

Hazardous chemicals in a selection of textile products manufactured in Shishi City & Huzhou City during 2013

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

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

Executive summary

In previous studies, we have shown that a wide range of textile products, manufactured and sold in many countries around the world, can contain an array of residues of hazardous substances, including hormone-disrupting alkylphenols and their ethoxylates, reprotoxic phthalates and, in some cases, azo dye precursors of carcinogenic amines. The current study extends this work to include a set of 85 additional clothing products manufactured in one of two cities in China (Shishi City in Fujian Province and the Zhili region of Huzhou City in Zhejiang Province), as well as extending the range of chemical residues tested for in sub-sets of the products to include organotins (in five articles with plastisol printed fabric), perfluorinated chemicals (PFCs, in one item of outdoor clothing) and antimony (in polyester products only).

10 of these products were purchased in June 2013, and the remaining 75 in October 2013. The first set of products were sent initially to the Greenpeace Research Laboratories, where the fabrics were representatively sub-sampled in a controlled laboratory environment to enable a range of different analyses to be carried out. Sub-samples were then forwarded to independent laboratories for all testing other than analysis of polyester samples for antimony (which was conducted in our laboratories). The second set of samples were sent directly to a different independent laboratory which carried out the sub-sampling and subsequent analyses. All ten of the first batch of items were tested for nonylphenol ethoxylates, as well as 40 of the 75 items in the second batch. Analyses for other chemical residues were carried out on specific sub-sets of items, selected according to colour, print type, waterproof properties and/or presence of polyester fibres.

Nonylphenol ethoxylates (NPEs)

All 10 items from the first set of samples tested positive for NPEs, at concentrations ranging from 1.6 to 1800 mg/kg (median 64 mg/kg). Four articles contained NPEs at concentrations above 100 mg/kg and, in one of these, over 1000 mg/kg (0.1% by mass).

Of the 40 articles selected for NPE analysis from the second batch and analysed in a different laboratory, NPEs were detected in 16 (40% of samples), with concentrations ranging from 62.3 to 860 mg/kg. In this case, the method detection limit for was far higher than for the first set (50 mg/kg compared to 1 mg/kg). This result both confirms the presence of NPEs residues in many clothing articles, at substantial levels of some of these, and highlights the importance of applying sensitive analytical methods in order to document the full extent of contamination.

The manufacture, use and release of NP and NPEs are not currently regulated in China, though NPEs and nonylphenol have recently been included on the 'List of toxic chemicals severely restricted for import and export in China' and their import or export now requires prior permission (MEP 2011). Furthermore, no regulations currently exist, in China or elsewhere, that restrict the sale of textile products containing NPE residues, though such a regulation is currently under development within the EU (KEMI 2012).

Azo dyes giving rise to carcinogenic amines

In this case, none of the four dark-coloured items tested, all from the first batch of 10 samples, showed the presence of such amines at levels above the detection limit of 5mg/kg.

Phthalates

All 6 of the 10 printed items from the first batch tested positive for phthalate esters, at levels above the detection limit of 3 mg/kg. Total phthalate concentrations in the printed sections of these articles ranged from 15 to 17 000 mg/kg, the highest level (with the phthalate DEHP present at almost 1.7% by weight) being found in a dress manufactured in Zhili, Huzhou City.

In the case of the 40 items from the second batch of samples which were tested at a different independent laboratory for phthalates, only one tested positive at a concentration above the higher detection limit of 50 mg/kg; this section of printed fabric from a coat purchased in Shishi City contained 4 400 mg/kg DEHP (0.44% by weight), as well as DINP at 860 mg/kg (0.086% by weight). It was not possible to determine whether any of the other 40 samples contained phthalates as process contaminants at concentrations below the 50 mg/kg detection limit.

The identification of phthalates at high concentrations in two of the articles tested indicates the ongoing use of phthalates as plasticisers, including the reprotoxic form DEHP, in some formulations used to produce plastisol prints on textile products. The sale of textiles products containing phthalates is not currently regulated in China, though draft limits on the presence of 6 phthalates (including DEHP and DINP) in clothes sold for babies and young children is under consideration.

Organotin compounds

Of the 5 articles, all from the first set of samples, which were analysed for organotin compounds none contained these compounds at levels above the method detection limit of 0.1 mg/kg.

Perfluorinated & polyfluorinated chemicals (PFCs)

Only one article in total was analysed for PFCs (both ionic and volatile forms) in this study, a waterproof jacket from the first set of samples. Two ionic PFCs were detected, PFOA at 4.73 µg/kg and the related perfluorodecanoic acid, (PFDA) at 3.25 µg/kg. No perfluorosulfonates (including PFOS) were found. However, the total concentration of volatile PFCs (1010 µg/kg) was over 120 times higher than that of ionic PFCs in the same sample, and was dominated by the fluorotelomer alcohols 8:2 FTOH (400 µg/kg) and 10:2 FTOH (130 µg/kg) as well as the fluorotelomer acrylates 8:2 FTA (370 µg/kg) and 10:2 FTA (110 µg/kg). Such compounds can act as an ongoing source of PFOA or PFDA through partial degradation.

Antimony

Concentrations of antimony, used as a catalyst during polyester manufacture, were generally higher in articles composed of 100% polyester than in other fabrics containing blends or polyester & other fibres, as anticipated. Concentrations were between 102 and 159 mg/kg for the two polyester samples analysed from the first batch, and ranged from 15-208 mg/kg (median 103 mg/kg) in the 36 positive samples from the sub-set of 40 analysed from the second batch, again primarily those comprised of 100% polyester.

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

Conclusions

Results from both sets of samples analysed in the current study are broadly consistent with the findings from our previous studies (Brigden *et al.* 2012, Greenpeace 2011, Greenpeace 2012a), though for NPEs the proportion of samples testing positive was somewhat higher in this case, suggesting that the commercial use of NPEs in the manufacture of textiles may be particularly prevalent in Shishi and Huzhou Cities. Previous research has demonstrated that residues of these toxic and persistent chemicals can subsequently be washed from finished clothing into sewer systems in significant quantities during laundering.

Overall, this study provides a further snapshot of what appears to be a more generic problem that is not restricted to the two manufacturing locations, and one that deserves further investigation including from a regulatory perspective.

1. Introduction

Finished textile products can contain certain hazardous chemicals used during their manufacture, either because of their use as components of materials incorporated within the product or due to residues remaining from the use within processes employed during manufacture.

This study follows on from, and extends, research recent published by Greenpeace that identified a number of hazardous chemicals in textile products sold by major brands (Brigden *et al.* 2012, Greenpeace 2011, Greenpeace 2012a). These previous studies determined the concentrations of nonyl phenol ethoxylates (NPEs) in a broad range of textile clothing products, and the later study also determined the concentrations of carcinogenic amines, released from azo dyes within dyed fabric, and phthalate esters (commonly referred to as phthalates) in fabrics bearing a plastisol print¹, as well using a broader qualitative chemical screening to identify the presence, as far as possible, of other hazardous chemicals present within some of the products. These previous studies also summarise information from other related studies which have reported the presence in textile products of NPEs (Brigden *et al.* 2012 and references within), carcinogenic amines released under reducing conditions from azo dyes (JRC 2008, Laursen *et al.* 2003) and phthalates in plastisol printed fabric (RAPEX 2012, Greenpeace 2004).

