# Hazardous Chemicals in Consumer Products

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## Summary

That hazardous chemicals are present in our environment is confirmed by several studies and is becoming increasingly well documented. However, only few people are aware that a number of these chemicals are used as additives in consumer goods we buy and use in our home everyday. In this study 33 consumer products, including body care products, toys, textiles, deodorizers and cleaners, have been tested for the presence of bisphenol-A, alkylphenols and ethoxylates, phthalates, musks and organotin compounds. Additionally a selected number of samples were analysed to identify other than the target compounds.

The results show that most polymer products, or products containing polymer parts, do contain nonylphenol and nonylphenol ethoxylates, phthalates or both. Especially the pyjamas with polymer prints contain high concentrations of DINP and DIDP up to 54,000 mg/kg. The concentrations of nonylphenol and nonylphenol ethoxylates in this samples averaged respectively 10 mg/kg and 1,000 mg/kg. A soft plastic baby toy contained, apart from nonylphenol and a number of target phthalates, high amounts of the plasticizer di-isooctyl adipate. Bisphenol-A was quantified in a polycarbonate baby bottle at 14 mg/kg while it was not found in canned food samples. Perfumes also contained phthalates, especially di-ethyl phthalate, and musks, mainly the polycyclic musk HHCB and in one case the nitro-musk MK. With one exception only low amounts of phthalates and musks were found in shampoos, deodorizers and cleaning products. Organotin compounds were quantified in one pyjama sample while others showed traces of these compounds.

## Contents

# 1. Introduction

## 1.1 Hazardous chemicals

The progress of the chemical industry in the past century has supplied the world with a vast amount of chemicals. At present roughly 100,000 chemicals are used and more than 500 new chemicals are introduced annually [1]. From these, several are known to cause adverse effects to man and animal life. The best documented are probably the persistent organic pollutants (POPs), such as the polychlorinated biphenyls (PCB) and the pesticide DDT. Although the use of chemicals as PCBs and DDT is forbidden for some time, it is still possible to measure these compounds in the environment worldwide. Meanwhile, new chemicals have replaced these compounds, and some of these chemicals, like phthalates, alkylphenols and alkylphenol ethoxylates and brominated flame retardants (BFR) are produced and used in huge amounts. Due to the production and use these compounds are found in sediments and surface waters. A recent TNO study, conducted for Greenpeace and focusing on the presence of hazardous chemicals in precipitation, showed that phthalates, alkylphenols, alkylphenol ethoxylates, artificial musk compounds and flame retardants were present in precipitation samples [2].

## 1.2 Hazardous chemicals in consumer products

That such compounds are present in our environment is confirmed by several studies and is becoming increasingly well documented [2, 3]. However, only few people are aware that many of these chemicals are used as additives in consumer goods we buy and use in our home everyday. This includes textiles, carpets and curtains, television and computer equipment and also cosmetic products. Phthalate esters and alkylphenol ethoxylates are used to soften PVC polymers used in toys and certain prints on textiles. The same compounds and artificial musks are used in personal care products. Organotin compounds are used to stabilise polymers and are therefore sometimes found in prints on T-shirts and pyjamas and in polymer parts of diapers. Of course, these additives are there for a reason; flame retardants are added to protect users against fire, while phthalates are added to soften plastics or as a carrier in perfumes. However, a consequence of their presence in consumer products is that the user is constantly exposed to these chemicals and that they will enter the environment during or after use of the products. The latter aspect became apparent in the study into the presence of these compounds in precipitation. While the results for AHTN, an artificial musk, indicated the presence of a localized emission source, the results for HHCB, another artificial musk, indicated that diffuse emissions by the domestic use of products containing this compound was probably the major source of emission to the environment.

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[1] Jackson T. In: Material Concerns. Pollution, profit and quality of life. Routledge, London, ISBN 0-415-13248-7, 40, **1996**.

[2] Vethaak A.D., Rijs G.B.J., Schrap S.M., Ruiter H., Gerritsen A., Lahr J. In: Estrogens and xeno-estrogens in the aquatic environment of the Netherlands. RIZA/RIKZ-report no. 2002.001, February **2002**.

[3] Kallenborn R., Gaterman R., Planting S., Rimkus G.G., Lund M., Schlabach M., Burkow I.C. J. Chromatogr. A, 846, 295-306, **1999**.

# 2. Study objective and approach

## 2.1 Objective of the Greenpeace study

A recent TNO study revealed the presence of a number of hazardous chemicals in precipitation[4]. The objective of this study is to determine whether these compounds are also present in consumer products. In an earlier Greenpeace study it was already shown that these compounds can be found in the dust in common homes [5]. This study presents the results for the presence and concentrations of compounds in typical consumer products like cosmetics, textiles, toys and cleaning products.

## 2.2 Chemical parameters

In this study the decision was made to concentrate on compounds similar to those determinated in the previous study in precipitation. The following chemical parameters were selected for this study:

- Bisphenol-A
- Alkylphenols and alkylphenol ethoxylates
- Phthalates
- Artificial musk compounds
- Organotin compounds
- "Non-target compounds" not included in the compound groups listed above and that can be identified in a screening analysis using gas chromatography in combination with mass spectrometry

The individual chemicals are listed in table 1. Some additional information about the use of these compounds can be found in chapter 4.

## 2.3 Samples

In total 33 samples were received, 28 from Greenpeace in the United Kingdom and 5 from Greenpeace in The Netherlands. The samples are common consumer products, including cosmetics, textiles, toys, air fresheners and cleaning products. All samples were purchased by Greenpeace in common shops in August 2003 and coded. Of most samples a duplicate sample was available. Table 2 provides an overview of the received samples.

[4] Peters RJB. Hazardous Chemicals in Precipitation. TNO report R 2003/198, May **2003**.
[5] Santillo D, Labunska I, Davidson H, Johnston P, Strutt M and Knowles O. Consuming Chemicals, Greenpeace Research Laboratories Technical Note 01/2003 (GRL-TN-01-2003), **2003**.

***Table 1. Compound groups and specific compounds included in this study.***

| Group | Specific compounds | Acronym |
|---|---|---|
| **Phthalates** | dimethyl phthalate | DMP |
| | diethyl phthalate | DEP |
| | di-iso-butyl phthalate | DIBP |
| | di-n-butyl phthalate | DBP |
| | benzylbutyl phthalate | BBP |
| | dicyclohexyl phthalate | DCHP |
| | di-(2-ethylhexyl) phthalate | DEHP |
| | di-n-octyl phthalate | DOP |
| | di-iso-nonylphthalate | DINP |
| | di-iso-decyl phthalate | DIDP |
| **Artificial musks** | galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-2-benzopyran) | HHCB |
| | tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene) | AHTN |
| | musk ambrette (2,6-dinitro-3-methoxy-4-t.butyltoluene) | MA |
| | musk ketone (4,6-dinitro-2-acetyl-5-t.butylxylene) | MK |
| | musk tibetene (2,6-dinitro-3,4,5-trimethyl-1-t.butylbenzene) | MT |
| | musk xylene (2,4,6-trinitro-5-t.butylxylene) | MX |
| **Bisphenol-A** | Bisphenol-A | BPA |
| **Alkylphenols and alkylphenol ethoxylates** | octylphenol | OP |
| | nonylphenol | NP |
| | octylphenol ethoxylates | OPEO |
| | nonylphenol ethoxylates | NPEO |
| **Organotins** | monobutyltin | MBT |
| | dibutyltin | DBT |
| | tributyltin | TBT |
| | tetrabutyltin | TeBT |
| | monooctyltin | MOT |
| | dioctyltin | DOT |
| | triphenyltin | TPT |
| **Non-target compounds** | Identified in GC/MS screening | |

