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Survey and environmental and health assessment of nonylphenol and nonylphenol ethoxylates in textiles

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Survey and environmental and health assessment of nonylphenol and nonylphenol ethoxylates in textiles

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Content

Preface

This project, ”Survey and environmental and health assessment of nonylphenol and nonylphenol ethoxylates in textiles” was carried out during the periode October 2009 to August 2012.

Nonylphenol ethoxylates (NPE) may be used in various processes in the manufacturing of textiles and residues of NPE and nonylphenol (NP), which is one of the degradations products of NPE, have been detected in textiles. NP is recognized as a health and environmentally hazardous substance.

The objective of this project is to contribute to an assessment of the extent to which the occurrence of nonylphenol (NP) and nonylphenol ethoxylates (NPE) in textiles constitutes a problem for the Danish consumers and the ambient (external) environment.

The project was implemented by DHI by a project team consisting of Senior Consultant Dorte Rasmussen (project manager), Tina Slothuus, Morten Bjergstrøm, Anne Rathmann Pedersen, Dorthe Nørgaard Andersen, Poul Bo Larsen and Brian Svend Nielsen. Eurofins Danmark A/S performed the chemical analyses. The English version was translated by Tove Krogsbøll Holt.

The project was advised by a steering committee consisting of Sidsel Dyekjær and Jette Rud Heltved, DEPA, and Tina Slothuus and Dorte Rasmussen, DHI.

Summary and conclusion

The overall objective of this project is to contribute to an assessment of the extent to which the occurrence of nonylphenol (NP) and nonylphenol ethoxylates (NPE) in textiles constitutes a problem for the Danish consumers and the ambient (external) environment.

NPEs are nonionic surfactants, i.e. non-electrically charged surfactants. NPE is used in the production of textiles and is i.a. used as an auxiliary agent for cleaning and rinsing of textiles, especially wool but also cotton, and for dyeing and bleaching of textiles.

NPE decomposes to i.a. NP, which has long been in focus because of its health and environmentally hazardous properties. The use of NP and NPE is regulated by REACH, the EU chemicals legislation. REACH lays down limitations of use of NP and NPE in textile production but there is no regulation of the amounts of NP and NPE allowed in imported textiles.

Alkyl phenol and –etholylates, including NP and NPE, may not be used in the production of textiles with the Nordic Swan ecolabel or the EU Flower ecolabel.

According to the trade organisation "Dansk tekstil og beklædning" (Danish textile and clothing), most Danish companies set limits for the amount of certain chemicals in textiles - including NP and NPE. Seven of the major buyers of textile products for Denmark were contacted. The majority reported that they have a limit for the acceptable amount of NPE in the finished textile products. This limit is between 100 and 250 mg NPE/kg textile. If this limit is exceeded, the import company tries to identify the source, and to have the content either reduced or eliminated. It is estimated that these limits are not based on health assessments. The textile producer may use alternatives to NPE, for example alcohol ethoxylates. When the concentrations remain below the limit, the import companies accept the content. The contacted companies indicated that NPE is used in many processes in imported textiles and fabrics, and perhaps in several stages within the product chain and, therefore, it is difficult to avoid the substances in the textiles.

A literature search was made for data on measured concentrations of NP and NPE in textile products, and a total of 116 analytical results were identified. In three of the analysis results, the concentration of NPE was higher than 6,000 mg NPE/kg textile, while the rest of the concentrations were below 3,200 mg NPE/kg textile. Some of the samples did not detect NP or NPE. The average concentration of nonylphenol ethoxylate was 670 mg/kg, and the highest concentration was measured to be 14,100 mg NPE/kg textile.

In the collected literature data, there was generally very little information on the country of origin for the analysed textile samples, and therefore it cannot be concluded whether there is a connection between the country of origin and the content of nonylphenol ethoxylate.

Based on the measured NP and NPE concentrations in textiles and based on assumptions about how quickly NP/NPEs are released to sweat and saliva, initial assessments were made on the extent of exposure of a person to NP/NPEs from clothes. This initial assessment was used in the selection of products for chemical analysis.

In this project, 15 textile samples were analysed for content of NP and NPE (before washing). The samples were chosen on the condition that the large exporting countries should be represented and on the basis of the preliminary exposure assessments, showing i.a. that children are exposed to NP and NPE in textiles to a higher extent than grown-ups. Therefore, children's wear (bed linen, mittens, underwear, jeans and T-shirts) from China (7 samples), Bangladesh (3 samples), India (2 samples), Pakistan, Turkey and Cambodia (1 sample from each country) were selected for acquisition and subsequent analysis.

As mentioned, some companies use limit values for the allowed amount of NPE in imported textiles, before they initiate closer examinations. The analyses of the purchased children's wear showed that 33% of the measurements were above the lowest limit value of 100 mg NPE/kg textile, and 20% were above the highest limit value of 250 mg/kg textile. For the literature data, 50% of the analytical results were higher than 100 mg NPE/kg textile, and 42% were higher than 250 mg NPE/kg textile. It should be noted that these limit values of 100 mg/kg textile and 250 mg/kg textile are hardly based on health assessments.

The highest concentration of NPE measured in the purchased children's wear was 310 mg NPE/kg textile, and the average concentration was 96 mg NPE/kg textile. No pattern was found regarding the types of textile (cotton or polyester, organic or non-organic) containing elevated concentrations of NP and NPE. Textiles with a higher concentration of NPE tend also to have one or more bright colours. Generally, the textiles from China - except a naturally coloured sweater - had higher concentrations of NPE.

In general, the concentrations were lower in the purchased children's wear than the concentrations found in the literature studies. But this may be mere coincidence as only a very limited number of textile samples were analysed. In order to investigate whether NP and NPE is removed by washing, the samples with a measured high content of NPE were washed and analysed. The results of these tests showed that washing reduces the total content of NPE in the textiles, but that there may still be residual concentrations of NPE in the textiles. The removal of NPE by one single washing varied between 25% and 99.9%. The analyses also showed that the content of NPE metabolites, e.g. short-chained ethoxylates and NP, increased by washing in some cases. This indicates that part of the observed removal of NPE by washing is the result of decomposition and not an actual removal.

As humans can absorb chemicals through the skin and the preliminary exposure assessments showed that dermal absorption may be an important route of exposure for NPE, tests with artificial sweat were performed on the textile types with a measured significant content of NPE. The tests showed that NPE can migrate to sweat, but also that the extent of the migration depends on the type of textile. Only a negligible migration of NPE to sweat from bed-linen was measured, while the measured migration to sweat from jeans was between 13% and 33% of the NPE content of the textile. NP was not detected in the sweat extract.

Only one test was made on the migration from the outside of mittens to saliva. The mittens were chosen because a considerable content of NPE had been detected in the mittens and because the initial exposure assessment showed that the absorption for a child sucking its mittens may be significant. However, only a very limited migration of 2% of the NPE content and less than 3% of the NP content in the mittens were measured in the test (the analysis is limited by the detection limit for NP).

In order to examine whether the content of NP and NPE can affect the consumers, the total absorption of NP and NPE was calculated based on the measured migrations and compared with the DNEL-value for NP. DNEL (Derived No Effect Level) is the largest amount of a chemical substance a consumer can absorb without a health risk. In this project, the DNEL for the allowed amount of NP absorption into the body was calculated to 0.005 mg NP/kg body weight per day, based on a NOAEL for the critical effect of the substance NP (nephrotoxic effects). Unlike most other substances, NPE forms a decomposition product (metabolite), which is more toxic than the precursor, namely NP. Therefore, NPE has been assigned to the same systemic toxicity as NP (measured as mg NP/kg body weight). This is obviously an approximation, since NPE does not always degrade 100% to NP and can be excreted from the body in the urine as a short-chain NPE. However, the U.S. EPA (2010) refers to other studies concluding that mammals convert NPE to NP.

Based on the analysis results obtained in this project, children's exposure to NPE from several pieces of clothing worn at the same time was calculated. The results showed that in a worst-case scenario, where a child wears new unwashed clothes 1 time every 2 weeks, and wears jeans, underwear and T-shirts that gives the highest absorption through the skin at the same time, the overall risk characterisation ratio (RCR) when using jeans, underwear and T-shirts (as well as gloves and bed-linen) is calculated to 1.4. According to these calculations, a child's absorption of NP when using new unwashed clothes can thus give an RCR above 1, indicating an increased health risk. At an average relative to the content of NP in the clothes, an RCR of 0.78 is seen when using new unwashed jeans, underwear and T-shirts at the same time over a period of 2 weeks. If the clothes have been washed once before use, a considerable reduction is seen in the exposure to NP/NPE, respectively, with a total RCR of 0.41 when using clothes with the highest concentrations of NPE.

An RCR value of 1.4 must also be interpreted in relation to the uncertainties and assumptions made in the calculations. It is thus assessed that the used DNEL value for NP is very prudent, as it is assumed in relation to the animal test used for the calculation that a systemic absorption of 10% only occurs after oral exposure of NP. In such an assumption, the DNEL value is set 10 times lower than if the systemic absorption is anticipated to be 100%. Furthermore, the exposure scenarios for skin contact with clothes assume an equally high release of NP and NPE in the migration tests, where clothing is extracted with artificial sweat. Then it is assumed in this study that 10% of the released substance is absorbed through the skin, which may be regarded as the highest possible absorption through the skin based on the available data - especially for NPE, the absorption could be expected to be lower than the 10% because of the higher molecular weight of this substance. All these anticipations may result in the calculation of a higher RCR value.

However, the literature reported significantly higher concentrations of NP/NPE in textiles than seen in this project. Textiles containing these substances are therefore assessed to be a significant source of exposure to NP/NPE in daily life. It therefore makes good sense to try and reduce the levels of NP and NPE in textiles as much as possible, partly to achieve better protection against nephrotoxicity effects, but also, because these substances are suspected of endocrine disrupting effects, to overcome any possible combination effects of NP/NPE, respectively, and other endocrine disruptors which humans may come into contact with in daily life.

Children and adults can also be exposed to NP and NPE from other sources, e.g. paints, varnishes, hair dyes, leather goods and stationery. However, the EU (EU, 2002) estimated that the systemic exposure to NP from most other consumer products is phased out and that the contribution from these sources therefore will be minimal.

In order to examine NP and NPE in textiles related to the aquatic the environment, a conservatively estimated average concentration in the aquatic environment was calculated (PEC - calculated environmental concentration) for NP based on data for 2007-2009 from wastewater treatment plants. PEC was calculated to be close to 0.02 μg NP/L, which is approx. 10 times below the predicted no effect concentration (PNEC) of 0.33 μg NP/L. The majority of Danish households are associated with wastewater treatment plants that remove a large proportion of NP and NPE in sewage. There is however still good reasons to reduce the emission given the fact that the Water Framework Directive includes a requirement that emissions and losses must cease.

The contribution of textiles to the total NP load of the aquatic environment was calculated to be approx. 86% (based on measurements in this work), and 200% (based on literature values), respectively, of the total NP load of the aquatic environment. Even though these results are based on very rough calculations, it may be used as a preliminary indication of the possible significance of the contribution of textiles to the total concentration of NP in the aquatic environment.

[1] When converting NPE into NP, figures are divided by 2.8

1. Introduction

Nonylphenol ethoxylates (NPE) are nonionic surfactants that are used i.a. as auxiliary agents in various industrial manufacturing processes, i.e. production of textiles. NPE decomposes to i.a. nonylphenol (NP), which has long been in focus because of its health and environmentally hazardous properties.

An EU risk assesment assessed that the consumer exposure to NP and NPE via textiles is negligible and no further assessment of this exposure route was made (EU, 2002). At the same time, however, over time analyses have been performed in Denmark and in other countries, e.g. Sweden and Norway, of the content of NP and NPE in textiles, which have proven a significant content in some cases. Therefore, the Danish Environmental Protection Agency (DEPA) has found it appropriate to have the content of NP and NPE in various imported types of textiles on the Danish market analysed and to require an environmentally and health assessment of nonylphenol and nonylphenol ethoxylates in textiles.

The overall objective of this project is to assess the content of NP and NPE in textiles and to contribute to an assessment of the extent to which the occurrence of NP and NPE in textiles constitutes a problem for the Danish consumers and the ambient (external) environment.

In this project, the health and environmental assessments are based on a collection of available literature data on the subject, supplemented by analyses of NP and NPE in textile samples chosen with a focus on clothing textiles and bed linen, from which human exposure is assessed to be significant.

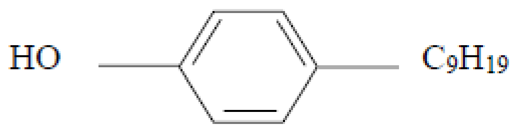
1.1 Characterisation of NP and NPE

An EU risk assessment has been made of nonylphenol (NP) and 4-nonylphenol (branched) (4-NP) (EU, 2002). In principle, NP covers all isomers of nonylphenol while 4-NP (branched) only covers 4-nonylphenols, of which the nonyl group is branched. The commercially manufactured NPs are primarily 4-NPs with a varied and undefined degree of branching.

The following data are taken from the above risk assessment report.

1.1.1 Physical-chemical properties (NP and 4-NP)

CAS No.: 25154-52-3 (NP)
84852-15-3 (4-NP)

Chemical structure	
Molecular weight:	220.3 g/mol
Boiling point:	287-310°C
Melting point:	-8-10°C
Density:	0.949-0.952 at 20°C
Vapour pressure:	0.9 Pa at 25°C
Solubility in water:	11 mg/L at 20°C (data from IUCLID, dependant of pH)
Log K_{OW}:	4.48

1.1.2 Physical-chemical properties (NPE)

CAS Nos: 68412-54-4
9016-45-9
26077-38-3
37205-87-1
127087-87-0

Among other things, the physical-chemical properties of NPE depend on the number of ethoxylate groups. NPE is more soluble in water than NP, has higher boiling and melting points and will be in a solid state at room temperature. Furthermore, NPE has a negligible vapour pressure. Its melecular weight depends on the number of ethoxylate groups (Table 1.1).

TABLE 1.1
RELATION BETWEEN THE NUMBER OF ETHOXY GROUPS AND THE MOLECULAR WEIGHT FOR NONYLPHENOL (NP) AND NONYLPHENOL ETHOXYLATES (NPE)

Number of ethoxy groups	Molecular weight (g/mol)	Notation used
0	220.3	NP
1	264.3	NPE_1
2	308.3	NPE_2
3	352.3	NPE_3
4	396.3	NPE_4
5	440.3	NPE_5
6	484.3	NPE_6
7	528.3	NPE_7
8	572.3	NPE_8
9	616.3	NPE_9
10	660.3	NPE_{10}
11	704.3	NPE_{11}
12	748.3	NPE_{12}
13	792.3	NPE_{13}
14	836.3	NPE_{14}
15	880.3	NPE_{15}

Often, the number of ethoxy groups in NPE is indicated by a subsequent number written in subscript. NPE_1 thus referers to nonylphenol ethoxylate with an ethoxy chain length of 1, NPE_2 refers to an ethoxy chain length of 2 and $NPE_{3\text{-}15}$ to an ethoxy chain length of between 3 and 15.

1.1.3 Classification of NP and NPE

From 1 December 2010, nonylphenol (NP) must be classified in accordance with the CLP Regulation:

- Repr. 2; H361fd (Reproductive toxicity. Category 2: May damage fertility. May damage the unborn child)
- Acute Tox. 4 H302 (Acute toxicity. Category 4: Harmful if swallowed)
- Skin Corr. 1B; H314 (Skin corrosion/irritation. Category 1B: Causes severe skin burns and eye damage)
- Aquatic Acute 1 H400 (Acute Hazard. Category 1: Very toxic to aquatic life)
- Aquatic Chronic 1 H410 (Chronic Hazard. Category 1: Very toxic to aquatic life with long lasting effects)

Until 1 June 2015, nonylphenol must also be classified according to the old regulation (DEPA, 2010):

- Xn (Harmful); R22: Harmful if swalloved
- C (Corrosive); R34: Causes burns
- Rep.3 (Reproductive toxicity); R62: Possible risk of impaired fertility
- Rep.3 (Reproductive toxicity); R63: Possible risk of harm to the unborn child

- N (Dangerous for the environment); R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Nonylphenol ethoxylates, NPEs, are not included in the DEPA list of hazardous substances. However, self classifications have been prepared for some NPE compounds but they vary somewhat from supplier to supplier (Table 1.2). However, NPE is generally classified as harmful (Xn R22: Harmful is swallowed) or irritant (Xi R41: Risk of serious damage to eyes or Xi R36/38: Irritating to eyes and skin). Furthermore, in most cases, NPE is classified with N R51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment, R52/53: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment or R53: May cause long-term adverse effects in the aquatic environment.

TABLE 1.2
SELF CLASSIFICATIONS OF NPE

CAS No.	EU classification
68412-54-4 **i-NPE-2,5***	Xi: R38 Xn: R22; Xi: R36/38; N: R51/53 Xi: R36/38; R53 Xn: R22 Xi: R41; N:R51/53 Xi: R36/38, N: R51/53 Xn: R22; Xi R36/38 N: R51/53 Xn: R22; Xi R36/38 R53 Xn: R22; Xi;R41 R53
9016-45-9 **NPE_{10}**	Xi: R36/38; N:R51/53 Xn: R22 Xi; R36/38 Xi R41 R52/53
26077-38-3	No information on self classification found**
37205-87-1 **(i-NPE_n)**	Xn: R22; Xi: R41 R53. Xi: R36/38; R53 Xn R22; Xi: R36/38, R53
127087-87-0 **Poly(oxy-1,2-ethanediyl), α-(4-nonylphenyl-ω-hydroxy-, branched**	No information on self classification found**

*) Isoform
**) Note: After the data search for this project, self classifications of many substances have been published at the ECHA website: www.ECHA.eu

1.1.4 Current regulation of nonylphenol and nonylphenol ethoxylates

NP and NPE are regulated under more regulations.

The use of NP and NPE is regulated via the REACH Regulation[2] Annex XVII Nos 46 a og b, which prescribes that NPE and NP should not be used at concentrations above 0.1% in preparations inteded to be used for a number of specific purposes, including manufacturing of textiles and leather, unless the use is conducted without discharge of waste water, i.e. in a closed system. NPE is also identified as a priority hazardous substance in the list of priority substances substances in annex X of the Water Framework Directive[3], which means that discharges, emissions and losses of the substance must be terminated. NPE is also in the OSPAR[4] List of Substances of Possible

[2] REACH. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
[3] Directive 2000/60/EC on water policy
[4] OSPAR: International cooperation between 15 European countries on the protection of the marine environment of the North-East Atlantic

Concern[5]. Furthermore, ”Statutory Order on the use of waste for agricultural purposes” (Statutory Order No. 1650 of 13 December 2006) defines a limit value for the sum of NPE and NP of 10 mg NP per kg dry matter in sludge for use as e.g. fertilizer for agricultural land.

In addition to this regulation, NP and NPE are on the DEPA List of undesirable substances as a subgroup under the group alkylphenol ethoxylates (DEPA, 2010) and in the EU priority list on substances that must be further investigated for endocrine-disrupting properties[6].

As no regulatory restrictions have been laid down regarding the presence of residues of NPE in textiles[7], NPE (and possibly its degradation products) may occur in textile products imported from outside the EU, where there are no restrictions on the use of NPE and NP in the production process. However, NPE and NP may also occur in EU-manufactured textiles produced or treated in a process, from which no waste water is discharged.

1.1.5 Risk to the external environment

Apart from NP, the most common degradation products from NPE are short-chained NPE with 1-2 ethoxylate units (NPE_{1-2}) and short-chained nonylphenoxy carboxylic acids (NPEC), all of which are relatively stable in the environment more environmentally hazardous than the parent NPE.

In the EU risk assessment report on NP (EU, 2002), a risk assessment was made for the aquatic environment. The results are summarized below.

A risk assessment can be made on the basis of calculation of a risk characterisation ratio (RCR):

$$RCR_{Env} = \frac{PEC}{PNEC}$$

Where

- PEC is the Predicted Environmental Concentration
- PNEC is the Predicted No Effect Concentration, i.e. the highest concentration, at which exposure to a substance is not expected to cause adverse effects. Corresponds to the AA-EQS (Annual Average Environmental Quality Standards) in the directive on environmental quality standards[8].

$RCR_{Env} > 1$ indicates that risk to the environment cannot be excluded and $RCR_{Env} < 1$ indicates that there is no risk to the environment.

In the EU risk assessment report, PNEC (the Predicted No Effect Concentration) for NP was calculated to be 0.33 µg/L (aquatic environment) (EU, 2002). This value is in accordance with the AA-EQS of 0.3 µg/L laid down in the Directive on environmental quality standards and thus also entered in the DEPA Statutory Order No. 1022 of 25 August 2010 as the environmental quality standard for waters and a requirement to discharge of pollutants to watercourses, lakes or the sea.