In addition to determining the concentrations of hazardous chemicals included in the previous reports, this current study also investigated the concentration of perfluorinated and polyfluorinated compounds (PFCs), and of antimony in certain products.

The study was carried out in two parts. In the first, the presence of a broad range of hazardous chemicals was investigated in 10 textile clothing articles manufactured in China, 5 manufactured in Shishi City (Fujian Province) and the other 5 in Zhili, Huzhou City (Zhejiang Province), all purchased in June 2013. All these items were analysed by independent laboratories for NPEs, carcinogenic amines (released under reducing conditions from azo dyes) were analysed for in dark or deeply coloured fabric, for phthalates and organotins within printed fabric of articles bearing a plastisol print, perfluorinated and polyfluorinated compounds in a single waterproof jacket, and (at the Greenpeace Research Laboratories) for antimony in articles containing polyester fabrics.

A subsequent set of analyses, conducted at a separate independent laboratory, investigated a wider range of articles (75 in total) manufactured in the same cities to determine the concentrations of NPEs, of phthalates within printed fabric, and of antimony in polyester fabrics. For each of these three chemical groups, a sub-set of 40 articles selected from the 75 was analysed. The methods used to determine the concentrations of NPEs, phthalates, or antimony in the second set of samples were less sensitive than those used in the first set of analysis, resulting in higher detection limits for these samples. All articles included in the second set of analysis were purchased in October 2013 from the online retailers Tmall or Taobao (<http://tmall.com>, <http://taobao.com>).

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

¹ Plastisol: A suspension of plastic particles, commonly PVC or EVA, in a plasticiser. Used as ink for screen-printing images and logos onto textiles

2. Materials and methods

All 85 articles were purchased either at stores in the manufacturing town, or *via* online stores. For the first set of products, once purchased each product was sealed in an individual clean polyethylene bag. Sealed bags containing the products were 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 laboratories for a range of analyses as detailed below. In addition, two articles with fabric composed of polyester were analysed at the Greenpeace Research Laboratories to determine the concentration of antimony within the polyester fibre. For the second set of products, the products were sent directly to a different independent laboratory which carried out the sub-sampling and subsequent analyses. Details of the individual articles are provided in Appendix 1.

2.1 Nonyl phenol ethoxylates (NPEs)

For the first set of samples, the concentrations of NPEs were quantified in a section of fabric from each of the 10 articles. 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.

For the second set of samples, the concentration of NPEs in extracts from each of 40 articles selected from the full batch of 75 was determined by high performance liquid chromatography – tandem mass spectrometry. The quantification was carried out for each of 15 individual nonylphenol ethoxylates, consisting of those with between 2 and 16 ethoxylate groups. The quantitative results presented below are the sum of the concentrations of the individual nonylphenol ethoxylates with 2-16 ethoxylate groups, with a detection limit of 50 mg/kg.

2.2 Carcinogenic amines released under reducing conditions

This analysis was only carried out for a sub-set of the first set of samples. Four articles which 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 European Union (EU) regulations (EU 2002), consistent with equivalent Chinese regulations (SAC 2012a), which involved the determination of certain aromatic amines derived from azo colourants 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.

2.3 Phthalates in plastisol prints

For the first set of samples, 6 articles bearing a large sized plastisol print of an image, logo or text were selected for determination of the concentrations of a range of phthalates within the printed section of fabric (i.e. in the print itself plus underlying fabric). Details of the individual phthalates quantified for each article are given in Appendix 2. A portion of each plastisol print sample 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 vaporizing (PTV) injector and a DB5ms column using deuterated (D10)-pyrene as an internal standard. The detection limit was 3 mg/kg for each individual phthalate.

For the second set of samples, the concentration of six phthalates were determined in plastisol printed fabric from 40 selected articles using gas chromatography / mass spectrometry, with a detection limit in this case of 50 mg/kg for each phthalate. Details of the individual phthalates quantified for each article are given in Appendix 2.

2.4 Organotins

This analysis was only carried out for the first set of samples. Five articles bearing a large plastisol print were analysed quantitatively for a range of organotins within the printed fabric. For some articles, which were composed of a mixture of print colours, a number of different sub-samples from the article were analysed. Details of the materials tested and the individual organotins quantified in each material 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. The detection limit was 0.1 mg/kg for each individual organotin.

2.5 Per- and poly-fluorinated chemicals (PFCs)

Analysis for perfluorinated and polyfluorinated compounds (PFCs) was conducted for only one article drawn from the first set of samples (a waterproof jacket). Details of the individual PFCs quantified in the article are given in Appendix 4. A sample was cut from the article where there was no printing or labelling. Two separate analyses were carried out on the 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

For the first set of samples, two articles with fabrics composed of polyester 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 followed by holding 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.

For the second set of samples, the concentration of antimony in extracts from each of the 40 articles was determined by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), with a detection limit of 10 mg/kg.

3. Results and Discussion

The results for the various substance groups are presented in the following sections. 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 Nonyl phenol ethoxylates (NPEs)

Of the 10 articles from the first set of samples in which NPEs were quantified, all tested positive for the presence of NPEs, at concentrations ranging from 1.6 to 1800 mg/kg (median 64 mg/kg). Four articles contained NPEs at concentrations above 100 mg/kg and, and 1 of these had a concentration over 1000 mg/kg (0.1% by mass).

For the 40 articles analysed from the second batch of samples, NPEs were detected in 16 samples (40% of samples), with concentrations in the range 62.3 – 860 mg/kg. Although NPEs were detected in a smaller fraction of samples in the second set, this is due in part to the fact that the detection limit for the second set was higher than for the first (50 mg/kg compared to 1 mg/kg). It may be that many of the samples from the second set in which NPEs were not detected contained NPEs at concentrations above 1 mg/kg, though it is not possible to confirm this.

Summaries of the number of samples containing NPEs within various ranges of concentration in the two sets are given in Tables 1a & 1b, and details for all articles is given in Appendix 1.

NPE concentration range (mg/kg)	First set: Number of samples, of 10
<1 (non-detect)	0
1-50	5
>50 – 100	1
>100 – 1 000	3
>1 000	1

Table 1a. Number of samples in the first set (of 10 articles tested) within various NPE concentration ranges.

NPE concentration range (mg/kg)	Second set: Number of samples (% of 40)
<50 non-detect)	24 (60%)
50 – 100	7 (18%)
>100 – 1 000	9 (22%)
>1 000	0

Table 1b. Number of samples in the second set (of 40 articles tested) within various NPE concentration ranges.

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 which 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 NP and NPEs are not currently regulated in China, though NPEs and nonylphenol have recently been included on the 'List of toxic chemicals severely restricted for import and export in China' and their import or export now requires prior permission (MEP 2011). In contrast, regulations do exist in some other countries. The use of these chemicals during textile manufacture has effectively been banned within the EU (EU 2003), with similar restrictions in place in the United States and Canada (CEPA 2004, USEPA 2010). NP has also been included as a 'priority hazardous substance' under the European Union (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). No regulations currently exist, in China or elsewhere, that restrict the sale of textile products containing NPE residues, though such a regulation is currently under development within the EU (KEMI 2012).

3.2 Carcinogenic amines released under reducing conditions

None of the 4 articles from the first set that were tested for the presence of carcinogenic amines released under the test conditions showed the presence of these compounds above the method detection limit (<5 mg/kg).