## *Table 2. Overview of samples and chemical parameters to be determined.*

| TNO Code | Greenpeace Code | Product Description | Chemical parameters to be determined | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | BpA | Musks | AP/APEO | Phthal | GC/MS | O-Tin |
| 52003227-001 | GP-NL-1 | Shampoo, Head&Shoulders | | X | | X | | X |
| 52003227-002 | GP-NL-2 | Shampoo, L'Oreal | | X | | X | | |
| 52003227-003 | GP-NL-3 | Shampoo: Fa | | X | | X | | |
| 52003227-004 | GP-NL-4 | Body Care: Nivea Body Milk | | X | | X | | |
| 52003227-005 | GP-NL-5 | Body Care: Dove Body Lotion | | X | | X | | |
| 52003227-006 | 1 and 1d | Poison 50ml, Christian Dior, Eau De Toilette Natural | | X | | X | | |
| 52003227-007 | 2 and 2d | Eternity 50ml, Calvin Klein, Eau De Toil | | X | | X | | |
| 52003227-008 | 3 and 3d | No.5, 50ml, Chanel, Eau de Parfum Vaporisateur spray | | X | | X | X | |
| 52003227-009 | 4 | 3 x packs of Tricky Putty, manufactured by Moose Enterprises Pty Ltd | | | | X | X | |
| 52003227-010 | 5 | Decorated Feeding Bottles (3 pack), Toys R Us | X | | | | | |
| 52003227-011 | 6 | Hamleys Magic Balloons (4 pack), Hamleys | | | | | X | |
| 52003227-012 | 7 and 7d | 2 x 2 packs of Sculpey oven-bake modelling clay, 'Red Hot Red', 56g each | | | | X | X | |
| 52003227-013 | 8 and 8d | Chad Valley Funky Bath Ducks ( 2 x 4 pack), | | | X | X | X | X |
| 52003227-014 | 9 and 9d | 2 x Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store | | | X | X | X | X |
| 52003227-015 | 10 and 10d | 2 x Piglet pyjamas for girls (ages 3-4 years), Disney | | | X | X | | X |
| 52003227-016 | 11 and 11d | 2 x Tigger pyjamas unisex with caption '100% Cheeky', (ages 12-18 months), Disney | | | X | X | | X |
| 52003227-017 | 12 and 12d | 2 x Tigger pyjamas for boys with caption 'Come on in little buddy. The Water's great!', (ages 12-18 months), Disney | | | X | X | | X |
| 52003227-018 | 13 and 13d | Bob The Builder pyjamas for boys (ages 1-1½), Mothercare | | | X | X | | X |
| 52003227-019 | 14 and 14d | 2 x Heinz 'Winnie the Pooh' pasta shapes in tomato sauce, 205g | X | | | | | |
| 52003227-020 | 15 and 15d | 2 x HP 'Bob The Builder' pasta shapes in tomato sauce, 213g | X | | | | | |
| 52003227-021 | 16 and 16d | 2 x Johnson's baby shampoo, camomile, 300ml and 500ml, Johnson and Johnson | | X | | X | | |
| 52003227-022 | 17 and 17d | 2 x Tesco kids 2 in 1 shampoo for curly/wavy hair, Cherry Crush, 250ml | | X | | X | | |
| 52003227-023 | 18 and 18d | 2 x Asda Bubbly Berry shampoo 2 in 1, 250ml | | X | | X | | |
| 52003227-024 | 19 and 19d | 2 x L'Oreal kids Fast Dry shampoo, melon, 250ml | | X | | X | X | |
| 52003227-025 | 20 and 20d | 2 x B&Q Colours, matt Magnolia, 75ml | | | X | X | | X |
| 52003227-026 | 21 | 2 x B&Q Colours, matt Lemon, 75 ml | | | X | X | X | X |
| 52003227-027 | 22 | Halford's Upholstery cleaner (high detergency formula), 500ml | | | X | X | X | |
| 52003227-028 | 23 | Turtle Wax original Minute Clean multi purpose cleaner | | | X | X | X | |
| 52003227-029 | 24 | Car Plan 'Matt Dash' low gloss protectant, 375ml | | | X | X | X | |
| 52003227-030 | 25 and 25d | Glade, Natural Breezes 'Cool Air' plug in refills (5 x 20ml), SC Johnson | | X | | X | | |
| 52003227-031 | 26 and 26d | Haze, Air Wick 'White Flowers' plug in refills (5 x 25ml), Reckitt Benckiser | | X | | X | X | |
| 52003227-032 | 27 and 27d | Ambi Pur parfume d'interieur Sky, 'Fresh Spring' (4 x 25ml), Sara Lee | | X | | X | X | |
| 52003227-033 | 28 and 28d | Ambi Pur Car 'Aqua' (8 x 8ml with diffusers and 2 x 8ml refills), Sara Lee | | X | | X | | |

# 3 Methods and materials

## 3.1 Sampling and sample pre-treatment

Samples were stored at room temperature until analysis. Samples consisting of a liquid or a suspension were homogenised by shaking for 10 minutes. From solid samples a proportional sub-sample, with respect to prints and coloured parts, was collected and cut into small pieces with clean scissors or a surgical knife. For textiles the pieces were smaller than 5 mm, for all other materials smaller than 2 mm. For pasta samples the entire sample was homogenised using a blender. Sticky samples like paints were mixed with sodium sulphate to obtain free flowing sub-samples. Depending on the type of analysis a sub-sample of 1, 2, 5 or 10 grams was collected for analysis.

## 3.2 Analytical procedures

### 3.2.1 Sample extraction

#### 3.2.1.1 Bisphenol-A in plastic

A sub-sample of the shredded material was dissolved in tetrahydrofuran. A known amount of $^{2}$D-biphenol-A ($^{2}$D-BPA) was added as an internal standard. The tetrahydrofuran solution was poured into excess ethanol to remove the polymer. After centrifugation and removal of the polymer, a part of the clear liquid was collected and evaporated to dryness. The residue was re-dissolved in a 50/50 mixture of HPLC water and methanol. Finally, the extract was filtered through a 0.45 µm filter and prepared for instrumental analyses.

#### 3.2.1.2 Bisphenol-A in pasta

A sub-sample of the homogenized sample was collected and $^{2}$D-BPA was added as an internal standard. The sample was extracted in an Ultra Turrax with a 50/50 mixture of heptane and acetonitrile. Following centrifugation the acetonitrile fraction was collected, and the remainder was extracted once more after the addition of fresh acetonitrile. The combined acetonitrile fractions were dried and evaporated to dryness. The residue was re-dissolved in a 50/50 mixture of HPLC water and methanol. Finally, the extract was filtered through a 0.45 µm filter and prepared for instrumental analyses.

#### 3.2.1.3 Alkylphenols and ethoxylates in liquid samples and suspensions

A sub-sample was mixed with methanol in a 100 ml vial, shaken for 2 minutes and heated in a water bath at 60°C for 15 minutes. Next, the vial was sonicated for 15 min until a homogenous suspension resulted, and stored in a refrigerator at 4°C for 60 min. The sample was centrifuged and a part of the clear liquid was evaporated to dryness. The residue was re-dissolved in a 50/50 mixture of HPLC water and methanol. Finally, the extract was filtered through a 0.45 µm filter and prepared for instrumental analyses.

#### 3.2.1.4 Alkylphenols and ethoxylates in solid samples

A sub-sample of the shredded material was soxhlet extracted overnight with dichloromethane. The extract was filtered if necessary and brought to a final volume of 100 ml with dichloromethane. A part

of this extract was evaporated to dryness under nitrogen. The residue was re-dissolved in a 50/50 mixture of HPLC water and methanol. Finally, the extract was filtered through a 0.45 µm filter and prepared for instrumental analyses.

### 3.2.1.5 Phthalates in liquid samples and suspensions

The sub-sample was mixed with hexane in a 100 ml vial and diphenyl phthalate (DPP) was added as an internal standard. The mixture was shaken for 2 minutes and heated in a water bath at 60°C for 15 minutes. Next, the vial was sonicated for 15 min until a homogenous suspension resulted, and stored in a refrigerator at 4°C for 60 min. The sample was centrifuged and a part of the clear liquid was concentrated, filtered through a 0.45 µm filter and brought to a final volume of 1 ml. Finally, 1,2,3,4-tetrachloronaphthalene was added as an injection standard.

### 3.2.1.6 Phthalates in solid samples

A sub-sample of the shredded material was brought into a soxhlet thimble and DPP was added as an internal standard. The sample was extracted overnight with dichloromethane. The extract was filtered if necessary and brought to a final volume of 100 ml with dichloromethane. A part of this extract was concentrated, filtered through 0.45 µm filter and brought to a final volume of 1 ml. Finally, 1,2,3,4-tetrachloronaphthalene was added as an injection standard.

### 3.2.1.7 Musks determination

A sub-sample was mixed with methanol in a 100 ml vial and phantolide (AHNI) was added as an internal standard. The mixture was shaken for 2 minutes and heated in a water bath at 60°C for 15 minutes. Next, the vial was sonicated for 15 min until a homogenous suspension resulted, and stored in a refrigerator at 4°C for 60 min. The sample was centrifuged and a part of the clear liquid was concentrated, filtered through a 0.45 µm filter and brought to a final volume of 1 ml. Finally, 1,2,3,4-tetrachloronaphthalene was added as an injection standard.

### 3.2.1.8 Organotin determination

A sub-sample was sonicated for 60 min in a sodium dithiocarbamate solution in ethanol after the addition of tripropyltin chloride (TPrT) as an internal standard. The extracts are left in the dark at room temperature overnight and sonicated a second time for 60 min. Next, the extracts were centrifuged and the sample residue removed. Two more internal standards, mono- and diheptyltin chloride (MHT and DHT) were added to control the extraction and derivatization procedure. After the addition of an acetate buffer (pH 4), HPLC water and a solution of sodium tetraethylborate (the derivatization agent) in ethanol, the mixture was extracted twice with hexane. The combined hexane fraction were dried and concentrated to a small volume. After purification of the extract using column chromatography on alumina, the extract is concentrated to a final volume of 1 ml and 1,2,3,4-tetrachloronaphthalene is added as an injection standard.

### 3.2.1.9 GC/MS screening

Extracts for GC/MS screening were prepared in the same way as those for the phthalates. For samples that were already extracted for phthalates, part of the phthalate extract was used for the GC/MS analysis.

