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TNO-report

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Chemical Additives in Consumer Products

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Summary

That man-made chemicals are present in our environment is confirmed by several studies and is becoming increasingly well documented. However, only few people are aware that several of these chemicals are used as additives in consumer goods we buy and use in our home everyday. In this study 12 consumer products, including household cleaning products, toys, textiles, electronic equipment and baby care products, have been tested for a range of compounds. Additionally, a selected number of samples were analysed to identify other than the target compounds.

The results show that both household cleaning products do not contain alkylphenols, alkylphenol ethoxylates, phthalates or artificial musks. In addition, the GC/MS screening did not reveal any special compounds other than low amounts of the preservative chlorobutanol in one of the samples. The toys and the (prints on the) textiles did contain high concentrations of especially di-isononyl phthalates up to about 150,000 mg/kg. The same products also contained nonyl- and octylphenol ethoxylates. Nonylphenol itself was found in four products. Surprisingly one of the baby care products contained both, nonylphenol and nonylphenol ethoxylates. One of the toys also contained substantial amounts of organotin compounds, especially octyltin compounds in a maximum concentration of 42 mg/kg for di-octyltin. In the DVD players limited amounts of brominated flame retardants were found, most likely originating from discrete electronic components and printed circuit boards. A GC/MS screening revealed that the majority of flame retardants in these products are organophosphate tri-esters. The baby care products both contained the artificial musk galaxolide in concentrations up to 327 mg/kg, as well as the older musk ketone. In addition one of these products contained di-ethyl phthalate in a concentration of 589 mg/kg while the other contained nonylphenol ethoxylate in a concentration of 98 mg/kg.

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1. Introduction

1.1 Man-made chemicals in consumer products

The progress of the chemical industry in the past century has supplied the world with a vast amount of chemicals. In the mid 1990's, it was estimated that roughly 100,000 chemicals were used and more than 500 new chemicals introduced annually¹. 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, other man-made chemicals have become increasingly widely used. Some of these chemicals, like phthalates, alkylphenols (AP), alkylphenol ethoxylates (APEO) and organotin compounds are produced and used in vast amounts. Due to their production and use, these compounds can be found in sediments and surface waters.

That such compounds are present in our environment is confirmed by several studies and is becoming increasingly well documented^{2,3,4}. 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. These include textiles, carpets and curtains, television, computer equipment and all kinds of personal care products⁵. Artificial musks and phthalates are used as a fragrance, fixative and carrier in perfumes, phthalates and APEO are used to soften PVC polymers in toys and certain prints on textiles. 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, 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.

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.

⁴ Peters R. *Hazardous Chemicals in Precipitation*. TNO report R 2003/198, May **2003**.

⁵ Peters R. *Hazardous Chemicals in Consumer Products*. TNO report R 2003/370, September **2003**.

2. Study objective and approach

2.1 Objective of the Greenpeace study

An earlier TNO study revealed the presence of a number of typical chemical additives in consumer products^{5,6}. In an earlier Greenpeace study it was already shown that these additives can be found in the dust in common homes⁷. The objective of this study is a follow up of the previous studies, however, broadening to other consumer products.

2.2 Chemical parameters

In this study the decision was made to concentrate on additives similar to those that were analysed in the previous studies. The following chemical parameters were selected for this study:

- Alkylphenols and alkylphenol ethoxylates
- Phthalates
- Artificial musk compounds
- Organotin compounds
- Brominated flame retardants
- “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 12 samples were received from Greenpeace Italy. The samples are common consumer products, including household cleaners, toys, textiles, DVD players and personal care products. Table 2 provides an overview of the received samples.

⁶ Peters RJB. *The Determination of Selected Additives in Consumer Products*. TNO report R 2004/002, December 2003.

⁷ 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
Alkylphenols and alkylphenol ethoxylates	octylphenol	OP
	nonylphenol	NP
	octylphenol ethoxylates	OPEO
	nonylphenol ethoxylates	NPEO
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
Brominated flame retardants	2,2',4,4'-tetrabromo diphenylether	BDE 47
	2,2',4,4',5-pentabromo diphenylether	BDE 99
	2,2',4,4',6-pentabromo diphenylether	BDE 100
	2,2',4,4',5,5'-hexabromo diphenylether	BDE 153
	2,2',3,4,4',5',6-heptabromo diphenylether	BDE 183
	decabromo diphenylether	BDE 209
	hexabromo cyclododecane	HBCD
	tetrabromo bisphenol-A	TBBPA
Organotins	monobutyltin	MBT
	dibutyltin	DBT
	tributyltin	TBT
	tetrabutyltin	TeBT
	monoocetyl tin	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	Class of product	Product and Company	Phthal	AP/APEO	Musks	BFR	O-Tin	Screen
52005041-001	1	Household goods	ACE Igiene casa: Procter&Gamble	X	X	X			X
52005041-002	2		Lysoform casa: Lever Fabergé Italia s.r.l.	X	X	X			X
52005041-003	3	Toys	Spider-man flip 'n zip: Giochi Preziosi s.p.a.	X				X	X
52005041-004	4		Barbie Fashion Fever: Mattel	X				X	X
52005041-005	5	Children's articles	Eva puzzle mats: Fantastiko s.r.l.	X		X		X	X
52005041-006	6		La Puzzone dei puzzones, Scarpone puzzone: Giochi Preziosi s.p.a.	X	X	X		X	X
52005041-007	7	Sport T-shirts	Girl collection 5 years: Emporio Junior s.r.l.	X	X			X	
52005041-008	8		K.T.Shirt MC Sport&Stripes: Champion Europe	X	X			X	
52005041-009	9	DVD Players	DVX PI@yer: Voxson	X			X		
52005041-010	10		DV - P 345 E: Hitachi	X			X		
52005041-011	11	Baby detergents	Babygella Bagno delicato: Rottapharm s.r.l.	X	X	X			X
52005041-012	12		Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	X	X	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. Sticky samples 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 Alkylphenols and alkylphenol ethoxylates