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 formulation to contain residues of amines used in their manufacture. Furthermore, certain carcinogenic amines have been detected as residues in other amines that are used for azo dye manufacture, providing an additional route for contamination of commercial azo dye formulations with carcinogenic amines (IARC 2008). These sources could contribute to the presence of carcinogenic amines at trace levels within textile products.

Legislation exists in certain countries, including EU member states and China, which prohibits the sale of products containing dyes that can degrade under specific test conditions to form carcinogenic amines at concentration above set limits, for textile articles which may come into direct and contact with human skin. The EU regulation lists 22 compounds, with a limit of 30 mg/kg (EU 2002). The regulation in China sets a limit of 20 mg/kg and lists the same compounds as the EU regulation, as well as two additional compounds (SAC 2012).

3.3 Phthalates in plastisol prints

For the first set of samples, one or more phthalate was present above the method detection limit (3 mg/kg) in plastisol printed fabric sections from each of the 6 articles tested, with the total phthalate concentrations in the printed section of each article ranging from 15 to 17 000 mg/kg.

For one article (CN13009), a dress manufactured in Zhili, Huzhou City, the printed fabric contained a very high phthalate concentration (17 000 mg/kg, 1.7% by mass), composed almost entirely of di-(2-ethylhexyl) phthalate (DEHP). The presence of DEHP at this concentration suggests its use as a plasticiser within the plastisol formulations used to manufacture the product.

Of the remaining 5 articles in which phthalates were detected at concentrations above 3 mg/kg, individual phthalates were detected below 100 mg/kg (0.01%). For these, the concentrations would be too low to be expected to have any significant plasticising function on their own. The identified phthalates are more likely present due to use within another component of the plastisol formulation (including inks or pigments), contamination of another substance used as a plasticisers within the plastisol formulation, 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.

For the second set of samples, phthalates were detected in only one of the 40 samples of printed fabric that were tested, at a concentration above the higher detection limit of 50 mg/kg. It is possible that many of the other samples from the second set in which phthalates were not detected could have contained one or more phthalate at concentrations below this higher detection limit, though clearly it is not possible to confirm this without further, more sensitive, analysis.

The single printed fabric sample from the second set in which phthalates were detected (sample 56, purchased in Shishi City, Fujian Province) contained DEHP at 4 400 mg/kg (0.44% by mass) as well as

di-iso-nonyl phthalate (DINP) at 860 mg/kg (0.086 %), indicating the use of DEHP, and possibly DINP, as plasticisers within the plastisol formulations used to manufacture the product.

Full details of the individual phthalate concentrations for all articles are presented in Appendix 2.

The phthalates present in two articles (1 from each set of analyses), at close to, or above, 0.1 % by mass, are toxic compounds. DEHP is known to exert reproductive toxicity, being toxic to the developing reproductive system in mammals (Ema & Miyawaki 2002, Mylchreest *et al.* 2002, Aso *et al.* 2005). Within the European Union, DEHP together with some other phthalates has been listed as a Substance of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013). DINP, though not currently among the phthalates of greatest regulatory concern, nonetheless does exhibit toxicity (primarily to the liver and kidney) at high doses. In addition, some hormone-disrupting (anti-androgenic) effects on reproductive development in rats have recently been reported for DINP (Boberg *et al.* 2011). Further background information on phthalate esters is provided in Box C.

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

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 plasticizers (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). All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal, principally because phthalates are not chemically bound but only physically associated to the polymer chains. Phthalates have been found to leach from food packaging materials and contaminate corresponding food products (Fierens *et al.* 2012, Fasano *et al.* 2012); from tubing material used for drug products manufacturing (Jenke *et al.* 2006) and from PVC blood bags which primarily contained DEHP (Ferri *et al.* 2012). Moreover, it has been shown that bacteria, which may grow on PVC plastics in wet conditions (e.g., shower curtains), may enhance DEHP leaching from plastic (Latorre *et al.* 2012). Thus, phthalates are widely found in the indoor environment, including in air and dust (Langer *et al.* 2010, Otake *et al.* 2001, Butte & Heinzow 2002, Fromme *et al.* 2004) at concentrations which commonly reflect the prevalence of plastics and certain textiles within the rooms sampled (Abb *et al.* 2009). Once plastic products are disposed to municipal landfills, phthalates 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 (Dalggaard *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 which do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children’s toys and childcare articles, first agreed as an emergency measure in 1999 and finally made permanent in 2005 (EU 2005). Very similar regulation in China has very recently been announced which 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.

Draft legislation has been proposed in China which would prohibit the presence of 6 phthalates, including DEHP and DINP, at concentrations above 0.1% by weight (1000 mg/kg) for the whole article, in clothes sold for babies and young children (under 36 months old) in China (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 European Union, 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 Organotin

Of the five articles from the first set of samples which were analysed for the presence of organotin compounds (in some cases, a number of different sub-samples representing different areas and

colours of print), none contained organotin compounds at levels above the method detection limit of 0.1 mg/kg for each organotin. Full details of the individual organotin data for all 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, though 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 poly-fluorinated chemicals (PFCs)

One article from the first set of samples, a waterproof jacket (CN13010), was analysed for a range of per- and poly-fluorinated chemicals (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 which 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.

More information on these PFCs is given in Box E.

Examples of both ionic and volatile PFCs were detected in the article. Details of the concentrations of individual PFCs by mass (ng/kg) and by area ($\mu\text{g}/\text{m}^2$) are given in Appendix 4. Two ionic PFCs were detected, PFOA (4.73 $\mu\text{g}/\text{kg}$) and the related compound perfluorodecanoic acid, (PFDA, 3.25 $\mu\text{g}/\text{kg}$), both of which are perfluorinated carboxylic acids. No perfluorosulfonates were detected in the sample.

The total concentration of volatile PFCs (1010 $\mu\text{g}/\text{kg}$) was over 120 times higher than that of ionic PFCs in the same sample. Four volatile PFCs were detected, each at considerably higher concentrations than those of the ionic PFCs. The volatile PFCs were the fluorotelomer alcohols

8:2 FTOH (400 µg/kg) and 10:2 FTOH (130 µg/kg), as well as the fluorotelomer acrylates 8:2 FTA (370 µg/kg) and 10:2 FTA (110 µg/kg). For both the fluorotelomer alcohols and the acrylates, the concentration of the 8:2 compound was approximately 3 times that of the 10:2 compound. See appendix 4 for concentrations by area (µg/m²).

The FTOHs (8:2 FTOH and 10:2 FTOH) and the FTAs (8:2 FTA and 10:2 FTA) can give rise to PFOA and PFDA, respectively (Frömel & Knepper 2010, Butt et al. 2013, Young & Mabury 2010). These PFCAs are highly persistent compounds which can bioaccumulate and exhibit a range of toxic properties (See Box E).

