composition of PFCs for the outdoor clothing article (Versace jacket, TX13109) was dominated by two fluorotelomer alcohols, 8:2 FTOH and, to a lesser extent, 10:2 FTOH. The FTOH concentrations were within the range of concentrations previously reported in earlier studies of outdoor clothing and related waterproof textiles (SSNC FoEN 2006, Greenpeace 2012c, Herzke *et al.* 2012, Schlummer 2013), though concentrations in TX13109 were at the lower end of ranges previously reported. Similarly, the other volatile PFC detected in this article, the fluorotelomer acrylate 8:2 FTA, was also present at a concentration consistent with limited previous data reported for outdoor clothing, again at the lower end of the range (Greenpeace 2012c). The concentrations of PFCAs detected in this article (PFOA and PFDA) were similar to those reported in some outdoor clothing articles, though considerably higher levels have been reported in certain articles (SSNC FoEN 2006, Greenpeace 2012c, Greenpeace 2014).

The composition of PFCs in the three items of footwear was different to those reported in previous studies. FTOHs, which were not detected in footwear from the current study, were reported to be the predominant PFCs. Similarly, PFSAAs including PFOS and PFBS were previously found to be the predominant ionic PFCs, though no PFSAAs were detected in the current study (Herzke *et al.* 2012, Greenpeace 2014). PFBA, the predominant PFC detected in footwear for the current study, has previously been found in some items of footwear, though at lower concentrations compared to those from the current study (Greenpeace 2014). The other PFCAs detected in individual articles, PFOA and PFDA, have not been detected in footwear from previous studies (Herzke *et al.* 2012, Greenpeace 2014).

Similarly, the composition of PFCs in the swimwear article sold by Giorgio Armani (TX13059), predominantly PFBA, was different to that in the single previous report for this type of article, which detected predominantly longer chain PFCAs, particularly PFOA (Greenpeace 2013b).

In some countries there are regulations relating to textile products. Within the EU a maximum limit of 1 $\mu\text{g}/\text{m}^2$ is set for PFOS in textiles (EU 2006). Even where regulation of PFOS in textile products is in place, no such limits are currently in place for any other PFCs, despite concerns about their hazardous nature and the fact that they can commonly be found at far higher concentrations in textiles. The one exception is that the sale of textiles containing PFOA above 1 $\mu\text{g}/\text{m}^2$ will be prohibited in Norway from June 2014 (NME 2013). In addition, PFOA and four other long-chain PFCAs (PFUnA, PFDoA, PFTrA, PFTeA) are also classified as substances of very high concern (SVHCs) within the EU under the REACH regulations (ECHA 2013), and certain long-chain PFCAs (PFNA, PFDA, PFUnA, PFDoA, PFTrA, PFTeA) have recently been added to a list of priority chemicals in Norway, meaning that releases to the environment must be eliminated or substantially reduced by 2020 (NEA 2013).

PFOS was not detected in any articles from this study. PFOA has some similar properties to PFOS and, though the EU regulatory limit for PFOS (1 $\mu\text{g}/\text{m}^2$) clearly does not apply to PFOA, it does provide a useful comparison for concentrations in textile articles. Furthermore, as noted above, PFOA will soon be prohibited above 1 $\mu\text{g}/\text{m}^2$ for textile products sold in Norway. PFOA was detected in two articles, Louis Vuitton ballerina shoes (TX13078, 0.533 $\mu\text{g}/\text{m}^2$) and a Versace jacket (TX13109, 0.333 $\mu\text{g}/\text{m}^2$), although in both cases the concentration per unit area was below 1 $\mu\text{g}/\text{m}^2$.

The other long-chain PFCA detected in two articles (PFDA), Louis Vuitton trainers (TX13077) and a Versace jacket (TX13109) is classified as a SVHC within the EU under the REACH regulations (ECHA 2013), and is a priority chemical in Norway whereby releases to the environment are required to be eliminated or substantially reduced by 2020 (NEA 2013).

One of our previous investigations (Greenpeace 2014) has shown that concentrations of ionic PFCs can vary widely not only between products but also within different parts of the same product. Differences in PFC levels measured for different parts reflect real variations in concentrations within each article, and do not result from the testing method itself. The variations are likely to be a characteristic of textile products treated with PFCs in general, and therefore an issue for all brands using PFCs in the manufacture of their products. The full extent of such variations, and the underlying causes, deserve further investigation.

The range of concentrations of antimony in polyester found in this study is consistent with levels reported in commercial polyester fibres (typically up to 300 mg/kg) (Duh 2002, Lacasse & Baumann 2004) and in clothing articles containing polyester fibres (in the range 1-200 mg/kg) (Laursen *et al.* 2003, Greenpeace 2012c, Greenpeace 2014, Kemi 2013).

Despite known and suspected toxicity for antimony trioxide, no regulations currently exist that prohibit use in textile manufacture, despite the availability of alternative catalysts for polyester manufacture. Within the EU, the Ecolabel

Regulation, which aims to promote products with a reduced environmental impact compared with other products in the same product group, requires that the antimony content in polyester fibres does not exceed 260 mg/kg for articles bearing the Ecolabel (EC 2009). For those fabrics analysed in the current study, antimony concentrations were below 260 mg/kg.

In this study, neither carcinogenic amines released under certain reducing conditions nor organotins were detected in any the samples investigated for these two chemical groups. Previous studies of textile products have, however, reported examples of organotins (BEUC 2012, Greenpeace 2004, Greenpeace 2012c, Laursen *et al.* 2003, TNO 2003, TNO 2005) and carcinogenic amines (JRC 2008, Laursen *et al.* 2003, Greenpeace 2012a), indicating their relevance for some textile products, though in the case of carcinogenic amines, a relatively low fraction of items commonly test positive.

Overall, this study has expanded the range of textile products that have been investigated for the presence and concentrations of a broad range of hazardous chemicals, highlighting their occurrence in luxury products across a range of brands, as well as a number of countries of manufacture and sale. The use of these and other hazardous chemicals during manufacture can be expected to result in releases from manufacturing facilities, including within wastewaters, in addition to the presence of chemical residues in the products themselves. In addition, there is the potential for losses of hazardous chemicals within the textile products following their sale, either directly such as in the case of phthalates within plastisol prints (Jenke *et al.* 2006, Fasano *et al.* 2012, Latorre *et al.* 2012), or when washed as part of their normal use, most notably for NPEs (Brigden *et al.* 2012, Greenpeace 2012b).

Although this study included a number of examples of articles from each of the brands included in the study, the number investigated is inevitably small compared to the large number of products sold by each brand. It cannot, therefore, be assumed that the results obtained in this study are representative of levels or presence of the chemicals investigated that may be expected for all such products from each brand. Rather, this study provides additional insight into what appears to be a generic problem for the textile sector that is not restricted to any particular brand, and is relevant to luxury textile products as well as other types of textile products previously investigated. The use of hazardous chemicals within this sector, and the presence of residues within final products, deserves further investigation, including from a regulatory and brand policy perspective.