For 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 minutes until a homogenous suspension resulted, and stored in a refrigerator at 4°C for 60 minutes.

For 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.

If necessary, sample extracts were 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.

3.2.2 Phthalates

For liquid samples and suspensions a 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 minutes until a homogenous suspension resulted, and stored in a refrigerator at 4°C for 60 minutes. Sample extracts were 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.

For 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 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 to all extracts.

3.2.3 Artificial musks

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 minutes until a homogenous suspension resulted, and stored in a refrigerator at 4°C for 60 minutes. 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.

3.2.4 Brominated flame retardants

The analytical sample was brought into a soxhlet thimble and 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 and filtered through 0.45 µm filter. Diazomethane was added for the derivatization of any free tetrabromobisphenol-A in the sample extract. Finally, the extract was concentrated to a volume of 1 ml and 1,2,3,4-tetrachloronaphthalene was added as an injection standard.

3.2.5 Organotin compounds

A sub-sample was sonicated for 60 minutes 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 minutes. 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.

3.2.6 GC/MS screening

Extracts for GC/MS screening were prepared in the same way as those for the phthalates.

3.2.7 Instrumental analysis

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 C₁₈ 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, brominated flame retardants 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.

3.2.8 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 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.

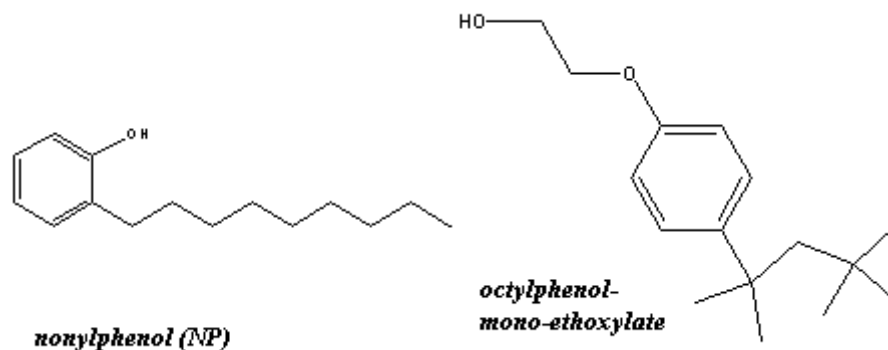
The identification of non-target compounds in the GC/MS screening was based on a comparison of mass spectra from the unknown compound peaks with reference mass spectra in a NIST/EPA/NIH Mass Spectral Library and the NBS75K library in the HP ChemStation. The compounds were considered positively identified if the correlation between spectra and library spectra was better than 90% and after visual confirmation by the analyst. Note, although confidence in the identities is high, it does not provide definitive identification

4. Results

4.1 Alkylphenol and alkylphenol ethoxylates

4.1.1 General information

Alkylphenols (AP) and alkylphenol ethoxylates (APEO) are used in plastics as additives and as surface-active ingredients in industrial detergents and emulsifiers. AP commonly used are nonylphenol (NP) and to a lesser extent octylphenol (OP), in both cases pre-dominantly the para-substituted isomers (> 90%). APEO are produced by a condensation reaction of AP 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 carpet cleaning, and as emulsifiers in solvents and agricultural pesticides⁸. As with the AP, nonylphenol ethoxylate (NPEO) is more used than octylphenol ethoxylate (OPEO). AP are moderately soluble in water while the APEO are generally more water soluble than the parent AP themselves. The chemical structure of n-nonylphenol and octylphenol-mono-ethoxylate (better known as Triton X-100) are presented below. NP has been found in PVC polymers where it is used as a stabilizer. NPEO is used in polymer prints on textile articles like T-shirts and pyjamas⁵.



4.1.2 Results for alkylphenols and alkylphenol ethoxylates in this study

In this study AP and APEO were determined in 8 consumer products. These included typical household cleaning products, toys, T-shirts and baby lotions. While octylphenol (OP) was found in none of the samples, nonylphenol (NP) was found in four of the samples in a maximum concentration of 8.9 mg/kg. Surprisingly,

⁸ Maguire R.J. Water Qual. Res. J. Canada 34, 37-78, 1999.

the highest NP concentration was found in one of the baby care products (52005041-011). The same product also contained nonylphenol ethoxylate (NPEO) in a concentration of 98 mg/kg. NPEO was found in four products with a maximum concentration of 354 mg/kg. Both T-shirts contained NPEO which probably originates from the polymer prints on the T-shirt. Octylphenol ethoxylate (OPEO) was found in only one of the samples. The complete results for AP and APEO are presented in table 3 in the appendix.