Studies have shown that NP has endocrine-disrupting (estrogenic) effects on fish, however, only at concentration levels significantly higher than the PNEC (EU, 2002).

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5 http://www.ospar.org/documents/dbase/publications/p00136_BD%20on%20nonylphenol.pdf

6 Endocrine Disrupters Website. European Commission Environment: http://ec.europa.eu/environment/endocrine/strategy/short_en.htm

7 In 2011, however, new discussions between the EU contries were initiated at Swedish initiative on the introduction of a ban under REACH.

8 Directive 2008/105/EC on environmetal quality standards in the field of water policy etc

To some extent, NP can accumulate in fish and a bioaccumulation factor (BCF)[9] of up to 1,300 has been measured in fish (EU, 2002). Furthermore, NP is characterized as inherently biodegradable (EU, 2002).

NP is only partly removed in wastewater treatment plants. Calculations indicate that approx. 34% is removed with the sludge, approx. 24% is degraded, just below 7% evaporates and the remaining 35% are discharged into the water environment (EU, 2002).

Therefore, NP may also end in the agricultural soil when sewage sludge is applied as fertilizer to the fields (BLST, 2010 (now the Danish Nature Agency). However, numerious studies have shown that NP is not taken up in plants and, therefore, humans will neither be exposed to NP via crops from sludge-applied fields nor through milk and meat from cattle having grazed on sludge-applied fields (theme at the Centre for Sustainable Land Use, 2001).

1.1.6 Risk of effects on human health

A risk assessment of effects on human health from contact with NP in textiles may as for effects on the environment be made on the basis of the calculation of a risk characterisation ratio (RCR_{Human}):

$$RCR_{Human} = \frac{U_{total}}{DNEL}$$

Where

U_{total} is the calculated total exposure to the substance in the human being

DNEL is the Derived No Effect Level; in this context, corresponding to the highest uptake of the substance in a human being when, even at repeated exposure over a long period of time, no effects are expected on the human being

RCR_{Human} >1 indicates an increased risk of effects on human health while RCR_{Human} <1 indicates an acceptable exposure level in relation to the protection against effects on human health.

According to the risk assessment of NP (EU, 2002), NP has a moderate acute toxicity. At oral ingestion (by mouth), LD_{50} was measured to be 1,200-2,400 mg/kg (studies in rats) and, for dermal exposure (skin contact), LD_{50} was measured to be 2,000 mg/kg (studies in rabbits). Furthermore, NP may cause skin burns and severe eye irritation. In a multi-generation study, increased occurrence of kidney damage was found in rats dosed orally with NP and a LOAEL (Lowest Observed Adverse Effect Level) of 15 mg/kg body weight per day was determined. In a series of tests, NP has demonstrated estrogenic effects. In a multi-generation reproduction study, in which rats were dosed orally with NP, disorders of the reproductive system (the ability to reproduce) were found in offspring, including accelerated sexual maturation, increased length of the sexual cycle, decreased weights of ovaries and reduced sperm count in 2^{nd} offspring generation (F2 generation). Based on the changes in the reproductive parameters in the above study, NOAEL (No Observed Adverse Effect level) of 15 mg/kg body weight per day was determined.

On the basis of the above data, an internal DNEL of 0.005 mg NP/kg body weight per day was calculated. The critical effect is histopathological changes in the kidney. Appendix B summarizes the applied data and describes the determination of the DNEL by use of assessment factors totaling 300 to account for the difference in toxicological response from animals to humans – differences in sensitivity between humans and extrapolation from a LOAEL level to a no-effect level (NOAEL). This DNEL can be described as the highest daily intake of NP that a person can tolerate before increased risk of effects occurs. NP is a degradation product of NPE and it is more toxic than the parent compound. NPE is here assigned to the same systemic toxicity as NP (measured as mg NP /

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9 BCF = the ratio of the concentration in fish (mg/kg wet weight) to the concentration in water (mg/kg water)

kg body weight). However, this is an approximation as NPE is not always completely degraded to NP in the body and it may be excreted from the body via the urine, e.g. as a short-chained NPE.

1.1.7 Other sources of NP and NPE

Children and adults may also be exposed to NP and NPE from other products and materials than textiles. Other sources of NP and NPE may include paints, varnishes, hair dyes, leather products and paper products. A Canadian study found that exposure to cosmetic products such as body lotions and perfumes as well as for cleaning agents containing NP and NPE caused the highest exposures (CEPA, 1999). In the EU risk assessment report, the highest exposure to NP was detected in humans who live close to textile mills using NP and NPE in the textile manufacturing. The systemic exposure to NPE from most consumer products was evaluated to be phased out in the near future and thus insignificant. The dose of NP by use of consumer products was estimated for the use of pesticides (dose by inhalation and skin contact is 0.00035 mg/kg body weight per application) and per hair dyeing (0.003 mg/kg body weight). For a person weighing 70 kg, who was also exposed to NP via food packaging, a systemic exposure was estimated to approx. 0.0006 mg/kg body weight per day (EU, 2002). This is much lower than the DNEL and demonstrates that other consumer products are not a major source of NP/NPE.

1.2 Summary

Nonylphenol ethoxylates (NPE) are used as auxiliary agents in the manufacturing of textiles. NPE decomposes to i.a. nonylphenol (NP), which has long been in focus because of its health and environmentally hazardous properties. Residues of NP and NPE have been detected in clothes available in the shops and the general consumer may thus be exposed to these substances. As NP and NPE will eventually be washed out of the clothes, the NP and NPEs will to a certain extent also end up in the environment.

NP degrades, but not rapidly, in the environment (EU, 2002). Furthermore, NP has a potential for accumulating in fish. In the aquatic environment, the highest concentration, at which exposure to NP is not expected to cause adverse effects, is 0.33 µg /L (PNEC). An assessment of the extent, to which the occurrence of NP constitutes a problem for the environment, implies that the predicted concentration in the aquatic environment (PEC) is determined and compared with PNEC. If PEC is lower than PNEC, NP is not expected to cause adverse effects in the environemnt. Furthermore, studies have shown that NP has endocrine-disrupting (estrogenic) effects on fish, however, only at concentration levels significantly higher than the PNEC.

NP is moderately acutely toxic and may cause skin burns and eye irritation. Long-term studies have shown that, i.a., NP may cause disorders of the reproductive system (the ability to reproduce). In order to assess the potential effects on a person due to regular and prolonged exposure to NP and NPE, an internal DNEL for prolonged exposure of 0.005 mg NP/kg body weight per day was calculated. I.e., that if, daily over a longer period, a person take up more than 0.005 mg/kg body weight per day, it cannot be excluded that there will be effects on the person.

2. Collection of information on nonylphenol and nonylphenol ethoxylates in textiles

This chapter describes the initial review of the available information in literature (including previous publications from DEPA) the Internet search for information on NP and NPE in textiles. The purpose of this part of the survey was to get an indication of which textiles had previously been analysed for NP/NPE and would thus be interesting to look at in further analytical work, both in terms of type of clothing, material and country of origin.

The initial studies included:

- Investigation of in which processes of textile production NPE is used, in order to assess which materials can be expected with a certain probability to contain NPE and NP, and the materials that are not immediately expected to contain NPEs and NP
- Collected statistics on import of textiles to Denmark from non-EU countries. On the basis of the collected statistics, a list was prepared of the countries, from which it would most relevant to buy clothes for further analysing.
- Available information on the presence of NP and NPE in textile products, including existing reports on chemicals in textiles, contact to purchasers, Ecolabelling Denmark and the Danish Technological Institute and a literature search via the Internet

2.1 Uses of NP and NPE in the textile industry

Especially, NPE with 7 to 15 ethoxylate units ($NPE_{7\text{-}15}$) are used in the manufacture of textiles but also short-chained NPE with 4 to 6 ethoxylate units ($NPE_{4\text{-}6}$) and long-chained NPE with more than 30 ethoxylate units ($NPE_{30\text{-}}$) are used in the production of textiles.

Examples of functions or operations, in which NPE is part of the manufacturing processes of textiles, include (EU, 2002; Miljöforvaltningen & Stockholm Vatten, 2007; RPA, 1999; SWEDWash & the Swedish Society for Nature Conservation (SSNC), 2008):

- An auxiliary agent for cleaning and rinsing of textiles, for the treatment of especially wool and to some extent cotton, from which fat and other impurities must be removed – i.a. for better dying
- Dying of textiles; NPE is used i.a. for dying cotton, acrylic and polyester
- An auxiliary agent in the bleaching as NPE increases the ability of the bleaching agent to penetrate into the textile
- Wetting agent for textiles
- Emulsifier for oils for textile fibers

In textile production, NPE is thus used in several process steps, including both the washing, dyeing and bleaching processes. Apparently, NPE is used both in the production of synthetic fabrics (acrylic, polyester) and in the production of natural textiles (e.g. cotton and wool). NP/NPE is thus expected to be present in all types of textile materials. However, the use of NPE in the treatment of wool and to some extent cotton is highlighted in several sources.

2.2 Import of textiles

As mentioned in the introduction, NP and NPE are regulated in Annex XVII of the REACH Regulation. However, this restriction on use does not cover the presence of NP and NPEs in imported textiles nor does any other legislation establish limits to the content of NP and NPE in textiles. Therefore, it is particularly interesting to look at textiles manufactured outside the EU and imported into Denmark as these may contain NP and NPE. In order to determine from which countries, textiles are mainly imported, and which would thus be relevant to include in the analysis, statistics were collected from StatBank Denmark (www.dst.dk) on import of a number textile products in 2008, such as T-shirts, sweaters, trousers, bed linen, towels, bathrobes and home textiles. Table 2.1 summarizes the information found and the three largest exporting countries for each of the investigated product groups. It should be emphasized that these textiles will not necessarily contain NP and NPE but the textiles are interesting as they are produced in countries that do not have the same regulation on the use of NP and NPE in textile manufacturing as the EU.

Table 2.1 shows that import of textiles into Denmark takes place mainly from countries outside the EU. Only for home textiles and bed linen, there are significant imports from another EU country to Denmark. The main export countries are China, India, Turkey, Pakistan, Bangladesh and India.

TABLL 2.1
IMPORT OF TEXTILES INTO DENMARK I 2008. SOURCE: STATBANK DENMARK (WWW.DST.DK)

Type of textile	Total (tons)	Largest exporter	Second largest exporter	Third largest exporter
Trousers	3,151	China 48%	Tyrkey 15%	Italy 8%
Underwear, towels and bathrobes	5,950	India 22%	Pakistan 19%	Columbia 16%
Home textiles	3,100	Ukraine 34%	Germany 16%	China 12%
Bed linen	11,809	Pakistan 44%	Sweden 13%	Bangladesh 10%
Sweaters	18,830	China 59%	Bangladesh 19%	Tyrkey 10%
T-shirts	16,341	Bangladesh 36%	Tyrkiet 24%	Kina 23%

2.2.1 Earlier textileprojects and projects relevant to this project

DEPA has published several project reports relevant to this project. The following experience can be drawn from these projects:

- A survey of chemical substances in textile fabrics (Environmental Project No. 23, 2003, in Danish) showed levels of NPE in cotton used for bed linen, cushions and children's wear, between 5.5 and 26.4 mg NPE/kg textile

- In Environmental Project No. 534 “Chemicals in textiles” (2000), the content of various chemicals, including NPE, was studied in 23 different textiles. In three of the textiles, NPE was detected at concentrations above the detection limit at a level of 26 mg NPE/kg textile to 85 mg NPE/kg textile. This was detected in trousers, towels and T-shirts made from polyester, wool and cotton (Environmental Project No. 534, 2000, in Danish).
- In the project "Preparing for REACH and development of relevant skills in the textile industry", which dealt with the implementation of REACH in the textile industry, a survey of the chemicals used in textile manufacturing was made (Environmental Project No. 1289, 2009, in Danish). The survey also included, as far as possible, an identification of the substances included in the applied chemical mixtures. The study found a mixture containing 10-30% NPE, suggesting that the rule that NPE and NP must not be used in concentrations above 0.1% in chemical mixtures in the production of textiles[10] is not always observed (Annex XVII No. 46 a and b, REACH Regulation)[11]. The content of NP and NPE in the finished textiles was not measured.

2.2.2 Google search

In connection with the initial survey, a broad Google search of existing data and information on the content of NP and NPE in textiles was carried out. This search yielded more results, particularly from studies conducted in Denmark and Sweden:

- In 2004, Greenpeace published the report ”Toxic childrenswear by Disney” on the content of chemicals in children’s wear from Disney. In most of the studied textiles, alkylphenol ethoxylates were detected at concentrations ranging from 34.1 mg NPE/kg textile to 1,700 mg NPE/kg textile (Greenpeace, 2004).
- In 2006, The Government Chemist, an independent analytical laboratory in England, which i.a. has the task of advising the British government, analysed 29 different textiles for the content of NPE and concentrations of NPE from 100 mg NPE/kg textile up to 14,100 mg NPE/kg textile were detected (Government Chemist, 2006). The high concentration of 14,100 mg NPE/kg textile was detected in multi-colored stripes on polyester satin twill. There has been no reason to doubt the validity of the analysis.
- The Swedish Society for Nature Conservation (SSNC) has studied the concentration of NP and NPE in textiles. A study of T-shirts thus showed NPE concentrations from less than 1 mg NPE/kg textile up to 940 mg NPE/kg textile with a detection limit of 1 mg NPE/kg textile. The study also showed that T-shirts produced outside the EU contained the highest concentrations and eco-labelled T-shirts produced within the EU contained the lowest concentrations of NPE. Most of the T-shirts contained NPE with approx. 8 ethoxylate groups (Hök *et al.*, 2007). A similar study showed levels of NPE in towels from less than 1 and up to 10,608 mg NPE/kg textile (Hök *et al.*, 2007). The number of ethoxylate units was 7-8.
- In 2007, the Swedish consumer magazine "Testfakta" examined the content of NPE in 13 snowsuits from different retailers and found a content of NPE between 970 mg NPE/kg textile and 1,200 mg NPE / kg textile (http://www.testfakta.se/Article.aspx? a = 21519, last updated 10 November 2007)
- In May 2009, the Danish Consumer Council magazine ”Tænk” (Think), published a study of i.a. chemicals in 10 men’s T-shirts. No NPE was detected in any of the T-shirts (http://www.taenk.dk/test/T-shirts/testresultater/).
- In 2009, the Swedish TV programme "Plus" had the content of a number of chemicals in jeans investigated. Four of the 6 studied jeans contained NPE above the detection limit at a concentration level from 7 mg NPE/kg textile and up to 2,200 mg NPE/kg textile

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[10]Unless the use is carried out without discharge to waste water, i.e. in a closed system.
[11] Annex XVII No. 46 a og b, REACH Regulation. (The same provision existed previously in a Danish Statutory Order, n2. 1006 of 12 October 2004 prepared in accordance with EU Directive)

(http://svt.se/2.109801/1.1685436/jeanstest_hela_testprotokollet, last updated 10 September 2009).

- On 2 October 2009, the Swedish newspaper "Göteborg Posten" published an article on toxic chemicals found in Björn Borg underwear. Two pairs of black coulored Björn Borg underwear had been sent for analysis. The analysis showed that a concentration of 860 mg NPE/kg was measured in the one pair and, in the second pair, a concentration of 490 mg of NPE/kg was measured. Björn Borg AB's own analysis of randomly selected batches of black coulored underwear showed a content of NPE of 120-200 mg NPE/kg textile (http://www.gp.se/konsument/tester/1.21943-borg-kalsonger-08, last updated October 2009).
- In 2009, the Norwegian Climate and Pollution Agency (the former SFT) examined 5 different different randomly selected jeans on the Norwegian market for content of i.a. NP and NPE without finding any content of these substances (http://www.sft.no/no/Aktuelt/Nyheter/2009/Oktober-2009/Har-ikke-funnet-antimuggmiddel-i-jeans-/?cid=40499).
- The Danish Information Centre for Environment and Health conducted a study of chemicals in scarves. In the test, 10 different brands of scarves were investigated and the result was i.a. that NP and NPE were not detected in scarves (http://www.miljoeogsundhed.dk/default.aspx?node=6649, not dated but downloaded in December 2009).
- For Greenpeace, TNO in the Netherlands conducted analyses on 5 pyjamas for children and detected NPE at concentrations between 17 and 1,930 mg NPE/kg textile and NP in 4 of pyjamas at concentrations between 6.9 and 49 mg NP/kg textile (http://www.uk.greenpeace.org.uk/files/pdfs/migrated/MultimediaFiles/Live/FullReport/6043.pdf from 2003).

The search results show that there is a focus on the presence of NP and NPE in textiles and studies have been conducted both in Denmark and abroad. The studies show that NPE and NP can occur at concentrations well above the detection limit. Thus, concentrations of up to 10,608 mg NPE/kg were detected in towels and up to 14,000 mg NPE/kg in one of the textiles that the British analytical laboratory, the Goverment Chemist, analysed.

2.2.3 Requirements to the content of NP and NPE in ecolabelled textiles

The "Flower" is the European Ecolabel and the "Swan" is the official ecolabel of the Nordic countries. The purpose of ecolabelling is to make it easy for buyers (both professionals and consumers) to buy environmentally friendly products and thereby contribute to a less environmentally harmful production and consumption.

The criteria document for the "Flower" and the "Swan" (EU, 2009) specifies a number of chemical substances that must not be used in production, including alkylphenol ethoxylates, of which NPE is a subgroup. In this project, it was therefore interesting to include textiles labelled with "Swan" and the "Flower" as references in the analytical programme.

2.2.4 Contact to importers

Seven of the major buyers of textile products in Denmark were contacted as part of the project. They were requested to complete a questionnaire in order to investigate whether there was knowledge of the presence of NP and NPE especially in imported textiles and whether requirements had been laid down in relation to the content of NP and NPE. The buyers were also asked about the types of textiles, cotton or synthetic, which most frequently contain NP and NPE, and whether they had standard test or control programmes, in which NP and NPE are included.

Appendix A presents a summary of the responses. Below some of main topics are presented:

- According to the trade organisation ”Dansk tekstil og beklædning” (Danish textile and clothing), most Danish companies impose requirements in terms of content and types of chemicals, including NPE/NP in textiles.
- The companies stated that they are aware of the presence of NP and NPE in textiles and that the presence is very likely. Generally, it is estimated that the presence is especially seen in imported products from China or India and to some extent from Turkey.
- The companies stated that the typical source of NP and NPE is the washing processes carried out at the end of the production process. At the same time, the probability of presence of NPE is highest in articles manufactured with washing processes comprising several wash steps.
- The companies stated that NPE is used in many processes and perhaps in several stages in the product chain. The majority, 5 of the 7 contacted companies have a limit for the acceptable amount of NPE in the finished textile products. The companies stated that when NPE content exceeds this limit, they try to identify the source and to have the NPE content either reduced or eleminated while they accept the content if the concentration is below the limit. The companies make use of spot tests for control rather than fixed monitoring programmes. The limit is between 100-250 mg NPE/kg textile. The limit of 100 mg NPE/kg textile is determined on the basis of the experience of the companies that concentrations exceeding this level typically indicates a technical use of NPE while concentrations below the approx. 100 mg NPE/kg textile indicates a more diffuse application, which can be difficult to track and control. No information was provided on how the 250 mg NP/kg textile limit had been determined.

2.3 Results of the literature search

Table 2.2 summarizes the results found in the literature search described in Sections 2.2.1 and 2.2.2. Appendix A lists the detailed results (Table A.1). A total of 116 test results was found.

The main facts are summarized below:

- All data are from before washing.
- There is large variation in the measured content of NP and NPE in clothes (for NPE, the measured values vary from less than 1 mg NPE/kg textile up to 14,100 mg NPE/kg textile).
- In three of the analytical results, a concentration higher than 6,000 mg NPE/kg textile was detected while, in the remaining samples, concentrations below 3,200 mg NPE/kg textile were measured. The high concentrations were detected in multi-colored stripes on a polyester satin twill (14,100 mg NPE/kg textile), in towels (10,608 mg NPE/kg textile) and in small red polka dots on white fabric (cotton-polyester) (6,400 mg NPE/kg textile). These very high concentrations indicate a lack of effective cleanings – e.g. rinsing - after treatment with an NPE-containing chemical mixture.
- Relatively high concentrations were measured in children textiles such as T-shirts (Disney), jeans and snowsuits.
- In a single measurement of NPE in towels, a concentration of 10,608 mg/kg textile was detected (Hök *et al.*, 2007). According to the report, the high content was verified by taking three more subsamples from different areas of the towels. The analyses showed that the distribution of these subsamples was less than 20% and the spread of nonylphenol ethoxylate must be considered homogeneous. Therefore, this measure is considered as valid. The other concentrations measured in the tested towels ranged from less than 1 mg NPE/kg textile to 1,277 mg NPE/kg textile. The geometric mean measured NPE concentration in the tested towels was 18 mg NPE/kg textile if disregarding the high NPE concentration. If not disregarding the high concentration, the average will be 25 mg NPE/kg textile instead.
- There are primarily measured for NPE. In the few analyses measuring for both NP and NPE, the ratio of NPE to NP was between 3:1 and 9:1 (when disregarding the analyses with pyjamas). For the pyjamas, the NPE:NP ratio was between 1:3 and 219:1.