Box E. Per- and poly-fluorinated chemicals (PFCs)

Per- and poly-fluorinated chemicals (PFCs) are a group of chemicals in which all (per-fluorinated), or most (poly-fluorinated), 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 (PFAS), 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 PFAS (for example perfluorooctane sulfonate, PFOS) and (PFCAs) (for example, perfluorooctanoic acid, PFOA), and for volatile poly-fluorinated chemicals which 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 PFASs 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 PFASs, including from being unintentional manufacturing byproducts 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, PFASs and FTOHs have frequently been reported in outdoor clothing and footwear articles and swimwear (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 and PFASs, 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 PFASs 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. 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 and PFSA 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 results 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 possible links between elevated blood levels of PFOA in humans has possible links with other diseases including thyroid diseases, elevated blood pressure & 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 been classified as a persistent organic pollutants (POP) 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).

For textile products, there are currently no regulations addressing the presence of PFCs in textile product sold in China, though in some other countries 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, other PFCs are not currently regulated 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). Within the EU certain long chain PFCAs, including PFOA and PFDA are classified as substances of very high concern (SVHCs) under the EU REACH regulations (ECHA 2013).

3.6 Antimony

Concentrations of antimony were determined for 2 of the first set of 10 articles, those which included fabrics containing polyester. In both cases the fabric was 100% polyester. Antimony was detected in both articles, with concentrations in the polyester fibre in the range 102-159 mg/kg.

For the second set of samples, antimony was determined for 40 samples, of which 35 were composed of 100% polyester. Three samples were composed of a blend of polyester and other fibres, and for two samples, no information on the fabric composition was given. For those fabrics reported to be composed of a blend of polyester and other fibres, the concentration of antimony was determined within the fabric blend and, from this, the concentration in the polyester fraction was calculated on the basis that all antimony arose from the polyester fibre within the fabric blend.

Antimony was detected in 36 of the 40 samples, with a detection limit of 10 mg/kg in the fabric. The concentrations of antimony in the fabrics were in the range 15 – 208 mg/kg (median = 103 mg/kg). For each of the 35 samples composed of 100% polyester, the concentration of antimony in the polyester fibre was the same as the concentration in the tested fabric. For the other 5 samples, the concentrations of antimony within the polyester fraction of the fabric was calculated from the fabric composition information where given. For the second set of samples, the concentrations of antimony within the polyester fraction of each fabric (calculated from the fabric composition information) were also in the range 15-208 mg antimony/kg polyester, though with a slightly higher median (107 mg/kg).

Details of antimony concentrations in individual articles from both sets of samples are presented in Appendix 1. The range of concentrations is consistent with reports that commercial polyester fibres commonly containing up to 300 mg/kg antimony (Duh 2002, Lacasse & Baumann 2004).

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).

Trivalent antimony, such as is present in antimony trioxide, is the more toxic form of antimony compounds, with effects including dermatitis, irritation of the respiratory tract, interference with the immune system (Kim et al. 1999). In addition, antimony trioxide is listed by the International Agency for Research on Cancer (IARC) as “possibly carcinogenic to humans” (group 2B), principally due to inhalation of dusts and vapours (IARC 1989), and antimony trioxide has been classified under the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) as suspected of causing cancer (H351). Inhalation exposure to antimony is more common in occupational settings, where as the general population is exposed to antimony mainly through ingestion of food and water. 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 which 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 which 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 Harmonized System of Classification and Labelling of Chemicals (GHS) as suspected of causing cancer (H351).

Inhalation exposure to antimony is more common in occupational settings, where as the general population is exposed to antimony mainly through ingestion of food and water. A previous study which found similar levels of antimony in polyester 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 which prohibit use in textile manufacture, despite the availability of alternative catalysts for polyester manufacture. Within the European Union (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 textile products, as either components of materials incorporated within the product or residues remaining from use within manufacturing processes.

Amongst these, the most commonly detected substances were NPEs, indicating that the use of NPEs is widespread within the international textile industry. In this way the results from both sets of samples are broadly consistent with the findings from previous studies (Brigden *et al.* 2012, Greenpeace 2011, Greenpeace 2012a). The fraction of samples in which NPEs were detected in the current study, however, was somewhat higher than for the two previous studies, indicating the use of NPEs in the manufacture of textiles in Shishi City (Fujian Province) and Zhili, Huzhou City (Zhejiang Province) may be more prevalent compared to the textile sector as a whole, and the textile sector in China.

For the first set of samples, NPEs were detected in all 10 samples (100%), while for previous studies using the same detection limit (1 mg/kg), NPEs were detected in a smaller fraction of articles, generally around two thirds of articles tested. A study of 78 articles detected NPEs in 67% of all articles, including in 19 of 28 articles reported to be manufactured in China (68%) (Brigden *et al.* 2012, Greenpeace 2011). A subsequent study of 141 articles detected NPE in 63%, including in 21 of 34 articles reported to be manufactured in China (62%) (Greenpeace 2012a).

For the second set of samples in the current study, NPEs were detected in a lower fraction of samples (40% of 40 samples), as might be expected due to the higher detection limit (50 mg/kg). By comparison, however, in previous studies, NPE concentrations above 50 mg/kg sample were found in 19% of samples in the study of 78 articles (and in 25% of the 28 of these articles manufactured in China) (Brigden *et al.* 2012, Greenpeace 2011) and in 26% of samples in the study of 141 articles (and in 32% of the 34 of these articles manufactured in China) (Greenpeace 2012a).

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 manufacture, use and release of NP and NPEs are not currently regulated in China, though NPEs and nonylphenol have recently been included on the 'List of toxic chemicals severely restricted for import and export in China' and their import or export now requires prior permission (MEP 2011). In contrast, regulations do exist in some other countries. The use of these chemicals during textile

manufacture has effectively been banned within the EU (EU 2003), with similar restrictions in place in the United States and Canada (CEPA 2004, USEPA 2010).

No regulations currently exist, in China or elsewhere, that restrict the sale of textile products containing NPE residues, though such a regulation is currently under development within the EU (KEMI 2012). In order to offer adequate protection, such regulations will need to set any limit for NPEs in products as low as possible and cover as wide a range of NPEs as possible.

In addition to the presence of NPEs, the identification of phthalates at high concentrations in two of the articles tested indicates the on-going use of phthalates as plasticisers in some formulations used to produce plastisol prints on textile products in both Huzhou City (Zhejiang Province) and Shishi City (Fujian Province). The levels and types of individual phthalates found in the two articles with high concentrations are broadly consistent with previous investigations of related textile products, though even higher concentrations were found in some articles analysed in previous studies (RAPEX 2012, Greenpeace 2004, Greenpeace 2012a).

The sale of textiles products containing phthalates in China is not currently regulated, though draft legislation has been proposed which would prohibit the presence of 6 phthalates, including DEHP and DINP, at concentrations above 0.1% by weight (1000 mg/kg) for the whole article, in clothes sold for babies and young children (under 36 months old) in China (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. Neither of the two articles in the current study in which DEHP was detected at a concentration above 0.1 % was intended for babies or children under 36 months old. The phthalate data presented in the current study are for sections of printed fabric rather than the whole article.

It has very recently been announced that regulation of certain phthalates in toys, including DEHP and DINP, however, will be introduced 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-iodecyl phthalate (DIDP) and di-n-octyl phthalate (DNOP) will be prohibited in such articles if they can be placed in the mouth (SAC 2013). Similar regulations of phthalates in toys also exist in other countries (EU 2005). While such regulations and initiatives do not relate directly to clothing articles, they do illustrate the level of concern regarding the toxicity of and exposure to phthalates, whatever their sources.