### 3.2.2 Instrumental analysis

BPA, APs and APEOs are analysed using liquid chromatography in combination with mass spectrometry (LC/MS). The LC/MS was a Hewlett Packard 1100 LC/ESI/MS system equipped with a guard column and a Waters Symmetry $C_{18}$ analytical column, length 15 cm, 3.9 mm i.d., 5 µm particle size. For BPA and APs negative ionisation was used, for APEOs positive ionisation. The mass spectrometer was used in the selected ion monitoring mode and typically three ions were monitored for BPA and APs. For APEOs fifteen ions (for n=1 to n=15, each separated by 44 mass units) were monitored.

Phthalates, musks and organotin compounds were analysed using gas chromatography in combination with mass spectrometry (GC/MS). The GC/MS was a Hewlett Packard 6890 gas chromatograph equipped with HP-5MS capillary column, length 30 m, 0.25 mm i.d., 0.25 µm film thickness, and interfaced to a Hewlett Packard 5973 mass spectrometer. The mass spectrometer was used in the selected ion monitoring mode and typically two or three ions were monitored for each compound. For the GC/MS screening the same instrument was used in the scan mode, allowing the identification of peaks in the chromatogram based on their mass spectrum.

### 3.2.3 Calculation of results

Identification of target compounds was based on retention time and qualifier ion ratio's. Quantification was based on external standards analysed within the same series as the sample extracts. The external standards were prepared from commercially available pure substances. The number of ethoxy units in the commercial alkylphenol ethoxylate standards ranged from n=5 to n=15 with a maximum around n=8-9. In all cases peak areas were used for calculations. The recovery of the added extraction standards was calculated but only the organotin results were corrected for this recovery. No correction for blank value was applied.

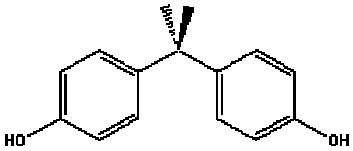
The identification of non-target compounds in the GC/MS screening was based on a comparison of mass spectra from the unknown compound peaks with reference mass spectra in a NIST/EPA/NIH Mass Spectral Library and the NBS75K library in the HP ChemStation. The compounds were considered positively identified if the correlation between spectra and library spectra was beter than 90%.

# 4 Results

## 4.1 Bisphenol-A

### 4.1.1 General information

Bisphenol-A (BPA) is a widely used intermediate in the production of epoxy resins, polycarbonate plastics and flame retardants, e.g. a substance used in an extensive range of products. Polycarbonate plastics are produced by the condensation of carbonyl chloride with diol monomers. The most common monomer for polycarbonates intended for food contact is BPA[6], which is reacted with carbonyl chloride in the presence of sodium hydroxide and a tertiary amine catalyst to form bisphenol-A polycarbonate. Not polymerised BPA may be released from the polycarbonate. Research of a few years ago indicated that BPA has estrogenic potency and is therefore generally included as one of the suspected endocrine disruptors [7]. BPA is moderately water soluble. The chemical structure of BPA is given in the figure below.




BPA was found in polycarbonate baby bottles in concentrations up to 20 mg/kg[8], but was not found to migrate into baby food[5]. However, BPA was found in canned food in concentrations up to 0.007 mg/kg[9], probably due to migration of polymer material on the inside of the can to the food.

### 4.1.2 Results for bisphenol-A in this study

Three samples, one baby bottle of polycarbonate and two canned food samples were analysed for BPA. BPA was quantified in the baby bottle polymer (52003227-010) at a level of 14 mg/kg which correlates well with known literature values[8]. In both canned food samples (52003227-019 and -020) no BPA was detected, probably for two reasons. First, the quantification limit of the method used in this study, 0.5 mg/kg, is much higher than the literature values found for BPA in canned food. Secondly, if BPA is found in canned food, this is always in foods with a moderate or high fat content. The pasta samples analysed in this study typically have a low fat content and therefore migration of BPA from the polymer to the food is probably not promoted.

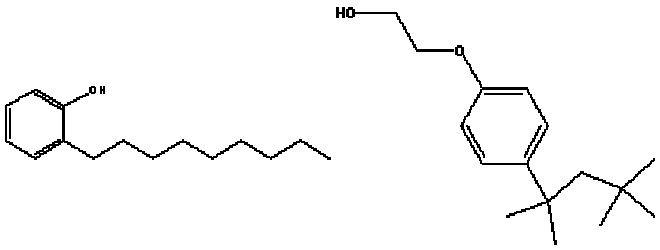
The results for BPA are presented in table 3 in the appendix.

## 4.2 Alkylphenol and alkylphenol ethoxylates

### 4.2.1 General information

[6] Mountfort KA, Kelly J, Jickels SM, Castle L. Food Additives and Contaminations, 56-63, *14*, **1997**.
[7] Toppari J. et al. Male reproductive health and evironmental chemicals with estrogenic effects. Miljöprojekt no. 290. Danisch Environmental Protection Agency, Denmark, **1995**.
[8] Sun Y, Wada M, Kuroda N, Hirayama K, Nakazawa H, Nkashima K. Analytical Sciences 697-702, *17*, **2001**.
[9] Goodson A, Summerfield W, Cooper I. Food Additives and Contaminants. 1-12, *19*, **2002**.

Alkylphenols (APs) and alkylphenol ethoxylates (APEOs) are used in plastics as additives and as surface-active ingredients in industrial detergents and emulsifiers. APs commonly used are nonylphenol (NP) and to a lesser extent octylphenol (OP), in both cases pre-dominantly the para-substituted isomers (>90%). APEOs are produced by a condensation reaction of APs with ethylene oxide. While the lower condensates (number of ethoxylate units about 4) are used as emulsifiers, the higher ethoxylates are used in textile and tapestry cleaning, and as emulsifiers in solvents and agricultural pesticides[10]. As with the APs nonylphenol ethoxylate (NPEO) is more used than octylphenol ethoxylate (OPEO). APs are moderately soluble in water while the APEOs are generally more water soluble than the parent APs themselves. The chemical structure of n-nonylphenol and octylphenol-mono-ethoxylate (better known as Triton X-100) are presented below.




4-NP has been found in PVC polymers where it is used as a stabilizer, in concentrations ranging from 1.4 to 1028 mg/kg[7]. We are not aware of data about the concentrations of APEOs in plastics.

### 4.2.2 Results for alkylphenols and alkylphenol ethoxylates in this study

In total 11 consumer products were analysed for APs and APEOs. These included children pyjamas, typical cleaning products and a baby toy. With the exception of sample 52003227-027, AP or APEO, or both were quantified in all other samples. In most cases the compounds found were NP, with concentrations ranging from 1.8 to 2,306 mg/kg, and NPEO with concentrations ranging from 2 to 1,930 mg/kg. OPEO was found in one sample (52003227-016) only with a concentration of 99 mg/kg. OP was not found in any of the samples. In part this may have been caused by the presence of an interfering compound, probably 2,4-di-(t-butyl) phenol, in a number of samples resulting in a higher quantification limit. A similar problem occurred with the determination of APEO in sample 52003227-013. This sample contains very high amounts of phthalates that seem to interfere with the quantification of APEO, again resulting in a higher quantification limit.

The complete results for AP and APEO are presented in table 4 in the appendix.

## 4.3 Phthalates

### 4.3.1 General information

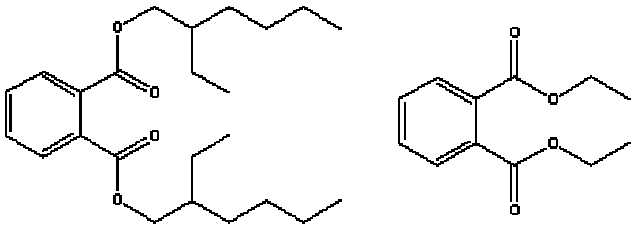
Phthalates are commonly found in cosmetic and personal care products, especially in nail polish, perfumes, hair sprays, household cleaners and deodorizers, as well as in soft plastics, baby toys, plastic garden furniture, shower curtains and so on. In the latter products phthalates are used as plasticizers to increase the flexibility of high molecular weight polymers. In some soft plastics phthalates may comprise up to 50% of the total weight. While until recently DEHP was the major phthalate used for this purpose, it now seems to be replaced by DINP.

[10] Maguire R.J. Water Qual. Res. J. Canada 34, 37-78, **1999**.

In perfumes phthalates are used as a carrier. The most important phthalate for this application is DEP. The Swedish Society for Nature Conservation performed an investigation about how common phthalates are in common cosmetic products[11]. Most products contained phthalates and in most cases DEP with concentrations ranging from less than 10 to 500 mg/kg for typical body care products and up to 19,000 mg/kg for perfumes. DBP was found also but to a much lesser extent.

Due to the presence of phthalates in common household products, cosmetics and toys, the potential for human exposure is very high. The EU has proposed a restriction for phthalates in articles for children in the age of 0-3 years, however, only temporary and for only 6 phthalates (DBP, BBP, DEHP, DOP, DINP and DIDP)[12]. Scientists at the US Center for Disease Control have documented human exposure to phthalates by determinations of the monoester metabolites in human urine[13].

The chemical structure of DEHP and DEP is presented below.