- Concentration levels far above 250 mg NPE/kg textile were detected in all investigated types of clothes (e.g. T-shirts and jeans) and, for some types of textiles, even concentrations around and over 1,000 mg NPE/kg textile were detected (e.g. T-shirts, towels, jeans and snowsuits).
- The average concentration of NPE in 10 T-shirts made from pure cotton was measured at 214 mg NPE/kg textile (from less than 1 mg NPE/kg textile and up to 940 mg NPE/kg textile) (Hök *et al.*, 2007) while the NPE concentration of 2 T-shirts made from pure polyester averaged 30.5 mg NPE/kg textile. Also in analyses made by the Government Chemist, a very high content of NPE was detected in polyester. Because of the very limited data material, it is not possible to conclude whether there is any connection between textile material (cotton, wool, silk) and the contents of NP and NPEs.
- There has carried out many measurements for cotton textiles.
- In the analyses carried out, clothes made from organic cotton had a lower content of NP and NPEs than clothing made from non-organic cotton. As however, there are only two analyses, no conclusion can be drawn on whether the NP and NPE content is generally lower in organic cotton textiles (Table A.1).
- In some cases, very large variation was measured in the content of NP and/or NPE for the same material and type of fabric, e.g. in towels, jeans and T-shirts. This may be explained by the fact that alternatives to NPEs are used in some manufacturing processes or, in some cases, the textile is washed thoroughly before it is marketed.
- There is tremendous variation in the measured levels of NPE in children's wear from Disney for the individual purchasing countries (Greenpeace, 2004). The lowest content was measured in clothing from Canada (34 mg NPE/kg textile) and the U.S. (49 mg NPE/kg textile). The highest content was measured in clothing from Turkey (1,190 mg NPE/kg textile), the Netherlands (1,220 mg NPE/kg textile), Thailand (1,390 mg NPE/kg textile) and Austria (1,700 mg NPE/kg textile). The content of clothes from Denmark was measured at 620 mg NPE/kg textile. Production countries were not provided in the study. No immediate explanation has been found for this large variation in the concentration of NPE in the clothes.
- In general, there is very little information on the the country of origin in the analytical reports found in the literature search. Therefore, it is not possible to conclude whether there is a genuine link between country of origin and content (see Figure 2.1). It may, however, be noted that the T-shirt with the highest content of NPE originated in China.

TABLE 2.2
OVERVIEW OF DETECTED CONCENTRATION LEVELS FROM THE LITERATURE SEARCH DISTRIBUTED ON DIFFERENT CLOTHING TYPES (MG NP(E)/KG TEXTILE). VALUES GIVEN IN BOLD AND ITALICS REFERS TO THE CONTENT OF NP WHILE THE OTHER VALUES REFER TO THE CONTENTS OF NPE

CHILDREN	Concentration levels found by the literature search (mg NPE per kg textile or mg NP per kg textile)						
	Minimum	Average	Standard deviation	Geometric mean	95% percentile	Maximum	Number
All	1	670	1,664	66	2,440	14,100	139
	0.1	***5.9***	***12.9***	***0.7***	***22.9***	***49***	***14***
T-shirts*	1	261	419	28	1,193	1,390	39
Textiles	1	1,608	2,753	282	4,960	14,100	30
	0.1	***2.2***	***2.9***	***0.9***	5.7	***6.4***	***4***
Towels	1	657	2,300	25	1,277	10,608	21
Snowsuits	2	421	411	158	1,074	1,200	13
Underwear	490	338	417	25	805	860	4
Jeans**	1	232	631	7	1,221	2,200	12
	<d.l.	***<d.l.***	***<d.l.***	***<d.l.***	***<d.l.***	***d.l.***	***5***
Pyjamas	17	1,038	701	585	1,861	1,930	7
	0.1	***14.7***	***19.5***	***4.8***	***41.0***	***49***	***5***
Other	491	670	1,664	199	620	620	13

*) For the study by the Danish Consumer Council of 10 men's T-shirts, in which no NP/NPE was detected, detection limits (d.l.) of 1 mg NPE/kg textile and 0.1 mg NP/kg textile were assumed

**) For the study by the Norwegian Climate and Pollution Agency of 5 randomly chosen jeans on the Norwegian market, in which no NP/NPE was detected, detection limits (d.l.) of 1 mg NPE/kg textile and 0.1 mg NP/kg textile were assumed

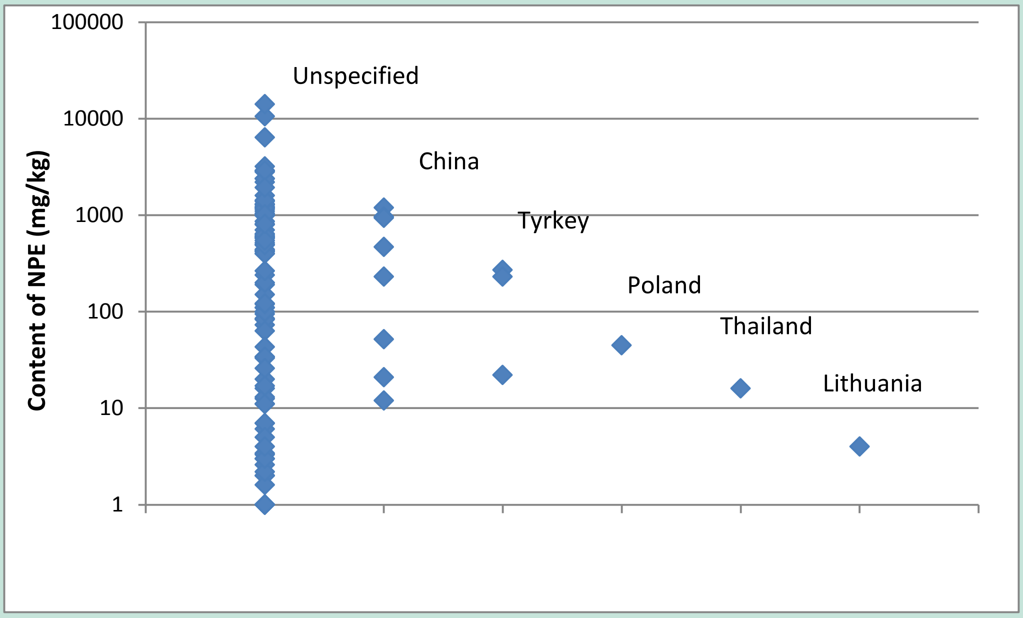

FIGURE 2.1
MEASURED CONTENT OF NPE IN TEXTILES IN RELATION TO REPORTED COUNTRY OF ORIGIN

2.4 Initial exposure assessments (health)

In order to decide which types of clothing, it was most appropriate to examine for contents of NP and NPE, an initial estimate was made of how much NP and NPE humans could be exposed to from textiles.

It is assumed that exposure via inhalation will be irrelevant as NP and NPE have very low vapour pressure and, therefore, very little NP and NPE can be expected to be released from textiles into the air. The other routes of exposure, skin contact and ingestion (i.e. by mouth by children sucking on clothes corners and mittens), were considered relevant exposure routes.

The types of textiles, for which exposure calculations were made, were selected according to whether NP and NPE were measured in clothing type, whether they represented typical clothing and whether they were assessed to have an effect in relation to exposure.

The following sections describe the standard models used for calculating the exposure.

2.4.1 Dermal exposure (ECHA, 2008a)

In ECHA (2008a), an equation for calculating the external dermal dose (L_{der}) is established for a non-volatile substance that migrates from an article and to the skin per day (see ECHA, R .15.3.2.2, Dermal Scenario B):

$$D_{der}\ (mg/kg\ bw/d) = Sd_{prod} \times C \times Fc_{migr} \times F_{contact} \times T_{skin} \times A_{skin} / BW \qquad \text{Equation (1)}$$

Where

D_{der}	Dose by contact with skin per day per kg body weight (mg/kg bw/d)
Sd_{prod}	Amount of textile per area unit (kg/m^2). This value is dependent on the textile as some fabrics are thicker than others. Here, it is thus calculated from the thickness of the fabric (TH) and density of the fabric (RHO): $Sd_{prod} = TH \times RHO$
TH	Layer thickness (m) (Table 2.3A)
RHO	Density of fabric. Here, it is set at 1,000 kg/m^3 (e.g. ECETOC TRA (http://www.ecetoc.org/tra))
A_{skin}	Area of contact between product and skin (m^2)
T_{skin}	Contact duration between article and skin per day (hours)
BW	Weight of the exposed person (kg body weight (kg bw)). Here, relatively low values were used - 60 kg for an adult and 10 kg for a child, corresponding to a child of almost 2 years. A 2-year-old child is often chosen as a model for assessment of consumer exposure to chemicals, partly because children are relatively much exposed to chemicals and partly because of children's relatively low weight
C	Concentration of NP (NPE) in the textile (mg NP (NPE)/kg textile)

Fc_{migr}	Rate of migration (mg/mg per hour), which, in the initial calculations, is set to 0.00125 mg NPE/NPE mg per hour, which corresponds to 2% NPE being assumed to migrate to sweat at 16 hours of exposure per day (Kraetke & Platzek, 2005), and 6.25×10^{-5} mg NP/mg NP per hour, corresponding to 0.1% NP being assumed to migrate during a 16-hour day (Kraetke & Platzek, 2005)[12]
$F_{contact}$	Fraction of contact area for skin, which is actually in contract with skin (here, set at 1)

The uptake via skin contact is less than the dose that can be calculated from the above equation as the skin itself constitutes an effective barrier. Therefore, the actual uptake per day per kg body weight (U_{skin}) is calculated based on the assumption that a maximum of 10% of the substance (NP and NPE) will be taken up through the skin (EU, 2002):

$$U_{skin}\ (mg/kg\ bw/d) = D_{skin} \times 10\% \qquad \text{Equation (2)}$$

The uptake through skin of NP and NPE from textiles depends on i.a. the rate of migration to sweat, Fc_{migr}, the rate with which NP or NPE penetrates the skin. The rate of migration to sweat for NPE is here assumed to be approx. 20 times higher than the rate of migration for NP, which reflects the higher solubility in water of NPE compared with that of NP. Furthermore, NP and NPE are assumed to penetrate the skin at the same rate, i.e. to have the same skin permeability rate. However, this is unlikely to actually be the case as NPE is expected to penetrate the skin more slowly than NP. This is illustrated in Figure 2.2, which presents the ratio of the calculated permeability rate of NPE to that of NP as a function of the number of ethoxylate units. As it is not known in what state NPE (the number of ethoxylate units on the migrated NPE) will migrate from the textile, it was decided to use the same value of 10% of the uptake through the skin (U_{skin}) for both NP and NPE though undoubtedly a very conservative estimate for the uptake of NPE through the skin.

[12] The release of substances from textiles will vary over time. Migration is also dependent on the type of textile fibers and fabric. Kraetke & Platzek (2005) have developed a simple screening model to estimate the migration of substances from textiles when worn for the first time. A distinction is made between dyes and auxiliary agents. For auxiliary agents, distinction is made between whether the auxiliary agent is expected to remain in the textile or not. Kraetke & Platzek (2005) has proposed the following migrations used as an estimate of how much substance is released from clothes over 16 hours when the person is wearing it for the first time.

Substance	Migration with sweat
Dye	0.5%
Hydrophilic auxiliary agent	2%
Hydrophobic afjuvant	0.1%

NP/NPE is characterized as an auxiliary agent. NPE is expected to remain in the textile and, therefore, a migration of 2% was applied whereas NP is hydrophobic and a migration of 0.1% is thus assumed. This corresponds to a release of o.00125 kg per kg per hour for NPE and 6.25×10^{-5} kg per kg per hour for NP (rough estimate).

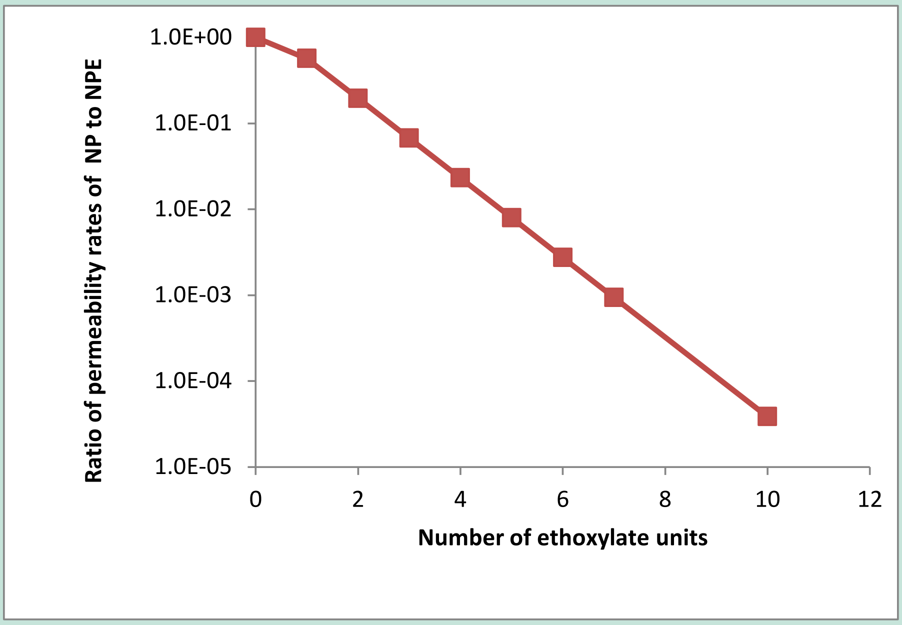

FIGURE 2.2
RATIO OF PERMEABILITY RATES OF NP TO NPE CALCULATED BY USE OF THE PROGRAM DERMWIN (VERSION 1.43A FROM 2008). THE PROGRAM IS PART OF EPISUITE, WHICH CAN BE FREELY DOWNLOADED FROM THE US EPA WEBSITE

2.4.2 Oral exposure

Oral exposure is assumed to occur as a result of a person (a child) sucking on the textile, and it is here calculated from the following equation, which is the equation that the tool ECETOC TRA (http://www.ecetoc.org/tra) uses for estimating the oral exposure, cf. ECHA guidance on estimating consumer exposure to chemicals (ECHA, 2008).

$$D_{oral}\ (mg/kg\ bw/d) = A_{oral} \times TH \times RHO \times C \times n_{mouth} \times F_{oral}/BW \qquad \text{Equation (3)}$$

Where

D_{oral}	Intake per day per kg body weight
A_{oral}	Area of the textile that the person has put in his mouth (cm^2)
n_{mouth}	Number of time a day that the person has sucked on the textile
BW	Weight of the exposed person (kg body weight (kg bw)). Here, relatively low values were used - 60 kg for an adult and 10 kg for a child, corresponding to a child of almost 2 years
C	Concentration of NP (NPE) in the textile (mg NP(E)/kg textile)
TH	Layer thickness (m)
RHO	Density of fabric. Here, it is set at 1,000 kg/m^3 (e.g. ECETOC TRA (http://www.ecetoc.org/tra))
F_{oral}	Fraction of NP (NPE) released by oral contact. It is set at 1. This is a conservative estimate as it is thus assumed that all NP (NPE) in the part of textile, which is in contact with the mouth, is released

The actual systemic uptake from a person sucking on the textile, U_{oral} = ingestion per kg body weight per day, is assumed to be 10% of the calculated exposure as the systemic bioavailability of NP after oral administration to rats was estimated to be 10% of initial dose due to "first pass" metabolism in the liver (EU, 2002):

U_{oral} (mg/kg bw/d) = D_{oral} × 10%   Equation (4)

2.4.3 Parameters applied in the exposure calculations

Tables 2.3a and b present an overview of the parameters used in the exposure calculations for the different types of textiles for children (a) and adults (b), respectively. It is assumed that childen are exposed orally when they are sucking on the textile as well as via skin contact. It is assumed that adults are only exposed via skin contact. The values for the parameters for the calculation of the oral exposure are taken from the ECETOC model, which is listed in the ECHA guidance on exposure assessments for the common consumer (ECHA, 2010). The exposed skin area was found by evaluation of the body part, which is in contact with the textile. In addition, the number of hours in the day, the clothes will be worn, are estimated conservative values.

TABLE 2.3A
OVERVIEW OF PARAMETERS USED FOR THE CALCULATIONS OF CHILDREN'S EXPOSURE TO NP/NPE

Type of textile	Body parts with skin contact (see Appendix C for skin area)	Area with skin contact to textile (cm^2)	Duration of skin contact per day T_{skin} (hours)	Justification for choice of parameter	Area of textile put into the mouth A_{oral} (cm^2)	Layer thickness TH (cm)	Comments
Towels	The whole body	6,410	0.5	Corresponds to the time it takes to dry off after a bath	10	0.01	From ECETOC TRA
Bed linen	The whole body	6,410	10	A 2-year old child will typically sleep approx. 10 hours a day	10	0.001	From ECETOC TRA
Snowsuits	None		-	Children wear clothes underneath, therefore no skin contact	10	0.01	From ECETOC TRA
Mittens	Hands	364	8	It is assumed that the child is outdoors all day in the day care	10	0.01	From ECETOC TRA
Socks	Feet	402	14	All day expect when the child is in bed	0	0.01	Oral contact with clothes not very likely
T-shirts	Torso + upper arms	2,300	14	All day expect when the child is in bed	0	0.01	Oral contact with clothes not very likely
Jeans	Legs	1,481	14	All day expect when the child is in bed	0	0.01	Oral contact with clothes not very likely
Underwear	Torso	2,276	24	The child is wearing underwear both day and night	0	0.01	Oral contact with clothes not very likely
Pyjamas	Arms + legs	2,314	10	A 2-year old child will typically sleep approx. 10 hours a day	10	0.01	From ECETOC TRA

TABLE 2.3B
OVERVIEW OF PARAMETERS USED FOR THE CALCULATIONS OF ADULTS' EXPOSURE TO NP/NPE

Type of textile	Body parts with skin contact (see Appendix C for skin area)	Area with skin contact to textile (cm^2)	Duration of skin contact per day T_{skin} (hours)	Justification for choice of parameter	Area of textile put into the mouth A_{oral} (cm^2)	Layer thickness TH (cm)	Comments
Towels	The whole body	17,160	0.5	Corresponds to the time it takes to dry off after a bath	-	0.01	Adults normally do not suck on their clothes
Bed linen	The whole body	17,160	8	Typical sleep duration	-	0.001	Adults normally do not suck on their clothes
Snowsuits	None		-	Adults typically do not use snowsuits	-	0.01	Adults normally do not suck on their clothes
Mittens	Hands	875	2	Corresponds to an adult using 1 hour to cycle back and forth to work	-	0.01	Adults normally do not suck on their clothes
Socks	Feet	1,115	16	All day expect when the adult is in bed	-	0.01	Adults normally do not suck on their clothes
T-shirts	Torso + upper arms	6,000	16	All day expect when the adult is in bed	-	0.01	Adults normally do not suck on their clothes
Jeans	Legs	5,560	16	All day expect when the adult is in bed	-	0.01	Adults normally do not suck on their clothes
Underwear	Torso	5,972	24	The adult is assumed to wear underwear both day and night	-	0.01	Adults normally do not suck on their clothes
Pyjamas	Arms + legs	7,962	8	Typical sleep duration	-	0.01	Adults normally do not suck on their clothes

2.5 Initial risk assessments

This section examines the risk assessment, which was made initially in order to be able to choose the textile types, for which would be appropriate to make chemical analyses.

As already mentioned (Section 1.1.6), a risk characterisation ration (RCR) is applied when it is assessed whether exposure from the use of a textile may constitute a risk to humans or not.

It appears from the previous section (Equations 1 and 3) that the calculated dermal and oral exposure (skin and oral contact) for NP or NPE from a textile is proportional to the concentration of NP and NPE in textile (C). The contribution from the use of a textile to the total RCR_{human} will thus be proportional to the concentration of NP or NPE in the textile. Therefore, one can also calculate the concentration of a piece of textile, in which the calculated total daily intake is equal to the DNEL, which corresponds to RCR_{human} is equal to 1. This concentration is hereinafter referred to as the no-effect concentration and is the roughly estimated maximum concentration that must be in the textile if the calculated daily uptake should not exceed DNEL for NP, and thus no health risk will occur from long-term contact with this piece of textile.