4.2 Phthalates

4.2.1 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 di-(2-ethylhexyl) phthalate (DEHP) was the major phthalate used for this purpose, it now seems to be replaced by diisononyl phthalate (DINP).

In perfumes phthalates are used as a carrier. The most important phthalate for this application is diethyl phthalate (DEP). The Swedish Society for Nature Conservation performed an investigation about how common phthalates are in cosmetic products⁹. 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. Similar results were found in a recent Greenpeace study of 36 perfume products¹⁰.

Due to the presence of phthalates in common household products, cosmetics and toys, the potential for human exposure is very high. The EU has imposed an emergency restriction for 6 phthalates (DBP, BBP, DEHP, DOP, DINP and DIDP) in articles for children in the age of 0-3 years¹¹. Scientists at the US Centre for Disease Control have documented human exposure to phthalates by determinations of the monoester metabolites in human urine¹² while WWF studies and a TNO study

⁹ Swedish Society of Nature Conservation. *Phthalates in European Cosmetic Products*. November, **2002**.

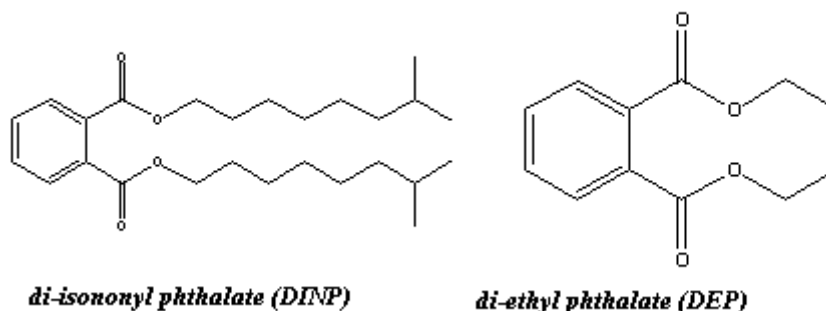
¹⁰ Peters RJB. *Phthalates and Artificial Musks in Perfumes*. TNO report R&I-A R 2005/011, January **2005**.

¹¹ Rastogi SC, Worsoe IM. Danish National Environmental Research Institute. NERI Technical Report No. 373, **2001**.

¹² Blount BC, Silca MJ, Cuadill SP, Needham JL, Pirkle JL, Sampson EJ, Lucier GW, Jackson RJ, Brock JW. *Levels of seven urinary phthalate metabolites in a human reference population*. *Environmental Health Perspectives*, **108**, 979-982, **2000**.

commissioned by Greenpeace have shown the presence of phthalates in human blood^{13,14}.

The chemical structure of DINP and DEP is presented below.



4.2.2 Results for phthalates in this study

All 12 products were analysed for phthalates. In the two household cleaning products, no phthalates were detected. Six products contained medium amounts of phthalates in concentrations below 1000 mg/kg. Four products, the two toys and two textiles as may be expected, contained higher amounts of certain phthalates. Interesting is that these were di-isononyl phthalates (DINP) and to a lesser extent di-isodecyl phthalates (DIDP), both phthalates that are increasingly replacing the older di-(2-ethylhexyl) phthalate (DEHP). The highest concentrations were found in sample 52005041-005 which contained 152000 mg/kg DINP and 11500 mg/kg DIDP. For the T-shirts, samples 52004041-007 and -008, it should be noted that the phthalate concentrations are based on the total product while the phthalates are probably present only in the print on the T-shirts. The complete results for the phthalates are in table 2 in the appendix.

4.3 Artificial musks

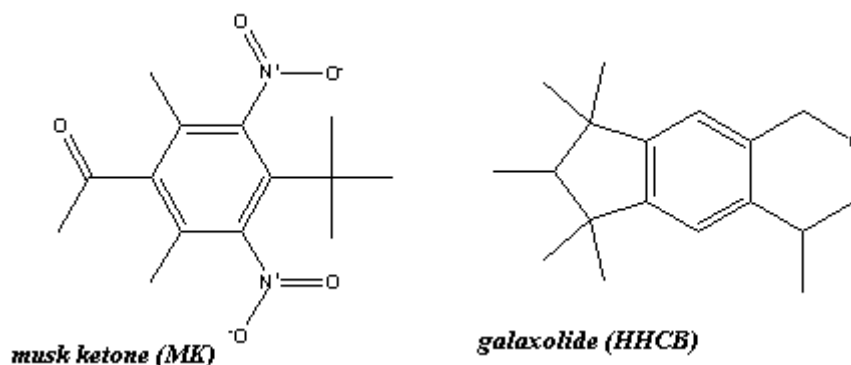
4.3.1 General information

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

¹³ Thomas GO, Hofson S, Jones KC. *WWF-UK National biomonitoring Survey 2003*, Appendix 3: Lancaster University Analytical Report, November **2003**.