5. References

- Abb M, Heinrich T, Sorkau E & Lorenz W (2009).** Phthalates in house dust. *Environment International* 35(6): 965-970
- Abdul-Ghani S, Yanai J, Abdul-Ghani R, Pinkas A & Abdeen Z (2012).** The teratogenicity and behavioral teratogenicity of di(2-ethylhexyl) phthalate (DEHP) and di-butyl phthalate (DBP) in a chick model. *Neurotoxicology and Teratology* 34(1): 56-62
- Adeoya-Osiguwa SA, Markoulaki S, Pocock V, Milligan SR & Fraser LR (2003).** 17-beta-estradiol and environmental estrogens significantly affect mammalian sperm function. *Human Reproduction* 18(1): 100-107
- Ahrens L (2011).** Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *Journal of Environmental Monitoring* 13: 20–31
- Andersen ME, Butenhoff JL, Chang S-C, Farrar DG, Kennedy GL, Lau C, Olsen GW, Seed J & Wallace KB (2008).** Perfluoroalkyl acids and related chemistries--toxicokinetics and modes of action. *Toxicological sciences* 102: 3–14
- Andrewes P, KitChendian KT & Wallace K (2004).** Plasmid DNA damage caused by stibine and trimethylstibine. *Toxicology and Applied Pharmacology* 194: 41-48
- Aso S, Ehara H, Miyata K, Hosyuyama S, Shiraishi K, Umamo T & Minobe Y (2005).** A two-generation reproductive toxicity study of butyl benzyl phthalate in rats. *Journal of Toxicological Sciences* 30(SI): 39-58
- BEUC (2012).** Chemicals in EURO 2012 shirts. The European Consumer Organisation (BEUC), <http://www.beuc.org/custom/2012-00422-01-E.pdf>; <http://www.beuc.org/custom/2012-00421-01-E.pdf>
- Blount BC, Silva MJ, Caudill SP, Needham LL, Pirkle JL, Sampson EJ, Lucier GW, Jackson RJ & Brock JW (2000).** Levels of seven urinary phthalate metabolites in a human reference population. *Environmental Health Perspectives* 108(10): 979-982
- Boberg J, Christiansen S, Axelstad M, Kledal TS, Vinggaard AM, Dalgaard M, Nellemann C & Hass U (2011).** Reproductive and behavioral effects of diisononyl phthalate (DiNP) in perinatally exposed rats. *Reproductive Toxicology* 31(2): 200-209
- Brigden K, Santillo D & Johnston P (2012).** Nonylphenol ethoxylates (NPEs) in textile products, and their release through laundering. Greenpeace Research Laboratories Technical Report 01/2012, 14pp. http://www.greenpeace.to/greenpeace/wp-content/uploads/2012/03/Dirty_Laundry_Product_Testing_Technical_Report_01-2012.pdf
- Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, De Voogt P, Jensen AA, Kannan K, Mabury SA & Van Leeuwen SP (2011).** Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integrated Environmental Assessment and Management* 7(4): 513–541
- Butt CM, Muir DC & Mabury SA (2013).** Biotransformation pathways of fluorotelomer-based polyfluoroalkyl substances: A review. *Environmental Toxicology & Chemistry*, doi: 10.1002/etc.2407. [Epub ahead of print]
- Butte W & Heinzow B (2002).** Pollutants in house dust as indicators of indoor contamination. *Reviews in Environmental Contamination and Toxicology* 175: 1-46
- Caldwell JC (2012).** DEHP: Genotoxicity and potential carcinogenic mechanisms—A review. *Mutation Research/Reviews in Mutation Research*, In Press, Corrected Proof, Available online 3 April 2012
- CEPA (2004).** Notice requiring the preparation and implementation of pollution prevention plans in respect of effluents from textile mills that use wet processing (TMEs) and nonylphenol (NP) and its ethoxylates (NPEs), under the Canadian Environmental Protection Act (CEPA), 1999. *Canada Gazette Part I*, Vol. 138, No. 49, 4 December 2004. <http://www.ec.gc.ca/planp2-p2plan/B2D19B6D-325F-458A-88E1-F69291E58DE3/g1-13849.pdf>
- Chitra KC, Latchoumycandane C & Mathur PP (2002).** Effect of nonylphenol on the antioxidant system in epididymal sperm of rats. *Archives of Toxicology* 76(9): 545-551

- Choe SY, Kim SJ, Kim HG, Lee JH, Choi Y, Lee H & Kim Y (2003).** Evaluation of estrogenicity of major heavy metals. *Science of the Total Environment* 312(1): 15–21
- Colon I, Caro D, Bourdony CJ & Rosario O (2000).** Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. *Environmental Health Perspectives* 108(9): 895-900
- Conder JM, Hoke RA, De Wolf W, Russell MH & Buck RC (2008).** Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environmental Science & Technology* 42: 995–1003
- Dalgaard M, Nellemann C, Lam HR, Sorensen IK & Ladefoged O (2001).** The acute effects of mono(2-ethylhexyl)phthalate (MEHP) on testes of prepubertal Wistar rats. *Toxicology Letters* 122: 69-79
- David A, Fenet H & Gomez E (2009).** Alkylphenols in marine environments: Distribution monitoring strategies and detection considerations. *Marine Pollution Bulletin* 58(7): 953-960
- De Boeck M, Kirsch-Volders M & Lison M (2003).** Cobalt and antimony: genotoxicity and carcinogenicity. *Mutation Research* 533: 135–152
- DeWitt J, Copeland C, Strynar M & Luebke R (2008).** Perfluorooctanoic acid-induced immunomodulation in adult C57BL/6J or C57BL/6N female mice. *Environmental Health Perspectives* 116 (5): 644-650.
- DME (2013).** Norway goes ahead with the ban on the pollutant PFOA. Danish Ministry of Environment (DME). <http://www.regjeringen.no/nb/dep/md/aktuelt/nyheter/2013/norge-gar-foran-med-forbud-mot-miljogift.html?id=735702>
- DoE (1991).** Environmental hazard assessment: Di(2-ethylhexyl)phthalate. Report TSD/2 Publ: United Kingdom Department of the Environment Toxic Substances Division. 51pp.
- Du G, Huang H, Hu J, Qin Y, Wu D, Song L, Xia Y & Wang X (2013).** Endocrine-related effects of perfluorooctanoic acid (PFOA) in zebrafish, H295R steroidogenesis and receptor reporter gene assays. *Chemosphere* 91: 1099-1106
- Duh B (2002).** Effect of antimony catalyst on solid-state poly-condensation of poly(ethylene terephthalate). *Polymer* 43(11): 3147–3154
- EC (2009).** Decision 2009/567/EC of 9 July 2009 establishing the ecological criteria for the award of the Community Ecolabel for textile products. *Official Journal of the European Communities* L197, 29.07.2009: 70-86. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:197:0070:0086:EN:PDF>
- ECHA (2013).** Candidate List of Substances of Very High Concern for Authorisation. European Chemicals Agency (ECHA). <http://echa.europa.eu/candidate-list-table>
http://echa.europa.eu/chem_data/authorisation_process/candidate_list_table_en.asp
- Ema M & Miyawaki E (2002).** Effects on development of the reproductive system in male offspring of rats given butyl benzyl phthalate during late pregnancy. *Reproductive Toxicology* 16: 71-76
- Eskes C, Honegger P, Jones-Lepp T, Varner K, Matthieu JM & Monnet-Tschudi F (1999).** Neurotoxicity of dibutyltin in aggregating brain cell cultures. *Toxicology In Vitro* 13(4-5): 555-560
- EU (2001).** Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the List of Priority Substances in the field of Water Policy and amending Directive 2000/60/EC, *Official Journal* L 249, 17/09/2002: 27-30
- EU (2002).** Directive 2002/61/EC of the European Parliament and of the Council of 19 July 2002 amending for the 19th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (azocolourants): <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2002:243:0015:0018:EN:PDF>
- EU (2003).** Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003 amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement) http://europa.eu.int/eur-lex/pri/en/oj/dat/2003/l_178/l_17820030717en00240027.pdf

EU (2005). Directive 2005/84/EC of the European Parliament and of the Council of 14 December 2005 amending for the 22nd time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (phthalates in toys and childcare articles):

<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:344:0040:0043:EN:PDF>

EU (2006). 2006/122/EC of the European Parliament and of the Council of 12 December 2006 amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the member states relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates). Official Journal L 372/32, 27.12.2006

<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:372:0032:0034:en:PDF>

EU (2010). Regulation 2010/276 of the European Parliament and of the Council of 31 March 2010 on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XVII (dichloromethane, lamp oils and grill lighter fluids and organostannic compounds).