The concentrations of the two PFCAs (PFOA and PFDA), and the two FTOHs (8:2 FTOH and 10:2 FTOH), were consistent with the lower values of concentration ranges previously reported in studies of outdoor clothing which detected these substances, though in each case each considerably higher concentrations of PFOA, PFDA and the two FTOHs were reported in certain outdoor clothing articles (Greenpeace 2012c, SSNC FoEN 2006, Herzke et al. 2012). The concentrations of the two FTAs was consistent with the limited previous data reported for these compounds in outdoor clothing (Greenpeace 2012c).

There are currently no regulations addressing the presence of PFCs in textile product sold in China, though in some other countries a maximum limit of 1 µg/m² is set for PFOS in textiles (EU 2006). PFOS was not detected in the article analysed in this study. PFOA has similar properties to PFOS, and although any regulatory limit for PFOS clearly does not apply to PFOA, it does provide a useful comparison for concentrations of this compound in textiles. Furthermore, though not applicable in

China, the sale of textiles containing PFOA above 1 µg/m² will be prohibited in Norway from June 2014 (NME 2013). PFOA was detected in the Jacket analysed in this study (CN13010), though the concentration by area (0.331 µg/m²) did not exceed the future Norwegian limit for PFOA, nor the more broadly applied PFOS limit.

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, Kemi 2013).

Despite known and suspected toxicity for antimony trioxide, no regulations currently exist which prohibit use in textile manufacture, despite the availability of alternative catalysts for polyester manufacture. Within the European Union (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). Antimony concentrations were below 260 mg/kg for all samples analysed in the current study.

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 provided an understanding of the presence and concentrations of a broad range of chemicals within textile products manufactured in Shishi City (Fujian Province) and Zhili, Huzhou City (Zhejiang Province). The use of these and other hazardous chemicals during manufacture will result in releases from manufacturing facilities, including within wastewaters, in addition to the presence of chemical residues in the products themselves.

This study also provides a snapshot of what appears to be a more generic problem that is not restricted to the two manufacturing locations, and one that deserves further investigation including from a regulatory perspective.

5. References

- Abb, M.; Heinrich, T.; Sorkau, E. and 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, S.A., Markoulaki, S., Pocock, V., Milligan, S.R. & Fraser, L.R. (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, M.E., Butenhoff, J.L., Chang, S.-C., Farrar, D.G., Kennedy, G.L., Lau, C., Olsen, G.W., Seed, J. & Wallace, K.B. (2008) Perfluoroalkyl acids and related chemistries--toxicokinetics and modes of action. *Toxicological sciences* 102: 3–14
- Andrewes, P., KitChendian, K.T. and 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. and 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, B.C., Silva, M.J., Caudill, S.P., Needham, L.L., Pirkle, J.L., Sampson, E.J., Lucier, G.W., Jackson, R.J. & Brock, J.W. (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, T.S., Vinggaard, A.M., 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, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A. & van Leeuwen, S.P. (2011) Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins. *Integrated Environmental Assessment and Management* 7(4): 513–541
- Butt, C.M., Muir, D.C., Mabury, S.A. (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, J.C. (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, 4th December 2004. <http://www.ec.gc.ca/planp2-p2plan/B2D19B6D-325F-458A-88E1-F69291E58DE3/g1-13849.pdf>
- Chitra, K.C., Latchoumycandane, C. & Mathur, P.P. (2002) Effect of nonylphenol on the antioxidant system in epididymal sperm of rats. *Archives of Toxicology* 76(9): 545-551
- Choe, S.Y., Kim, S.J., Kim, H.G., Lee, J.H., Choi, Y., Lee, H. and Kim, Y. (2003) Evaluation of estrogenicity of major heavy metals. *Science of the Total Environment* 312(1): 15–21
- Colon, I., Caro, D., Bourdony, C.J. & 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, J.M., Hoke, R.A., De Wolf, W., Russell, M.H. & Buck, R.C. (2008) Are PFCA's bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds. *Environmental Science & Technology* 42: 995–1003
- Dalgaard, M., Nellemann, C., Lam, H.R., Sorensen, I.K. & 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. and Lison, M. (2003) Cobalt and antimony: genotoxicity and carcinogenicity. *Mutation Research* 533: 135–152
- DeWitt, J., Copeland, C., Strynar, M. and Luebke, R. (2008). Perfluorooctanoic acid-induced immunomodulation in adult C57BL/6J or C57BL/6N female mice. *Environmental Health Perspectives* 116 (5): 644-650.
- 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 polycondensation 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>
- ECHA (2013) Candidate List of Substances of Very High Concern for authorization. European Chemicals Agency. 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
- 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) Directive 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). <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:372:0032:0034:en:PDF>
- EU (2010) Regulation 276/2010 of 31 March 2010 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council 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, J.K., 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, E.T., 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 Henauw, 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. and 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, T.P. (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. & Rüdén 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, S.A., 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, J.P. & Kannan, K. (2001) Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environmental Science & Technology* 35(7): 1339–1342
- Grande, S. W., Andrade, A. J., Talsness, C. E., 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, E.W., 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 Jr, L. E. 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, A.K., Letcher, R.J., Sonne, C., Dietz, R. & Born, E.W. (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/en/publications/reports/Dirty-Laundry-2/>
- 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
- 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, E.L., Borghini, F., Corsi, I. and Focardi, S.I. (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, A.O., Muir, D.C.G. & Letcher, R.J. (2011) Monitoring of perfluorinated compounds in aquatic biota: an updated review. *Environmental Science & Technology* 45: 7962–7973