¹⁴ Peters RJB. *Man-made chemicals in Human Blood*. TNO-report R 2004/493, November **2004**.

most well known artificial musks nowadays are the polycyclic musks galaxolide (HHCB) and tonalide (AHTN). Until recently the nitromusks musk ketone (MK) and musk xylene (MX) were also used, but these are expected to be phased out by 2010¹⁵. The structures of MK and HHCB are presented below.



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-musks¹⁶. 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. In a recent study for Greenpeace TNO determined artificial musks in perfumes. With one exception only low concentrations of nitro musks were found. However, polycyclic musks, especially HHCB and AHTN were found in concentrations up to almost 78000 mg/kg for HHCB¹⁰.

4.3.2 Results for artificial musks in this study

In this study artificial musks were determined only in the two household cleaning products and the two baby care products. Musks were found only in the two baby care products, 52005041-011 and -012. These products not only contained the polycyclic musk galaxolide (HHCB), but also the older nitromusk musk ketone (MK). The latter is remarkable since nitromusks in perfumes are almost completely replaced by polycyclic musks and only older types of perfumes still contain substantial amounts of nitromusks¹⁰. The highest concentrations were 327 mg/kg for HHCB and 106 mg/kg for MK, both in sample 52005041-012. Other artificial musks that were identified in these samples are ADBI, MX and AHTN. The complete results are in table 3 in the appendix.

¹⁵ Bester K, Hühnerfuss H, Lange W, Rinkus GG, Theobald N. *Water Res.* **32**, 1857-1858, **1998**.

¹⁶ Rooselaar J, Weijland JW. De bepaling van nitromuskverbindingen in cosmetische producten met behulp van GC en GC/MS. Project EN 94-3, February **1997**.

4.4 Brominated flame retardants

4.4.1 General information

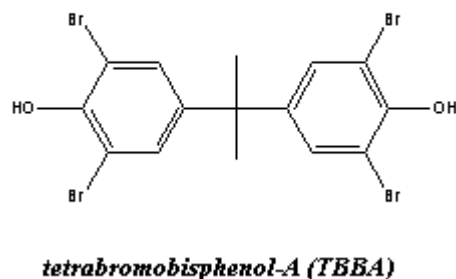
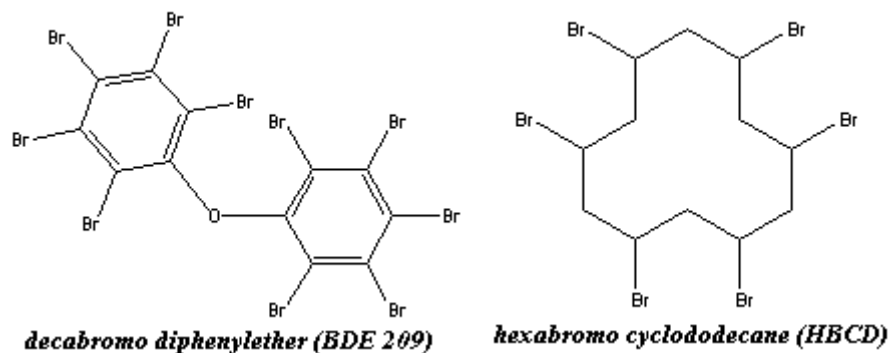
Flame retardants are added to polymers used in a wide range of materials such as electric and electronic equipment, paint, textiles and in cars and aircraft to prevent them from catching fire. Within the group of the brominated flame retardants two types of flame retardants can be distinguished. Polybrominated diphenyl ethers (PBDE) are so-called additive flame retardants. PBDEs are used as commercial mixtures such as Bromkal, with different degrees of bromination². Typically, PBDEs may comprise up to 5% to 20% of the total weight of a product to which they are added. Since these chemicals are not chemically bound they may “leak” from the polymer product, thus entering the environment. Hexabromocyclodecane (HBCD) is a cyclo-aliphatic brominated chemical meant to partially replace PBDEs because of their known toxicity. HBCD is also an additive flame retardant and can enter the environment in much the same way.

Tetrabromobisphenol-A (TBBA) can be used as both a reactive and an additive flame retardant. In its more common reactive use, it is added to materials as a co-polymer, which means that it is chemically bound to, and part of, the polymer material itself. TBBA is used in this way in epoxy polymers such as printed circuit boards in electronic equipment like computers and television sets. Even when used in this manner, small amounts of the TBBA monomer will not be polymerized and can “leak” into the environment. In other cases, mostly in ABS plastics, TBBA is used as an additive flame retardant in concentrations up to 16% by weight^{17,18}. Its use in this additive mode can result in proportionately much higher losses to the environment from products during use than when used reactively.

¹⁷ Luijk R. PhD dissertation, Formation of polyhalogenated dibenzo-p-dioxins and benzofurans during thermal degradation processes. University of Amsterdam, may 1993.

¹⁸ Danish Environmental Protection Agency, Environmental Project no. 494 1999, *Brominated Flame Retardants*, www.mst.dk/udgiv/Publications/1999/87-7909-416-3/html/default_eng.htm. 1999.

The chemical structure of decabromodiphenylether (BDE-209), HBCD and TBBA are presented below.