<http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:086:0007:0012:en:PDF>

Fasano E, Bono-Blay F, Cirillo T, Montuori P & Lacorte S (2012). Migration of phthalates, alkylphenols, bisphenol A and di(2-ethylhexyl)adipate from food packaging. *Food Control* 27(1): 132-138

Fei C, McLaughlin JK, Lipworth L & Olsen J (2009). Maternal levels of perfluorinated chemicals and subfecundity. *Human Reproduction* 24: 1200–1205

Ferri M, Chiellini F, Pili G, Grimaldi L, Florio ET, Pili S, Cucci F & Latini G (2012). Di-(2-ethylhexyl)-phthalate migration from irradiated poly(vinyl chloride) blood bags for graft-vs-host disease prevention. *International Journal of Pharmaceutics* 430(1–2):Pages 86-88

Fierens T, Servaes K, Van Holderbeke M, Geerts L, De Henauf S, Sioen I & Vanermen G (2012). Analysis of phthalates in food products and packaging materials sold on the Belgian market. *Food and Chemical Toxicology* 50(7): 2575-2583

Filella M, Belzile N & Chen Y-W (2002). Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry. *Earth-Science Reviews* 59: 265–285

Fries E & Püttmann W (2004). Occurrence of 4-nonylphenol in rain and snow. *Atmospheric Environment* 38(13): 2013-2016

Frömel T & Knepper TP (2010). Biodegradation of fluorinated alkyl substances. *Reviews of Environmental Contamination and Toxicology* 208: 161–177

Fromme H, Lahrz T, Piloty M, Gebhart H, Oddoy A & Rüden H (2004). Occurrence of phthalates and musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany). *Indoor Air* 14 (3): 188-195

Fromme H, Tittlemier SA, Völkel W, Wilhelm M & Twardella D (2009). Perfluorinated compounds--exposure assessment for the general population in Western countries. *International Journal of Hygiene and Environmental Health* 212: 239–270

Fu M, Li Z & Wang B (2008). Distribution of nonylphenol in various environmental matrices in Yangtze River estuary and adjacent areas. *Marine Environmental Science* 27(6): 561-565

Giesy JP & Kannan K (2001). Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environmental Science & Technology* 35(7): 1339–1342

Grande SW, Andrade AJ, Talsness CE, Grote K & Chahoud I (2006). A dose–response study following in utero and lactational exposure to di(2-ethylhexyl)phthalate: effects on female rat reproductive development. *Toxicol. Sci.* 91: 247–254

Grandjean P, Andersen EW, Budtz-Jørgensen E, Nielsen F, Mølbak K, Weihe P & Heilmann C (2012). Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *Journal of the American Medical Association* 307(4): 391-7

Gray LE Jr, Laskey J & Ostby J (2006). Chronic di-n-butyl phthalate exposure in rats reduces fertility and alters ovarian function during pregnancy in female Long Evans hooded rats. *Toxicol. Sci.* 93: 189–195

Greaves AK, Letcher RJ, Sonne C, Dietz R & Born EW (2012). Tissue-specific concentrations and patterns of perfluoroalkyl carboxylates and sulfonates in East Greenland polar bears. *Environmental Science & Technology* 46: 11575–11583

Greenpeace (2004). Finding Chemo - Toxic Childrenswear by Disney. Greenpeace International, pp18.
<http://www.greenpeace.org/international/en/publications/reports/finding-chemo-toxic-children/>

Greenpeace (2011). Dirty Laundry 2: Hung Out to Dry - Unravelling the toxic trail from pipes to products, pp32.
http://www.greenpeace.org/international/Global/international/publications/toxics/Water%202011/Textilemanufacture_China.pdf

Greenpeace (2012a). Toxic Threads: The Big Fashion Stitch-Up.
<http://www.greenpeace.org/international/en/publications/Campaign-reports/Toxics-reports/Big-Fashion-Stitch-Up/>

Greenpeace (2012b). Dirty Laundry: Reloaded - How big brands are making consumers unwitting accomplices in the toxic water cycle, pp48.
<http://www.greenpeace.org/international/en/publications/Campaign-reports/Toxics-reports/Dirty-Laundry-Reloaded/>

Greenpeace (2012c). Chemistry for any weather: Greenpeace tests outdoor clothes for perfluorinated toxins;
<http://www.greenpeace.org/romania/Global/romania/detox/Chemistry%20for%20any%20weather.pdf>

Greenpeace (2013a). Toxic Threads: Polluting Paradise. A story of big brands and water pollution in Indonesia, pp 44; including the accompanying Technical Report, pp30.
<http://www.greenpeace.org/international/en/publications/Campaign-reports/Toxics-reports/Polluting-Paradise/>

Greenpeace (2013b). Greenpeace: Bademoden mit gefährlichen Chemikalien belastet (German).
http://www.greenpeace.de/fileadmin/gpd/user_upload/themen/chemie/Factsheet_Bademode.pdf

Greenpeace (2013c). Schadstoffe in G-Star Produkten (German)
http://www.greenpeace.de/fileadmin/gpd/user_upload/themen/chemie/20130408_Factsheet_PFOS_in_G-Star-Produkten.pdf

Greenpeace (2014). A Little Story about the Monsters in Your Closet; and accompanying Technical Report.
<http://www.greenpeace.org/eastasia/publications/reports/toxics/2014/little-story-monsters-closet/>

Guenther K, Heinke V, Thiele B, Kleist E, Prast H & Raecker T (2002). Endocrine disrupting nonylphenols are ubiquitous in food. *Environmental Science and Technology* 36(8): 1676-1680

Guerranti C, Sbordoni I, Fanello EL, Borghini F, Corsi I & Focardi SI (2012). Levels of phthalates in human milk samples from central Italy. *Microchemical Journal*, In Press, Corrected Proof, Available online 8 July 2012

Herzke D, Olsson E & Posner S (2012). Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in consumer products in Norway – A pilot study. *Chemosphere* 88: 980–987

Houde M, De Silva AO, Muir DCG & Letcher RJ (2011). Monitoring of perfluorinated compounds in aquatic biota: an updated review. *Environmental Science & Technology* 45: 7962–7973

Howdeshell KL, Wilson VS, Furr J, Lambright CR, Rider CV, Blystone CR, Hotchkiss AK & Gray LE Jr (2008). A mixture of five phthalate esters inhibits fetal testicular testosterone production in the Sprague Dawley rat in a cumulative dose additive manner. *Toxicol. Sci.* 105: 153–165

IARC (1987). Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42, supplement 7. International Agency for Research on Cancer (IARC).
<http://monographs.iarc.fr/ENG/Monographs/suppl7/index.php>

IARC (1989). International Agency for Research on Cancer (IARC) Monographs programme on the evaluation of carcinogenic risks to humans: Some Organic Solvents, Resin Monomers and Related Compounds, Pigments and Occupational Exposures in Paint Manufacture and Painting vol. 47, pp. 291–306