A high calculated concentration in the textile, which gives an uptake of NP or NPE corresponding to DNEL, implies that person who is wearing the clothes is taking up only a small fraction of NP or NPE in textile. I.e., the higher the calculated no-effect concentration is, the smaller the fraction is taken up by the person wearing the clothes. Therefore, the calculated highest concentrations are higher for NP than for NPE as NPE is more mobile than the NP.

Tables 2.4a and b present the calculated no-effect concentrations. Calculation Box 2.1 provides an example of how the uptake of NP through the skin and by ingestion is calculated, and shows how the concentration in the textile, which results in an uptake corresponding to DNEL, is calculated for each type of textile (assuming that the migration of NP from the textile is 6.25 × 10-5 mg NP/mg NP per hour). Calculated no-effect concentrations higher than 50,000 mg NP/kg textile are listed as ”>50,000 mg NP/kg”. This high concentration has been applied for the types of textiles, for which the contact area is very small and for which it is not expected that the person sucks on the textile. The limit is chosen as a theoretical value, which is undoubtedly much higher than the concentrations that can be found in the textiles. In the tables, it is also indicated how much (in %) of the total uptake that, according to the calculations, originates from the skin and the oral intake, respectively. As an example of this, a calculated no-effect concentration for NPE of to 3,570 mg NP/kg textile for exposure of children to towels (Table 2.4a) with the uptake through the skin contributing 28.6%, i.e., 1,021 mg NP/kg textile, and the oral intake contributing 71.4%, i.e., 2,549 mg NP/kg textile.

As seen in Tables 2.4a and b, the calculated no-effect concentrations are lower for children than for adults. This reflects the fact that children have the highest uptake of NP or NPE (indicated as amount of substance per kg body weight). It is not surprising as children weigh less, have a larger surface area per kg body weight and not least because they suck more on things. Tables 2.4a and b also show that the lowest values for the 'no-effect concentration' for NP or NPE are for the types of textiles, on which it is assumed that children suck and from which a high uptake of the substances in the body is calculated.

The results of these calculations should of course be used with great caution as they are based on some conservative assumptions. For example, relatively high exposure times and a high migration from textile to saliva were used and it was not taken into account that the textiles might be washed before use. The calculations only reflect a theoretical maximum daily uptake from a single, new and unwashed type of textile. The no-effect concentrations may be used as e.g. a step 1 warning level. If, for a piece of textile, concentrations of NP and NPE are measured above the calculated no-effect concentration for the type of textile, there may be reason to look at the situation. It should also be noted that for all the investigated types of textiles, the calculated no-effect concentrations are higher than the limit values of 100 and 250 mg NPE/kg textile, which companies use as a limit value for carrying out further investigations (Section 2.2.4). This suggests that the limit values, which some companies already use, are low enough to protect the consumer.

TABLE 2.4A

CALCULATIONS OF CHILDREN'S UPTAKE OF NP/NPE EXPRESSED AS NO-EFFECT CONCENTRATIONS, WHERE THE CALCULATED (THEORETICAL AND CONSERVATIVELY SPECIFIED) TOTAL DAILY UPTAKE (INTERNAL DOSE) FROM THE INDIVIDUAL TYPES OF TEXTILES DOES NOT EXCEED DNEL. FURTHERMORE, THE PERCENTAGES (%) THAT, ACCORDING TO THE CALCULATIONS, ORIGINATE FROM THE SKIN AND THE ORAL INTAKE, RESPECTIVELY, ARE INDICATED.

Type of textile	NP			NPE		
	Calculated no-effect concentration (mg NP/ kg textile)	% contribution via skin	% contribution via oral intake	Calculated no-effect concentration (mg NP/ kg textile)	% contribution via skin	% contribution via oral intake
Towels	4,902	2.0	98.0	3,570	28.6	71.4
Bed linen	35,698	28.6	71.4	5,548	11.1	89.9
Snowsuits	5,000	0.0	100	5,000	0.0	100
Mittens	4,911	1.8	98.2	3,666	26.7	73.3
Socks	>50,000	100	0.0	7,107	100	0.0
T-shirts	24,845	100	0.0	1,242	100	0.0
Jeans	38,584	100	0.0	1,929	100	0.0
Underwear	14,646	100	0.0	732	100	0.0

TABLE 2.4B

CALCULATIONS OF ADULTS' UPTAKE OF NP/NPE EXPRESSED AS NO-EFFECT CONCENTRATIONS, WHERE THE CALCULATED (THEORETICAL AND CONSERVATIVELY SPECIFIED) TOTAL DAILY UPTAKE (INTERNAL DOSE) FROM THE INDIVIDUAL TYPES OF TEXTILES DOES NOT EXCEED DNEL. FURTHERMORE, THE PERCENTAGES (%) THAT, ACCORDING TO THE CALCULATIONS, ORIGINATE FROM THE SKIN AND THE ORAL INTAKE, RESPECTIVELY, ARE INDICATED.

Type of textile	NP			NPE		
	Calculated no-effect concentration (mg NP/ kg textile)	% contribution via skin	% contribution via oral intake	Calculated no-effect concentration (mg NP/ kg textile)	% contribution via skin	% contribution via oral intake
Towels	>50,000	100	0.0	27,972	100	0.0
Bed linen	>50,000	100	0.0	17,483	100	0.0
Snowsuits	Adults are not assumed to be exposed to NP/NPE from use of snowsuits					
Mittens	>50,000	100	0.0	>50,000	100	0.0
Socks	>50,000	100	0.0	13,453	100	0.0
T-shirts	>50,000	100	0.0	2,500	100	0.0
Jeans	>50,000	100	0.0	2,698	100	0.0
Underwear	33,490	100	0.0	1,674	100	0.0

CALCULATION BOX 2.1
EKSAMPLE OF CALCULATION OF THE TOTAL UPTAKE

Calculation of a child's uptake of NPE when using ***mittens***

Uptake through skin (internal dose per kg body weight per day):

U_{skin} (mg/kg bw/d): $Sd_{prod} \times Fc_{migr} \times F_{contact} \times T_{skin} \times A_{skin} \times C \times 10\%/BW$

Where

BW:	Weight of exposed person	10 kg bw for a child
Sd_{prod}:	Amount of textile per area unit	= 0.0001 m × 1,000 kg/m³ = 0.1 kg textile/m²
Fc_{migr}:	Rate of migration	= 0.00125 (mg NPE/mg NPE per hour) (conversion of values in Kraetke & Platzek (2005)
$F_{contact}$	Faction of contact area for skin	1 (assumption)
T_{skin}:	Contact duration per day	8 hours per day (Table 1.4a) (assumption)
A_{skin}:	Area for skin contact	364 cm² (two hands) = 0.0364 m² (from ECETOC TRA)
C:	Concentration of NPE in textile (mg/kg textile)	To be calculated/inserted

By inserting the above values, the following result is obtained:
U_{skin} = 0.1 kg textile/m² × 0.00125 mg NPE/mg NPE per hour × 1 × 8 hours/day × 0.0364 m² × C × 0.1/10 kg = $3.64 \cdot 10^{-7}$ × C kg textile/day/kg bw

Oral uptake

U_{oral} (mg/kg bw/d) = $A_{oral} \times TH \times RHO \times n_{mouth} \times C \times 10\%/BW \times F_{oral}$

Where

A_{oral}:	Area of textile in oral contact	10 cm² = 0.0010 m² (from ECETOC TRA – Table 2.3a)
TH:	Layer thickness	Thickness of textile = 0.01 cm = 0.0001 m (from ECETOC TRA – Table 2.3a)
RHO:	Density of textile	1,000 kg/m³ (from ECETOC TRA)
n_{mouth}:	Number of times per day	1 (assumption)

By inserting the above values, the following result is obtained:
U_{oral} = 0.0010 m² × 0.0001 m × 1,000 kg/m³ × C × 0.1 /10 kg × 1 = $1.0 \cdot 10^{-6}$ × C kg textile/day/kg bw

The total uptake in a 10-kg child via migration from mittens is thus:
U = ($3.64 \times 10^{-7} + 1.0 \times 10^{-6}$) × C kg textile/day/kg lgv = 1.364×10^{-6} × C kg tekstil/day/kg bw

The concentration, C, that results in an uptake corresponding to a DNEL of 0.005 mg/day/kg bw, can then be estimated to:

C = 0.005 mg/day/kg bw/(1.364×10^{-6} × C kg textile/day/kg bw) = 3,666 mg/kg textile

Table 2.5 shows a comparison between the calculated no-effect concentrations for NPE (from Table 2.3a - children's exposure) and the measured NPE concentration levels that were found in the literature search (from Table 2.2). The no-effect concentrations are indicated both in the NP units and in NPE units. The study on towels showed a uniform distribution of NPE in the various samples with a maximum of approx. 7-8 ethoxylate groups. NPE units have been converted to NP units by assuming 9 ethoxylate units per NP.

Example of conversion from NPE(weight) to NP units (weight)

The molucar weight for NP is 220 g NP/mol, for NPE_9 616 g NPE/mol. For towels, a higher no-effect concentration of 3,570 mg NP/kg textile, which corresponds to 3,570 mg NP/kg textile × (616 g NPE per mol)/(220 g NP per mol) = 9,996 mg NPE/kg textile.

This means that the uptake of NPE can be converted to uptake of NP by dividing by 2.8.

Table 2.5 shows that the calculated no-effect concentration is higher than the measured concentration for al the studied types of textiles when it is calculated for one type of textile at a time – except for one case. For towels, a single measurement showed a NPE content higher than the calculated no-effect concentration, which might indicate a special case.

If the 95% percentile of the measured data is used, which is normal in risk assessment, it appears that all 95% percentiles are below the calculated no-effect concentrations.

Assessed on the basis of the literature values for content of NP or NPE in textiles and the calculations presented in this chapter, NP or NPE in textiles does not constitute a health risk when exposure is calculated for an individual pieace of textile.

In this chapter, no calculations were made of the concentrations resulting from exposure to NP and NPE from more pieces of textiles on the same day as the initial exposure calculation was only made with a view to selecting types of textiles that would be relevant to test in chemical analysis. The selection is presented in Chapter 3. Chapter 4 contains calculation of the total exposure from more pieces of textiles based on analytical data from Chapter 3

TABLE 2.5
CALCULATED NO-EFFECT CONCENTRATIONS FOR FOR NPE I DIFFERENT TYPES OF TEXTILES COMPARED WITH MEASURED LITERATURE-BASED NPE CONCENTRATION LEVELS

Type of textile	Calculated no-effect concentration*		Measured NPE concentration level found in literature search			
	(mg NP/kg textile)	(mg NPE/kg textile)	95% percentile (mg NPE/kg textile)	Highest measured concentration (mg NPE/kg textile)	Geometric mean value (mg NPE/kg textile)	Mean (mg NPE/kg textile)
Towels	3,570	9,996	1,277	**10,608**	25	657
Bed linen	5,548	15,534	-	-	-	-
Snowsuits	5,000	14,000	1,074	1,200	158	421
Mittens	3,666	10,264	-	-	-	-
Socks	7,107	19,901	-	600 (only one measurement)	-	-
T-shirts	1,242	3,478	1,193	1,390	28	261
Jeans	1,929	5,402	1,221	1,200	7	232
Underwear	732	2,050	805	860	25	338

*) Please refer to Calculation Box 2.1

3. Analyses of NP and NPE in textile products

3.1 Selection of products for analysis

In the preparation of this report, a small analysis programme was carried out on selected textiles. Based on the initial literature search, contact to the buyers and the initial exposure assessment, the analysis programme was established on the basis the following considerations:

- The analysis programme should both provide information on the presence of NP and NPE in a range of consumer textile products and provide quantitative measurements of the migration of the substances and leaching from the textiles.
- The initial exposure assessments (Tables 2.4a and b) clarified that the total uptake of NP and NPE is generally highest for children as they are exposed both through the skin and by uptake through the mouth, and it was considered most appropriate to focus on children's wear.
- Primarily, the textile types that immediately cause the highest exposure (Tables 2.4a and b), and, at the same time, have not been thoroughly studied in previous studies, i.e. underwear, bed linen and mittens, were selected. Underwear was chosen because it has much contact with the skin and because children may wear it all day. Bed linen is relevant because children, especially infants, will be in contact with the bed linen many hours a day. Mittens are relevant as children may suck on their mittens and oral uptake may thus occur.
- A number of textiles (jeans, T-shirts, sweaters) were chosen because these types of clothing have shown elevated concentrations of NP and NPE. And, at the same time, these types of clothing represent different types of fabric (cotton, polyester, etc.) and they are often used by children.
- Many textile products are imported from non-EU countries. These countries are interesting as textiles produced in non-EU countries are not subject to the same regulation (legislation) as textiles produced within the EU. In this context, especially China, Bangladesh, Turkey and India are interesting as large quantities of textiles are imported from these countries (Table 3.1).
- Various exporting countries were selected for two clothing groups - bed linen and underwear - to assess whether the country of origin is important.
- Different materials (cotton, polyester, etc.) were selected to get an idea of the importance of the textile type. Also coloured synthetic materials were selected.
- Eco-labelled textiles (Flower and the Swan) were included as reference textiles as it is interesting to see whether there is a difference between eco-labelled and non-eco-labelled textiles.

TABLE 3.1
OVERVIEW OF ANALYSES PERFORMED ON SELECTED TEXTILES FOR CHILDREN

Type of textile	Country of origin	Description	Quantitative analysis before washing	Migration with artificial sweat	Migration with artificial saliva	Washing water after textile washing
Bed linen	India	100% eco-cotton Light beige stripes	X			
	Pakistan	100% cotton. Coloured print in red/blue etc.	X	X		X
	Bangladesh	100% cotton. Pink with coloured hearts	X			
Mittens	China	100% acrylics. Light blue	X			
	China	100% polyester. Brown	X			
	China	100% polyester. Pink	X		X	X
Underwear	India	95% cotton/ 5% elastan. Solid pink	X			
	China	100% eco-cotton. Green/white striped	X			X
	Bangladesh	95% cotton/ 5% elastan. White with butterfly print	X			
Jeans	Tyrkey	100% cotton. Light blue	X			
	China	100% cotton. Dark blue	X	X		X
	Kina	100% cotton. Black	X	X		X
T-shirt	Bangladesh	100% cotton. Pink with owl print	X			X
T-shirt	Cambodia	100% polyester. Pink	X			
Sweater	China	100% cotton. Natural colour	X			
Number of analyses			15	3	1	6

3.2 Chemical analyses

The content of NP and NPE (NPE_1, NPE_2, $NPE_{3\text{-}15}$), respectively, was measured in all the selected textiles in duplicate. A representative subsample was taken from each piece of textile (approx. 2 g, which was weighed) and this subsample was extracted by shaking with 40 mL of methanol for 2 hours at room temperature. Then, the extract was analysed for NP, NPE and OPE (octylphenol ethoxylate), respectively. GC/MS (gas chromatography-mass spectrometry - detection limit: 0.2 mg/kg and the relative standard deviation (RSD) of 12%) was used to analyse the short-chained ethoxylates and LC/MS (liquid chromatography-mass spectrometry – detection limit: 0. 2 mg / kg and RSD of 15% of the long-chained ethoxylates (3-15).

For some of the selected textiles, chemical analyses were also performed of the clothes after washing. The textile samples were washed in an ordinary washing machine according to the textile care label and then air dried.

For a few relevant textiles, migration tests were made with artificial sweat and saliva (before washing, see Table 3.4). A representative subsample was taken from each textile and this subsample was extracted for 2 hours either with artificial sweat (produced in accordance with DIN 53160-2) or with artificial saliva (produced in accordance with DIN 53160-1) while the sample was shaken. Then, the extract was analysed. Migration test with artificial sweat was made on the textiles, for which skin was considered a significant route of exposure and for which significant concentrations of NP and NPE, respectively, had been measured (bed linen and jeans). Migration test with artificial saliva was made on mittens as it was estimated that children's oral intake from mittens can be significant.

3.3 Results of chemical analyses

Table 3.2 presents the results of the analyses before washing. Furthermore, it shows the calculated concentration of NP units (NPs). This concentration is calculated from the molecular weight of NP and NPE assuming that the number of ethoxylate groups is 9 for the long-chained NPE (average of 3 and 15)[13].

13 The molecular weight of NPE9 is 616 g/mol and the molecular weight of NP is 220 g/mol. A NPE concentration of e.g. 310 mg NPE/kg thus corresponds to 310/616 × 220 mg NP/kg = 111 mg NP/kg textile. I.e. that NPE is converted into number of NP units by dividing by 2.8 (616/310 = 2.8)

TABLE 3.2
ANALYTICAL RESULTS. MEASURED CONTENT OF NONYLPHENOL AND NONOLPHENOL ETHOXYLATE (NP/NPE) IN TEXTILES BEFORE WASHING

Type of textile	Country of origin	Material/ description	Measured concentrations in the textile (mg NP(E)/kg textile)					
			NP	NPE1	NPE2	NPE3-15	Total concentra-tion of NP	Total concentra-tion of NPs
Bed linen	India	100% eco-cotton. Light beige stripes	1	0.4	0.3	6.5	7,2	3,9
	Pakistan	100% cotton. . Coloured print in red/blue etc.	**1.1**	**0.4**	**0.5**	**310**	**311**	**112,6**
	Bangladesh	100% cotton. Pink with coloured hearts	0.9	<0.2	<0.2	0.27	<0,67	1,2
Mittens	China	100% acrylics. Light blue	2.1	3.5	5.4	57	65,9	29,3
	China	100% polyester. Brown	2.8	1.4	1.9	25	28,3	14,3
	China	100% polyester. Pink	**1.7**	**0.8**	**0.2**	**85**	**86**	**32,9**
Underwear	India	95% cotton/ 5% elastan. Solid pink	2.4	5.8	12	98	115,8	50,8
	China	100% eco-cotton. Green/white striped	**1.1**	**0.4**	**0.3**	**250**	**250,7**	**91,0**
	Bangladesh	95% cotton/ 5% elastan. White with butterfly print	0.7	0.7	1.3	1.8	3,8	2,9
Jeans	Tyrkey	100% cotton. Light blue	1	0.3	0.3	2.6	3,2	2,4
	China	100% cotton. Dark blue	**1.4**	**0.6**	**1.3**	**250**	**251,9**	**92,2**
	China	100% cotton. Black	**1.2**	**0.6**	**0.7**	**180**	**181,3**	**66,5**
T-shirt	Bangladesh	100% cotton. Pink with owl print	**3.7**	**1.6**	**1.4**	**120**	**123**	**48,9**
T-shirt	Cambodia	100% polyester. Pink	2.3	<0.2	<0.2	4.1	<4,5	3,9
Sweater	China	100% cotton. Natural colour	1.3	0.2	<0.2	1.6	<2,0	2,1
Mean			1,6	1,1	1.7	92.8	96	37.0
Spread			0,8	1,6	3.1	106.7	107	38.3
Geometric mean			1,5	0,6	0.6	23.0	26	15.2

Note: Number of ethoxylategroups is indicated.
NPs refers to the total concentration of NPE expressed as "nonylphenol units"
The textiles, which had the highest concentrations of NP/NPE (in **bold**), were selected for analysis for migration to artificial sweat and saliva.

3.3.1 Results - analyses on textiles before washing

Table 3.2 shows that

- The highest concentrations of NPE (3-15 ethoxylate groups) were measured in bed linen with coloured print in red, blue etc., in green and white striped underwear, dark blue and black jeans and in pink T-shirt with owl print.
- No relation can be demonstrated between the types of textile (cotton or polyester, organic or non-organic) and high concentrations of NP and NPE, respectively.
- Small amounts (below 10 mg NP or NPE/kg textile) were detected in a ecolabelled textile. This may be caused by the use of NP/NPE in the production or it maybe because of a contamination from a parallel production of non-ecolabelled textiles.
- NPE was detected in textiles both made from cotton (120-250 mg NPE/kg textile), from polyester (pink mittens from China: 85 mg NPE/kg textile) and from eco-cotton (underwear from China: 250 mg NPE/kg textile). Furthermore, a high concentration (310 mg NPE/kg textile) was detected in the OEKO-TEX-labelled bed linen with primarily red and blue coloured print. An OEKO-TEX labelled product contained above 100 mg NPE/kg textile, but below the limit on 1000 mgNPE/ kg textile, which is the limit that applies to this label.
- The textiles with high concentrations of NPE also had one or more strong colours. This is seen very clearly in jeans, in which the dark blue and black jeans had very high concentrations of NPE compared with the light blue jeans.
- The bed linen with a primarily strong red and blue print had a markedly higher concentration than the bed linen with a light colour.
- Especially the textiles from China have high concentrations of NPE. However, one of the analyses of textiles from China (sweater) showed a low concentration of NPE. This garment differs from the other types of textiles as it is natural colour and does not contain any strong colours. However, it should be noted here that 7 of the 15 studied textiles originated from China.