4.4.2 Results for brominated flame retardants in this study

A number of relevant PBDE, HBCD and TBBA were determined in the DVD players. For the interpretation of the data, especially those of the electronic equipment, it is necessary to understand how the final sample is prepared. For the DVD players all metal parts and wiring was removed. From all remaining parts that could be differentiated visually, proportional sub-samples were collected. No differentiation has been made between printed circuit boards and other polymers. The amounts of these sub-samples were based on the estimated total amount of that particular part or material in the product. This means that only small sub-samples are collected from small parts while large sub-samples are collected from, for instance, the outside material of the product.

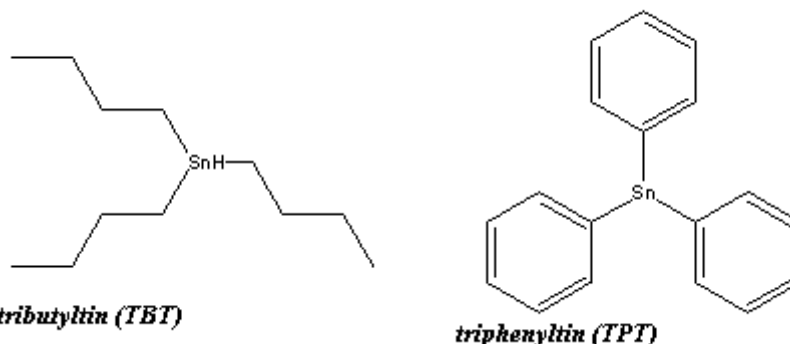
The results for the brominated flame retardants are presented in table 4 in the appendix. In general, only small amounts of brominated flame retardants were found in the two samples, 52005041-009 and -010. Maximum concentrations were found for BDE-183 of 12 and 23 mg/kg respectively. HBCD was not found while only low amounts of TBBA were found in both samples. It is expected that TBBA originates from the printed circuit boards and it should be kept in mind that the

amount of TBBA found only reflects the amount of free, e.g. non-polymerized, TBBA in the samples. Since most of the TBBA will be polymerised the actual TBBA concentration will be higher but this is chemically bound in the epoxy material of the printed circuit boards and thus less available for the environment.

4.5 Organotin compounds

4.5.1 General information

There are three major applications for organotin compounds. First, the use of tributyltin (TBT) in anti-fouling paints for ships, secondly, the use of triphenyltin (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 compounds¹⁹. In some occasions organotin compounds are used as fungicides on textiles that are exposed to extreme weather conditions, such as canvas. The structures of TBT and TPT are presented below.



TNO has a lot experience with the analyses of these compounds in environmental samples as well as in (textile) products. Until few years ago mainly TBT and its degradation products dibutyltin (DBT) and monobutyltin (MBT) were found. Nowadays, it is more often di-octyltin (DOT) and mono-octyltin (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.

¹⁹ Gaikema F.J., Alberts P.J. Gaschromatografische bepaling van residuen van organotinverbindingen in textielproducten. De Ware(n)-Chemicus 1999, 23-33.

4.5.2 Results for organotin compounds in this study

In this study six samples, four toys and two T-shirts are analysed for nine individual organotin compounds. Organotin compounds were found in all samples but especially in sample 52005041-003 with 42 mg/kg of di-octyltin (DOT), 34 mg/kg of mono-octyltin (MOT) and 28 mg/kg of di-butyltin (DBT). The organotin concentrations in the other five samples were all around or below 0.1 mg/kg. The complete results are in table 5 in the appendix.

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 complex showing many peaks. This was especially the case for the chromatograms of one of the household cleaning products and the two baby care products (52005041-002, -011 and -012). Not surprisingly these products contained many terpenes and terpenoids, and other fragrances like phenylethyl alcohol, phenylmethyl acetate and methyl dihydrojasmonate. The GC/MS screening also confirmed the presence of HHCB and MK in both baby care products (52005041-011 and -012) by their full scan mass spectrum. This was also the case for the presence of di-ethyl phthalate (DEP) in the latter product.

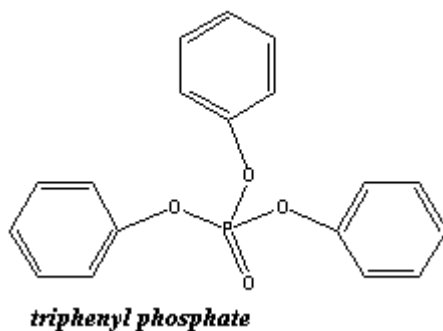
One of the household cleaning products (52005041-001) contained small amounts of chlorinated preservative, chlorobutanol. The toys (52005041-003 and -004) both contained mainly DINP while the puzzle mats (52005041-005) contained mainly alkanolic acids (mainly hexa- and octadecanoic acids) that are used (in the form of their metal salts) as stabilizers and plasticizers in polymers. Erucylamide, identified in the same sample, is used as a slip agent in polymers and can be found in polyolefins and as an additive in adhesives for food packaging.