IARC (1998). Aromatic amines. In: International Agency for Research on Cancer (IARC) monographs on the evaluation of the carcinogenic risk of chemicals to humans. Volume 4; Some aromatic amines, hydrazine and related substances, N-nitroso compounds and miscellaneous alkylating agents, updated 1998.
<http://monographs.iarc.fr/ENG/Monographs/vol4/volume4.pdf>

- IARC (2008).** International Agency for Research on Cancer (IARC) monographs on the evaluation of the carcinogenic risk of chemicals to humans. Volume 99; Some Aromatic Amines, Organic Dyes, and Related Exposures. <http://monographs.iarc.fr/ENG/Monographs/vol99/mono99.pdf>
- Iwata M, Eshima Y, Kagechika H & Miyaura H (2004).** The endocrine disruptors nonylphenol and octylphenol exert direct effects on T cells to suppress Th1 development and enhance Th2 development. *Immunology Letters* 94(1-2): 135-139
- Jaffe M & East AJ (2007).** Polyester fibres. In: Lewin, M. Handbook of fibre chemistry. 3rd Ed CRC press ISBN 0-8247-2565-4
- Jenke DR, Story J & Lalani R (2006).** Extractables/leachables from plastic tubing used in product manufacturing. *International Journal of Pharmaceutics* 315(1–2): 75-92
- Jenkins SM & Barone S (2004).** The neurotoxicant trimethyltin induces apoptosis via capase activation, p38 protein kinase, and oxidative stress in PC12 cells. *Toxicology Letters* 147 (1): 63-72
- Jenkins SM, Ehman K & Barone S (2004).** Structure-activity comparison of organotin species: dibutyltin is a developmental neurotoxicant in vitro and in vivo. *Developmental Brain Research* 151 (1-2): 1-12
- Jensen A & Leffers H (2008).** Emerging endocrine disrupters: perfluoroalkylated substances. *International Journal of Andrology* 31: 161-169
- Jobling S, Sheahan D, Osborne JA, Matthiessen P & Sumpter JP (1996).** Inhibition of testicular growth in rainbow trout (*Oncorhynchus mykiss*) exposed to estrogenic alkylphenolic chemicals. *Environmental Toxicology and Chemistry* 15(2): 194-202
- Jobling S, Reynolds T, White R, Parker MG & Sumpter JP (1995).** A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspectives* 103(6): 582-587
- Joensen UN, Bossi R, Leffers H, Jensen AA, Skakkebaek NE & Jørgensen N (2009).** Do perfluoroalkyl compounds impair human semen quality? *Environmental Health Perspectives* 117: 923–927.
- JRC (2008).** European survey on the presence of banned azodyes in textiles, EUR 23447 EN – 2008. Joint Research Commission, Institute for Health and Consumer Protection, European Commission. ISBN 978-92-79-09118-6. http://publications.jrc.ec.europa.eu/repository/bitstream/11111111/1321/1/eur_23447_en_fr_aa.pdf
- KEMI (2013).** Hazardous chemicals in textiles – report of a government assignment, The Swedish Chemical Agency, Report no. 3/13. <http://www.kemi.se/Documents/Publikationer/Trycksaker/Rapporter/Rapport-3-13-textiles.pdf>
- Kergosien DH & Rice CD (1998).** Macrophage secretory function is enhanced by low doses of tributyltin-oxide (TBTO), but not tributyltin-chloride (TBTCI). *Arc. Environ. Contam. Toxicol.* 34: 223-228
- Kim HA, Heo Y, Oh SY, Lee KJ & Lawrence DA (1999).** Altered serum cytokine and immunoglobulin levels in the workers exposed to antimony. *Human and Experimental Toxicology* 18(10): 607-613
- Koch HM, Preuss R & Angerer J (2006).** Di(2-ethylhexyl)phthalate (DEHP): human metabolism and internal exposure—an update and latest results. *Int. J. Androl.* 29: 155–165
- Lacasse K & Baumann W (2004).** Textile Chemicals: Environmental data and facts. Springer- Verlag ISBN 3-540-40815-0
- Langer S, Weschler CJ, Fischer A, Bekö G, Toftum L & Clausen G (2010).** Phthalate and PAH concentrations in dust collected from Danish homes and daycare centers. *Atmospheric Environment* 44(19):2294-2301
- Langer V, Dreyer A & Ebinghaus R (2010).** Polyfluorinated compounds in residential and nonresidential indoor air. *Environmental Science & Technology* 44(21): 8075-81
- Latorre I, Hwang S, Sevillano M & Montalvo-Rodríguez R (2012).** PVC biodeterioration and DEHP leaching by DEHP-degrading bacteria. *International Biodeterioration & Biodegradation* 69:73-81
- Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A & Seed J (2007).** Perfluoroalkyl Acids: A Review of monitoring and toxicological findings. *Toxicological Sciences* 99: 366-394.

Lau JH, Wong CP, Lee NC & Ricky Lee SW (2003). Electronics Manufacturing with Lead-Free, Halogen-Free & Conductive-Adhesive materials. McGraw-Hill. ISBN 0071386246

Laursen SE, Hansen J, Drøjdahl A, Hansen OC, Pommer K, Pedersen E & Bernth N (2003). Survey of chemical compounds in textile fabrics. Survey no. 23, on behalf of the Danish Environmental Protection Agency. <http://www.mst.dk/NR/rdonlyres/B9CDE217-9E41-4F27-A8A3-921D5B50A737/0/23.pdf>

Lin H, Ge R-S, Chen G-R, Hu G-X, Dong L, Lian Q-Q, Hardy DO, Sottas CM, Li X-K & Hardy MP (2008). Involvement of testicular growth factors in fetal Leydig cell aggregation after exposure to phthalate in utero. Proc. Natl Acad. Sci. USA 105(20): 7218–7222

Liu C, Deng J, Yu L, Ramesh M & Zhou B (2010). Endocrine disruption and reproductive impairment in zebrafish by exposure to 8:2 fluorotelomer alcohol. Aquatic Toxicology 96(1): 70-6

Liu C, Yu L, Deng J, Lam PK, Wu RS & Zhou B (2009). Waterborne exposure to fluorotelomer alcohol 6:2 FTOH alters plasma sex hormone and gene transcription in the hypothalamic-pituitary-gonadal (HPG) axis of zebrafish. Aquatic Toxicology 93(2-3): 131-7

Liu H, Liang Y, Zhang D, Wang C, Liang H & Cai H (2010). Impact of MSW landfill on the environmental contamination of phthalate esters. Waste Management 30(8–9):1569-1576

Loi EIH, Yeung LWY, Taniyasu S, Lam PKS, Kannan K & Yamashita N (2011). Trophic magnification of poly- and perfluorinated compounds in a subtropical food web. Environmental Science & Technology 45: 5506–5513

Lopez-Espinosa MJ, Freire C, Arrebola JP, Navea N, Taoufiki J, Fernandez MF, Ballesteros O, Prada R & Olea N (2009). Nonylphenol and octylphenol in adipose tissue of women in Southern Spain. Chemosphere 76(6): 847-852

Lovekamp-Swan T & Davis BJ (2003). Mechanisms of phthalate ester toxicity in the female reproductive system. Environmental Health Perspectives 111(2): 139-145

Lui JY, Li JG, Zhao YF, Wang YX, Zhang L, Wu YN (2010). The occurrence of perfluorinated alkyl compounds in human milk from different regions of China. Environment International 36 (5): 433-438.