- Howdeshell, K. L., Wilson, V. S., Furr, J., Lambright, C. R., Rider, C. V., Blystone, C. R., Hotchkiss, A. K. & Gray Jr, L. E. (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, A.J. (2007) Polyester fibres. In: Lewin, M. Handbook of fibre chemistry. 3rd Ed CRC press ISBN 0-8247-2565-4
- Jenke, D.R., Story, J. & Lalani, R. (2006) Extractables/leachables from plastic tubing used in product manufacturing. *International Journal of Pharmaceutics* 315(1–2): 75-92
- Jenkins S.M. & Barone S. (2004). The neurotoxicant trimethyltin induces apoptosis via caspase activation, p38 protein kinase, and oxidative stress in PC12 cells. *Toxicology Letters* 147 (1): 63-72
- Jenkins S.M., 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 disruptors: 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, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspectives* 103(6): 582-587
- Joensen, U.N., Bossi, R., Leffers, H., Jensen, A.A., Skakkebaek, N.E. & 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/111111111/1321/1/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, D.H. & Rice, C.D. (1998) Macrophage secretory function is enhanced by low doses of tributyltin-oxide (TBTO), but not tributyltin-chloride (TBTCl). *Arc. Environ. Contam. Toxicol.* 34: 223-228
- Kim, H.A., Heo, Y., Oh, S.Y., Lee, K.J. and Lawrence, D.A. (1999) Altered serum cytokine and immunoglobulin levels in the workers exposed to antimony. *Human and Experimental Toxicology* 18(10): 607-613
- Koch, H. M., 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, C.J., Fischer, A., Bekö, G., Toftum, L. and 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., Sevilano, 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, J.H., Wong, C.P., Lee, N.C. and Ricky Lee, S.W. (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, D.O., Sottas, C.M., Li, X.-K. & Hardy, M.P. (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, P.K., Wu, R.S. & 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, E.I.H., Yeung, L.W.Y., Taniyasu, S., Lam, P.K.S., 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, M. J., Freire, C., Arrebola, J. P., Navea, N., Taoufik, J., Fernandez, M. F., 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 B.J. (2003) Mechanisms of phthalate ester toxicity in the female reproductive system. *Environmental Health Perspectives* 111(2): 139-145
- Lui, J.Y., Li, J.G., Zhao, Y.F., Wang, Y.X., Zhang, L., Wu, Y.N. (2010). The occurrence of perfluorinated alkyl compounds in human milk from different regions of China. *Environment International* 36 (5): 433-438.
- Lye, C.M., Frid, C.L.J., Gill, M.E., Cooper, D.W. & Jones, D.M. (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, A. J., Morais, R. N., Botelho, G. G., Muller, G., Grande, S. W., Carpentieri, G. B., Leão, G. M. & Dalsenter, P. R. (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, M.H., Henley, W.E., Galloway, T.S. (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, D.G. & Foster, P.M.D. (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-ver stinglista/> (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)
- 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>
- 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, G.W., Lange, C.C., Ellefson, M.E., Mair, D.C., Church, T.R., Goldberg, C.L., Herron, R.M., Medhizadehkashi, Z., Nobiletti, J.B., Rios, J.A., Reagen, W.K. & Zobel, L.R. (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, T.J., Ngo, M., Aronov, P.A., Reznikova, T.V., Green, P.G. & Rice, R.H. (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. and Keil, D. (2008). Suppression of humoral immunity in mice following exposure to perfluorooctane sulphonate. *Toxicological Sciences* 104 (1): 144-154.
- Peters, R.J.B., Beeltje, H. & van Delft, R.J. (2008) Xeno-estrogenic compounds in precipitation. *Journal of Environmental Monitoring* 10: 760-769
- Poulsen, P.B. & Jensen, A.A. (2005) More environmentally friendly alternatives to PFOS-compounds and PFOA Danish Environmental Protection Agency Environmental Project No. 1013 Miljøprojekt
- Rand, A.A., Mabury, S.A. (2012) In vitro interactions of biological nucleophiles with fluorotelomer unsaturated acids and aldehydes: fate and consequences. *Environmental Science & Technology* 46(13): 7398-406
- Rice, C. P., Schmitz-Afonso, I., Loyo-Rosales, J. E., Link, E., Thoma, R., Fay, L., Altfater, D. & Camp, M.J. (2003) Alkylphenol and alkylphenol-ethoxylates in carp, water, and sediment from the Cuyahoga River, Ohio. *Environmental Science & Technology* 37(17): 3747–3754
- Rosenmai, A.K., Nielsen, F.K., Pedersen, M., Hadrup, N., Trier, X., Christensen, J.H. & Vinggaard, A.M. (2013) Fluorochemicals used in food packaging inhibit male sex hormone synthesis. *Toxicology & Applied Pharmacology* 266: 132–142
- Rudel R.A., Camann D.E., Spengler J.D., Korn L.R. & Brody J.G. (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
- 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, T.M., Steenland, K., Thun, M.J. & Rinsky, R.A. (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, M.J., Barr, D.B., Reidy, J.A., Malek, N.A., Hodge, C.C., Caudill, S.P., Brock, J.W., Needham, L.L. & Calafat, A.M. (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, S.H., Main, K.M., Liu, F., Stewart, S.L., Kruse, R.L., Calafat, A.M., Mao, C.S., Redmon, J.B., Ternand, C.L., Sullivan, S. & Teague, J.L. (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, E.L., Tanabe, S., and 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, U.K. (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, L.S., Stigum, H., Frøshaug, M., Broadwell, S.L. & 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, E.C.M., de Groot, D.M.G, Penninks, A.H., Waalkens-Berendsen, I.D.H., Wolterbeek, A.P.M., Piersma, A.H., 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, E.C.M., Verhoef, A., de la Fonteyne, L.J.J., Waalkens-Berendsen, I.D.H., Wolterbeek, A.P.M., van Loveren, H., Piersma, A.H. (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* 159(1): 125-32
- White, S.S., Fenton, S.E. & Hines, E.P. (2011) Endocrine disrupting properties of perfluorooctanoic acid. *Journal of Steroid Biochemistry and Molecular Biology* 127: 16–26

- Ying, G.G., Kookana, R.S., 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, C.J. & Mabury, S.A. (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

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

Sample code	Brand	Place of sale /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)
CN13001	小玩皮 S·NAUGHTY	Shishi City	t-shirt	100% cotton	1.7	<5	15	<0.1	-	-	-
CN13002	舒美捷 SUMJOR	Shishi City	shorts	100% cotton	220	<5	-	-	-	-	-
CN13003	B&S	Shishi City	shorts & t-shirt set	not specified	140	-	18	<0.1	-	-	-
CN13004	one way	Shishi City	Dress & shorts set	not specified	90	-	43	-	-	-	-
CN13005	野豹 YeBao	Shishi City	t-shirt	100% polyester	38	<5	-	-	-	-	102
CN13006	今童王 Jintongwang	Zhili, Huzhou City	t-shirt	100% cotton	1.6	-	21	<0.1	-	-	-
CN13007	Toozaizai	Zhili, Huzhou City	shorts	100% cotton	1800	-	-	-	-	-	-
CN13008	小澄童 XCTONG	Zhili, Huzhou City	shorts & t-shirt set	98% cotton, 2% elastane	2.8	-	15	<0.1	-	-	-
CN13009	咿儿呀 yierya	Zhili, Huzhou City	dress	outshell 100% cotton; lining chemical fiber fabric	2.2	-	17000	<0.1	-	-	-
CN13010	小澄童 XCTONG	Zhili, Huzhou City	jacket	100% polyester	430	<5	-	-	7.97	1010	159

Table A1a. Details of all articles from the first set of samples, 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 (sum) 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; '-' indicates not tested.

Sample Number	Place of manufacture	Type of product	Fabric	NPEs (mg/kg)	phthalate total (mg/kg)	Antimony in fabric (mg/kg)	Antimony polyester (mg/kg)*
1	Zhili, Huzhou City	girl's pant in yellow colour	cotton and polyester	85.7	<50	-	-
2	Zhili, Huzhou City	girl's suit in orange colour	cotton and polyester	121	<50	-	-
3	Zhili, Huzhou City	blue baby suit with superman print	cotton and polyester	<50	<50	-	-
4	Zhili, Huzhou City	children suit	cotton and polyester	<50	<50	-	-
5	Zhili, Huzhou City	children down-filled coat	no fabric info in the tag	-	-	48.5	..**
6	Zhili, Huzhou City	children T-shirt with panda printing	cotton	<50	<50	-	-
7	Zhili, Huzhou City	children pant with printing	cotton and polyester	<50	<50	-	-
8	Zhili, Huzhou City	red and black down-filled coat	100% polyester	-	-	38.8	38.8
9	Zhili, Huzhou City	green T-shirt with printing	cotton and polyester	<50	<50	-	-