As mentioned in paragraph 4.4 only limited amounts of brominated flame retardants were found in the DVD players (52005041-009 and -010). To see if any other type of flame retardants were used, a GC/MS screening was applied to the extracts of these samples. As it turns out, both samples contain triphenyl- and mixed phenyl-tolyl-phosphates. Organophosphate tri-esters are widely used as additive flame retardants and plasticizers in numerous common commercial products, for instance electronic equipment, furniture, textiles and building materials. Since they are not covalently bonded to the matrix they may leak to the environment and organophosphate tri-esters have been found in indoor environments^{20,21}. The structure

²⁰ Sjodin A, Carlsson H, Thuresson K, Sjolín A, Bergman A, Ostman C. *Environ. Sci. Technol.* 448-454, 35, **2001**.

²¹ Otake T, Yoshinaga J, Yanagisawa Y. *Environ. Sci. Technol.* 3099-3102, 35, **2001**.

of one of the identified compounds (in this case triphenyl phosphate) is shown below.



A summary of the compounds identified in the samples is presented in table 6 in the appendix.

4.7 Quality control measurements

4.7.1 Method validation parameters

All methods applied were already used on earlier occasions and were validated in according to research and development protocols. 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 toys and T-shirts, 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 10 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.

4.7.2 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, may not properly represent the quality of the extraction of chemicals in the product itself. Especially for the phthalates the quality of the extraction was tested in earlier studies by extracting the same sample three times in a row. Analyses showed that, of the total quantity of phthalates extractable from the sample, 100% was found in the first extract.

4.7.3 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 2 mg/kg. Results were not corrected for this blank value, but the quantification limit for DEHP was raised to 10 mg/kg.

5. Conclusions

In this study 12 consumer products have been tested for the presence of the typical man-made chemicals. A selected number of these products were analysed for alkylphenols and alkylphenol ethoxylates, phthalates, artificial musks, brominated flame retardants and organotin compounds. In addition a GC/MS screening was performed on a selected number of samples.

- Eight products were analysed for AP and APEO. NPEO was found in four products in concentrations ranging from 26 to 354 mg/kg. NP was also found in four products in concentrations ranging from 1.8 to 8.9 mg/kg. NP and NPEO were both found in one of the baby care products. OPEO was both found in a single sample while OP was not found at all.
- All twelve products were analysed for phthalates. Typically, high DINP concentrations were found in a number of products with a maximum concentration of over 150,000 mg/kg in sample 52005041-004. In general DINP was the dominant phthalate in these samples. DEHP was found but only in a limited number of samples and in concentrations far lower than DINP. DEP was found in both baby care products, in one of them in a concentration of 589 mg/kg.
- Four products were analysed for artificial musk compounds, nitro- and polycyclic musks. The two household cleaning products did not contain any artificial musks while both baby care products contained the polycyclic musk HHCB as well as the nitro-musk MK.
- Two samples, the DVD players, were analysed for brominated flame retardants. These were found but in limited concentrations up to 23 mg/kg for BDE-183. A GC/MS screening showed that other flame retardants, triphenyl phosphates, were present in these samples.
- Organotin compounds were determined in six samples. While most of them contained only low amounts of organotin compounds, sample 52005041-003 contained higher amounts of octyl- and butyltins in concentrations up to 42 mg/kg for DOT.
- The additional GC/MS screenings on eight samples mainly revealed compounds that can be expected in these kinds of products. Generally, fragrances, plasticizers, preservatives and solvents were identified. In a number of cases the presence of phthalates and artificial musks could be confirmed by the full scan mass spectra of these compounds. In addition, the presence of organophosphate flame retardants, replacing typical brominated flame retardants, was shown.

6. QA/QC statement

TNO Environment and Geosciences operates in compliance with the Quality System standard ISO 9001 (certificate no. 07246-2003-AQ-ROT-RvA). The analytical determinations in this study are performed in compliance with that quality standard.

7. Authentication

Name and address of the principal:

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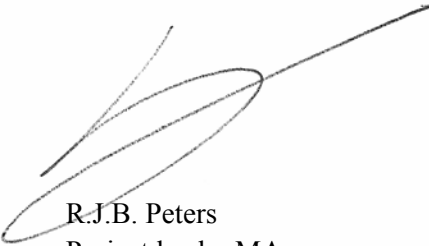
Names and functions of the cooperators:

Dr. R.J.B. Peters	Project Leader
Ing. H. Beeltje	Technician
Drs. R.J. van Delft	Technician

Date upon which, or period in which, the research took place:

February 2005 – March 2005

Signature:



R.J.B. Peters
Project leader MA

Approved by:



Dr. M.P. Keuken
Head of Department MA

Appendix Full results of all product analysis

In the result tables the acronyms given in table 1 are being used. 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 when concentrations of several thousands of mg/kg are reported. In general no more than two significant numbers apply, so that for DINP in sample 52005041-003 (table 2) the result of 85528 mg/kg should be read as 86000 mg/kg.