Lye CM, Frid CLJ, Gill ME, Cooper DW & Jones DM (1999). Estrogenic alkylphenols in fish tissues, sediments, and waters from the UK Tyne and Tees estuaries. Environmental Science & Technology 33(7): 1009-1014

Martino-Andrade AJ, Morais RN, Botelho GG, Muller G, Grande SW, Carpentieri GB, Leão GM & Dalsenter PR (2008). Coadministration of active phthalates results in disruption of foetal testicular function in rats. Int. J. Androl., Dec. 2008: 9pp. (DOI 10.1111/j.1365-2605.2008.00939)

Matthews G (1996). PVC: Production, Properties and Uses. The Institute of Materials, London: 379 pp.

Mayer T, Bennie D, Rosa F, Palabrica V, Rekas G, Schachtschneider J & Marvin C (2008). Dispersal of Contaminants from Municipal Discharges as Evidenced from Sedimentary Records in a Great Lakes Coastal Wetland, Cootes Paradise, Ontario. Journal of Great Lakes Research 34(3): 544-558

Melzer D, Rice N, Depledge MH, Henley WE & Galloway TS (2010). Association between serum perfluorooctanoic acid (PFOA) and thyroid disease in the U.S. National Health and Nutrition Examination Survey. Environmental Health Perspectives 118(5): 686–692

MEP (2011). List of Toxic Chemicals Severely Restricted on the Import and Export in China (2011). Ministry of Environmental Protection (MEP), The People's Republic of China. http://www.crc-mep.org.cn/news/NEWS_DP.aspx?TitID=267&T0=10000&LanguageType=CH&Sub=125

Micic V & Hofmann T (2009). Occurrence and behaviour of selected hydrophobic alkylphenolic compounds in the Danube River. Environmental Pollution 157(10): 2759-2768

Mylchreest E, Sar M, Wallace DG & Foster PMD (2002). Fetal testosterone insufficiency and abnormal proliferation of Leydig cells and gonocytes in rats exposed to di(n-butyl) phthalate. Reproductive Toxicology 16: 19-28

Nam S-H, Yang C-Y & An Y-J (2009). Effects of antimony on aquatic organisms (Larva and embryo of *Oryzias latipes*, *Moina macrocopa*, *Simocephalus mixtus*, and *Pseudokirchneriella subcapitata*). Chemosphere 75: 889–893

- NEA (2013).** Flere stoffer på ver Stinglista (additional substances added to the priority list), Norwegian Environment agency (NEA). <http://www.miljodirektoratet.no/no/Nyheter/Nyheter/2013/November-2013/Flere-stoffer-pa-verstinglista/> (Norwegian)
- Nilsson H, Kärrman A, Rotander A, Van Bavel B, Lindström G & Westberg H (2013).** Biotransformation of fluorotelomer compound to perfluorocarboxylates in humans. *Environment International* 51: 8-12
- NME (2013).** Norway goes ahead with the ban on the pollutant PFOA. Norwegian Ministry of Environment (NME). <http://www.regjeringen.no/nb/dep/md/aktuelt/nyheter/2013/norge-gar-foran-med-forbud-mot-miljogift.html?id=735702> (Norwegian)
- OECD-UNEP (2013).** Synthesis paper on per- and polyfluorinated chemicals (PFCs). OECD/UNEP Global PFC Group, Organisation for Economic Cooperation and Development (OECD) & United Nations Environment Program (UNEP). <http://www.oecd.org/env/ehs/risk-management/synthesis-paper-on-per-and-polyfluorinated-chemicals.htm>
- Olsen GW, Lange CC, Ellefson ME, Mair DC, Church TR, Goldberg CL, Herron RM, Medhdzidehkashi Z, Nobiletti JB, Rios JA, Reagen WK & Zobel LR (2012).** Temporal Trends of Perfluoroalkyl Concentrations in American Red Cross Adult Blood Donors, 2000–2010. *Environmental Science & Technology* 46: 6330-6338
- OSPAR (1998).** OSPAR Strategy with Regard to Hazardous Substances, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR 98/14/1 Annex 34
- OSPAR (2004).** Nonylphenol/nonylphenolethoxylates, OSPAR Priority Substances Series 2001, updated 2004, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London, ISBN 0-946956-79-0: 20 pp.
- OSPAR (2011).** OSPAR Background Document on Organic Tin Compounds, OSPAR Priority Substances Series, Publication Number: 535/2011. OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London. ISBN 978-1-907390-76-0
- Otake T, Yoshinaga J & Yanagisawa Y (2001).** Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD. *Environmental Science and Technology* 35(15): 3099-3102
- Pang K, Kotek R & Tonelli A (2006).** Review of conventional and novel polymerization processes for polyesters. *Progress in Polymer Sciences*, 31(11): 1009–1037
- PARCOM (1992).** PARCOM Recommendation 92/8 on nonylphenol-ethoxylates, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR Commission, London: 1 p.
- Patterson TJ, Ngo M, Aronov PA, Reznikova TV, Green PG & Rice RH (2003).** Biological activity of inorganic arsenic and antimony reflects oxidation state in cultured human keratinocytes. *Chemical Research in Toxicology* 16(12): 1624-1631
- Peden-Adams M, Keller J, EuDaly J, Berger J, Gilkeson G & Keil D (2008).** Suppression of humoral immunity in mice following exposure to perfluorooctane sulphonate. *Toxicological Sciences* 104 (1): 144-154.
- Peters RJB, Beeltje H & Van Delft RJ (2008).** Xeno-estrogenic compounds in precipitation. *Journal of Environmental Monitoring* 10: 760-769
- Poulsen PB & Jensen AA (2005).** More environmentally friendly alternatives to PFOS-compounds and PFOA Danish Environmental Protection Agency Environmental Project No. 1013 Miljøprojekt
- Rand AA & Mabury SA (2012).** In vitro interactions of biological nucleophiles with fluorotelomer unsaturated acids and aldehydes: fate and consequences. *Environmental Science & Technology* 46(13): 7398-406
- Rice CP, Schmitz-Afonso I, Loyo-Rosales JE, Link E, Thoma R, Fay L, Altfater D & Camp MJ (2003).** Alkylphenol and alkylphenol-ethoxylates in carp, water, and sediment from the Cuyahoga River, Ohio. *Environmental Science & Technology* 37(17): 3747–3754
- Rosenmai AK, Nielsen FK, Pedersen M, Hadrup N, Trier X, Christensen JH & Vinggaard AM (2013).** Fluorochemicals used in food packaging inhibit male sex hormone synthesis. *Toxicology & Applied Pharmacology* 266: 132–142