As the octylphenol ethoxylatates (OPE) were part of the analysis packages although not focussed on in the project, the analytical results of these chemicals are also included here. In 8 of textiles, the content was below the detection limit (0.2 mg OPE/kg textile) and no concentrations above 10 mg OPE/kg textile were measured. The mean of all the measurements were below 1.6 mg OPE/kg textile, which is less than 2% of the mean value of the measured NPE concentrations.

3.3.2 Resultats – analyses on textiles after washing

In order to assess how much NP and NPE that may be removed by washing, some selected textiles were analysed for NP and NPE after a single washing. The results are shown in Table 3.3, in which the percentage decrease in the concentration of long-chained NPE by washing is indicated in parentheses.

TABLE 3.3
ANALYTICAL RESULTS. MEASURED CONTENT OF NONYLPHENOL AND NONYLPHENOL ETHOXYLATE (NP/NPE) IN TEXTILES BEFORE (B) AND AFTER (A) WASHING

Type of textile	Country of origin	Material/ description	Before washing (B) After washing (A)	Measured concentrations in the textile (mg NP(E)/kg textile) NP	NPE1	NPE2	NPE3-15	Total concentration of NPE	Total concentration of NPs
Bed linen (washed at 60°C)	Pakistan	100% cotton. Coloured print in red/blue etc.	B A	1.1 0.43	0.4 <0.2	0.5 <0.2	310 0.29 (99.9%)	311 <0.49	112.6 0.7 (99.4%)
Mittens (washed at 40°C)	China	100% polyester Pint	B A	1.7 2.3	0.8 2	0.2 1.1	85 28 (67%)	86 31.1	32.9 14.8 (55.0%)
Underwear (washed at 40°C)	China	100% eco-cotton. Green/white striped	B A	1.1 1.7	0.4 5.1	0.3 6.7	250 15 (94%)	251 26.8	91.0 16.1 (82.3%)
Jeans (washed at 40°C)	China	100% cotton. Dark blue	B A	1.4 1.1	0.6 0.44	1.3 1.2	250 110 (56%)	252 112	92.2 41.6 (54.9%)
	China	100% cotton. Black	B A	1.2 0.37	0.6 <0.2	0.7 <0.2	180 35 (81%)	181 35	66.5 13.0 (80.5%)
T-shirt (washed at 40°C)	Bangladesh	100% cotton. Pink with owl print	B A	3.7 0.78	1.6 0.9	1.4 1.1	120 90 (25%)	123 92	48.9 34.5 (29.4%)

Note: Number of ethoxylategroups is indicated.
NPs refers to the total concentration of NPE expressed as "nonylphenol units"
Decrease in the concentration of NPE_{3-15} (3-15 ethoxy groups) after a single washing is indicated in parentheses (%).

The analytical results (Table 3.3.) show that

- The total content of NP and NPE in the textiles generally decreases by washing but NPE was detected in the textiles after washing at concentrations up to 112 mg/kg textile.
- The removal of NPE by a single washing varies from 25% up to 99.9%. Most NPE was removed by washing the bed linen at 60°C. The other washing tests were made at 40°C. This may indicate that more NPE is removed by washing at higher temperatures. However, data are too sparse to draw any definite conclusions.
- In some cases, the content of short-chained NPE and NP increased by washing. This indicates that a small part of the observed removal of the long-chained NPE is due to degradation of the ethoxylate chain to the more short-chained NPE and not an actual removal of NP. This was observed when washing the mittens, in which the content increased from 0.8 to 2 NPE_1/kg textile and from 0.2 to 1.1 mg NPE_2/kg textile. It was also observed when washing the underwear, in which the content of NP increased from 1.1 to 1.7 mg NP/kg textile, the content of NPE_1 increased from 0.4 to 5.1 mg NPE_1/kg textile and of NPE_2 from 0.3 to 6.7 mg NPE_2/kg textile. The release of NP and the short-chained NPE from the textile to sweat and saliva is expected to be much slower than the release of the long-chained NPE but, on the other hand, NP and the short-chained NPE are expected to be taken up more rapidly than the long-chained NPE via the skin (Figure 2.2). However, it is difficult to quantify the significance of this.

Overall, it is estimated, however, that as the total NP concentration (NPs) decreased by washing, for the mittens by 55% and for the underwear by 82.3%, washing the textiles before use will reduce the total uptake of NP.

In the same test, the removal of octylphenol ethoxylates (OPE) by washing was also measured. The removal varied between 13% and 89%, i.e. similar to that of NPE.

3.3.3 Results and discussion – analyses with artificial sweat and saliva

The textiles with the highest concentrations of NP and NPE (in **bold** in Table 3.2) before washing were selected for analysis with artificial sweat and saliva, i.e. the bed linen, jeans (both dark blue and black) and the mittens. These textiles will potentially cause relatively high exposure and are thus interesting from a health perspective.

Table 3.4 presents the results of the migration analyses with artificial sweat and artificial saliva. The analyses were made on the textiles before washing and the concentrations of NP and NPE in the textile before washing are indicated in the table for comparison.

TABLE 3.4
RESULTS OF MIGRATION ANALYSES ON TEXTILES (B: BEFORE WASHING) WITH ARTIFICIAL SWEAT (SW) AND SALIVA (SA). THE RESULTS ARE GIVEN AS MG MIGRATED NP/NPE PER KG TEXTILE

Type of textiles	Country of origin	Material/ description	Before washing (B) Extraction with sweat (sw)/saliva (sa)	Measured migrations from the textile (mg migrated NP(E)/kg textile) NP	NPE1	NPE2	NPE3-15	NPE_1 + NPE2+ NPE3-15	Total concentration of NPs
Bed linen	Pakistan	100% cotton. Coloured print in red/blue etc.	B sw	1.1 <0.05 (<4.5%)	0.4 <0.05	0.5 <0.05	310 <0.2 (<0.1%)	311 <0.3	112.6 <0.1 (<0.1%)
Jeans	China	100% cotton. Dark blue	B sw	1.4 <0.05 (<3.6%)	0.6 <0.05	1.3 <0.05	250 32 (13%)	252 32	92.2 11.5 (12%)
	China	100% cotton. Black	B sw	1.2 <0.05 (<4.1%)	0.6 <0.05	0.7 <0.05	180 60 (33%)	181 60	66.5 21.5 (32%)
Mittens outer fabric	China	100% polyester Pink	B sa	1.7 <0.05 (<3%)	0.8 <0.05	0.2 <0.05	85 1.9 (2%)	86 1.9	32.9 0.7 (2%)

Note: Measured migration of nonylphenol and nonylphenol ethoxylates (NP/NPE) from textiles. Unit: mg (migrated) per kg textile
Number of ethoxylate groups is indicated by subscript.
NPs indicates the total concentration of NPE indicated in "nonylphenol units"

The results of the migration analyses (Table 3.4) show that

1. The migration of NPE from the bed linen to artificial sweat was apparently very limited (<0.1% of the NPE content in the textile). For comparison, a significant migration of NPE to artificial sweat was measured in the dark jeans (13-33% of the NPE content in the textile).
2. The only test with artificial saliva showed a migration to saliva of 2% of the NPE content in the textile and less than 3% of the NP content of the textile (the analysis is limited by the detection

limit for NP), i.e. that, for the studied pink mittens, there was only minor migration of NPE to saliva.

3. Compared with the figures of migration used in the initial exposure calculation in Chapter 2, the measured values are higher. For NP, migration was thus assumed to be 0.1% and measured to be <3%, which is the detection limit and, for NPE, migration was assumed to be 2% and measured from <0.1% up to 33%.

In the same migration test, the migration of octylphenol ethoxylates (OPE) to sweat and saliva was measured. The migration to sweat was measured up to 70% and to saliva up to 93%. Indicated in mg/kg, the migration of OPE to sweat constitutes less than 2% of the migration of NPE to sweat and the migration of OPE to saliva constitutes less than the migration of NPE to saliva. Overall, it is assessed that, compared with NP/NPE, OP/OPE will contribute only to a very limited extent to a potential overall risk from wearing clothes with a content of alkylphenols[14].

3.4 Summary of analytical results

For all studies types of textiles (before washing), the average of the total NPE concentration in the textile was determined to be 96 mg NPE/kg textile with a standard deviation of 107 mg NPE/kg textile and a geometric mean of 26 mg NPE/kg textile (Table 3.2). Measured as NPs, an average content of 37 mg NPE/kg textile, a spread of 38 mg NPE/kg textile and a geometric mean of 15 mg NPE/kg textile were measured. No relation was demonstrated between the types of textile (cotton or polyester, organic or non-organic) and high concentrations of NP and NPE, respectively. There is a tendency that the textiles with high concentrations of NPE also have one or more strong colours. The textiles from China – except for a natural-coloured sweater – had high concentrations of NPE. Finally, NP/NPE was detected in small amounts in an ecolabelled textile.

The measurements showed that the total content of NP and NPE in the textiles decreases by washing but measurable concentrations of NPE may still be present in the textiles after a single washing. The removal of NPE by a single washing varied between 25% and up to 99.9%. Most NPE was removed by washing of the bed linen at 60°C. For a few textiles, a slightly higher content of the short-chained NPE and NP was detected after one washing, indicating that a minor part of the observed removal of the long-chained NPE is due to degradation of the ethoxylate chain into the more short-chained NPE and not an actual removal of NP.

The measurements showed that NPE can migrate to sweat and that the extent of migration varies considerably between the different textile samples. An insignificant migration of NPE was measured from bed linen to artificial sweat and a migration from jeans to artificial sweat of between 13 and 33% of the NPE content in the textile.

No NP was detected in the sweat extract. This shows that migration op NP apparently is below 4% of the NP content (determined by the detection limit of the NP) in the fabric, even at a very intense two-hour extraction with artificial sweat.

Only a single test of migration to artificial saliva was made, in which limited migration was measured of 2% of the NPE content in the textile and less than 3% of the NP content in the textile (the analysis was limited by the detection limit for NP).

The analyses also included octylphenol ethoxylates (OPE). The measurements showed that OPE represents only a very small faction of the total content of alkylphenols in textiles and that the migration of OP/OPE to sweat and saliva is significantly less than the migration of NP/NPE. Therefore, it is assessed that, compared with NPE, OPE will only contribute to a very limited extent to a potential risk from the presence of alkylphenols in textiles.

[14] Note that OP is also considered an endocrine disrupter.

3.5 Comparison with literature values

Table 3.5 compares the analytical results from this study with the data found in literature. As shown in the table, generally lower concentrations were measured in the selected textile samples than the concentrations found in the analytical results from literature (cf. Chapter 2).

As described in Section 2.2.4, a number of Danish companies uses limit values, determining how much NPE purchased textiles must contain before they launch further investigations. The limit of the interviewed companies is set at 100 and 250 mg NPE/kg textile.

Table 3.5 shows the proportion of samples that cannot pass the two limit values of 100 and 250 mg NPE/kg textile, respectively.

Assuming that the concentrations found in this study are representative of the concentration levels generally detected in the textiles imported to and marketed in Denmark, then, in 1 of 3 cases (5 of 15 textile samples), the concentration of NPE is above the lowest limit value of 100 mg NPE/kg textile and, in 1 of 5 cases (3 of 15 textile samples), the concentration of NPE is above the upper limit value of 250 mg NPE/kg textile. However, two of the samples are very close to the 250 mg NPE/kg textile limit. For the literature data, the concentration of NPE is above 100 mg NPE/kg textile in 50% of the samples and above 250 mgNPE/kg textile in 42% of the samples.

As analysis is only made on a limited number of textile samples, the above difference between the measurements in this study and the literature values may be a coincidence.

As already mentioned, a concentration higher than 6 g NPE/kg textile was only detected in 3 of the 139 analytical results (2%) from literature while the concentrations in the remaining tests were evenly distributed between 1 mg/kg textile and up to 3,200 mg NPE/kg textile. The measurements are considered reliable. The fact that high concentrations above 6 g NPE/kg of textile were only measured in a few textile samples, indicates that this will not occur under normal production, and that it is rather occurs only at abnormal operation, e.g., by accident or if the rinsing processes have not worked properly. If these 3 results are considered outliers and therefore can be neglected, only very slightly lower average concentrations are estimated (Table 3.5). Therefore, it does not alter the fact that, apparently, higher concentrations are generally reported in the literature than the concentrations found in this study. It was decided to use all the values in the further calculations.

TABLE 3.5
COMPARISON OF LITERATURE DATA AND ANALYTICAL RESULTS FOR NPE CONCENTRATION LEVELS IN TEXTILES

Type of textile	Literature values (mg NPE/kg textile)			Analytical values (mg NPE/kg textile)		
	Geometric mean	Average	Highest value	Geometric mean	Average	Highest value
Towels	25	657	10,608	-	-	-
Bed linen	-	-	-	11	106	311
Snowsuits	158	421	1,200	-	-	
Mittens	-	-	-	54	60	86
Socks	600	600	600	-	-	
T-shirts	28	261	1,390	24	64	123
Jeans	7	232	2,200	53	145	252
Underwear	25	338	860	48	123	251
Pyjamas	585	1,038	1,930	-	-	-
All samples	66	670	14,100	28	96	311
All samples minus the three highest concentrations	59	456	3,200	-	-	-
Higher than 100 mg NPE/kg textile		50%			33%	
Higher than 250 mg NPE/kg textile		42%			20%	

4. Health and environmental assessments

The health and environmental assessments described in this chapter are based partly on the measurements made in this study and partly on the literature values described in Chapter 2.

4.1 Health assessments

It was examined whether the content of NP and NPE in the textiles may pose a health risk to the consumers (children). For this purpose, the risk characterisation ratio RCR_{human} was calculated, cf. Section 1.1.6.

$$RCR_{human} = \frac{U_{total}}{DNEL}$$

In the calculation of U_{total}, the uptake of NP and NPE (mg/kg body weight per day) from contact with skin and from sucking on the textile, the results of the migration measurements for the textiles were applied (Table 3.4). The calculation of U_{total} is presented in this chapter.

The measurements of the migration to artificial sweat showed that NPE can migrate to sweat but the measurements also indicated that the extent of the migration depends on the type of textile. At two hours of intensive contact, a low migration of NPE was measured from the bed linen to sweat (<0.1%) while the migration of NPE from jeans was between 13 and 33% of the NPE content.

However, no NP was detected in the sweat extract, suggesting that the migration of NP from textiles is very limited, i.e. less than 4% of the NP content in the textile. The test also demonstrates that the NP is not removed to a greater extent by use but will remain in the textile. This is consistent with the preliminary assumptions (Section 2.4).

The migration to artificial saliva (from a pair of mittens) showed a limited migration to saliva for both NPE and NP. The migration was 2% of the NPE content of the textile and less than 3% of the NP content in the textile (this analysis is limited by the detection limit of the NP) (Table 3.4).

4.1.1 Exposure by use of new unwashed textiles for which migration has been measured

Children's daily uptake of NP and NPE by use of different types of new unwashed of textiles is estimated.

It is assumed that a child does not normally wear new unwashed clothes every day and that the clothes will typically be washed after each use. Therefore, it is assumed that, on average, 2-year old child wears new unwashed clothes once every 14 day. The estimated uptake is thus an estimate of how much NP and NPE that a child will take up daily on average over a period of 14 days, via skin contact with bed linen and jeans and from sucking on the mittens.

As only a few migration tests were made for the types of textile, for which the test before washing showed the highest content of NP and NPE, i.e. the mittens, bed linen and two pairs of jeans, the calculations of the total uptake thus do not account for the fact that the child is also wearing other chlothes during a day, e.g. underwear and T-shirt and that the child may also suck on e.g. the bed linen (migration to saliva was not measured for bed linen).

The migration per hour is calculated by dividing the measured migration by the test duration of extraction of sweat and saliva (2 hours). However, in the calculations, the restriction that the maximum migration cannot exceed the actual quantity in the textiles, was imposed. This calculation method is hereinafter referred to as "normalized" migration (MiG_{sweat} and MiG_{saliva}, respectively).

The following equation is applied in the calculation of the amount of NP (NPE) that is taken up **through the skin** per kg body weight per day (D_{skin}) (cf. ECHA, 2008a, Dermal Scenario B) as a result of the contact of the textiles with the skin, and in which the actual uptake (U_{skin}) is limited to 10% due to the ability of the skin barrier.

$$U_{skin}\ (mg/kg\ bw/d) = D_{skin} \times 10\% \qquad \text{Equation (2)}$$

$$D_{skin}\ (mg/kg\ bw/d) = Sd_{prod} \times MiG_{sweat} \times T_{skin} \times A_{skin}/BW \qquad \text{Equation (5)}$$

Where

D_{skin}	Dose on the skin barrier in mg per kg body weight per day
Sd_{prod}	Amount of textile per area unit (kg/m^2), calculated from the thickness of the fabric (TH) and density of the fabric (set at 1,000 kg/m^3) (RHO): Sd_{prod} = TH × RHO
MiG_{sweat}	Measured migration of NP or NPE from the textile to sweat per hour (mg NP or NPE/kg/hour)
T_{skin}	Total duration of skin contact per day (hours per day) based on an assumption of the frequency of how often new unwashed textiles are used; in this case, with the assumption that new unwashed clothes are used on average every 14 days.
A_{skin}	Area of contact between skin and the textile in question, cf. Chapter 2 (m^2)
BW	Weight of exposed person (kg body weight (kg bw)). It is set at a relatively low value of 10 kg for a child – corresponding to a child of almost 2 years

The following equation is applied in the calculation of the amount of NP (NPE) that is taken up **through the mouth** per kg body weight per day (D_{oral}) as a result of sucking on the textile, and in which the actual uptake (U_{oral}) is assumed to be 10% uptake of the dose.

$$U_{oral}\ (mg/kg\ bw/d) = D_{oral} \times 10\% \qquad \text{Equation (4)}$$

$$D_{oral}\ (mg/kg\ bw/d) = Sd_{prod} \times MiG_{saliva} \times T_{oral} \times A_{oral}/BW \qquad \text{Equation (6)}$$

Where

D_{oral}	Dose taken up by sucking on the textile in mg per kg body weight per day
Mig_{saliva}	Measured migration of NP or NPE from the textile to saliva per hour (mg NP or NPE/kg/hour)
Sd_{prod}	Amount of textile per area unit (kg/m^2), calculated from the thickness of the fabric (TH) and density of the fabric (set at 1,000 kg/m^3) (RHO): Sd_{prod} = TH × RHO

T_{oral}	Total duration of oral contact per day (hours per day) based on an assumption of the frequency of how often new unwashed textiles are used; in this case, with the assumption that new unwashed clothes are used on average every 14 days
A_{oral}	Area of the textile that the person has put in his mouth
BW	Weight of exposed person (kg body weight (kg bw)). It is set at a relatively low value of 10 kg for a child – corresponding to a child of almost 2 years

In the calculations, T_{oral} is applied, which is the total time of oral contact with the textile as the migration is indicated per hour. In the initial caculations in Chapter 2, the figure for the number of time per day that the person sucked on the textile was used.

Table 4.1 presents the calculated average uptake of NP and NPE in children (body weight of 10 kg) when wearing new unwashed clothes in a 14-day period. The measured migrations are applied, in which the results of the migration measurements are normalized by 2 hours to mg/kg textile/hour. The uptake of NPE is converted into uptake of NP units. As previously (e.g. Sections 2.5 and 3.3), it is assumed that uptake of NPE can be converted to uptake of NP by dividing by 2.8.