Table 1 Concentrations of alkylphenols and ethoxylates in consumer products

TNO Code	Greenpeace Code	Product and Company	OP mg/kg	NP mg/kg	OPEO mg/kg	NPEO mg/kg
52005041-001	1	ACE Igiene casa: Procter&Gamble	< 1	< 1	< 2	< 2
52005041-002	2	Lysoform casa: Lever Fabergé Italia s.r.l.	< 1	< 1	< 2	< 2
52005041-005	5	Eva puzzle mats: Fantastiko s.r.l.	< 1	4.2	18	59
52005041-006	6	La Puzzone dei puzzones, Scarpone puzzone: Giochi Preziosi s.p.a.	< 1	2.4	< 2	< 2
52005041-007	7	Girl collection 5 years: Emporio Junior s.r.l.	< 1	1.8	< 2	354
52005041-008	8	K.T.Shirt MC Sport&Stripes: Champion Europe	< 1	< 1	< 2	26
52005041-011	11	Babygella Bagno delicato: Rottapharm s.r.l.	< 1	8.9	< 2	98
52005041-012	12	Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	< 1	< 1	< 2	< 2

Table 2 Concentrations of phthalates in consumer products

TNO Code	Greenpeace Code	Product and Company	DMP	DEP	DBP	DIBP	BBP
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
52005041-001	1	ACE Igiene casa: Procter&Gamble	< 1	< 1	< 1	< 1	< 1
52005041-002	2	Lysoform casa: Lever Fabergé Italia s.r.l.	< 1	< 1	< 1	< 1	< 1
52005041-003	3	Spider-man flip 'n zip: Giochi Preziosi s.p.a.	< 1	< 1	< 1	< 1	< 1
52005041-004	4	Barbie Fashion Fever: Mattel	< 1	< 1	< 1	< 1	< 1
52005041-005	5	Eva puzzle mats: Fantastiko s.r.l.	< 1	< 1	< 1	1.6	< 1
52005041-006	6	La Puzzone dei puzzones, Scarpone puzzone: Giochi Preziosi s.p.a.	< 1	< 1	< 1	< 1	< 1
52005041-007	7	Girl collection 5 years: Emporio Junior s.r.l.	< 1	< 1	2.6	8.8	57
52005041-008	8	K.T.Shirt MC Sport&Stripes: Champion Europe	< 1	< 1	7.9	1.4	359
52005041-009	9	DVX Pl@yer: Voxson	< 1	< 1	< 1	5.6	45
52005041-010	10	DV - P 345 E: Hitachi	< 1	< 1	< 1	< 1	11
52005041-011	11	Babygella Bagno delicato: Rottapharm s.r.l.	< 1	2.4	< 1	< 1	< 1
52005041-012	12	Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	< 1	589	1.3	< 1	< 1

TNO Code	Greenpeace Code	Product and Company	DCHP	DEHP	DOP	DINP	DIDP
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
52005041-001	1	ACE Igiene casa: Procter&Gamble	< 1	< 10	< 1	< 10	< 10
52005041-002	2	Lysoform casa: Lever Fabergé Italia s.r.l.	< 1	< 10	< 1	< 10	< 10
52005041-003	3	Spider-man flip 'n zip: Giochi Preziosi s.p.a.	< 1	< 10	< 1	85528	< 10
52005041-004	4	Barbie Fashion Fever: Mattel	3.4	24	< 1	151916	11455
52005041-005	5	Eva puzzle mats: Fantastiko s.r.l.	< 1	< 10	< 1	228	< 10
52005041-006	6	La Puzzone dei puzzones, Scarpone puzzone: Giochi Preziosi s.p.a.	< 1	898	< 1	34	< 10
52005041-007	7	Girl collection 5 years: Emporio Junior s.r.l.	13	79	< 1	12051	< 10
52005041-008	8	K.T.Shirt MC Sport&Stripes: Champion Europe	< 1	718	< 1	6969	713
52005041-009	9	DVX Pl@yer: Voxson	< 1	19	< 1	162	< 10
52005041-010	10	DV - P 345 E: Hitachi	< 1	17	< 1	319	< 10
52005041-011	11	Babygella Bagno delicato: Rottapharm s.r.l.	< 1	< 10	< 1	< 10	< 10
52005041-012	12	Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	< 1	< 10	< 1	< 10	< 10

Table 3 Concentrations of musks in consumer products

TNO Code	Greenpeace Code	Product and Company	ADBI mg/kg	AHTN mg/kg	ATTI mg/kg	DPMI mg/kg	HHCB mg/kg
52005041-001	1	ACE Igiene casa: Procter&Gamble	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
52005041-002	2	Lysoform casa: Lever Fabergé Italia s.r.l.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
52005041-011	11	Babygella Bagno delicato: Rottapharm s.r.l.	0.8	0.2	< 0.1	< 0.1	9.3
52005041-012	12	Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	0.4	2.0	< 0.1	< 0.1	327

TNO Code	Greenpeace Code	Product and Company	MA mg/kg	MK mg/kg	MT mg/kg	MX mg/kg
52005041-001	1	ACE Igiene casa: Procter&Gamble	< 0.1	< 0.1	< 0.1	< 0.1
52005041-002	2	Lysoform casa: Lever Fabergé Italia s.r.l.	< 0.1	< 0.1	< 0.1	< 0.1
52005041-011	11	Babygella Bagno delicato: Rottapharm s.r.l.	< 0.1	42	< 0.1	0.2
52005041-012	12	Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	< 0.1	106	< 0.1	0.9