10	Zhili, Huzhou City	grey suit with panda printing	cotton and polyester	141	<50	-	-
11	Zhili, Huzhou City	green colour suit for boys	no fabric info in the tag	-	-	78.5	-**
12	Zhili, Huzhou City	blue T-shirt with printing	cotton and polyester	<50	<50	-	-
13	Zhili, Huzhou City	green suit with panda printing	outer cotton & polyester; inner 100% polyester	<50	<50	118	118
14	Zhili, Huzhou City	grey suit with printing	100% polyester	<50	<50	-	-
15	Zhili, Huzhou City	red sport suit	20% cotton and 80% polyester	62.3	<50	-	-
16	Zhili, Huzhou City	pink coat for girls	100% polyester	-	-	<10	<10
17	Zhili, Huzhou City	pink dress for girls	90% polyester and 10% cotton	-	-	<10	<11
18	Zhili, Huzhou City	pink down-filled jacket	100% polyester	-	-	101	101
19	Zhili, Huzhou City	black down-filled jacket	100% polyester	-	-	101	101
20	Zhili, Huzhou City	T-shirt with rabbit printing for girls	95% cotton and 5% polyester	113	<50	-	-
21	Zhili, Huzhou City	suit with Mickey mouse printing	cotton	<50	<50	-	-
22	Zhili, Huzhou City	blue jacket for boys	100% polyester	-	<50	<10	<10
23	Zhili, Huzhou City	pink down-filled jacket for girls	100% polyester	-	-	<10	<10
24	Zhili, Huzhou City	black trousers for girls	100% polyester	-	-	72.6	72.6
25	Zhili, Huzhou City	red waistcoat for girls	100% polyester	<50	-	151	151
26	Zhili, Huzhou City	pink jacket for girls	100% polyester	-	-	201	201
27	Zhili, Huzhou City	green T-shirt for girls	cotton and polyester	-	<50	130	130
28	Zhili, Huzhou City	pink T-shirt for girls	cotton	<50	<50	-	-
29	Zhili, Huzhou City	waistcoat	100% polyester	<50	-	16.4	16.4
30	Zhili, Huzhou City	orange colour suit with printing	70% cotton and 30% polyester	<50	<50	-	-
31	Zhili, Huzhou City	blue T-shirt with printing for boys	80% cotton and 20% polyester	<50	<50	-	-
32	Zhili, Huzhou City	down-filled coat for boys	100% polyester	116	-	47.9	47.9
33	Zhili, Huzhou City	black suit with printing for boys	cotton and polyester	<50	<50	-	-
34	Zhili, Huzhou City	dark blue suit for boys	cotton and polyester	<50	<50	-	-
35	Zhili, Huzhou City	jeans with printing for kids	cotton and polyester	76.2	<50	-	-
36	Zhili, Huzhou City	baby suit with light blue colour	100% polyester	-	-	138	138
37	Zhili, Huzhou City	white jacket for girls	100% polyester	-	-	15.3	15.3
38	Zhili, Huzhou City	black jacket for boys	100% polyester	-	-	66.3	66.3
39	Zhili, Huzhou City	girls suit with Mickey mouse printing	cotton and polyester	860	<50	-	-
40	Zhili, Huzhou City	baby suit with printing	cotton and polyester	62.7	<50	-	-
41	Zhili, Huzhou City	dress for girls	cotton and polyester	-	-	173	173
42	Zhili, Huzhou City	waistcoat for girls	cotton and polyester	-	-	92.9	92.9
43	Zhili, Huzhou City	pink down-filled jacket for girls	100% polyester	-	-	127	127
44	Zhili, Huzhou City	green T-shirt for girls	cotton and polyester	<50	<50	-	-
45	Zhili, Huzhou City	T-shirt with printing	cotton and polyester	689	<50	-	-
46	Zhili, Huzhou City	blue jacket for boys	100% polyester	-	-	64.6	64.6
47	Zhili, Huzhou City	black jacket for boys	100% polyester	86.1	-	85.2	85.2

48	Shishi City	blue T-shirt for boys	cotton and polyester	-	<50	-	-
49	Shishi City	red sport suit for boys	100% polyester	-	-	110	110
50	Shishi City	yellow T-shirt with printing	cotton	<50	<50	-	-
51	Shishi City	blue suit for boys	cotton and polyester	-	-	162	162
52	Shishi City	blue and grey colour suit	100% polyester	-	-	190	190
53	Shishi City	T-shirt for boys	cotton and polyester	<50	<50	-	-
54	Shishi City	black suit for boys	100% polyester	-	-	64.2	64.2
55	Shishi City	dark blue down-filled jacket	100% polyester	-	-	90.6	90.6
56	Shishi City	pink coat with cat-image printing	cotton and polyester	100	5300	-	-
57	Shishi City	yellow sport suit	cotton and polyester	<50	<50	-	-
58	Shishi City	red T-shirt with printing	cotton and polyester	111	<50	-	-
59	Shishi City	black jacket	cotton and polyester	-	-	19.7	65.7
60	Shishi City	orange T-shirt	cotton and polyester	123	<50	-	-
61	Shishi City	grey sport suit	100% polyester	64.1	<50	97.4	97.4
62	Shishi City	yellow jacket for boys	100% polyester	-	-	208	208
63	Shishi City	green down-filled jacket	100% polyester	-	-	56.6	56.6
64	Shishi City	grey and blue sport suit	100% polyester	-	-	190	190
65	Shishi City	black sport trouser	99% polyester	-	-	146	147
66	Shishi City	sport suit with yellow and blue colour	100% polyester	-	<50	127	127
67	Shishi City	blue suit for boys	cotton and polyester	565	<50	-	-
68	Shishi City	pink suit for girls	cotton and polyester	<50	<50	-	-
69	Shishi City	blue T-shirt	cotton	<50	<50	-	-
70	Shishi City	blue T-shirt	cotton	<50	<50	-	-
71	Shishi City	down-filled coat with red and blue colour	100% polyester	-	-	104	104
72	Shishi City	blue waistcoat	100% polyester	-	-	158	158
73	Shishi City	grey T-shirt	cotton and polyester	<50	<50	-	-
74	Shishi City	pink dress for girls	100% polyester	-	-	208	208
75	Shishi City	red T-shirt	100% polyester	-	-	153	153

Table A1b. Details of all articles from the second set of samples, including the concentrations of NPEs, phthalates and antimony. For phthalates, the total concentration (sum) of the quantified individual compounds is given, with data for individual phthalates in Appendix 2; '-' indicates not tested. * Where fabric was composed of mixed fibres, the concentration of antimony in polyester was calculated from fabric composition information, on the basis that all antimony arose from the polyester fibre within the fabric blend. ** fabric composition information not given

Appendix 2. Concentrations of individual phthalates in the 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)
CN13001	小玩皮 S·NAUGHTY	t-shirt	<3.0	<3.0	<3.0	7.4	<3.0	7.1	<3.0	<3.0	<3.0	15
CN13003	B&S	shorts & t-shirt set	<3.0	<3.0	<3.0	10	<3.0	7.6	<3.0	<3.0	<3.0	18
CN13004	one way	Dress & shorts set	9.9	<3.0	<3.0	26	<3.0	7.5	<3.0	<3.0	<3.0	43
CN13006	今童王 Jintongwang	t-shirt	4.8	<3.0	<3.0	<3.0	<3.0	16	<3.0	<3.0	<3.0	21
CN13008	小澄童 XCTONG	shorts & t-shirt set	<3.0	<3.0	<3.0	15	<3.0	<3.0	<3.0	<3.0	<3.0	15
CN13009	咿儿呀 yierya	dress	<3.0	<3.0	<3.0	12	<3.0	17000	<3.0	<3.0	<3.0	17000