TABLE 4.1
CALCULATED UPTAKE OF NP AND NPE IN 2-YEAR OLD CHILDREN WHEN WEARING NEW UNWASHED CLOTHES ONCE EVERY 14 DAYS. THE MIGRATIONS OF NPE MEASURED IN THIS STUDY FROM BED LINEN, MITTENS AND JEANS ARE APPLIED (SEE ALSO TABLE 3.4)

Type of textile and route of exposure	Amount of textile per area unit	Measured migration	Duration of contact with the textile from frequency of use of new unwashed textiles	Contact area on skin or in mouth	Estimated uptake in child of 10 kg (U_{total})	
	Sd_{prod}	Oral: MiG_{saliva} or Dermal: MiG_{sweat}	T_{oral} or T_{skin}	A_{oral} or A_{skin}	U_{oral}: 10% D_{oral} or U_{skin}: 10% D_{skin}**	
	(kg textile/ m^2)	(mg NPE/ kg textile/ hour)	(hours/day)	(m^2)	(mg NPE/ kg bw/day)	(mg NP/ kg bw/day converted from NPE)***
Mittens (oral)	0.1	0.95	0.21	0.001	2.03E-07	7.27E-08
Bed linen (skin)	0.01	<0.1	0.71	0.6410	4.59E-06	1.64E-06
Blue jeans (skin)	0.1	16	1	0.1481	2.37E-03	8.46E-04
Black jeans (skin)	0.1	30	1	0.1481	4.44E-03	1.59E-03
Average of two pairs of jeans					3.41E-03	1.22E-03
Total uptake from mittens (oral), bed linen (skin) and jeans (skin)					3.41E-03	1.22E-03

* The duration of contact with the textile is calculated as the number of hours/day over 14 days as it is assumed that children only wear new unwashed clothes containing NP and NPEs once every 14 day. Therefore, the number of hours per time is divided by 14, e.g. use of mittens is 3 hours per time/14 days, corresponding to 0.21 hours/day.

** U_{oral}: 10% × D_{oral} = 10% × Sd_{prod} × MiG_{saliva} × T_{oral} × A_{oral}/bw
U_{skin}: 10% × D_{skin} = 10% × Sd_{prod} × MiG_{sweat} × T_{skin} × A_{skin}/bw

*** NPE is converted into NP by dividing by 2.8

If the migration measurements for new unwashed textiles are normalized only by the duration of the extraction (2 hours), an overall uptake from jeans, mittens and bed linen of 0.0012 mg NP/kg bw/day is calculated (Table 4.1). Table 4.1 shows that the uptake from skin contact with jeans makes the main contribution to the total calculated uptake (nearly 100%) of NP and NPE, respectively.

The calculations in Table 4.1 only include the textiles, for which migration tests were made in this study. As already mentioned, the calculations do not take into account that the child may also wear other new unwashed clothes containing NP and NPE.

4.1.2 Exposure by use of new unwashed textiles for which migration has not been measured

In the analyses of textiles before washing performed in this study, the following NPE concentrations were measured in three different pieces of underwear: 3.8 mg NPE/kg textile, 115.8 mg NPE/kg textile and 250.7 NPE mg/kg textile (Table 3.2). For comparison, the following NPE concentrations were measured in three types of jeans: 3.2 mg NPE/kg textile, 181.3 mg NPE/kg textile and 251.9 mg NPE/kg textile (Table 3.2). Very similar levels were thus measured in underwear and jeans. Slightly lower NPE concentrations were measured in T-Shirts (123 mg NPE/kg textile and 1.6 mg NPE/kg textile) compared with jeans and underwear.

Migration to sweat from jeans were measured at 32 mg NPE/kg textile and 60 mg NPE/kg textile at 2 hours extraction in migration test of two pairs of jeans. When converting to migration per hour, 16 mg NPE/kg textile and 30 mg NPE/kg textile, respectively, are obtained. A normalized migration regarding both the extraction time and the initial concentration of NPE in the textile is thus:

$$\frac{16 \text{ mg NPE/kg textile/hour}}{250 \text{ mg/kg textile}} = 0.06 \text{ mg NPE/mg NPE/hour}$$

$$\frac{30 \text{ mg NPE/kg textile/hour}}{180 \text{ mg/kg textile}} = 0.17 \text{ mg NPE/mg NPE/hour}$$

An average normalized migration can thus be estimated at 0.12 mg NPE/mg NPE/hour, i.e. 12% may migrate per hour. It means that all NPE in textile with skin contact will have migrated to sweat after approx. 8 hours of contact at an unchanged migration rate

The contribution from underwear and T-shirts to the total uptake of NP and NPE, respectively, in a 2-year old child wearing new unwashed clothes is calculated in Table 4.2. As the migration from underwear and T-shirts to sweat was not measured in this study, the average normalized (with respect to time and concentration in the textile) migration rate to sweat from jeans of 0.12 mg NPE/mg NPE/hour was used.

The following equation is applied in the calculation of the (theoretic) uptake of NP or NPE through the skin. The actual uptake (U_{skin}) is limited to 10% due to the ability of the skin barrier.

$$U_{skin} \text{ (mg/kg bw/d)} = D_{skin} \times 10\% \qquad \text{Equation (2)}$$

$$D_{skin} \text{ (mg/kg bw/d)} = Sd_{prod} \times MiG_{sweat} \times C_{textile} \times T_{skin} \times A_{skin}/BW \qquad \text{Equation (7)}$$

Where MiG_{sweat} is specified as a normalized migration dependent on the amount of NPE in the textile (mg NPE/NPE mg/hour) and $C_{textile}$ indicates the amount of NPE in the textile (NPE mg/kg textile).

TABLL 4.2
CALCULATED UPTAKE OF NP AND NPE IN 2-YEAR OLD CHILDREN WEARING NEW UNWASHED CLOTHES ONCE EVERY 14 DAYS. AN ESTIMATED NORMALIZED MIGRATION OF 0.12 MG NPE/MG NPE/HOUR IS APPLIED FOR UNDERWEAR AND T-SHIRT

Type of textile	Amount of textile per area unit	Estimated normalized migration to sweat	Contact area for skin	Duration of contact with the textile from frequency of use of new unwashed textiles*	Initial conc. in the textile	Calculated uptake in child of 10 kg (U_{total})	
	S_d	MiG_{sweat}	A_{skin}	T_{skin}	$C_{textile}$	U_{total} **	
	(kg textile/ m²)	(mg NPE/ mg NPE/ hour)	(m²)	(hours/day)	(mg NPE/ kg textile)	(mg NPE/ kg bw/day)	(mg NP/ kg bw/day)
Underwear	0.1	0.12	0.2276	1.71	115.8	5.41E-03	1.93E-03
Underwear	0.1	0.12	0.2276	1.71	250.7	1.17E-02	4.18E-03
Underwear	0.1	0.12	0.2276	1.71	3.8	1.77E-04	6.34E-05
Average for underwear						*5.76E-03*	*2.06E-03*
T-shirt	0.1	0.12	0.2300	1	123	3.39E-03	1.21E-03
T-shirt	0.1	0.12	0.2300	1	<4.5	<1.24E-04	<4.44E-05
Average for T-shirts						*1.76E-03*	*6.28E-04*

* The duration of contact with the textile is calculated as the number of hours/day over 14 days as it is assumed that children only wear new unwashed clothes containing NP and NPEs once every 14 day. Therefore, the number of hours per time is divided by 14, e.g. use of underwear is 24 hours per time/14 days, corresponding to 1.71 hours/day

** $U_{total} = 10\% \times Sd_{prod} \times MiG_{sweat} \times C_{textile} \times T_{skin} \times A_{skin} / bw$ (for NP, $U_{total} = U_{total\ for\ NPE}/2.8$) [15]

On average, the total contribution to exposure to NP by a 2-year child's use of new unwashed clothes is 0.002 mg/kg bw/day for underwear and 0.0006 mg/kg bw/day for T-shirts. The reason for the higher contribution from underwear is that this garment is assumed to be worn 24 hours a day while T-shirts are only assumed to be used 14 hours a day.

4.1.3 Exposure by use of new washed textiles

Washing the new textiles before use can reduce the amount of NP/NPE in the textiles. The measurements (Table 3.3) showed that between approx. 29% and up to 99% was removed by a single wash. For jeans and underwear, removals by washing of between approx. 55% and 82% were measured (Table 3.3) and for T-shirts of approx. 29%.

Tabel 4.3 shows the calculated uptake in children wearing various clothes that have been washed once befor use.

[15] NPE is converted into NP by dividing by 2.8

TABLE 4.3
CALCULATED UPTAKE OF NP AND NPE IN 2-YEAR OLD CHILDREN WEARING NEW WASHED CLOTHES ONCE EVERY 14 DAYS. AN ESTIMATED NORMALIZED MIGRATION OF 0.12 MG NPE/MG NPE/HOUR IS APPLIED

Type of textile	Amount of textile per area unit	Estimated normalized migration to sweat	Contact area for skin	Duration of contact with the textile from frequency of use of new unwashed textiles*	Initial conc. in the textile	Calculated uptake in child of 10 kg (U_{total})	
	S_d	MiG_{sweat}	A_{skin}	T_{skin}	$C_{textile}$	U_{total} **	
	(kg textile/ m²)	(mg NPE/ mg NPE/ hour)	(m²)	(hours/day)	(mg NPE/ kg textile)	(mg NPE/ kg bw/day)	(mg NP/ kg bw/day)
Jeans	0.1	0.12	0.1481	1	110	1.95E-03	6,98E-04
Jeans	0.1	0.12	0.1481	1	35	6.22E-04	2,22E-04
Average for jeans						*1.29E-03*	*4.60E-04*
Underwear	0.1	0.12	0.2276	1,71	-	-	-
Underwear	0.1	0.12	0.2276	1,71	26.8	1.25E-03	4,47E-04
Underwear	0.1	0.12	0.2276	1,71	-	-	-
Average for underwear						*1.25E-03*	*4.47E-04*
T-shirt	0.1	0.12	0.2300	1	92	2.54E-03	9,07E-04
T-shirt	0.1	0.12	0.2300	1	-	-	-
Average for T-shirts						*2.54E-03*	*9.07E-04*

* The duration of contact with the textile is calculated as the number of hours/day over 14 days as it is assumed that children only wear new washed clothes once every 14 day. Therefore, the number of hours per time is divided by 14, e.g. use of underwear is 24 hours per time/14 days, corresponding to 1.71 hours/day

** $U_{total} = 10\% \times Sd_{prod} \times MiG_{sweat} \times C_{textile} \times T_{skin} \times A_{skin} / bw$ (for NP, $U_{total} = U_{total\ for\ NPE}/2.8$)[16]

'-' indicates that no value was found for the concentration of NPE after washing and U_{total} can thus not be calculated

4.1.4 Risk assessment

In the previous sections (Sections 4.1.1-3), calculations were made of the average daily uptake of NP and NPE when a 2-year old child (10 kg) wear new either unwashed or washed clothes.

DNEL for NP taken up is estimated to be 0.005 mg NP/kg body weight per day. The critical effect is histopathological changes in kidney (Section 1.1.6). Appendix B summarizes the applied toxicological data and describes the determination of the DNEL. This DNEL can be described as the highest daily intake of NP, which does not lead to an increased risk of adverse health effects. In this context, it is important to note that the DNEL is determined from LOAEL of damage to the kidney by repeated impact with NP over time. This means that DNEL is a measure of how much NP a human can tolerate on average per day over time. A child will typically not wear new clothes every day, and the clothes will typically be washed after each use. Therefore, more realistic calculations were based on the assumption that a child wears new unwashed clothes once every 14 day at the most.

Table 4.4 shows that for a child who wears new unwashed clothes once every 14 days and, at the same time, wears the jeans, underwear and T-shirt yielding the highest uptake through the skin, the

[16] NPE is converted into NP by dividing by 2.8

overall risk characterisation ratio (RCR) by use of jeans, underwear and T-shirt (and mittens and bed linen) is calculated to 1.4. According to these calculations, a child's uptake of NP by the use of new unwashed clothes thus provides an RCR above 1, indicating a health risk. Considering the measured contents of NP in the various textiles, an average total RCR of 0.78 is seen for wearing new unwashed jeans, underwear and T-shirt at the same time over a 14-day period. For wearing clothes that are washed once before use, a significant reduction in exposure to NP and NPE, respectively, is seen with a total RCR of 0.41 when wearing clothes with the highest concentrations of NPE. This shows how important a single washing of clothes before use is, regarding a minimisation of the risk from use.

TABLE 4.4
CALCULATED UPTAKE OF NPE AND NP IN 2-YEAR CHILDREN USING EITHER NEW UNWASHED CLOTHES OR NEW WASHED CLOTHES (JEANS, UNDERWEAR AND T-SHIRTS) OVER A PERIOD OF 14 DAYS. THE CONTRIBUTION TO RISK CHARACTERISATION RATIO (RCR) IS CALCULATED FOR NP WITH A DNEL OF 0.005 MG/KG (SECTION 1.1.6)

Type of textiles	Calculated uptake in child of 10 kg using *new unwashed clothes*		RCR_{NP}	Calculated uptake in child of 10 kg using *new washed clothes*		RCR_{NP}
	(mg NPE/kg bw/day)	(mg NP/kg bw/day)	(U_{skin}/DNEL)	(mg NPE/kg bw/day)	(mg NP/kg bw/day)	(U_{skin}/DNEL)
Jeans	$2.37 \cdot 10^{-3}$	8.46E-04	0.17	6.22E-04	2.22E-04	0.04
Jeans	$4.44 \cdot 10^{-3}$	1.59E-03	0.32	1.95E-03	6.98E-04	0.14
Underwear	5.41E-03	1.93E-03	0.39	-	-	-
Underwear	1.17E-02	4.18E-03	0.84	1.25E-03	4.47E-04	0.09
Underwear	1.77E-04	6.34E-05	0.01	-	-	-
T-shirt	3.39E-03	1.21E-03	0.24	2.54E-03	9.07E-04	0.18
T-shirt	<1.24E-04	<4.44E-05	0.01	-	-	-
Total uptake based on highest values for jeans, underwear and T-shirt		6.98E-03	**1.40**	-	2.05E-03	0.41
Total uptake based on average of jeans, underwear and T-shirt		3.90E-03	0.78	-	1.81E-03	0.36

The calculations in this study show that the concentrations in the textiles can be so high that the contents of NP and NPE in textiles can constitute a significant source of exposure to NP/NPE, especially if the clothes are not washed before use. However, it should be noted that the assessment is based on a limited data material.

It is a relatively small exceeding with an RCR value of 1.4, which must also be seen in relation to the uncertainties and assumptions made in the calculations. It is thus assessed that the applied DNEL for NP taken up is very prudent as, in the animal experiment used for the calculation of DNEL, it was assumed that there is only a systemic uptake of 10% after oral exposure to NP. If a higher systemic uptake had been assumed in the study used for determining the DNEL, the result would have been a higher DNEL and thus a lower risk in the calculations made in this study (please refer to the calculations in Appendix B for additional information).

Furthermore, in the exposure scenarios for skin contact with textiles, an equally high release of NP and NPE is assumed as in migration tests, in which soaked textiles are extracted with artificial sweat. Subsequently, it is assumed that 10% of the released substance is absorbed through the skin, which must be considered an upper limit on the basis of the available experimental data; especially for NPE, the absorption is likely to be lower due to the higher molecular weight of the substance (see also Appendix B).

In addition, the DNEL for NP is applied to NPE, which means that NPE is assigned the same systemic toxicity as NP (measured as mg NP/kg body weight). This is, of course, an approximation as NPE is not always degraded 100% to NP and may be excreted from the body in the urine as a short-chained NPE.

At the same time, it is also important to note that the DNEL is determined on the basis of NOAEL for nephrotoxic effects by repeated impact with NP over time. The duration of the exposure to NP/NPE, which it takes to cause damage to the kidney, appears to be longer than the time that consumers actually wear new clothes even if a child were to use new unwashed clothes several days in a row.

Assuming that, at the most, a 2-year old child wears new unwashed clothes every 14 days with the NP/NPE-levels in textiles observed in this study, in a worst-case (highest values for all the new unwashed textiles used), an increased health risk to children may be associated with NP/NPE in textiles. In most cases, it is estimated, however, that there is no health risk associated with the use of new unwashed clothes every 14 days if the textiles contain no more NPE than is seen in this study. In literature, however, so high concentrations of NP/NPE in textiles are reported that textiles containing these substances may be a significant source of exposure to NP/NPEs in everyday life. In literature, measured concentrations are reported for jeans at almost 10 times the level (2,200 mg NPE/kg textile) measured in this study (Table 3.5). For underwear, a content that is 3-4 times higher than the content measured in this study is described and, for T-shirts, a content of NPE of more than 10 times the level measured in this study is reported. However, the validity of the literature values is unknown and has not been assessed in this study.

Therefore, it may make good sense to try to reduce the content of NP and NPE in textiles as much as possible, partly to achieve better protection against nephrotoxic effects, and partly to address potential combination effects between the NP and NPE, respectively, and other endocrine disrupters, with which people may come into contact in everyday life as these substances are under suspicion of endocrine disrupting effects.

4.2 Environmental assessments

In this section, the contribution to the textiles to the total emission of NP and NPE, respectively, to the environment is assessed. As the most common degradation product of NPE is NP, which is more hazardous than NPE, the environmental impact is calculated in terms of NP-units (NPs).

For the analysis, the measured concentrations of the content of NP in the inlet and discharge for 2004-2006 and in the discharge for 2007-2009 are used (BLST, 2010, 2011). Table 4.5 shows these concentrations. It can be seen that the concentration in the effluent is reduced by a factor of approx. 4-6 from 2004-2006 until 2007-2009. This is in line with the rapidly declining consumption of NP/NPE in Denmark. According to the so-called SPIN database[17], the NP/NPE consumption has decreased by more than 80% in the period from 2006 to 2008 as the NP/NPE consumption in 2006 was 1,422 tonnes, in 2007, it was 1,418 tonnes and in 2008 237 tonnes/year[18].

The fate of NP/NPE in the wastewater treatment plant (WWTP) is complex. A degradation of NP and NPE will take place in the WWTP. As a result of degradation, the average chain length of NPE will become shorter in the WWTP. Short-chained nonylphenol carboxylates (NPECx) will be formed

17 http://195.215.251.229/fmi/xsl/spin/SPIN/maininfo.xsl?-db=SPINstof&-lay=SPINnavn&-view)

18 CAS numbers used in the search: 25154-52-3, 84852-15-3, 68412-54-4, 9016-45-9, 26077-38-3, 37205-87-1, 127087-87-0.

as a degradation of NP will occur. In addition, to a certain extent, NP and the short-chained NPE will be concentrated in the sludge. The measurement data in Table 4.5 indicate a removal from the water at about 70-90%, of which almost 10% ends up in the sludge[19].

Based on these measured concentrations in the discharge from WWTPs, a conservatively predicted environmental concentration (PEC[20]) for NP was estimated at 0.02 µg/L. It is calculated by applying the 95% percentile of the discharge concentration for 2007-2009 (0.24 g/L), a background concentration of approx. 0.0001 µg/L[21] (Environmental Project No. 1182, 2007) and a default value for the dilution of 10 (ECHA, 2010)[22]. By dividing by the predicted no-effect concentration (PNEC for NP) of 0.33 µg/L (Section 1.1.4), a risk characterisation ratio (RCR) of 0.06 is calculated. There are only measurements of NP and the calculations do not account for the fact that longer chained NPE will also occur in the effluents. But even if the longer chained NPE in the discharge was also taken into account, RCR would hardly exceed 1. If assuming, e.g., a ratio NP:NPE of 1:4 in the discharge (see below), and if it is also assumed that NPE is as toxic as NP[23], RCR would only be 0.24.

Also, in the inlet to WWTPs, only NP and not NPE was measured. For an estimate of how much NPs that occur in the inlet in total, measured data on the content of NP and the different chain lengths of NPE in the inlet to two Danish WWTPs were used (Environmental Project No. 704, 2002). Here, a molar ratio of NP to NPE between 1:1.4 and 1:3.0 was measured, i.e. for each mole of NP, 1.4 moles of NPE and 3 moles of NPE, respectively, were found. The average of these molar ratios, i.e. 1:2.2, was applied in the calculations. For comparison, it may be mentioned that Ahel *et al.* (1994) measured a ratio of NP to NPE of approx. 1:4 – i.e. a significantly higher NP:NPE ratio than that used in this study.

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19 See also Section 1.1.5.

20 PEC: Predicted Environmental Concentration (expected concentration in the environment) cf. Section 1.1.4

21 In this context, the term "background concentration" is used as a 'steady-state' background concentration, i.e. the concentration that was already there. It is assumed that approx. 700 mill m^3 of waste water is emitted annually (BLST, 2011) with a content of NP of 0.065 µg/L - corresponding to the mean concentration in the effluent from wastewater treatment plants (BLST, 2011), a total water volume in Denmark of 2×10^{11} m^3 (Environmental Project No. 307, 1995), a half-life of NP in surface water of 150 days corresponding to a degradation rate constant of 0.0046 d^{-1} (EU, 2002) and an assumption that the water that Denmark exchanges with other countries has the same concentration of NP (i.e. the net exchange with other countries is 0).
$PEC_{background} = 700 \times 10^6/365 \times 0.065 / (2 \times 10^{11} \times 0.0046)$ g/L = 0.0001 g/L.