Table 4 Concentrations of brominated flame retardants in consumer products

TNO Code	Greenpeace Code	Product and Company	BDE 47 mg/kg	BDE 99 mg/kg	BDE 100 mg/kg	BDE 153 mg/kg	BDE 154 mg/kg
52005041-009	9	DVX Pl@yer: Voxson	< 0.1	0.2	< 0.1	3.1	0.2
52005041-010	10	DV - P 345 E: Hitachi	< 0.1	0.2	< 0.1	6.4	0.4

TNO Code	Greenpeace Code	Product and Company	BDE 183 mg/kg	BDE209 mg/kg	HBCD mg/kg	TBBPA mg/kg
52005041-009	9	DVX Pl@yer: Voxson	12	< 0.1	< 0.1	1.1
52005041-010	10	DV - P 345 E: Hitachi	23	< 0.1	< 0.1	0.6

Table 5 Concentrations of organotin compounds in consumer products

TNO Code	Greenpeace Code	Product and Company	MBT	DBT	TBT	TeBT
			mg/kg	mg/kg	mg/kg	mg/kg
52005041-003	3	Spider-man flip 'n zip: Giochi Preziosi s.p.a.	3.6	28	0.08	0.02
52005041-004	4	Barbie Fashion Fever: Mattel	< 0.01	0.06	< 0.01	< 0.01
52005041-005	5	Eva puzzle mats: Fantastiko s.r.l.	< 0.01	0.12	< 0.01	< 0.01
52005041-006	6	La Puzzone dei puzzones, Scarpone puzzone: Giochi Preziosi s.p.a.	< 0.01	< 0.01	< 0.01	< 0.01
52005041-007	7	Girl collection 5 years: Emporio Junior s.r.l.	< 0.01	< 0.01	< 0.01	< 0.01
52005041-008	8	K.T.Shirt MC Sport&Stripes: Champion Europe	< 0.01	0.02	< 0.01	< 0.01

TNO Code	Greenpeace Code	Product and Company	MOT	DOT	MPT	DPT	TPT
			mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
52005041-003	3	Spider-man flip 'n zip: Giochi Preziosi s.p.a.	34	42	< 0.01	< 0.01	< 0.01
52005041-004	4	Barbie Fashion Fever: Mattel	0.02	0.03	< 0.01	< 0.01	< 0.01
52005041-005	5	Eva puzzle mats: Fantastiko s.r.l.	0.02	0.09	< 0.01	< 0.01	< 0.01
52005041-006	6	La Puzzone dei puzzones, Scarpone puzzone: Giochi Preziosi s.p.a.	< 0.01	0.02	< 0.01	< 0.01	< 0.01
52005041-007	7	Girl collection 5 years: Emporio Junior s.r.l.	< 0.01	0.06	< 0.01	< 0.01	< 0.01
52005041-008	8	K.T.Shirt MC Sport&Stripes: Champion Europe	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Table 6 Additional “non-target” compounds identified in GC/MS screening

TNO Code	Greenpeace Code	Product Description	Additional compounds identified in products with GC-MS screening
52005041-001	1	ACE Igiene casa: Procter & Gamble	Simple chromatogram. Mainly dimethylpentanol. Traces of octanol, dimethyloctanol, chlorobutanol and benzophenone.
52005041-002	2	Lysoform casa: Lver Fabergé Italia s.r.l.	Complex chromatogram. Fragrances: terpenes like pinene, carene, limonene and eucalyptol. Traces of diphenylether
52005041-003	3	Spider-man flip 'n zip: Giochi Preziosi s.p.a.	Simple chromatogram. Mainly di-isononyl phthalate. Traces of some alkanes and styrene.
52005041-004	4	Barbie Fashion Fever: Mattel.	Simple chromatogram. Mainly di-isononyl phthalate. Traces of some alkanes, alkanolic acids (and esters) and other phthalates (DEHP, DIDP).
52005041-005	5	Eva puzzle mats: Fantastiko s.r.l.	Complex chromatogram. Mainly hexa- and octadecanoic acid, erucylamide and acetophenone. Alkanes in the range of C ₂₀ -C ₃₀ and trace of DINP.
52005041-006	6	La Puzzone dei puzzones, Scarpone puzzone: Cgiochi Preziosi s.p.a.	Simple chromatogram. Plasticisers: di-(ethylhexyl) phthalate. Traces of alkylated benzenes, styrene, methylphenol and other phthalates (DINP).
52005041-011	11	Babygelle Bagno delicato: Rottapharm s.r.l.	Complex chromatogram. Mainly glycerol tricaprylates. Fragrances: terpenes as pinene and limonene, phenylmethyl acetate, musk ketone (MK) and a trace of galaxolide (HHCB). Mixture of n-, iso- and cycloalkanes and alkenes in the range of C ₁₂ -C ₂₀ .
52005041-012	12	Mustela babygel, bain mousse e'veil: Laboratoires Expanscience	Complex chromatogram. Fragrances: many terpenes or terpenoids, phenylethyl alcohol, phenylmethyl acetate, methyl dihydrojasmonate, galaxolide (HHCB), musk ketone (MK). Carrier: diethyl phthalate