### 4.3.2 Results for phthalates in this study

In total 29 products were analysed for phthalates. These include body care products, perfumes, toys, textiles with prints and deodorizers. In four of these products no phthalates were quantified. In 12 products only small amounts of phthalates were found, with concentrations of the individual phthalates below 10 mg/kg. This indicates that these phthalates are probably not true additions, but more likely residues resulting from the raw production materials or otherwise. In the remaining 13 products higher concentrations of phthalates were found. This group can roughly be split into two groups; body care products, perfumes and deodorizers on one side, and toys and textiles with prints on the other side.

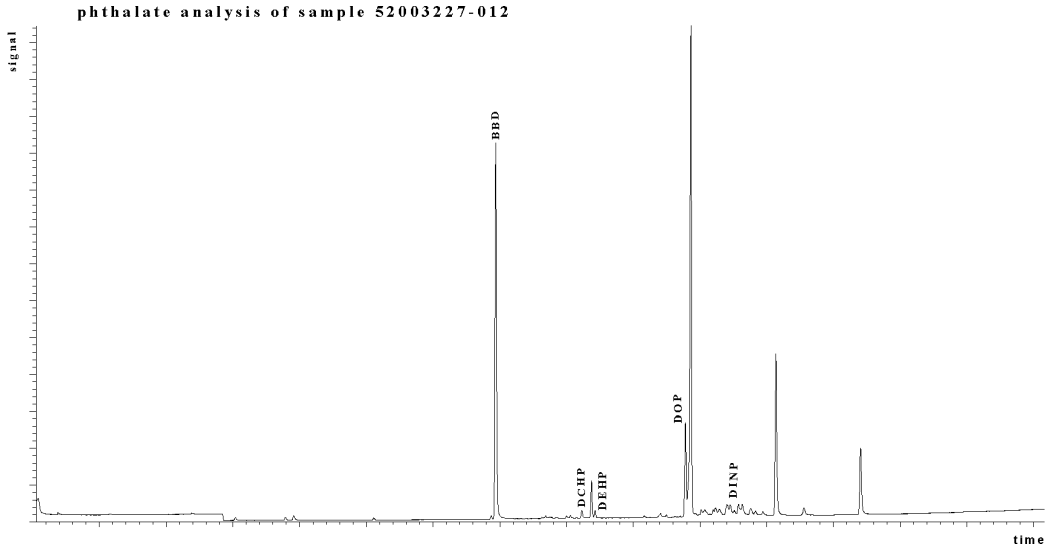
In the body care products and deodorizers mainly DEP was found in concentrations ranging from less than 10 mg/kg up to 168 mg/kg. Only small amounts of other phthalates, DEHP, with a maximum of 19 mg/kg were found in these products. As expected, high concentrations of DEP, ranging from 325 to 22,300 mg/kg, were found in the three perfume samples (52003227-006, -007 and -008).

In the toys, modelling clay and bath ducks (52003227-012 and -013) high concentrations of phthalates were quantified. The modelling clay mainly contained BBP and DINP in concentrations of respectively 32,300 mg/kg and 18,500 mg/kg. DCHP, DEHP and DOP were also found in this sample in concentrations up to 4,000 mg/kg. In the bath ducks (52003227-013) at first only DINP and DIDP were quantified in concentrations up to 7,300 and 6,200 mg/kg respectively. However, this seems rather low for this soft type of PVC material. The GC/MS screening revealed that another softener, di-iso-octyl adipate, was present in this sample. Although the amount was not quantified, the concentration was estimated by comparison with DINP and DIDP in this sample, and is expected to be at least 200,000 mg/kg, e.g. 20% by weight.

[11] Swedish Society of Nature Conservation. Phthalates in European Cosmetic Products. November, **2002**.
[12] Rastogi SC, Worsoe IM. Danisch National Environmental Research Institute. NERI Technical Report No. 373, **2001**.
[13] Blount BC et al. Environmental Health Perspectives, 108, 979-982, **2000**.

In three of the five pyjama samples (52003227-014, -017 and -018) high concentrations of phthalates were quantified. All three were found to contain DINP in concentrations ranging from 27,500 mg/kg to 54,000 mg/kg. Two of the three samples also contained DIDP, in both cases about 10% of the DINP concentration, indicating that the DIDP is probably an impurity of the DINP. Finally, one of those two samples also contained BBP, DCHP and DEHP in amounts up to 3,400 mg/kg. In all cases it may be expected that these phthalates originate from the prints on the front of the pyjamas, and not from the fabric itself. Since these samples were sub-sampled proportionally, and the print is about 10% of the total surface of the top of the pyjama, the actual phthalate concentrations in the print material will be much higher than the results presented here.

The chromatogram beneath is that of the extract of sample 52003227-012 showing the different phthalates identified in this sample. The complete results of the phthalate analysis are presented in table 5 (two pages) in the appendix.

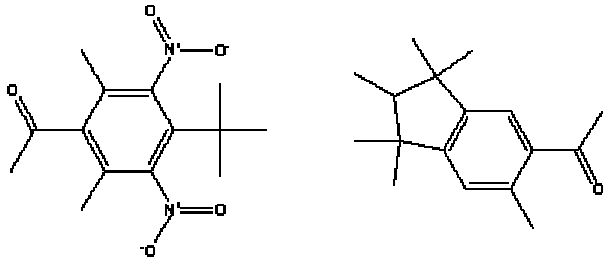



## 4.4 Musks

### 4.4.1 General information

Originally, musk is a male sexual scent signal and is since ancient times aspired to humans who have used it for medicines and as a fixative in perfumes. However, the increasing demand resulted in the production of artificial musk fragrances. The most well known artificial musks are musk xylene (MX), musk ketone (MK), and the polycyclic musks tonalide (AHTN) and galaxolide (HHCB). Due to their toxicity and persistence, nitro musks are no longer produced in Europe and replaced by the synthetic polycyclic musks [14]. The structures of MK and AHTN are presented below.

[14] Bester K, Hühnerfuss H, Lange W, Rinkus GG, Theobald N. Water Res. 32, 1857-1858, **1998**.

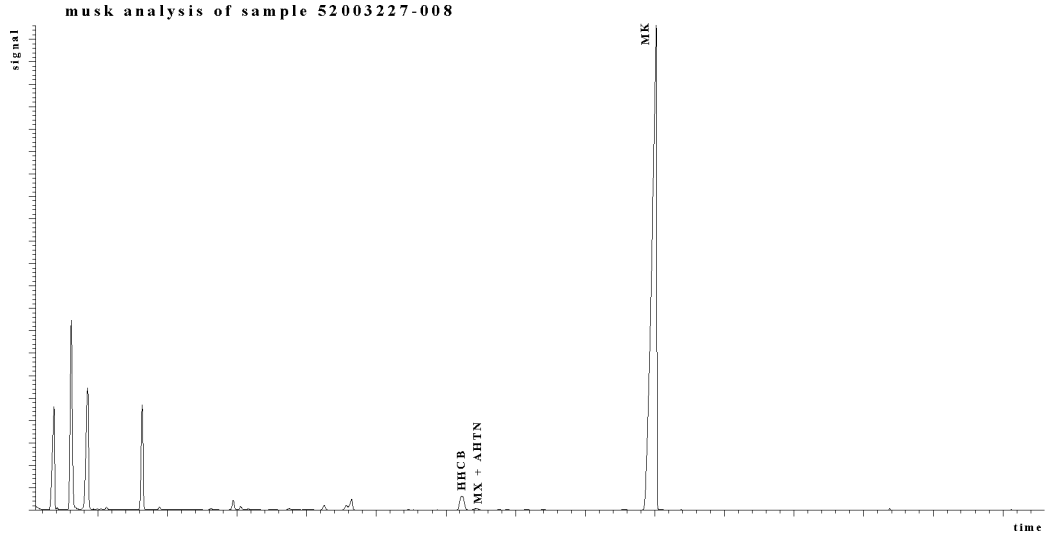


Musks are used as additives for perfumes, in detergents and soaps, in body lotions and deodorizers. Only limited information was found in the literature about the concentrations of musks in these types of products. In a study by the Dutch Keuringsdienst van Waren 114 cosmetic products were tested for nitro-musks[15]. MK was the most prominent musk and found in about 50% of the samples, with concentrations ranging from 1 to 24,000 mg/kg, the latter found in perfume.

### 4.4.2 Results for musks in this study

In this study MK, 4,600 mg/kg, was found in only one sample (52003227-008, Chanel No. 5) together with a small amount of MX, and some HHCB. Higher amounts of HHCB were found in both other perfume samples; Poison from Christian Dior and Eternity from Calvin Klein contained respectively 6,200 mg/kg and 8,000 mg/kg HHCB. The same polycyclic musk was also found in two shampoo's both from L'Oreal in concentrations of 350 mg/kg and 540 mg/kg. All the products containing higher amounts of HHCB also contained low amounts of AHTN, roughly 0.5% to 10% of the HHCB content. AHTN was found in a high concentration of 9,100 mg/kg in only one sample, Ambi Pur perfume d'interieur Sky (52003227-032). The other nitro-musks MA and MT were not found in any of the samples analysed for musks.