22 PEC = 0.0001 µg/L + 0.24 µg/L/10 = 0.02 µg/L

23 NPE is known to be less toxic to aquatic organisms than NP

TABLE 4.5
MEASURED CONCENTRATIONS OF NP IN INLET AND DISCHARGE FROM WASTEWATER TREATMENT PLANTS AND IN SLUDGE (2004-2006, 2007-2009) INDICATED WITH 5% PERCENTILE, 50% (MEDIAN), 95% PERCENTILE, THE MEAN VALUE AND AN ESTIMATED TOTAL NP CONCENTRATION IN THE INLET (NPs)

Para-meter	Unit	Period	Result of monitoring programme for NP in inlet, discharge and sludge, 2004-2006, 2007-2009 (BLST, 2010,2011)				Estimated total NP concentration (NPs) (this study)
			5% percentile	Median	95% percentile	NP (mean)	NPs (mean)
Inlet	µg NP/L	2004-2006	0.06	2.03	4.7	2.05	6.6 (=2.05 + 2.2 × 2.05)
		2007-2009					1.41)
Discharge	µg NP/L	2004-2006	<d.l.	0.03	1.5	0.3	-
		2007-2009	<d.l.	<d.l.	0.24	0.065	-
Sludge	mg NP/kg DM	2004-2006	0.05	1.9	10	2.6	-

1) Estimated from the inlet concentrations in 2004-2006 and a set of outlet concentrations for 2004-2006 and 2007-2009, respectively, by assuming that the percentage removal (approx. 85%) of NP/NPE in the wastewater treatment plants has not changed significantly in this period.

Table 4.5 shows that the estimated total concentration of NPs in the inlet to WWTPs is 1.4 µg NP/L. This is significantly higher than the no-effect concentration of 0.33 µg NP/L and indicates that the NP concentration may exceed this concentration locally in areas without sewage treatment. But as 90% of the waste water in Denmark is led to WWTPs and these reduce the concentration significantly, the NPE concentration in the environment will be considerably lower.

On the basis of the annual amounts of imported texiles (59,181 tonnes per year - Table 2.1), an annual volume of waste water in 2004-2006 of approx. 700 mill. m^3/year and the assumption that all NP/NPE in the textile is washed out and discharged to the WWTP that year, the contribution of the imported textiles to the concentration of NP/NPE in the inlets to the WWTPs was calculated. This was simply made by dividing the total volume of NP/NPE in the imported textiles by the total amount of waste water led to WWTPs in a year.

Furthermore, the potential impact of an imposition of a limit value for the amount of NP that textiles may contain was examined. In this context, the theoretical NP contribution of the textiles was calculated using the proposed limit values for NP/NPE in textiles (Section 2.2.4), i.e. 100 mg NPE/kg textile and 250 mg NPE/kg textile. For each of the proposed limit values, the geometric mean concentration of NPE in the textile samples that comply with the limit values was calculated. The difference between using the geometric mean concentration of NPE from the values measured in this study and from the values found in literature is only significant for the total number of textile samples (Table 4.6). For textile samples with concentrations less than 100 and 250 mg NPE/kg, the the measured values and the literature values are not significantly different. In literature, a few samples with very high concentrations were found, which caused the very high calculated geometric mean concentration for all textile samples.

The calculated geometric mean concentrations were used to calculate the contribution of the textiles to the WWTPs (Table 4.6).

Based on the measured concentrations of NP for 2007-2009, the calculations indicate that NP/NPE in the textiles accounts for about 86% of the total NP load of the waste water and thus the environmental impact of NP. If the average of literature values is applied, the contribution of NP from textiles is 200% (Table 4.6). This indicates that there is considerable uncertainty associated with these rough estimates.

TABLE 4.6
CALCULATED CONCENTRATION CONTRIBUTIONS OF NP FROM TEXTILES IN INLET TO WWTPS

Variable	NPE concentrations measured in this study			NPE concentrations from literature		
	All textile samples	Only textile samples with <100 mg NPE/kg textile	Only textile samples with <250 mg NPE/kg textile	All textile samples	Only textile samples with <100 mg NPE/kg textile	Only textile samples with <250 mg NPE/kg textile
Geometric mean concentration NPE (mg NPE/kg textile)	28	7.2	15.1	66	6.1	9.2
NPs (mg NP/kg textile)	13.3	3.4	7.2	32	2.9	4.4
Contribution to inlet concentration (µg NPs/L)	1.2[24]	0.3	0.6	2.8	0.3	0.4
% contribution of estimated content of NPs in inlet (Table 4.5)	86 (= 1.2/1.4 × 100%)	21	43	200	21	29

Table 4.6 also shows that the total amount of NP led to the waste water will be significantly reduced if a limit value to the NP or NPE in textiles is imposed. A limit value of 250 mg NPE/kg textile will reduce the NP contributionsfrom textiles to the inlet concentration of 1.2 µg NPs/L to 0.6 µg NPs/L, and a limit value of 100 mg NPE/kg textile will reduce the NP contribution from textiles to 0.3 µg NPs/L.

Overall, on the basis of these calculations, it is assessed that the NP/NPE contribution of the textiles to the external environment is significantly compared to the total load of the external environment of NP/NPE and although there may be no immediate widespread risk to the aquatic environment in Denmark where approx. 90% of waste water is led to WWTPs, it still makes good sense to try to further reduce NP emissions to the external environment, i.a. to meet the Water Framework Directive target of cessation of emissions and losses of NP/NPE.

[24] =13.3 mg NP/kg textile × 59,181 tonnes of imported textiles per year/700 × 10^6 m^3 per year=1.2 µg NP/L

5. Conclusion and recommendations

Clothes for children and adults may contain residues of the chemicals used in the manufacture of textiles. One of these chemicals is NPE, which, by degradation, forms nonylphenol (NP). NP and NPE are found to be both health and environmentally hazardous.

There are generally reported higher NP and NPE concentrations in literature (mean 670 mg NPE/kg textile, geometric mean 66 mg NPE/kg textile, standard deviation of 1.664 NPE/kg textile and highest concentration of 14,100 mg NPE/kg textile) than measured in this study (mean 96 mg NPE/kg textile, geometric mean 27 mg NPE/kg textile, standard deviation of 107 mg NPE/kg textile and highest concentration of 311 mg NPE/kg textile). As only a limited number of textile samples is analysed, this difference may be random; however, it may also be the result of importers becoming more aware of imposing requirements concerning the NP (E) content in textiles.

There seems to be no pattern in the types of textile (cotton or polyester, organic or non-organic) containing high concentrations of NP and NPEs. There is a tendency that the textiles having a higher concentration of NPE also have one or more bright colours. The textiles from China - except for a natural-coloured sweater - generally had higher concentrations of NPE.

Tests with artificial sweat showed that NPE can migrate to sweat but also that the level varies a great deal. An insignificant migration of NPE from bed linen to sweat was measured but a migration of NPE from jeans to sweat between 13 and 33% was detected. No NP was detected in the sweat extract.

Only a single analysis of migration to artificial saliva was performed, in which a limited migration of both NPE and NP was measured. The content of NP in the saliva extract was below the detection limit, and the migration of NPE was measured to be between <0.1% and up to approx. 32%. It is not possible to draw definitive conclusions on migration of NP and NPE from textiles to saliva on the basis of this one analysis but it is likely that migration is dependent on the type of textile, dyeing, etc.

Based on the analytical results obtained in this study, calculations were carried out of children's exposure to NPE from more pieces of clothes at the same time. The results showed that, in a worst-case scenario, in which a child wears new unwashed clothes once every 14 days and wears the jeans, underwear and T-shirt, yielding the highest uptake through the skin at the same time, the overall risk characterisation ratio (RCR) using jeans, underwear and T-shirt (and an insignificant contribution from mittens and bed linen) is calculated to be 1.4. According to these calculations, a child's uptake of NP using new unwashed clothes may thus result in an RCR above 1, indicating a health risk under the assumptions made in the calculations of this study. At an average consideration regarding the content of NP in the clothes, an RCR of 0.78 using new, unwashed jeans, underwear and T-shirts simultaneously over a 14-day period is seen. When using clothes that are washed once before use, a significant reduction in exposure to NP and NPE, respectively, is seen with a total RCR of 0.41 for the textiles with the highest concentrations of NPE. This shows the importance of a single washing of clothes before use is, regarding a minimisation of the risk from use.

Furthemore, significantly higher concentrations of NP/NPE in textiles were reported in literature than measured in this study. Therefore, textiles containing these substances are considered a significant source of exposure to NP/NPEs in everyday life. It may thus make good sense to try to reduce the levels of NP and NPE in textiles as much as possible, partly to achieve greater protection against nephrotoxic effects, and partly to address potential combination effects between NP and NPE, respectively, and other endocrine disrupters, which humans may come in contact with in everyday life as these substances are under suspicion of endocrine disrupting effects.

It should be mentioned that the calculations are based on a flimsy data material as only a limited number of clothing samples was included in the study just as a conservative interpretation was made of migration measurements in the saliva and sweat and skin absorption tests.

Furthermore, simple calculations of the NP and NPE contribution from imported textiles to the aquatic environment suggested that, potentially, the textiles constitute a major source of the total NP load on waste water and thus also to the environment.

In summary it may be recommended that importers of textiles ask their supplier to limit the content of Np/NPE in textiles and that consumers wash new clothes before use.

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Appendix A: Background material of the survey

TABLE A.1
RESULTS FROM THE SURVEY/LITERATURE SEARCH

Product No.	Country of manufacture	Type of textile	Concentration (mg NPE/kg)	Concentration (mg NP/kg)
T-shirts [a)]				
1	Poland	100% polyester	45	-
2	Thailand	100% polyester	16	-
3	-	100% cotton	<1	-
4	Tyrkey	100% eco-cotton	22	-
5	Lithuania	91% polyamide 9% elasthane	4	-
6	-	85% ”dri-release” 15% cotton	13	-
7	-	100% cotton	430	-
8	China	100% cotton	940	-
9	-	100% cotton	11	-
10	-	100% cotton	63	-
11	-	100% cotton	33	-
12	-	100% cotton	43	-
13	-	100% cotton	120	-
14	Tyrkey	100% cotton	270	-
15	-	92% cotton 8% elasthane	3	-
16	Portugal	100% eco-cotton (ecolabelled with the Swan)	4	-
17	Tyrkey	100% cotton	230	-
Towels [b)]				
1	-	Terry cloth	<1	-
2	-	Terry cloth	94.6	-
3	-	Terry cloth	2	-
4	-	Terry cloth	6.1	-

Product No.	Country of manufacture	Type of textile	Concentration (mg NPE/kg)	Concentration (mg NP/kg)
5	-	Terry cloth	11.1	-
6	-	Terry cloth	239	-
7	-	Terry cloth	517	-
8	-	Terry cloth	190.5	-
9	-	Terry cloth	1,277	-
10	-	Terry cloth	577	-
11	-	Terry cloth	10,608	-
12	-	Terry cloth	3.4	-
13	-	Terry cloth	2.6	-
14	-	Terry cloth	3.3	-
15	-	Terry cloth	7	-
16	-	Terry cloth	<1	-
17	-	Terry cloth	1.6	-
18	-	Terry cloth	150.7	-
19	-	Terry cloth	12.6	-
20	-	Terry cloth	2.2	-
***Fabrics* c)**				
1 Bed linen/cushions/ clothes (i.a. trousers/ shirt) for children	-	100% cotton	5	0.5
2 Bed linen/cushions/ clothes (i.a. skirt, dress, shirt) for children	-	100% cotton	16	1.8
3 (Blouse with teddybear print for children)	-	100% cotton	<3	<0.1
4 (Oilcloth)	-	100% cotton	20	6.4
***Underwear* d)**				
Björn Borg	-	-	860	-
Björn Borg	-	-	490	-
***Jeans* e)**				
Nudie	-	100% cotton	<1	-
Cheap Monday	-	98% cotton, 2% elasthane	2,200	-

Product No.	Country of manufacture	Type of textile	Concentration (mg NPE/kg)	Concentration (mg NP/kg)
Miss Sixty	-	98% cotton, 2% elasthane	7	-
Wrangler	-	100% cotton	<1	-
Crocker	-	85%cotton, 13% elasthane multi ester, 2% elasthane	110	-
Lee	-	100% cotton	420	-
Snowsuits f)				
H&M	-	-	1,200	-
Kapp-Ahl	-	-	990	-
Lindex	-	-	970	-
Nanook	-	-	12	-
Altitude 8848	-	-	52	-
Polarn & Pyret Skidoverall	-	-	110	-
Reima Essen	-	-	2	-
Europris Boys & Girls	-	-	420	-
Didriksons Mountain Goat	-	-	470	-
Coop Friends	-	-	21	-
Helly Hansen K Mount skisuit	-	-	230	-
Polarn & Pyret Bävernylon	-	-	580	-
Åhléns	-	-	420	-
Disney textiles g) (sum of alkylphenol ethoxylates)				
Tigger vest, Denmark	-	-	620	-
Mickey Mouse T-shirt, Belgium	-	-	264.3	-
Princess T-shirt, Canada	-	-	34,1	-
Donald Duck T-shirt, Netherlands	-	-	1,220	-
Minnie Mouse T-shirt, Spain	-	-	122	-
Finding Nemo T-shirt, UK	-	-	1,045	-
Mickey Mouse T-shirt, USA	-	-	49	-

Product No.	Country of manufacture	Type of textile	Concentration (mg NPE/kg)	Concentration (mg NP/kg)
Tigger baby bib, Slovakia	-	-	1,153	-
Snow White T-shirt, New Zealand	-	-	440	-
Minnie Mouse Pyjamas, Austria	-	-	1,700	-
Finding Nemo T-shirt, Turkey	-	-	1,190	-
Mickey Mouse underwear, Norway	-	-	*	-
Treasure Planet pyjamas, Mexico	-	-	357	-
Snow White underwear, France	-	-	*	-
Buzz Lightyear vest, Philippines	-	-	548	-
Princess Ariel T-shirt, Argentina	-	-	640	-
Mickey Mouse sweatshirt, China	-	-	83	-
Snow White T-shirt, Thailand	-	-	1,390	-
Winnie the Pooh PVC raincoat, Germany	-	-	73.2	-
Government Chemist h)				
Plastisol print on cotton woven T-shirt	-	Cotton	400	-
Pigment printed jersey fabric (viscose - elastane)	-	Viscose-elasthane	200	-
Black cord fabric	-		600	-
Waterbase print on cotton - polyester fabric	-	Cotton-polyester	100	-
Small red polka dots on white (cotton-polyester) fabric	-	Cotton-polyester	6,400	-
Black cord fabric	-		600	-
100% cotton woven fabric with pigment print	-	Cotton	400	-
Pink elastic ribbon	-		1,300	-
Printed viscose fabric	-	Viscose	2,800	-
White nylon net fabric	-	Nylon	ND	-

Product No.	Country of manufacture	Type of textile	Concentration (mg NPE/kg)	Concentration (mg NP/kg)
Waterbase print on cotton – polyester shirt	-	Cotton-polyester	2,900	-
Purple velour (polyester - viscose) fabric	-	Polyester-viscose	2,400	-
Black jersey (viscose-elastane) fabric	-	Viskose-elasthane	1,300	-
Blue and green flower pigment print on white cotton fabric	-	Cotton	1,100	-
Pigment print on cotton - polyester fabric	-	Cotton	1,200	-
100% cotton fibre reactive print towel	-	Cotton	800	-
Black acrylic scarf	-	Acrylics	ND	-
Discharge print on rayon lining	-	Rayon	700	-
Jersey fabric with placement print	-		100	-
Plastisol print on cotton - polyester fabric	-	Cotton-polyester	1,600	-
Plastisol print on cotton fabric	-	Cotton	3,200	-
Grey silk fabric	-	Silk	2,400	-
Burgundy silk fabric	-	Silk	2,900	-
Plastisol and waterbase print on cotton fabric	-	Cotton	ND	-
Multi-coloured stripes on polyester satin twill	-	Polyester satin	14,100	-
Plastisol print on lycra	-	Lycra	500	-
Waterbase print on cotton shirt	-	Cotton	100	-
Plastisol print on cotton fabric	-	Cotton	600	-
Cotton (polyester- nylon-elastane) rich anti-slip gripper socks	-	Cotton, polyester-nylon-elasthane	600	-
Environmental Project No. 534 i)				
Dark blue, coloured, washable habit trousers	-	Polyester/wool	34	-
Dark green, coloured terry towel	-	Cotton	85	-

Product No.	Country of manufacture	Type of textile	Concentration (mg NPE/kg)	Concentration (mg NP/kg)
Yellow, coloured T-shirt with PVC print	-	Polyester	26	-
TNO – MEP [j]				
2 × Buzz Lightyear pyjamas for boys (ages 2-3 years), exclusive to Disney Store	-	-	17	49
2 × Piglet pyjamas for girls (ages 3-4 years), Disney	-	-	1,430	6.9
2 × Tigger pyjamas unisex with caption '100% Cheeky', (ages 12-18 months), Disney	-	-	1,017	ND
2 × Tigger pyjamas for boys with caption 'Come on in little buddy. The Water's great!', (ages 12-18 months), Disney	-	-	812	8.8
Bob The Builder pyjamas for boys (ages 1-1½), Mothercare	-	-	1,930	8.8
Danish Consumer Council magazine "Tænk" (Think) [k]				
10 T-shirts testet	-	-	-	-
Danish Consumer Council magazine "Tænk" (Think) [k]				
Bjørkvin, Black International, Cottonfield, Divided, H&M, Jack & Jones, Jim Avignon Spreadshirt / BC, Stanfield, Tiger	-	-	ND	-
Norwegian Climate and Pollution Agency (the former SFT) [l]				
5 jeans testet	-	-	ND	-

a) Swedish EPA, 2008
b) Swedish EPA, 2007
c) Environmental Project No. 23, 2003
d) http://www.gp.se/konsument/tester/1.21943-borg-kalsonger-08;
e) http://svt.se/content/1/c8/01/68/54/36/jeans_del1.pdf; http://svt.se/2.109801/1.1685436/jeanstest_hela_testprotokollet
f) http://www.testfakta.se/Article.aspx?a=21510
g) http://www.greenpeace.org/raw/content/denmark/press/rapporter-og-dokumenter/finding-chemo-toxic-children.pdf
h) http://www.governmentchemist.org.uk/dm_documents/Determination%20of%20specific%20alkylphenol%20ethoxylates%20in%20textiles_6sQz8.pdf
i) Environmental Project No. 534, 2000
j) TNO (2003): Hazardous Chemicals in Consumer Products. Downloaded from http://www.uk.greenpeace.org.uk/files/pdfs/migrated/MultimediaFiles/Live/FullReport/6043.pdf
- Not available
k) http://www.taenk.dk/test/t-shirts/testresultater/).
l) http://www.sft.no/no/Aktuelt/Nyheter/2009/Oktober-2009/Har-ikke-funnet-antimuggmiddel-i-jeans-/?cid=40499).

Figures A.1 and A.2 show the distribution of the measured concentrations in textiles. The values in the figures are thus taken from Table A.1.