Table A2a. Concentrations (mg/kg), in plastisol printed fabric from the first set of samples, of the following phthalates; dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-iso-butyl phthalate (DIBP), butylbenzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-iso-nonyl phthalate (DINP) and di-iso-decyl phthalate (DIDP). * Total concentration (sum) to 2 significant figures

Sample Number	Type of product	DnBP (mg/kg)	BBP (mg/kg)	DEHP (mg/kg)	DnOP (mg/kg)	DINP (mg/kg)	DIDP (mg/kg)	Total* (mg/kg)
01	girl's pant in yellow colour	<50	<50	<50	<50	<50	<50	<300
02	girl's suit in orange colour	<50	<50	<50	<50	<50	<50	<300
03	blue baby suit with superman print	<50	<50	<50	<50	<50	<50	<300
04	children suit	<50	<50	<50	<50	<50	<50	<300
06	children T-shirt with panda printing	<50	<50	<50	<50	<50	<50	<300
07	children pant with printing	<50	<50	<50	<50	<50	<50	<300
09	green T-shirt with printing	<50	<50	<50	<50	<50	<50	<300
10	grey suit with panda printing	<50	<50	<50	<50	<50	<50	<300
12	blue T-shirt with printing	<50	<50	<50	<50	<50	<50	<300
13	green suit with panda printing	<50	<50	<50	<50	<50	<50	<300
14	grey suit with printing	<50	<50	<50	<50	<50	<50	<300
15	red sport suit	<50	<50	<50	<50	<50	<50	<300
20	T-shirt with rabbit printing for girls	<50	<50	<50	<50	<50	<50	<300
21	suit with Mickey mouse printing	<50	<50	<50	<50	<50	<50	<300
22	blue jacket for boys	<50	<50	<50	<50	<50	<50	<300
27	green T-shirt for girls	<50	<50	<50	<50	<50	<50	<300

28	pink T-shirt for girls	<50	<50	<50	<50	<50	<50	<300
30	orange colour suit with printing	<50	<50	<50	<50	<50	<50	<300
31	blue T-shirt with printing for boys	<50	<50	<50	<50	<50	<50	<300
33	black suit with printing for boys	<50	<50	<50	<50	<50	<50	<300
34	dark blue suit for boys	<50	<50	<50	<50	<50	<50	<300
35	jeans with printing for kids	<50	<50	<50	<50	<50	<50	<300
39	girls suit with Mickey mouse printing	<50	<50	<50	<50	<50	<50	<300
40	baby suit with printing	<50	<50	<50	<50	<50	<50	<300
44	green T-shirt for girls	<50	<50	<50	<50	<50	<50	<300
45	T-shirt with printing	<50	<50	<50	<50	<50	<50	<300
48	blue T-shirt for boys	<50	<50	<50	<50	<50	<50	<300
50	yellow T-shirt with printing	<50	<50	<50	<50	<50	<50	<300
53	T-shirt for boys	<50	<50	<50	<50	<50	<50	<300
56	pink coat with cat-image printing	<50	<50	4400	<50	860	<50	5300
57	yellow sport suit	<50	<50	<50	<50	<50	<50	<300
58	red T-shirt with printing	<50	<50	<50	<50	<50	<50	<300
60	orange T-shirt	<50	<50	<50	<50	<50	<50	<300
61	grey sport suit	<50	<50	<50	<50	<50	<50	<300
66	sport suit with yellow and blue colour	<50	<50	<50	<50	<50	<50	<300
67	blue suit for boys	<50	<50	<50	<50	<50	<50	<300
68	pink suit for girls	<50	<50	<50	<50	<50	<50	<300
69	blue T-shirt	<50	<50	<50	<50	<50	<50	<300
70	blue T-shirt	<50	<50	<50	<50	<50	<50	<300
73	grey T-shirt	<50	<50	<50	<50	<50	<50	<300

Table A2b. Concentrations (mg/kg), in plastisol printed fabric from the second set of samples, of the following phthalates; 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 (sum) to 2 significant figures

Appendix 3. Concentrations of individual organotins in the printed fabric from 5 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)
CN13001a	小玩皮 S·NAUGHTY	t-shirt	fabric / print plastic turquoise+white	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CN13001b	小玩皮 S·NAUGHTY	t-shirt	print plastic blue+yellow-orange	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CN13003	B&S	shorts & t-shirt set	fabric / print plastic black+multicolour	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CN13006a	今童王 Jintongwang	t-shirt	fabric / print white-grey	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CN13006b	今童王 Jintongwang	t-shirt	print plastic black+brown	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CN13008	小澄童 XCTONG	shorts & t-shirt set	fabric / print plastic black-red+white-purple	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CN13009	咿儿呀 yierya	dress	fabric / print plastic white	<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; monobutyl tin (MBT), dibutyl tin (DBT), dioctyltin (DOT), Tributyltin (TBT), Triphenyltin (TPhT), Monooctyltin (MOT), Tetrabutyltin (TTBT), Tricyclohexyltin (TCHT)

Appendix 4. Concentrations of individual PFCs in the article tested (CN13010)

sample Code	Total (µg/kg)	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)
CN13010	7.97	< 2170	< 2170	< 2170	< 1450	< 2170	< 1450	< 1450	< 1450	< 1450	4730	< 1450	3250

Table A4a. Concentrations of ionic PFCs* by mass (ng/kg) in CN13010; 1000 ng/kg = 1 µg/kg

sample Code	PFUnA (ng/kg)	PFDoA (ng/kg)	PFTTrA (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)
CN13010	< 1450	< 1450	< 1450	< 1450	< 1450	< 2900	< 2900	< 2900	< 2170

Table A4a. continued; concentrations of ionic PFCs* by mass (ng/kg) in CN13010; 1000 ng/kg = 1 µg/kg

sample Code	Total (µg/m²)	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)
CN13010	0.558	<0,151	<0,151	<0,151	<0,101	<0,151	<0,101	<0,101	<0,101	<0,101	0.331	<0,101	0.227

Table A4b. Concentrations of ionic PFCs* by area (µg/m²) in CN13010; 1000 ng/kg = 1 µg/kg

sample Code	PFUnA (µg/m²)	PFDoA (µg/m²)	PFTTrA (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)
CN13010	<0,101	<0,101	<0,101	<0,101	<0,101	<0,202	<0,202	<0,202	<0,151

Table A4b. Continued; concentrations of ionic PFCs* by area (µg/m²) in CN13010; 1000 ng/kg = 1 µg/kg

sample Code	Total (µg/kg)	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)
CN13010	1010	< 14	370	110	< 47	< 160	400	130	< 9	< 9	< 9	< 9

Table A4c. Concentrations of volatile PFCs* by mass (µg/kg) in CN13010; 1000 ng/kg = 1 µg/kg

sample Code	Total (µg/m²)	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)
CN13010	70.7	<0,98	25.9	7.70	<3,29	<11,2	28.0	9.10	<0,63	<0,63	<0,63	<0,63

Table A4d. Concentrations of volatile PFCs* by area (µg/m²) in CN13010; 1000 ng/kg = 1 µg/kg

* 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)