The chromatogram beneath is that of the extract of Chanel No.5 (52003227-008) with the musks indicated. The results of the musk analysis are presented in table 6 in the appendix.

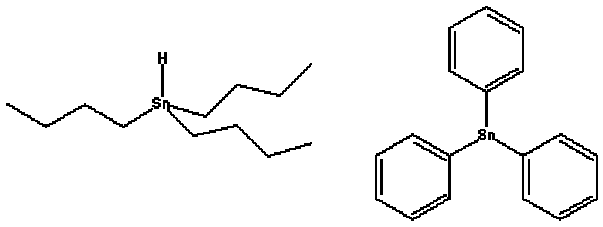



[15] Rooselaar J, Weijland JW. De bepaling van nitromuskverbindingen in kosmetische producten met behulp van GC en GC/MS. Project EN 94-3, February **1997**.

## 4.5 Organotin compounds

### 4.5.1 General information

There are three major applications for organotin compounds. First, the use of TBT in anti-fouling paints for ships, secondly, the use of TPT as a pesticide, and third, the use of butyl- and octyltin compounds as stabilisers in polymers. Therefore, many textile products containing polymer parts, like T-shirts with prints, sanitary bandages, plasters and diapers, can contain organotin compounds[16]. In some occasions organotin compounds are used as fungicides on textiles that are exposed to extreme whether conditions, such as canvas. The structures of TBT and TPT are presented below.



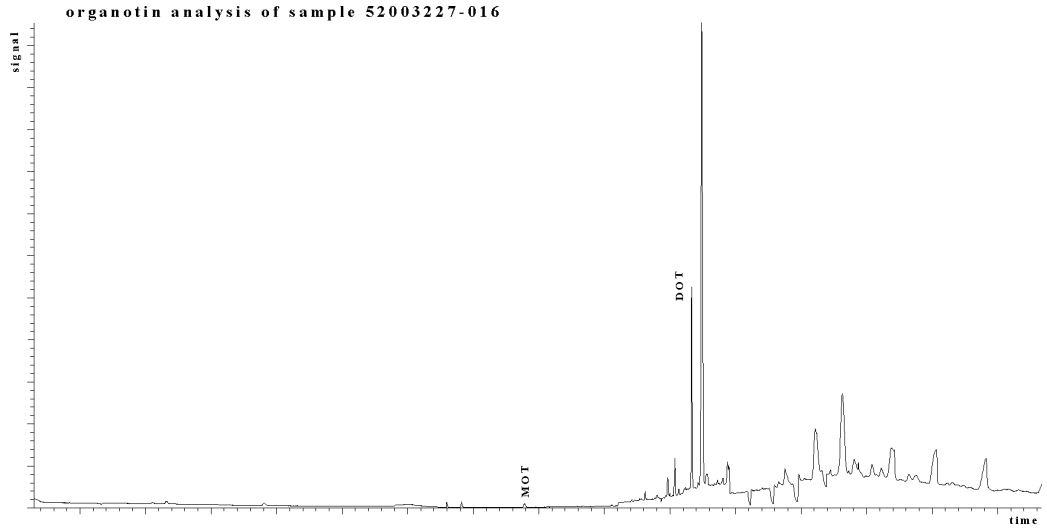

TNO has a lot experience with the analyses of these materials. Until few years ago mainly TBT and its degradation products DBT and MBT were found. Nowadays, it is more often DOT and MOT that are found, always in the polymer parts (foam, plastic or adhesives) used in these of products. Concentrations ranging from 0.01 mg/kg up to more than 2 mg/kg for textile products, and up to more than 50 mg/kg for polymer parts of products, have been found.

### 4.5.2 Results for organotin compounds in this study

In this study nine samples, a shampoo, three toys or related products, and five pyjamas are analysed for seven individual organotin compounds. Organotin compounds, DOT, MOT and a trace of TBT (below the quantification limit) where found in one pyjama sample (52003227-016) in concentrations up to 1.4 mg/kg product. The chromatogram of this sample is shown directly underneath. As with the phthalates it should be remembered that the sub-sampling was done proportionally, meaning that the organotin concentrations in the polymer print on the pyjamas will even be higher. Traces of MOT, DBT and MBT were further found in sample 52003227-015 while sample 52003227-017 showed traces of TBT and DBT. All the traces mentioned are above the detection limit of the method, 0.002 mg/kg, but below the quantification limit of 0.01 mg/kg.

The chromatogram beneath is that of the extract of sample 52003227-016. The peaks of DOT and MOT are indicated. The results of the organotin determinations are presented in table 7 in the appendix.

[16] Gaikema F.J., Alberts P.J. Gaschromatografische bepaling van residuen van organotinverbindingen in textielproducten. De Ware(n)-Chemicus 1999, 23-33.



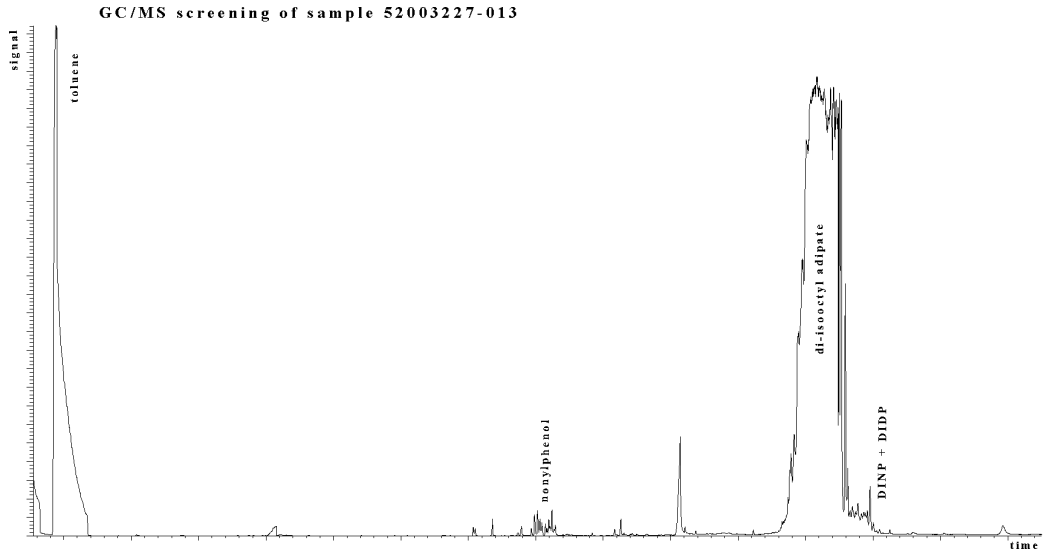

## 4.6 GC/MS screening

In the GC/MS screenings some additional compounds were identified in a number of samples. For some samples the chromatogram was very complex showing many peaks. This was especially the case for the chromatograms of the perfume and the deodorizer samples (52003227-008, -030, -031 and -032). Not surprisingly these products contain a many terpenes and terpenoids, and other fragrances like phenylethyl alcohol and methyl dihydrojasmonate. In the perfume sample an additional phthalate was identified, di-isooctyl phthalate , which was not on the target list. The same phthalate was found in the modelling clay, together with three more phthalates that were not on the target list. Since the pyjama sample (52003227-014) also contained di-isooctyl phthalate, and even in high concentrations, it is advised to add this phthalate to the target list of phthalates so that it will be monitored in additional product samples.

Terpenes were also found in Hamleys Magic Balloons (52003227-011), together with a low concentration of even numbered n-alkanes. The chromatogram of the extract of Tricky Putty (52003227-009) shows a series of peaks that were identified as a homologue series of polymethylsiloxanes and polymethylcyclosiloxanes. In the three cleaning products (52003227-027, -028 and -029) typical industrial solvent like 2-butoxyethanol, ethoxyethoxyethanol and the alkanes/cycloalkane mixture were found.

In the GC/MS screening of the bath ducks (52003227-013) an additional plasticizer was found in a very high concentration. It was identified as di-isooctyl adipate, an ester of hexadioic acid. This sample also contained toluene. A chromatogram of this sample is shown beneath with the identified compounds indicated.

No chlorinated compounds or pesticides were found in any of the samples. A summary of the additional compounds identified in the samples is presented in table 8 in the appendix.




## 4.7 Quality control measurements

### 4.7.1 Method validation parameters

All methods used were already used on earlier occasions and are validated in a limited way. The linearity of the instrumental analysis is known but the linearity of the complete method is not a very useful parameter since the concentrations in the products can be so far apart that extracts have to be concentrated or diluted for the result to fall in the linear range of the instrumental analysis.

The repeatability for each of the methods is determined by replicate analyses of the same sample. For homogenous samples, most liquids and suspensions, the repeatability is better than 15 % . For not homogenous solid samples, like the pyjamas with prints, the repeatability is better than 25%.

The quantification limits are given in the result tables in the appendix and generally vary between 0.01 mg/kg and 1 mg/kg, depending on the type of analyses and expected result. In some cases the quantification limits were raised to higher values due to interferences.

### 4.2.2 Recovery of extraction standard

To all samples extraction standards were added. The recovery of the extraction standards for phthalates and musks was in all cases above 80%. For the organotin compounds, the alkylphenols, alkylphenol ethoxylates and bisphenol-A, the recovery was above 70%. With the exception of the organotin determination the results are not corrected for the recovery of this extraction standard.