- Rudel RA, Camann DE, Spengler JD, Korn LR & Brody JG (2003).** Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. *Environmental Science and Technology* 37(20): 4543-4553
- SAC (2012a).** GB18401-2010, National general safety technical code for textile products. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Standardization Administration of the People's Republic of China (SAC)
- SAC (2012b).** The safety technical code for infants and children textile products (edition for authorizing/approval). General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China & Standardization Administration of the People's Republic of China (SAC).
<http://www.cttc.net.cn/Upload/fck/E85819E943C6D099FFB911B819472341C442E47D.pdf>
- SAC (2013).** Toys safety, Part 1: Basic Code, GB 6675.1—201. SAC (Standardization Administration of the People's Republic of China http://www.sac.gov.cn/zwgk/wtotb/tbttb/201307/t20130702_138723.htm (Chinese)
- Saito I, Onuki A & Seto H (2004).** Indoor air pollution by alkylphenols in Tokyo. *Indoor Air* 14(5): 325-332
- Schlummer M, Gruber L, Fiedler D, Kizlauskas M & Müller J (2013).** Detection of fluorotelomer alcohols in indoor environments and their relevance for human exposure. *Environment International* 57-58: 42-9
- Schnorr TM, Steenland K, Thun MJ & Rinsky RA (1995).** Mortality in a cohort of antimony smelter workers. *American Journal of Industrial Medicine* 27(5): 759-770
- Shue MF, Chen FA & Chen TC (2010).** Total estrogenic activity and nonylphenol concentration in the Donggang River, Taiwan. *Environmental Monitoring and Assessment*, 168: 91-101
- Silva MJ, Barr DB, Reidy JA, Malek NA, Hodge CC, Caudill SP, Brock JW, Needham LL & Calafat AM (2004).** Urinary levels of seven phthalate metabolites in the U.S. population from the National Health and Nutrition Examination Survey (NHANES) 1999-2000. *Environmental Health Perspectives* 112(3): 331-338
- SSNC FoEN (2006).** Fluorinated pollutants in all-weather clothing. Norwegian Society for the Conservation of Nature/Friends of the Earth Norway and Swedish Society for Nature Conservation, January 2005, ISBN 91558 0721 6: 43 pp.
- Swan SH, Main KM, Liu F, Stewart SL, Kruse RL, Calafat AM, Mao CS, Redmon JB, Ternand CL, Sullivan S & Teague JL (2005).** Decrease in anogenital distance among male infants with prenatal phthalate exposure. *Environmental Health Perspectives* 113(8): 1056-1061
- Tao L, Ma J, Kunisue T, Libelo EL, Tanabe S & Kannan K (2008).** Perfluorinated compounds in human breast milk from several Asia countries, and infant formula and dairy milk from the United States. *Environmental Science and Technology* 42: 8597-8602
- Thiele UK (2004).** Quo vadis polyester catalyst? *Chemical Fibres International* 54: 162-163.
- Thier-Grebe R & Rabe M (2000).** Polyester with titanium dioxide catalyst 'C-94'. Property Acordis, October: 1–11. In Pang K, Kotek R, Tonelli A (2006). Review of conventional and novel polymerization processes for polyesters. *Progress in Polymer Sciences*, 31(11): 1009–1037
- Thomsen C, Haug LS, Stigum H, Frøshaug M, Broadwell SL & Becher G (2010).** Changes in concentrations of perfluorinated compounds, polybrominated diphenyl ethers, and polychlorinated biphenyls in Norwegian breast-milk during twelve months of lactation. *Environmental Science and Technology* 44: 9550–9556
- TNO (2003).** Hazardous Chemicals in Consumer Products. TNO Netherlands Organisation for Applied Scientific Research.
<http://www.greenpeace.org/international/PageFiles/24502/hazardous-chemicals-in-consume.pdf>
- TNO (2005).** Chemical Additives in Consumer Products. TNO Netherlands Organisation for Applied Scientific Research.
<http://www.greenpeace.org/international/Global/international/planet-2/report/2005/4/chemical-additives-in-consumer.pdf>
- Tonk ECM, De Groot DMG, Penninks AH, Waalkens-Berendsen IDH, Wolterbeek APM, Piersma AH, Van Loveren H (2011b).** Developmental immunotoxicity of di-n-octyltin dichloride (DOTC) in an extended one-generation reproductive toxicity study. *Toxicology Letters* 204(2–3): 156-163

- Tonk ECM, Verhoef A, De la Fonteyne LJJ, Waalkens-Berendsen IDH, Wolterbeek APM, Van Loveren H, Piersma AH (2011a).** Developmental immunotoxicity in male rats after juvenile exposure to di-n-octyltin dichloride (DOTC). *Reproductive Toxicology* 32(3): 341-348
- UNEP (2009).** Adoption of amendments to Annexes A, B and C of the Stockholm Convention on Persistent Organic Pollutants under the United Nations Environment Programme (UNEP).
<http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP-NOTIF-DN-CN524-2009.English.pdf>
- USPEA (2010).** Nonylphenol (NP) and Nonylphenol Ethoxylates (NPEs) Action Plan. Unites States Environmental Protection Agency (USEPA), August 18, 2010.
<http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/np-npe.html>
- Weinberg I, Dreyer A & Ebinghaus R (2011).** Waste water treatment plants as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air, *Environmental Pollution* 59(1): 125-32
- White SS, Fenton SE & Hines EP (2011).** Endocrine disrupting properties of perfluorooctanoic acid. *Journal of Steroid Biochemistry and Molecular Biology* 127: 16–26
- Ying GG, Kookana RS, Kumar A & Mortimer M (2009).** Occurrence and implications of estrogens and xenoestrogens in sewage effluents and receiving waters from South East Queensland. *Science of the Total Environment* 407(18): 5147-5155
- Young CJ & Mabury SA (2010).** Atmospheric perfluorinated acid precursors: chemistry, occurrence, and impacts. *Reviews of Environmental Contamination and Toxicology* (208): 1–109
- Yu Y, Zhai H, Hou S & Sun H (2009).** Nonylphenol ethoxylates and their metabolites in sewage treatment plants and rivers of Tianjin, China. *Chemosphere* 77(1): 1-7

For more information, contact:
pressdesk.int@greenpeace.org

Greenpeace International
Ottho Heldringstraat 5
1066 AZ Amsterdam
The Netherlands
Tel: +31 20 7182000

greenpeace.org

Appendix 1:

Concentration of NPEs, carcinogenic amines, phthalates, organotins, ionic PFCs, volatile PFCs and antimony in all articles tested