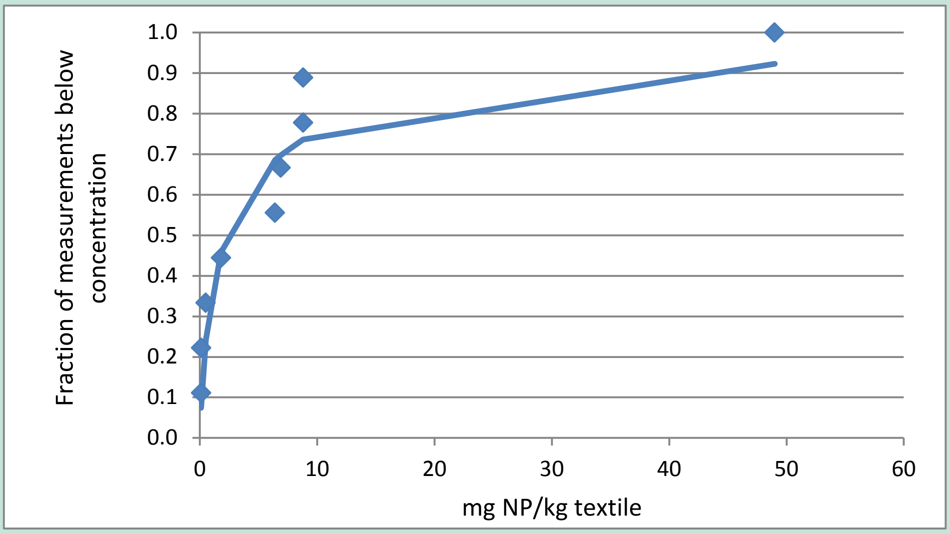

FIGURE A.1
DISTRIBUTION OF MEASURED NP CONCENTRATIONS IN TEXTILES. LOGARITHMIC NORMAL DISTRIBUTION IS ASSUMED

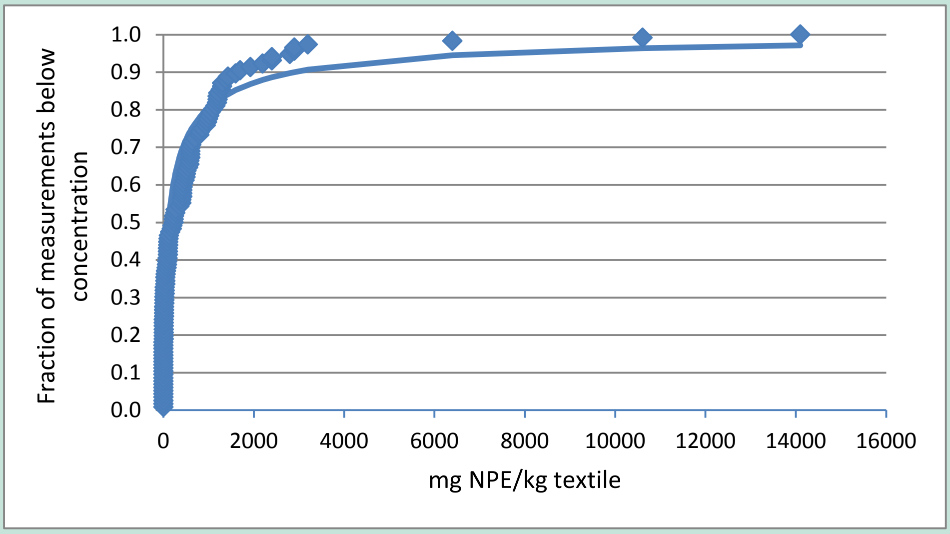

FIGURE A.2
DISTRIBUTION OF MEASURED NPE CONCENTRATIONS IN TEXTILES. LOGARITHMIC NORMAL DISTRIBUTION IS ASSUMED

Questionnaire

7 COMPANIES IMPORTING AND SELLING TEXTILES WERE CONTACTED. ALL THE COMPANIES ARE ANONYMIZED IN THIS REPORT.

Question	Company						
	1	2	3	4	5	6	7
Do you pose requirements to chemicals in textiles purchased?	Will introduce systematic monitoring of compliance with the law	Yes	Yes	Yes	Yes	Yes	Yes
What are the requirements?	Yes, all Danish & European legislation is obeyed	Max 250 mg/kg textile is accepted*	Requirement prohibiting NPE in approx. 10 years. The requirement is difficult to meet as NPE still	Chemical restrictions, Ban on APO and other degradation products. Accepts, however, 100 mg/kg textile**	All Danish & European legislation is obeyed	Suppliers manual with rules contains a list of chemicals, for which there are requirements	All suppliers must sign an agreement, which i.a. contains a list with chemicals that cannot be applied in the production. The list contains i.a. NP and NPE
To which legislation/regulation do you refer?		Referring to DIR 2003/53/EC					The national legislation in the individual sales countries is obeyed. Now the majority of the national legislation is included under REACH, except for some exemptions

Question	Company 1	2	3	4	5	6	7
Do you pose any requirements on the content of nonylphenol ethoxylates and nonylphenol?	No we do not pose any requirements on NPE		If the presence is >100 mg/kg textile, it is investigated, from where in the process NPE originates	At >100 mg/kg, it is most likely that APO is applied in the process while, at <100 mg/kg, it is most likely that APO originates for elsewhere, e.g. contaminations	No we do not pose any requirements on NPE		Our restriction list contains far more chemicals than those regulated under REACH
Do you have standard test or monitoring programmes, e.g. ecolabellig	Yes, i.a. ecolabelling, the EU Flower and faith in textiles	In 2007, spot checks were made, which showed that the require-ment to NPE was met. No checks have been made since	Ad hoc checks are made for NPE No commonly accepted analytical standard exists (Methods: LC-MS, ST-IR, LC-DAD)	Spot checks	Yes, i.a. ecolabelling, the EU Flower and faith in textiles	Testing with the rules. Testing with Oeko-tex when required	Yes. Our own test programmes are followed. Many suppliers have Oeko-tex.
Are nonylphenol ethoxylates and nonylphenol included in the test programme?	No			Measure NPE, OPE, NP and OP	No		NP and NPE are frequently tested as part of the company test programme.
Nonylphenol ethoxylates and nonylphenol **Do you have knowledge of any presence of these substances in the textiles?** **What is the concentration level, if known?** **Do you have knowledge**	No	NPE is used in the manufacture of cotton. Cleaning of fibers, subsequent cleaning process Used as emulsifier in dyeing pigments	Auxiliary agent in dyeing and cleaning processes. Detergent, scouring agent, wetting agent, emulsifier, dipersing, impregnative. Leather: Dyeing and degreasing Silk:	Yes Occur often: Several places and at high concentrations. Rarely > 1,000 mg/kg textile At >100 mg/kg textile, the source is search and remedied. The source is typically	No	Not answered	NP and NPE occur quite frequently NP and NPE are used as detergents, dispersing, emulsifying and impregnation agents in paste for printing. NP and NPE

Question	Company 1	2	3	4	5	6	7
of use of NPE during manufacturing/ treatment? **Do you know the extent of the use and how large the amount is?**			Degumming Used i.a. in the manufacture of jeans where many cleaning processes are applied	cleaning processes at the end of the process			are not allowed in our products. There has been tested for the substances over the past two years. The substances are detected very rarely. However, when the tests started, NP and NPE were detected in approx. 20% of products.
The following questions are for textiles, for which presence of NPE/NP is known							
Where are the textiles manufactured? **Within the EU** **Outside the EU** **Which non-EU country?**	Not answered	Especially India and China	Especially the far East. A study from 2004 showed a sing case out of 50, in which high concentrations of NPE were detected.	Especially China	Not answered	Not answered	Now, NP and NPE are found very rarely. When the tests were started, NP and NPE were primarily detected in textiles form China, India and Turkey.
Types of texstiles: **Cotton** **Synthetic** **Viscose** **Mixture** **Others**	Not answered	Not answered	Not answered	Different types	Not answered	Not answered	Cotton Synthetic

Question	Company						
	1	2	3	4	5	6	7
Use of the textiles: **Clothing** **Towels** **Bed linen** **Home textiles: Carpets, curtains, etc.** **Others**	Not answered	Not answered	Not answered	Not answered	Not answered	Not answered	Towels Home textiles

* Level for NPE established in cooperation with suppliers in the Far East. A total ban was not realistic.
** Level for NPE established on the basis of results of laboratory measurements from a major study of NPE in textiles

Appendix B: Nonylphenol (NP) - Derivation of systemic DNEL for the common consumer

B.1 Introduction

This appendix explains the derivation of a systemic DNEL for the common consumer. The derivation is based on toxicological data from animal studies, in which the critical effects, i.e. the effects resulting from the lowest exposure levels are identified. Furthermore, assessment factors are used to account for the uncertainties inherent in extrapolating results from animal studies to effects on humans.

B.2 Method

The derivation of a DNEL for the common consumer is based on toxicological data from the risk assessment report for NP (EU, 2002).

DNEL is derived from:

$$DNEL = \frac{NOAEL}{AF_1 \times AF_2 \times AF_3 \times AF_4 \times AF_5 \times AF_6 \times AF_7}$$

where
NOAEL (No Observed Adverse Effect Level) is the critical effect

AF_1, AF_2,...AF_7 are assessment factors accounting for the uncertainties inherent in extrapolating results from animal studies to the human situation. The applied assessment factors are based on the ECHA guidance (ECHA, 2008) and are described in details in Section B.3.

The toxicological profile of nonylphenol (NO) is described in EU (2002) and a short description is given below. The acute oral LD_{50} is between 1,200 and 2,400 mg/kg body weight (bw) and the dermal LD_{50} is about 2,000 mg/kg bw. LC_{50} is not known but due to the corrosive properties of NP, acute toxicity via inhalation cannot be excluded. Slight respiratory irritation is observed at 400 ppm but not at 30 ppm. The potential for mutagenicity and carcinogenicity is assessed to be low. In an oral study (administered by gavage) investigating the toxicological effects of NP on early stages of development, NOAEL values of 75 mg/kg bw/day and 300 mg/kg bw/day for maternal (dam) and fetal (fetus) toxicity, respectively, were identified. A LOAEL value of 100 mg/kg bw/day for testicular toxicity was determined on the basis of a repeated-dose oral (gavage) study.

A LOAEL value of 15 mg/kg bw/day for histopathological (tissue) changes in the kidneys was determined from a multi-generation study. Groups of 30 Sprague-Dawley rats (male/female) were exposed to NP via feed at concentrations of 0 (control) 200, 650 or 2,000 ppm for up to 20 weeks. Calculated NP intakes were 0, 15, 50 and 160 mg/kg bw/day. The following effects were demonstrated: Reduced body weight, increased kidney weights at 50 and 160 mg/kg bw/day, histopathological changes in the kidney including tubular degeneration and extension at 15, 50 and 160 mg/kg bw/day.

Also from a multi-generation reproduction study (F1, F2 and F3), a NOAEL of 15 mg/kg bw/day was determined for effects on the reproductive system. Groups of 30 Sprague-Dawley rats (male/female) were exposed to NP via feed at concentrations of 0 (control) 200, 650 or 2,000 ppm for 3 generations. Calculated NP intakes were 0, 15, 50 and 160 mg/kg bw/day in the non-reproductive phase, rising to 0, 30, 100 and 300 mg/kg bw/day during lactation. The following effects were detected over several generations: Disorders of the reproductive system of offspring including minor changes in the length of the oestrous cycle, timing of vaginal opening, ovarian weight and number of sperm/sperma time at 50 and 160 mg/kg bw/day. Functional changes in reproduction were not induced at 15, 50 and 160 mg/kg bw/day.

Based on data from the toxicological profile of NP, the EU has assessed the critical effects to be histopathological changes in the kidneys and reproductive parameters, both identified in a multi-generation study. Hereinafter, the NOAEL and LOAEL values of 15 mg/kg bw/day established from oral studies, in which administation of NP is via the feed, were applied in the derivation of a relevant systemic DNEL for the common consumer. These studies are considered more relevant in relation to human exposure than studies with oral administration of NP via gavage.

B.3 Assessment factors

The applied assessment factors are based on the guidance given in ECHA (2008). No data were available and no considerations were made regarding the level of the actual assessment factors in the EU risk assessment report (2002).

Based on the method described in ECHA (2008), the following assessment factors are considered relevant for deriving DNEL for the common consumer:

AF_1: Interspecies variation: A total assessment factor of 10 is applied to correct for differences between rat and human. The assessment factor of 10 can be divided into an assessment factor of 4 for differences in body weight and an assessment factor of 2.5 for other differences (toxico dynamics).

AF_2: Intraspecies variation: An assessment factor of 10 is applied to account for differences in toxicological response and sensitivity in different population groups.

AF_3: Duration of exposure: An assessment factor of 1 is applied as both studies are multi-generation studies.

AF_4: Dose-response relation: Assessment factors of 1 and 3 are applied for the NOAEL value and the LOAEL value, respectively, for a dose-response relation, i.e. when based on LOAEL, a factor of 3 is applied for extrapolating to a no-effect level.

AF_5: Quality of data: An assessment factor of 1 is applied. The derived NOAEL and LOAEL values are based on multi-generation studies performed in accordance with the GLP principles and OECD guideline.

The calculation of DNEL is as follows:

$$\mathrm{DNEL} = \frac{\mathrm{LOAEL}}{\mathrm{AF_1} \times \mathrm{AF_2} \times \mathrm{AF_3} \times \mathrm{AF_4} \times \mathrm{AF_5}}$$

$$\mathrm{DNEL}_{\mathrm{oral}} = \frac{15\ \mathrm{mg\ NP/kg\ bw/day}}{10 \times 10 \times 1 \times 3 \times 1} = 0.05\ \mathrm{mg\ NP/kg\ bw/day}$$

B.4 Absorption conditions for calculation of internal DNEL

According to the EU risk assessment report (2002), the systemic bioavailability of NP after oral administration in rat was estimated at 10% of the initial dose due to"first pass" metabolism in the liver.

According to the EU risk assessment report (2002), percutaneous absorption is limited although skin penetration may occur, especially in stratum corneum. In an 8-hour in-vitro study using ^{14}C-labelled NP (labelled in the benzene ring), absorption of less than 0.15% for both pig and rat skin was measured. The penetration through the skin was measured at around 3% for pig skin and 6% for rat skin. Other studies reported in the EU (2002) gave similar results. Based on this information, it was evaluated in the EU (2002) that a maximum of 10% can be absorbed through the skin. An absorption factor (Abs_{oral}) of 10 is applied for dermal absorption. This factor converts $NOAEL_{oral}$ into $NOEL_{dermal}$.

Based on $DNEL_{oral}$ and applying the oral absorption factor, the internal dose corresponding to $DNEL_{internal}$ is calculated:

$$DNEL_{internal} = \frac{0.05 \text{ mg NP/kg bw/day}}{10} = 0.005 \text{ mg / kg bw/day}$$

This $DNEL_{internal}$ applies regardless of the route of exposure as the actual exposure for a given route of exposure is converted into internal dose by applying the relevant absorption factor for the route of exposure. Then, the internal dose (possibly the sum of the internal dose for all relevant routes of exposure) is compared with $DNEL_{internal}$ value.

Uncertainty analysis in connection with the calculated DNEL values

The applied absorption factors for oral and dermal exposure are the same values as those used in the risk characterisation in the EU risk assessment report on nonylphenol (EU, 2002).

An oral absorption ratio of 10% is applied for nonylphenol. When this value is applied, this is in relation to the systemic absorption of unmetabolized nonylphenol alone (in the form of non-conjugated nonylphenol), and thus does not include the amount of metabolites (sulfate and glucuronide conjugates), which, however, are reported to constitute the highest concentration in the blood. The total absorption of nonylphenol expressed as systemically absorbed quantity of nonylphenol + metabolites must thus be assumed to be significantly more than 10% by oral exposure. This is also stated in the EU risk assessment report (EU, 2002), which assumed 100% absorption of nonylphenol by oral exposure, while as mentioned only 10% is assumed to be absorbed as non-conjugated nonylphenol.

When the internal dose is calculated only for 10% of the external dose, it is thus assumed that the toxicity attributes solely to the unmetabolized nonylphenol and not its metabolites, i.e. conjugated nonylphenol. However, no data illustrating the difference between the toxicity of free nonylphenol and the toxicity of metabolites of nonylphenol are stated, which is why application of an absorption factor (Abs_{oral}) of 10 for a conversion of an external oral DNEL value to an internal DNEL value must be considered conservative in this case.

The reverse applies in assessment of dermal absorption, in which it is assumed that up to 10% of the dermal dose can be taken up systemically. In-vitro studies on skin of rats, pigs and humans indicate that less than 0.15% of the dose was recovered in the diffusion chamber under the skin while up to 6% was retained in the skin. Thus, there is reason to believe that the actual bioavailable part of NP is significantly less than 10% for dermal exposure.

Under these conditions, as specified in the EU risk assessment report, the application of the specified absorption ratios of 10% for both oral and dermal exposure must be considered conservative.

As this may be essential for the risk characterisation, it is important to specify this as significant uncertainties in the assessment as more exact knowledge on absorption ratios most likely will result in lower values for the risk characterisation ratio (RCR).

Table B.1 shows the DNEL values that can be calculated from the relevant toxicological data.

B.5 Conclusion

The critical effect is assessed to be histopathological changes in the kidneys based on the LOAEL value of 15 mg/kg bw/day, which indicates a lower NOAEL value than the 15 mg/kg bw/day.

$DNEL_{oral}$ can be calculated at 0.05 mg/kg/day from a LOAEL value of 15 mg/kg/day and applying a total assessment factor of 300.

In relation to exposure via multiple exposure routes with various degrees of absorption, it is necessary to calculate an internal (systemic) DNEL, in which exposure is also calculated as total systemic or internal dose, and which takes into account the varying degrees of absorption of the different routes of exposure, ie.:

$$DNEL_{internal} = DNEL_{oral} \times Abs_{oral}$$

The systemic bioavailability of NP after oral administration in rat is assessed to be 10% of initial dose due to “first pass” metabolism in the liver. Based on the above, the internal DNEL for the common consumer from oral exposure is derived to be 0.015 and 0.005 mg/kg bw/day from the oral NOAEL and LOAEL values, respectively, both at 15 mg/kg bw/day.

As no NOAEL or LOAEL values were found for dermal exposure, an internal DNEL for the common consumer from dermal exposure is based on the oral NOAEL and LOAEL values of 15 mg/kg bw/day. Then, the dermal exposure was converted into internal dose using the dermal absorption (Abs_{dermal}). The systemic bioavailability of NP after dermal absorption is assessed to be 10% of initial dose due to an estimated dermal absorption of 10%. Based on the above, the internal DNEL for the common consumer from dermal exposure is derived to be 0.015 and 0.005 mg/kg bw/day from the oral NOAEL and LOAEL values, respectively, both at 15 mg/kg bw/day.

For use in the health assessments, the total internal dose is calculated, i.e. the uptake via skin contact and the uptake via oral exposure are summed up in the calculations and compared with the internal DNEL of 0.005 mg NP/kg bw/day.

Nonylphenol, which is a degradation product of nonylphenol ethoxylate (NPE), has been shown to be more toxic than the actual NPE. NPE will be partly transformed into NP in humans. US EPA (2010) thus refers to studies, in which it was concluded that mammals convert NPE into NP. In this study, it is assumed that NPE taken up in the body is fully transformed into NP in the human body, which is a conservative assumption. Therefore, NPE assigned the same DNEL value as NP.

In conclusion, the internal DNEL for the common consumer is 0.005 mg NP/kg bw/day. The same DNEL value is applied for NPE as NPE is transformed into NP in the body.

TABLE B.1
CALCULATED EXTERNAL AND INTERNAL DNEL VALUES

Exposure (systemic effect)	NOAEL/LOAEL	Effect	Effect level	Absorption ratio (oral)	Assessment factors					Derived external DNEL (mg/kg bw/day)	Derived internal DNEL (mg/kg bw/day)
					Inter-species variation (AF_1)	Intra-species variation (AF_2)	Duration of exposure (AF_3)	Dose-response relation (AF_4)	Quality of data (AF_5)		
Chronic oral	NOAEL Multi-generation reproduction study in rat (oral administration via feed)	Changes in reproductive parameters	15 mg/kg bw/day	10%	10	10	1	1	1	0.15	0.015
Chronic oral	LOAEL Multi-generation reproduction study in rat (oral administration via feed)	Histopathological changes in the kidneys	15 mg/kg bw/day	10%	10	10	1	3	1	0.05	0.005
Chronic inhalation										Not relevant	Not relevant
Acute oral										Not relevant	Not relevant
Acute dermal										Not relevant	Not relevant
Acute inhalation										Not relevant	Not relevant

Chronic inhalation: Not relevant as the critical route of exposure is oral
Acute oral, dermal and inhalation: Not relevant to systemic effect. The acute oral LD50 is between 1,200-2,400 mg/kg bw (rat), and the dermal LD50 is about 2,000 mg/kg bw (rabbit). LC50 for inhalation is not known.

Appendix C: Surface area of children and adults

TABLE C.1
APPLIED SURFACE AREA OF CHILD AND ADULT

Body part	Child (10 kg)		Adult (60 kg)	
	Surface area (cm^2)	(%)[2)]	Surface area (cm^2)	(%)[4)]
Whole body	6,410 [1)]	100	17,160 [3)]	100
Head	1,058	16.5	1,218	7.1
Torso	2,276	35.5	5,972	34.8
Arms	833	13	2,402	14
Hands	364	5.68	875	5.1
Legs	1,481	23.1	5,560	32.4
Feet	402	6.27	1,115	6.5

1) From Exposure Factors Handbook. Calculated from the average ratio of surface area (m^2) to weight (kg) for 0-2-year olds of 0.0641. Weight =10 kg applied.
2) From Exposure Factors Handbook. Average values for 1-2-year olds applied.
3) From Exposure Factors Handbook. Calculated from the average ratio of surface area (m^2) to weight (kg) for >18- year olds of 0.0286. Weight = 60 kg applied.
4) From Exposure Factors Handbook. Average values for >18-year olds applied.

Survey and environmental and health assessment of nonylphenol and nonylphenlethoxylates in textiles

Nonylphenol and nonylphenolethoxylates (NP/NPE) are used in the production of textiles and residues may be found in the final textile product. An assessment of the exposure of children has shown that under normal conditions the concentrations in textiles do not constitute a health risk. An assessment of the emissions to the environment showed that textiles may be a significant source, but also that efficient waste water treatment plants remove a large proportion of NP/NPE.

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