It should be mentioned that the addition of an extraction standard to a solid product sample, finely cut pieces of plastic for instance, does not say much about the quality of the extraction. Especially for the phthalates the quality of the extraction was tested additionally by extracting the same sample (52003227-013) three times. Analyses showed that 100% of the phthalates were found in the first extract.

### 4.2.3 Blank samples

With each series blank samples were included. These blank consisted of a complete analysis in the same series as the samples, however, without the addition of sample material. With the exception of

phthalates no blank values were observed. For the phthalates blank values were observed for DEHP, corresponding 1 to 5 mg/kg. Results were not corrected for this blanc value, but the quantification limit for DEHP was raised to 10 mg/kg.

# 5. Conclusions

In this study 33 consumer products have been tested for the presence the hazardous chemicals. A selected number of these 33 products were analysed for bisphenol-A, alkylphenols and ethoxylates, phthalates, musks and organotin compounds. In addition a GC/MS screening was performed on a selected number of samples.

- Three samples, a polycarbonate baby bottle and two canned food samples were analysed for BPA. BPA was found in the baby bottle in a concentration of 14 mg/kg but not in the canned food samples.

- APs and APEOs were analysed in 11 products, one plastic toy, five pyjamas, two paints and three cleaning products. With the exception of the cleaning products NP or NPEO or both were found in all products, NP in concentrations around 10 mg/kg with one high concentration of 2306 mg/kg, NPEO in concentrations up to 1930 mg/kg. The highest concentrations were found in the plastic toy and four of the five pyjamas. OP was not found while OPEO was found in one sample with a concentration of 99 mg/kg.

- 29 out of 33 products were analysed for phthalates. Typically, high concentrations of DEP were found in perfumes, while polymer materials contained mainly the phthalates DINP and DIDP, seemingly replacing DEHP that was found in a much lesser extent in this study. High concentrations of BBP and other phthalates were found in a sample of modelling clay. The additional GC/MS screening revealed that the plastic baby toy, apart from the target phthalates, contained high amounts of di-isooctyl adipate. Phthalates were generally not found, or only in low concentrations, in the shampoos, skin lotions, deodorizers and cleaning products tested in this study.

- Seven shampoos, two skin lotions, three perfumes and four deodorizers were tested for musk compounds. The artificial musk HHCB was the most prominent, mainly in perfumes and to a lesser extent in one brand of shampoo. The other shampoos and skin lotions did not contain any of the target musks. AHTN was found in low concentrations in the perfumes and in a high concentration in one brand of deodorizer. Two nitro-musks, MK and to a much lesser extent MX were found in one brand of perfume.

- Organotin compounds were tested in one shampoo, five pyjamas two paint samples. DOT and MOT were found in one of the pyjamas while traces of MBT, DBT and TBT where found in two more pyjamas.

- The additional GC/MS screenings on 14 samples mainly revealed compounds that can be expected in these kinds of products. Generally, fragrances, plasticizers other than the target phthalates, preservatives and solvents were identified. Di-isooctyl phthalate and di-isooctyl adipate were identified in more than one of the samples containing polymer parts, sometimes in high concentrations. Therefore, it should be considered to add these to the list of the target phthalates.

## 6. QA/QC statement

The analytical determinations in this study are performed in compliance with NEN-EN-ISO/IEC 17025 and STERLAB accreditation no. 54, “The development and application of methods for the determination of organic contaminants in environmental matrices, wastes and materials”. TNO Environment, Energy and Process Innovation is listed in the STERLAB register under no. L 026. STERLAB is part of the Dutch Council for Accreditation (RvA) and is a member of the European co-operation for Accreditation (EA) and the International Laboratory Accreditation Co-operation (ILAC). TNO Environment, Energy and Process Innovation operates in compliance with the Quality System standard ISO 9001 (certificate no. 00680-97-AQ-ROT-RvA)

# 7. Authentication

Name and address of the principal:

Greenpeace Nederland
Keizersgracht 174
1016 DW Amsterdam

Name and functions of the cooperators:

| | |
|---|---|
| Dr. R.J.B. Peters | Project Leader |
| Ing. R. Geenen | Technician |
| Drs. R.J. van Delft | Technician |
| Ing. J.A.D. van Renesse | Technician |

Names and establishments to which part of the research was put out to contract:
-

Date upon which, or period in which, the research took place:
February 2003 – May 2003

| Signature: | Appoved by: |
|---|---|
| R.J.B. Peters | Dr. M.P. Keuken |
| Project leader MA | Head of Department MA |

## Appendix: Full results of all product analysis

In the result tables the following acronyms are being used:

| Group | Specific compounds | Acronym |
|---|---|---|
| **Phthalates** | dimethyl phthalate | DMP |
| | diethyl phthalate | DEP |
| | di-iso-butyl phthalate | DIBP |
| | di-n-butyl phthalate | DBP |
| | benzylbutyl phthalate | BBP |
| | dicyclohexyl phthalate | DCHP |
| | di-(2-ethylhexyl) phthalate | DEHP |
| | di-n-octyl phthalate | DOP |
| | di-iso-nonylphthalate | DINP |
| | di-iso-decyl phthalate | DIDP |
| **Artificial musks** | galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-2-benzopyran) | HHCB |
| | tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene) | AHTN |
| | musk ambrette (2,6-dinitro-3-methoxy-4-t.butyltoluene) | MA |
| | musk ketone (4,6-dinitro-2-acetyl-5-t.butylxylene) | MK |
| | musk tibetene (2,6-dinitro-3,4,5-trimethyl-1-t.butylbenzene) | MT |
| | musk xylene (2,4,6-trinitro-5-t.butylxylene) | MX |
| **Bisphenol-A** | Bisphenol-A | BPA |
| **Alkylphenols and alkylphenol ethoxylates** | octylphenol | OP |
| | nonylphenol | NP |
| | octylphenol ethoxylates | OPEO |
| | nonylphenol ethoxylates | NPEO |
| **Organotins** | monobutyltin | MBT |
| | dibutyltin | DBT |
| | tributyltin | TBT |
| | tetrabutyltin | TeBT |
| | monooctyltin | MOT |
| | dioctyltin | DOT |
| | triphenyltin | TPT |

**Note:** When reading the tables in this appendix please note that while results are always rounded to the correct decimal number, they are not always rounded to the correct number of significant units. Due to the uncertainty in the results (for instance the repeatability of the method), the number of significant units is limited. This is especially true for when concentrations of several thousands of mg/kg are reported. In general no more than two significant numbers apply, so that for DEP in sample 52003227-007 (table 5) the result of 22999 mg/kg should be read as 23000 mg/kg.

### *Table 3. Concentrations of bisphenol-A in consumer products*

| TNO Code | Greenpeace Code | Product Description | Bisphenol-A<br>BpA<br>mg/kg |
|---|---|---|---|
| 52003227-010 | 5 | Decorated Feeding Bottles (3 pack), Toys R Us | 14 |
| 52003227-019 | 14 and 14d | 2 x Heinz 'Winnie the Pooh' pasta shapes in tomato sauce, 205g | < |
| 52003227-020 | 15 and 15d | 2 x HP 'Bob The Builder' pasta shapes in tomato sauce, 213g | < |

<: below quantification limit of 0.5 mg/kg for BpA

### *Table 4. Concentrations of alkylphenols and ethoxylates in consumer products*

| TNO Code | Greenpeace Code | Product Description | Alkylphenol and alkylphenol ethoxylates | | | |
|---|---|---|---|---|---|---|
| | | | OP mg/kg | NP mg/kg | OPEO mg/kg | NPEO mg/kg |
| 52003227-013 | 8 and 8d | Chad Valley Funky Bath Ducks ( 2 x 4 pack), Woolworths | < | 2306 | < 10 | < 10 |
| 52003227-014 | 9 and 9d | 2 x Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store | < 5 | 49 | < | 17 |
| 52003227-015 | 10 and 10d | 2 x Piglet pyjamas for girls (ages 3-4 years), Disney | < 5 | 6.9 | < | 1430 |
| 52003227-016 | 11 and 11d | 2 x Tigger pyjamas unisex with caption '100% Cheeky', (ages 12-18 months), Disney | < 5 | < | 99 | 1017 |
| 52003227-017 | 12 and 12d | 2 x Tigger pyjamas for boys with caption 'Come on in little buddy. The Water's great!', (ages 12-18 months), Disney | < 5 | 8.8 | < | 812 |
| 52003227-018 | 13 and 13d | Bob The Builder pyjamas for boys (ages 1-1½), Mothercare | < 5 | 8.8 | < | 1930 |
| 52003227-025 | 20 and 20d | 2 x B&Q Colours, matt Magnolia, 75ml | < | 1.8 | < | 246 |
| 52003227-026 | 21 | 2 x B&Q Colours, matt Lemon, 75 ml | < | 2.5 | < | 350 |
| 52003227-027 | 22 | Halford's Upholstery cleaner (high detergency formula), 500ml | < | < | < | < |
| 52003227-028 | 23 | Turtle Wax original Minute Clean multi purpose cleaner | < | < | < | 41 |
| 52003227-029 | 24 | Car Plan 'Matt Dash' low gloss protectant, 375ml | < 5 | < | < | 2 |