Sample code	Brand	Place of sale	Place of manufacture	Type of product	Fabric	NPEs (mg/kg)	Amines (mg/kg)	Phthalate total (mg/kg)	Organotin total (mg/kg)	Ionic PFCs (µg/kg)	Volatile PFCs (µg/kg)	Antimony in fabric (mg/kg)	Antimony polyester (mg/kg)*
TX13033	Dior	China	Morocco	t-shirt	100% cotton	560	-	13	-	-	-	-	-
TX13034	Dior	Taiwan	Morocco	polo shirt	100% cotton	460	-	-	-	-	-	-	-
TX13035	Dior	France	unknown	t-shirt	92% cotton, 8% elastane	<1.0	-	-	-	-	-	-	-
TX13036	Dior	France	Italy	trainers	not specified	75	-	-	-	6.88	ND	-	-
TX13037	Dior	Italy	unknown	t-shirt	main 100% cotton; ribbing 97% cotton, 3% elastane	<1.0	-	-	-	-	-	-	-
TX13038	Dior	Russia	Morocco	t-shirt	100% cotton	4.0	-	48	-	-	-	-	-
TX13039	Dior	Switzerland	Italy	knitted top	70% cashmere, 30% silk	400	<5	-	-	-	-	-	-
TX13045	Dolce & Gabbana	Hong Kong	Italy	t-shirt	100% cotton	6.1	-	4.1	<0.1	-	-	-	-
TX13046	Dolce & Gabbana	Italy	Italy	t-shirt	50% cotton, 50% polyester	2.1	-	-	-	-	-	117	234
TX13047	Dolce & Gabbana	Russia	Hungary	skirt	100% cotton	<1.0	<5	-	-	-	-	-	-
TX13059	Giorgio Armani	China	China	swimsuit	outshell-1 80% polyamide, 20% elastane; outshell-2 100% polyester; lining 92% polyamid, 8% elastane	<1.0	-	-	-	4.50	ND	-	-
TX13060	Giorgio Armani	Italy	China	t-shirt	100% cotton	<1.0	<5	-	-	-	-	-	-
TX13061	Giorgio Armani	Italy	China	shorts	fabric 1 100% cotton; fabric 2 55% cotton, 45% polyester	<1.0	<5	-	-	-	-	54	120
TX13062	Giorgio Armani	Italy	China	t-shirt	100% cotton	<1.0	<5	-	-	-	-	-	-
TX13070	Hermes	China	Italy	baby shawl	100% cotton	<1.0	-	-	-	-	-	-	-
TX13071	Hermes	France	unknown	baby booties	dipped lambskin	380	<5	-	<0.1	-	-	-	-
TX13076	Louis Vuitton	Hong Kong	Italy	shoes	upper calf leather; sole rubber	370	-	-	<0.1	-	-	-	-
TX13077	Louis Vuitton	France	Italy	trainers	suede	100	-	-	<0.1	2.52	ND	-	-
TX13078	Louis Vuitton	Switzerland	Italy	ballerina shoes	suede	760	<5	-	<0.1	16.9	31	-	-
TX13079	Marc Jacobs	Italy	Thailand	body suit	93% cotton 7% elastane	1.7	-	40	-	-	-	-	-
TX13080	Marc Jacobs	Italy	Turkey	t-shirt	100% cotton	<1.0	-	46	<0.1	-	-	-	-
TX13081	Marc Jacobs	Denmark	India	t-shirt	100% cotton	<1.0	<5	-	<0.1	-	-	-	-
TX13103	Trussardi	Italy	unknown	t-shirt	96% cotton, 4% elastane	<1.0	<5	-	-	-	-	-	-
TX13104	Trussardi	Italy	Turkey	t-shirt	95% cotton, 5% elastane	<1.0	<5	-	-	-	-	-	-
TX13105	Trussardi	Italy	unknown	t-shirt	96% cotton, 4% elastane	<1.0	-	-	-	-	-	-	-
TX13109	Versace	Italy	Italy	jacket	fabric 1 100% polyester; fabric 2 100% cotton; lining component 96% cotton, 4% elasthan	<1.0	-	-	-	8.41	374	110	110
TX13110	Versace	UK	Italy	t-shirt	96% cotton, 4% elasthan	<1.0	<5	-	-	-	-	-	-

Table A1. Details of all articles, including the concentrations of NPEs, carcinogenic amines, phthalates, organotins, PFCs and antimony. For carcinogenic amines “<5 mg/kg” indicates that all quantified amines were below the detection limit (<5 mg/kg). For phthalates, organotins and PFCs, the total concentration of the quantified individual compounds in each group is given, with data for individual phthalates, organotins and PFCs provided in Appendices 2, 3 and 4 respectively. ND = not detected. “-” indicates not tested.

* Where fabric was composed of mixed fibres, the concentration of antimony in the polyester portion was calculated from fabric composition information, on the basis that all antimony arose from the polyester fibre within the fabric blend.

Appendix 2:

Concentration of individual phthalates in the five articles tested

Sample code	Brand	Type of product	DiBP (mg/kg)	DMP (mg/kg)	DEP (mg/kg)	DnBP (mg/kg)	BBP (mg/kg)	DEHP (mg/kg)	DnOP (mg/kg)	DiNP (mg/kg)	DiDP (mg/kg)	Total* (mg/kg)
TX13033	Dior	t-shirt	<3.0	<3.0	<3.0	<3.0	<3.0	4.4	<3.0	8.1	<3.0	13
TX13038	Dior	t-shirt	8.9	<3.0	19	4.3	<3.0	16	<3.0	<10	<10	48
TX13045	Dolce & Gabbana	t-shirt	<3.0	<3.0	<3.0	<3.0	<3.0	4.1	<3.0	<3.0	<3.0	4.1
TX13080	Marc Jacobs	t-shirt	12	<3.0	<3.0	3.4	<3.0	25	<3.0	<3.0	<3.0	40
TX13081	Marc Jacobs	t-shirt	8.0	26	<3.0	6.4	<3.0	6.0	<3.0	<3.0	<3.0	46

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

* Total concentration to 2 significant figures

Appendix 3:

Concentrations of individual organotins in the seven articles tested

Sample code	Brand	Type of product	Material analysed	MBT (mg/kg)	DBT (mg/kg)	DOT (mg/kg)	TBT (mg/kg)	TPhT (mg/kg)	MOT (mg/kg)	TTBT (mg/kg)	TCHT (mg/kg)	Total (mg/kg)
Plastisol print												
TX13045a	Dolce &	t-shirt	print black & grey	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13045b	Gabbana		print blue, red, blue, light blue	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13080a	Marc Jacobs	t-shirt	fabric/print plastic white	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13080b			print plastic dark blue	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13081	Marc Jacobs	t-shirt	fabric/print plastic white & black	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Footwear												
TX13071	Hermes	baby booties	leather orange & white (side wall)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13076a	Louis Vuitton	shoes	leather white & grey	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13076b			plastic white & foam grey	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13077	Louis Vuitton	sneakers	leather brown & white	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TX13078	Louis Vuitton	ballerina shoes	leather black	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table A3. Concentrations (mg/kg) of the following organotins; monobutyltin (MBT), dibutyltin (DBT), dioctyltin (DOT), tributyltin (TBT), triphenyltin (TPhT), mono-octyltin (MOT), tetrabutyltin (TTBT), tricyclohexyltin (TCHT). Data for two individual subsamples is given for some articles where more than one type of fabric was analysed.

Appendix 4:

Concentrations of individual PFCs in the five articles tested

Sample code	Brand	Type of product	PFBS (ng/kg)	PFHxS (ng/kg)	PFHpS (ng/kg)	PFOS (ng/kg)	PFDS (ng/kg)	PFBA (ng/kg)	PFPA (ng/kg)	PFHxA (ng/kg)	PFHpA (ng/kg)	PFOA (ng/kg)	PFNA (ng/kg)	PFDA (ng/kg)	PFUnA (ng/kg)	PFDoA (ng/kg)	PFTra (ng/kg)	PFTeA (ng/kg)	PFOSA (ng/kg)	PF-3,7-DMOA (ng/kg)	HPFHpA (ng/kg)	H2PFDA (ng/kg)	H4PFOS; 6:2 FTS (ng/kg)	Total (µg/kg)
TX13036	Dior	trainers (footwear)	< 1750	< 1750	< 1750	< 1160	< 1750	6880	< 1160	< 1160	< 1160	< 1210	< 1160	< 1160	< 1160	< 1160	< 1160	< 1160	< 1160	< 2330	< 2330	< 2330	< 1750	6.88
TX13077	Louis Vuitton	trainers (footwear)	< 846	< 846	< 846	< 564	< 846	1650	< 564	< 564	< 564	< 564	< 564	868	< 564	< 564	< 564	< 564	< 564	< 1130	< 1130	< 1130	< 846	2.52
TX13078	Louis Vuitton	ballerina shoes (footwear)	< 966	< 966	< 966	< 644	< 966	15700	< 644	< 644	< 644	1190	< 644	< 644	< 644	< 644	< 644	< 644	< 644	< 1290	< 1290	< 1290	< 966	16.9
TX13059	Giorgio Armani	swimwear (swimwear)	< 758	< 758	< 758	< 505	< 758	3180	< 505	< 505	< 505	< 505	< 505	< 505	< 505	< 505	< 505	< 505	< 505	< 1010	1320	< 1010	< 758	4.5
TX13109	Versace	jacket (waterproof)	< 1970	< 1970	< 1970	< 1320	< 1970	< 1320	< 1320	< 1320	< 1320	4750	< 1320	3660	< 1320	< 1320	< 1320	< 1320	< 1320	< 2630	< 2630	< 2630	< 1970	8.41