<: below quantification limit of 1 mg/kg for OP, NP, OPEO and NPEO unless stated otherwise

## *Table 5. Concentrations of phthalates in consumer products*

| TNO Code | Greenpeace Code | Product Description | Phthalates | | | | |
|---|---|---|---|---|---|---|---|
| | | | DMP mg/kg | DEP mg/kg | DIBP mg/kg | DBP mg/kg | BBP mg/kg |
| 52003227-001 | nd | Shampoo, Head&Shoulders | < | 1.1 | < | < | < |
| 52003227-002 | nd | Shampoo, L'Oreal | < | 168 | < | < | < |
| 52003227-003 | nd | Shampoo: Fa | < | 0.9 | < | < | < |
| 52003227-004 | nd | Body Care: Nivea Body Milk | < | 0.9 | < | < | < |
| 52003227-005 | nd | Body Care: Dove Body Lotion | < | 33 | < | < | < |
| 52003227-006 | 1 and 1d | Poison 50ml, Christian Dior, Eau De Toilette Natural Spray | < | 5675 | 33 | 14 | < |
| 52003227-007 | 2 and 2d | Eternity 50ml, Calvin Klein, Eau De Toil | < | 22299 | 38 | 14 | < |
| 52003227-008 | 3 and 3d | No.5, 50ml, Chanel, Eau de Parfum Vaporisateur spray | < | 325 | < | < | < |
| 52003227-009 | 4 | 3 x packs of Tricky Putty, manufactured by Moose Enterprises Pty Ltd | 1.6 | 1.6 | 17 | 16 | 3.6 |
| 52003227-012 | 7 and 7d | 2 x 2 packs of Sculpey oven-bake modelling clay, 'Red Hot Red', 56g each | < | < | 196 | 162 | 32349 |
| 52003227-013 | 8 and 8d | Chad Valley Funky Bath Ducks ( 2 x 4 pack), Woolworths | < | 1.6 | 37 | 26 | < |
| 52003227-014 | 9 and 9d | 2 x Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store | < | < | 44 | 15 | 1709 |
| 52003227-015 | 10 and 10d | 2 x Piglet pyjamas for girls (ages 3-4 years), Disney | < | 4.1 | 20 | 56 | 1.6 |
| 52003227-016 | 11 and 11d | 2 x Tigger pyjamas unisex with caption '100% Cheeky', (ages 12-18 months), Disney | < | 1.6 | 20 | 10 | < |
| 52003227-017 | 12 and 12d | 2 x Tigger pyjamas for boys with caption 'Come on in little buddy. The Water's great!', (ages 12-18 months), Disney | < | < | 108 | 25 | < |
| 52003227-018 | 13 and 13d | Bob The Builder pyjamas for boys (ages 1-1½), Mothercare | < | < | 139 | 22 | < |
| 52003227-021 | 16 and 16d | 2 x Johnson's baby shampoo, camomile, 300ml and 500ml, Johnson and Johnson | < | 1.5 | < | < | < |
| 52003227-022 | 17 and 17d | 2 x Tesco kids 2 in 1 shampoo for curly/wavy hair, Cherry Crush, 250ml | < | < | < | < | < |
| 52003227-023 | 18 and 18d | 2 x Asda Bubbly Berry shampoo 2 in 1, 250ml | < | 1.2 | < | < | < |
| 52003227-024 | 19 and 19d | 2 x L'Oreal kids Fast Dry shampoo, melon, 250ml | < | < | < | < | < |
| 52003227-025 | 20 and 20d | 2 x B&Q Colours, matt Magnolia, 75ml | < | < | 24 | 5.7 | < |
| 52003227-026 | 21 | 2 x B&Q Colours, matt Lemon, 75 ml | < | < | 35 | 7.3 | < |
| 52003227-027 | 22 | Halford's Upholstery cleaner (high detergency formula), 500ml | < | < | < | < | < |
| 52003227-028 | 23 | Turtle Wax original Minute Clean multi purpose cleaner | < | < | < | < | < |
| 52003227-029 | 24 | Car Plan 'Matt Dash' low gloss protectant, 375ml | < | 5.9 | < | < | < |
| 52003227-030 | 25 and 25d | Glade, Natural Breezes 'Cool Air' plug in refills (5 x 20ml), SC Johnson | < | 122 | < | < | < |
| 52003227-031 | 26 and 26d | Haze, Air Wick 'White Flowers' plug in refills (5 x 25ml), Reckitt Benckiser | < | 2.9 | < | < | < |
| 52003227-032 | 27 and 27d | Ambi Pur parfume d'interieur Sky, 'Fresh Spring' (4 x 25ml), Sara Lee | < | 108 | < | < | < |
| 52003227-033 | 28 and 28d | Ambi Pur Car 'Aqua' (8 x 8ml with diffusers and 2 x 8ml refills), Sara Lee | < | 6.9 | < | < | < |

<: below quantitation limit of 1 mg/kg unless stated otherwise

## *Table 5 (continued). Concentrations of phthalates in consumer products*

| TNO Code | Greenpeace Code | Product Description | Phthalates | | | | |
|---|---|---|---|---|---|---|---|
| | | | DCHP mg/kg | DEHP mg/kg | DOP mg/kg | DINP mg/kg | DIDP mg/kg |
| 52003227-001 | nd | Shampoo, Head&Shoulders | < | <10 | < | < | < |
| 52003227-002 | nd | Shampoo, L'Oreal | < | <10 | < | < | < |
| 52003227-003 | nd | Shampoo: Fa | < | <10 | < | < | < |
| 52003227-004 | nd | Body Care: Nivea Body Milk | < | 11 | < | < | < |
| 52003227-005 | nd | Body Care: Dove Body Lotion | < | <10 | < | < | < |
| 52003227-006 | 1 and 1d | Poison 50ml, Christian Dior, Eau De Toilette Natural Spray | < | 167 | < | < | < |
| 52003227-007 | 2 and 2d | Eternity 50ml, Calvin Klein, Eau De Toil | < | 88 | < | < | < |
| 52003227-008 | 3 and 3d | No.5, 50ml, Chanel, Eau de Parfum Vaporisateur spray | < | 20 | < | < | < |
| 52003227-009 | 4 | 3 x packs of Tricky Putty, manufactured by Moose Enterprises Pty Ltd | < | <10 | < | < | < |
| 52003227-012 | 7 and 7d | 2 x 2 packs of Sculpey oven-bake modelling clay, 'Red Hot Red', 56g each | 388 | 364 | 3988 | 18493 | < |
| 52003227-013 | 8 and 8d | Chad Valley Funky Bath Ducks ( 2 x 4 pack), Woolworths | < | <10 | < | 7297 | 6247 |
| 52003227-014 | 9 and 9d | 2 x Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store | 3445 | 797 | < | 27533 | 2303 |
| 52003227-015 | 10 and 10d | 2 x Piglet pyjamas for girls (ages 3-4 years), Disney | 1.8 | 12 | < | 64 | 4.2 |
| 52003227-016 | 11 and 11d | 2 x Tigger pyjamas unisex with caption '100% Cheeky', (ages 12-18 months), Disney | | 12 | < | 15 | 2.5 |
| 52003227-017 | 12 and 12d | 2 x Tigger pyjamas for boys with caption 'Come on in little buddy. The Water's great!', (ages 12-18 months), Disney | 75 | 201 | < | 53664 | 6113 |
| 52003227-018 | 13 and 13d | Bob The Builder pyjamas for boys (ages 1-1½), Mothercare | 35 | 73 | < | 49803 | < |
| 52003227-021 | 16 and 16d | 2 x Johnson's baby shampoo, camomile, 300ml and 500ml, Johnson and Johnson | < | <10 | < | < | < |
| 52003227-022 | 17 and 17d | 2 x Tesco kids 2 in 1 shampoo for curly/wavy hair, Cherry Crush, 250ml | < | <10 | < | < | < |
| 52003227-023 | 18 and 18d | 2 x Asda Bubbly Berry shampoo 2 in 1, 250ml | < | <10 | < | < | < |
| 52003227-024 | 19 and 19d | 2 x L'Oreal kids Fast Dry shampoo, melon, 250ml | < | <10 | < | < | < |
| 52003227-025 | 20 and 20d | 2 x B&Q Colours, matt Magnolia, 75ml | < | <10 | < | < | < |
| 52003227-026 | 21 | 2 x B&Q Colours, matt Lemon, 75 ml | < | <10 | < | 24 | < |
| 52003227-027 | 22 | Halford's Upholstery cleaner (high detergency formula), 500ml | < | <10 | < | < | < |
| 52003227-028 | 23 | Turtle Wax original Minute Clean multi purpose cleaner | < | <10 | < | < | < |
| 52003227-029 | 24 | Car Plan 'Matt Dash' low gloss protectant, 375ml | < | <10 | < | < | < |
| 52003227-030 | 25 and 25d | Glade, Natural Breezes 'Cool Air' plug in refills (5 x 20ml), SC Johnson | < | <10 | < | < | < |
| 52003227-031 | 26 and 26d | Haze, Air Wick 'White Flowers' plug in refills (5 x 25ml), Reckitt Benckiser | < | <10 | < | < | < |
| 52003227-032 | 27 and 27d | Ambi Pur parfume d'interieur Sky, 'Fresh Spring' (4 x 25ml), Sara Lee | < | <10 | < | < | < |
| 52003227-033 | 28 and 28d | Ambi Pur Car 'Aqua' (8 x 8ml with diffusers and 2 x 8ml refills), Sara Lee | < | 19 | < | 2.9 | < |

<: below quantitation limit of 1 mg/kg unless stated otherwise

## *Table 6. Concentrations of musks in consumer products*

| TNO Code | Greenpeace Code | Product Description | Musk compounds | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | HHCB mg/kg | AHTN mg/kg | MA mg/kg | MK mg/kg | MT mg/kg | MX mg/kg |
| 52003227-001 | nd | Shampoo, Head&Shoulders | < | < | < | < | < | < |
| 52003227-002 | nd | Shampoo, L'Oreal | 351 | 60 | < | < | < | < |
| 52003227-003 | nd | Shampoo: Fa | < | < | < | < | < | < |
| 52003227-004 | nd | Body Care: Nivea Body Milk | < | < | < | < | < | < |
| 52003227-005 | nd | Body Care: Dove Body Lotion | < | < | < | < | < | < |
| 52003227-006 | 1 and 1d | Poison 50ml, Christian Dior, Eau De Toilette Natural Spray | 6248 | 20 | < | < | < | < |
| 52003227-007 | 2 and 2d | Eternity 50ml, Calvin Klein, Eau De Toil | 7992 | 50 | < | < | < | < |
| 52003227-008 | 3 and 3d | No.5, 50ml, Chanel, Eau de Parfum Vaporisateur spray | 73 | 3.2 | < | 4592 | < | 2.2 |
| 52003227-021 | 16 and 16d | 2 x Johnson's baby shampoo, camomile, 300ml and 500ml, Johnson and Johnson | 131 | 15 | < | < | < | < |
| 52003227-022 | 17 and 17d | 2 x Tesco kids 2 in 1 shampoo for curly/wavy hair, Cherry Crush, 250ml | < | < | < | < | < | < |
| 52003227-023 | 18 and 18d | 2 x Asda Bubbly Berry shampoo 2 in 1, 250ml | < | < | < | < | < | < |
| 52003227-024 | 19 and 19d | 2 x L'Oreal kids Fast Dry shampoo, melon, 250ml | 537 | 2.1 | < | < | < | < |
| 52003227-030 | 25 and 25d | Glade, Natural Breezes 'Cool Air' plug in refills (5 x 20ml), SC Johnson | < | < | < | < | < | < |
| 52003227-031 | 26 and 26d | Haze, Air Wick 'White Flowers' plug in refills (5 x 25ml), Reckitt Benckiser | < | < | < | < | < | < |
| 52003227-032 | 27 and 27d | Ambi Pur parfume d'interieur Sky, 'Fresh Spring' (4 x 25ml), Sara Lee | < | 9058 | < | < | < | < |
| 52003227-033 | 28 and 28d | Ambi Pur Car 'Aqua' (8 x 8ml with diffusers and 2 x 8ml refills), Sara Lee | 6.3 | < | < | < | < | < |

<: below quantification limit of 0.5 mg/kg

## *Table 7. Concentrations of organotin compounds in consumer products*

| TNO Code | Greenpeace Code | Product Description | Organotin compounds | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | MBT mg/kg | DBT mg/kg | TBT mg/kg | TeBT mg/kg | MOT mg/kg | DOT mg/kg | TPT mg/kg |
| 52003227-001 | nd | Shampoo, Head&Shoulders | < | < | < | < | < | < | < |
| 52003227-013 | 8 and 8d | Chad Valley Funky Bath Ducks ( 2 x 4 pack), Woolworths | < | < | < | < | < | < | < |
| 52003227-014 | 9 and 9d | 2 x Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store | < | < | < | < | < | < | < |
| 52003227-015 | 10 and 10d | 2 x Piglet pyjamas for girls (ages 3-4 years), Disney | < | < | < | < | < | < | < |
| 52003227-016 | 11 and 11d | 2 x Tigger pyjamas unisex with caption '100% Cheeky', (ages 12-18 months), Disney | < | < | < | < | 0.06 | 1.4 | < |
| 52003227-017 | 12 and 12d | 2 x Tigger pyjamas for boys with caption 'Come on in little buddy. The Water's great!', (ages 12-18 months), Disney | < | < | < | < | < | < | < |
| 52003227-018 | 13 and 13d | Bob The Builder pyjamas for boys (ages 1-1½), Mothercare | < | < | < | < | < | < | < |
| 52003227-025 | 20 and 20d | 2 x B&Q Colours, matt Magnolia, 75ml | < | < | < | < | < | < | < |
| 52003227-026 | 21 | 2 x B&Q Colours, matt Lemon, 75 ml | < | < | < | < | < | < | < |

<: below quantification limit of 0.01 mg/kg

## *Table 8. Additional "non-target" compounds identified in GC/MS screening*

| TNO Code | Greenpeace Code | Product Description | Additional compounds identified in products with GC-MS screening |
|---|---|---|---|
| 52003227-008 | 3 and 3d | No.5, 50ml, Chanel, Eau de Parfum Vaporisateur spray | Complex chromatogram. Mainly fragrances: many terpenes or terpenoids, phenylethyl alcohol, phenylmethyl acetate, benzenepropanol, phenylpropenol, phenylpropenol acetate, benzyl benzoate, methyl tetradecanoate. Preservatives: benzyl benzoate, 2-hydroxy benzoic acid. Plasticisers: di-isooctyl phthalate. |
| 52003227-009 | 4 | 3 x packs of Tricky Putty, manufactured by Moose Enterprises Pty Ltd | Simple chromatogram. Characteristic pattern of polymethylsiloxanes and polymethylcyclosiloxanes |
| 52003227-011 | 6 | Hamleys Magic Balloons (4 pack), Hamleys | Simple chromatogram. Fragrances:terpenes like pinene, carene and limonene. Alkanes: even numbered in the range of $C_{10}$ to $C_{18}$ (low concentrations) |
| 52003227-012 | 7 and 7d | 2 x 2 packs of Sculpey oven-bake modelling clay, 'Red Hot Red', 56g each | Simple chromatogram. Fragrances: hexadecanoic acid, octadecanoic acid. Plasticisers: diheptyl phthalate, di-isooctyl phthalate, decyloctyl phthalate, isodecyloctyl phthalate |
| 52003227-013 | 8 and 8d | Chad Valley Funky Bath Ducks ( 2 x 4 pack), Woolworths | Simple chromatogram. Solvents: toluene. Plasticisers: di-isooctyl adipate (very high concentration) |
| 52003227-014 | 9 and 9d | 2 x Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store | Simple chromatogram. Plasticisers: di-isooctyl phthalate (amount comparable with DINP) |
| 52003227-024 | 19 and 19d | 2 x L'Oreal kids Fast Dry shampoo, melon, 250ml | Simple chromatogram. Fragrances: dimethyl octanol, methyl dihydrojasmonate. Solvents: tetradecene |
| 52003227-026 | 21 | 2 x B&Q Colours, matt Lemon, 75 ml | Simple chromatogram. Preservatives: 2,4-di-(1,1-dimethylethyl)phenol |
| 52003227-027 | 22 | Halford's Upholstery cleaner (high detergency formula), 500ml | Simple chromatogram. Solvents: 2-butoxyethanol, 1-decanol, 1-undecanol |
| 52003227-028 | 23 | Turtle Wax original Minute Clean multi purpose cleaner | Simple chromatogram. Solvents: 2-Ethoxyethoxyethanol |
| 52003227-029 | 24 | Car Plan 'Matt Dash' low gloss protectant, 375ml | Simple chromatogram. Fragrances: limoneen. Solvents: mixture of alkanes and cycloalkanes in the range of $C_{12}$-$C_{17}$ |
| 52003227-030 | 25 and 25d | Glade, Natural Breezes 'Cool Air' plug in refills (5 x 20ml), SC Johnson | Complex chromatogram. Mainly fragrances: many terpenes or terpenoids, phenylethyl alcohol, phenylmethyl acetate, methyl dihydrojasmonate, alpha-methyl benzenemethanol acetate |
| 52003227-031 | 26 and 26d | Haze, Air Wick 'White Flowers' plug in refills (5 x 25ml), Reckitt Benckiser | Complex chromatogram. Fragrances: many terpenes and terpenoids, methyl dihydrojasmonate, benzyl benzoate |
| 52003227-032 | 27 and 27d | Ambi Pur parfume d'interieur Sky, 'Fresh Spring' (4 x 25ml), Sara Lee | Complex chromatogram. Fragrances: many terpenes and terpenoids, phenylethyl alcohol, phenylmethyl acetate, methyl dihydrojasmonate. Preservatives: Butylated hydroxytoluene |