Table A4a. Concentrations of ionic PFCs* by mass (ng/kg; 1000 ng/kg = 1 µg/kg) in waterproof clothing, footwear or swimwear, with total concentration for 21 compounds (µg/kg)

Sample code	Brand	Type of product	PFBS (µg/m²)	PFHxS (µg/m²)	PFHpS (µg/m²)	PFOS (µg/m²)	PFDS (µg/m²)	PFBA (µg/m²)	PFPA (µg/m²)	PFHxA (µg/m²)	PFHpA (µg/m²)	PFOA (µg/m²)	PFNA (µg/m²)	PFDA (µg/m²)	PFUnA (µg/m²)	PFDoA (µg/m²)	PFTra (µg/m²)	PFTeA (µg/m²)	PFOSA (µg/m²)	PF-3,7-DMOA (µg/m²)	HPFHpA (µg/m²)	H2PFDA (µg/m²)	H4PFOS; 6:2 FTS (µg/m²)	Total (µg/m²)	
TX13036	Dior	trainers (footwear)	<0.972	<0.972	<0.972	<0.644	<0.972	3.82	<0.644	<0.644	<0.644	<0.672	<0.644	<0.644	<0.644	<0.644	<0.644	<0.644	<0.644	<0.644	<1,294	<1,294	<1,294	<0.972	3.82
TX13077	Louis Vuitton	trainers (footwear)	<0.823	<0.823	<0.823	<0.548	<0.823	1.61	<0.548	<0.548	<0.548	<0.548	<0.548	0.845	<0.548	<0.548	<0.548	<0.548	<0.548	<0.548	<1,099	<1,099	<1,099	<0.823	2.45
TX13078	Louis Vuitton	ballerina shoes (footwear)	<0.433	<0.433	<0.433	<0.288	<0.433	7.04	<0.288	<0.288	<0.288	0.533	<0.288	<0.288	<0.288	<0.288	<0.288	<0.288	<0.288	<0.288	<0,578	<0,578	<0,578	<0.433	7.58
TX13059	Giorgio Armani	swimwear (swimwear)	<0.151	<0.151	<0.151	<0.101	<0.151	0.636	<0.101	<0.101	<0.101	<0.101	<0.101	<0.101	<0.101	<0.101	<0.101	<0.101	<0.101	<0,202	0.264	<0,202	<0.151	0.900	
TX13109	Versace	jacket (waterproof)	<0.137	<0.137	<0.137	<0.092	<0.137	<0.092	<0.092	<0.092	<0.092	0.333	<0.092	0.256	<0.092	<0.092	<0.092	<0.092	<0.092	<0.092	<0,184	<0,184	<0,184	<0.137	0.589

Table A4b. Concentrations of ionic PFCs* by area (µg/m²) in waterproof clothing, footwear or swimwear, with total concentration for 21 compounds (µg/m²)

Sample code	Brand	Type of product	6:2 FTA (µg/kg)	8:2 FTA (µg/kg)	10:2 FTA (µg/kg)	4:2 FTOH (µg/kg)	6:2 FTOH (µg/kg)	8:2 FTOH (µg/kg)	10:2 FTOH (µg/kg)	MeFOSE (µg/kg)	EtFOSE (µg/kg)	MeFOSA (µg/kg)	EtFOSA (µg/kg)	Total (µg/kg)
TX13036	Dior	trainers (footwear)	< 14	< 14	< 14	< 47	< 160	< 120	< 56	< 9	< 9	< 9	< 9	ND
TX13077	Louis Vuitton	trainers (footwear)	< 12	< 12	< 12	< 38	< 130	< 100	< 46	< 8	< 8	< 8	< 8	ND
TX13078	Louis Vuitton	ballerina shoes (footwear)	< 14	31	< 14	< 45	< 150	< 120	< 54	< 9	< 9	< 9	< 9	31
TX13059	Giorgio Armani	swimwear (swimwear)	< 14	< 14	< 14	< 46	< 160	< 120	< 55	< 9	< 9	< 9	< 9	ND
TX13109	Versace	jacket (waterproof)	< 15	34	< 17	< 51	< 170	210	130	< 10	< 10	< 10	< 10	374

Table A4c. Concentrations of volatile PFCs* by mass (µg/kg) in waterproof clothing, footwear or swimwear, with total concentration for 11 compounds (µg/kg)

Sample code	Brand	Type of product	6:2 FTA (µg/m²)	8:2 FTA (µg/m²)	10:2 FTA (µg/m²)	4:2 FTOH (µg/m²)	6:2 FTOH (µg/m²)	8:2 FTOH (µg/m²)	10:2 FTOH (µg/m²)	MeFOSE (µg/m²)	EtFOSE (µg/m²)	MeFOSA (µg/m²)	EtFOSA (µg/m²)	Total (µg/m²)
TX13036	Dior	trainers (footwear)	<7.20	<7.20	<7.20	<24.1	<82.3	<61.7	<28.8	<4.63	<4.63	<4.63	<4.63	ND
TX13077	Louis Vuitton	trainers (footwear)	<12.5	<12.5	<12.5	<39.8	<136.	<104.	<48.2	<8.38	<8.38	<8.38	<8.38	ND
TX13078	Louis Vuitton	ballerina shoes (footwear)	<6.27	13.9	<6.27	<20.1	<67.2	<53.7	<24.2	<4.03	<4.03	<4.03	<4.03	13.9
TX13059	Giorgio Armani	swimwear (swimwear)	<2.94	<2.94	<2.94	<9.66	<33.6	<25.2	<11.5	<1.89	<1.89	<1.89	<1.89	ND
TX13109	Versace	jacket (waterproof)	<1.05	2.38	<1.19	<3.57	<11.9	14.7	9.10	<0.70	<0.70	<0.70	<0.70	26.2

* Individual PFCs included the following;

Ionic PFCs:

Perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS), perfluorobutanoate (PFBA), perfluoropentanoate (PFPA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorotridecanoate (PFTra), perfluorotetradecanoate (PFTeA), perfluorooctane sulfonamide (PFOSA), perfluoro-3,7-dimethyloctanoate (PF-3,7-DMOA), 7H-dodecafluoroheptanoate (HPFHpA), 2H,2H-perfluorodecanoate (H2PFDA), 2H,2H,3H,3H-perfluoroundecanoate (H4PFUnA)

Volatile PFCs:

1H,1H,2H,2H-perfluorooctylacrylate (6:2 FTA), 1H,1H,2H,2H-perfluorodecylacrylate (8:2 FTA), 1H,1H,2H,2H-perfluorododecylacrylate (10:2 FTA), 1H,1H,2H,2H-perfluoro-1-hexanol (4:2 FTOH), 1H,1H,2H,2H-perfluoro-1-oktanol (6:2 FTOH), 1H,1H,2H,2H-perfluoro-1-decanol (8:2 FTOH), 1H,1H,2H,2H-perfluoro-1-dodecanol (10:2 FTOH), 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (MeFOSE), 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (EtFOSE), N-methylperfluoro-1-octanesulfonamide (MeFOSA), N-ethylperfluoro-1-octanesulfonamide (EtFOSA)