Ministry of Environment and Food of Denmark
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Survey and risk assessment of chemical substances in bicycle helmets

Survey of chemical substances in consumer products No. 162a

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Preface

This project describes which materials bicycle helmets for young children are made of and which chemical substances that can be found in bicycle helmets for children. An information collection was made and based on this, selected bicycle helmets for children were analysed for selected chemical substances. The results of the information collection and the chemical analyses are presented in this report.

This project was carried out in the period March 2017 to December 2017.

The project is conducted by FORCE Technology with subcontractors for some of the analyses. Eurofins have made a quantitative analysis of foam material for content of chlorinated phosphorus-based flame retardants as well as a quantitative analysis of bicycle straps for content of different perfluoroalkyl and polyfluoroalkyl substances (PFASs). Furthermore, Eurofins have also made migration analysis for the same groups of substances.

The participants of the project were:

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- Charlotte Merlin, FORCE Technology
- Anders Schmidt, FORCE Technology (quality assurance)

The project was followed by a working group consisting of Jesper Gruvmark, Bettina Ørsnes Larsen and Shima Dobel from the Chemical Division, Danish EPA as well as Pia Brunn Poulsen, FORCE Technology.

The project was financed by the Danish Environmental Protection Agency

Summary and conclusions

Today, most children wear bicycle helmet, also the quite young children. Parts of the bicycle helmet have direct skin contact at the forehead, at the ears and the strap has direct skin contact on the cheeks and under the chin. It might also be expected that the youngest children put some parts of the bicycle helmet into the mouth, for instance the strap and the closing mechanism.

The purpose of the project
The purpose of this project has been to investigate which materials that bicycle helmets typically consist of and if there are any problematic substances in the parts of the bicycle helmets which have direct contact with the skin or in the parts which the youngest children can be expected to put into the mouth. Furthermore, the purpose of the project has been to examine whether the content of the possibly problematic chemical substances in bicycle helmets can be hazardous to children's health .

The scope of the project
The project is limited to focus on bicycle helmets for young children, i.e. primarily children at the age under 3 years. Focus has been on bicycle helmets intended to a cranial circumference of between 42 and 52 cm corresponding to the cranial circumference of children up to 3 years. Neither ski helmets nor bicycle airbag/inflatable bicycle helmets have been included in this report.

Survey
In the first phase of the project, information about bicycle helmets for children was collected. The following methods were used:
- Contact to the trade, for instance trade association and selected suppliers of bicycle helmets
- Internet search
- Shop visits
- Use of the app "Check the chemistry" made by the Danish Consumer Council and the Danish EPA
- Literature search, for instance the Danish EPA's previous projects regarding chemicals in consumer products as well as foreign tests of bicycle helmets for children

The survey showed that a lot of different bicycle helmets for children are available on the market. In total 39 different brands/producers of bicycle helmets were identified. Each of these produces different types of bicycle helmets in different colours and printed patterns. The different types of bicycle helmets can be the more common bicycle helmets with vent holes ('racer helmets'), skater helmets (a more closed helmet with a few vent holes) and more special bicycle helmets designed as for instance animal heads.

The price of the analysed bicycle helmets for children in this project varies between 89.90 DKK and 769 DKK. The bicycle helmets are mainly produced in China but a few European brands have their own production in Europe (Germany or Italy).

The survey shows that bicycle helmets consist of the following parts which are mainly produced in the following materials:
- Outer shell in PC (polycarbonate). However, they are also produced in ABS (acrylonitrile butadiene styrene), and in a few cases in PVC (polyvinyl chloride), PS (polystyrene) or EPS (expanded polystyrene).
- Inner shell in EPS (expanded polystyrene).

- Pads/padding and possibly chin pad in PU (polyurethane) foam either with a thin textile layer or entirely encircled by textile (a pocket of textile) most likely of PES (polyester). The pads in the helmet might be glued on or be fastened with Velcro. In the latter case, there are several small pads (pockets of textile with foam filling).
- Possibly a hard plastic strap inside (of unknown material) making the helmet adjustable to the size of the head.
- Strap of nylon, PES (polyester) or PP (polypropylene)
- Chin buckle of hard plastic (of unknown material or POM (polyoxymethylene)).

Parts in contact with the skin when the bicycle helmet is worn
When a bicycle helmet is worn correctly the child is not in direct skin contact with either outer shell or inner shell. They are only in direct skin contact with:
- The pads inside in the helmet – i.e. there is a direct contact with the textile on or around the foam. Direct skin contact is primarily on the forehead – at other places the child's hair will be in between.
- The bicycle strap at the ears, cheeks and under the chin where a direct skin contact will occur at several places on the strap.
- The chin buckle where direct skin contact will occur with the plastic buckle or possibly the padding around the buckle (which is typically made of the same material as the padding inside the helmet).

Content of potentially problematic chemical substances in bicycle helmets
Use of the app "Check the chemistry" made by the Danish Consumer Council and the Danish EPA showed that none of the six bicycle helmets where the app was used contained substances from the candidate list in a concentration above 0.1%. In 7 other cases, where the app was used, no reply was received.

According to previous consumer tests of bicycle helmets from 2010, 2012 and 2013, phthalates have been found in small amounts in the padding as well as organic tin compounds and PAHs (polyaromatic hydrocarbons). PAHs are today restricted via REACH for plastic products in contact with the skin, and organic tin compounds are today restricted via REACH in all kinds of articles. Previous surveys have identified phthalates in small amounts – however, small amounts are more an indication of impurities than a deliberate use. It was therefore decided that the focus had to be on other problematic substances for the analyses. It was decided to focus on a possible use of flame retardants in the foam material and a possible use of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in the bicycle strap. For examination of a content of possibly other problematic substances, an element analysis/screening analysis was performed on both the bicycle strap and the foam material.

Screening analyses of 16 bicycle helmets for young children
In total 16 different bicycle helmets for young children in different brands and in different price ranges (from 90 DKK to 599 DKK) were purchased. Most of these were ('racer') bicycle helmets (10 pcs.), 5 pcs. were skater helmets and one bicycle helmet was designed as an animal head. The vast majority of the purchased bicycle helmets were produced in China (11 pcs.), 3 pcs. were produced in the EU and for the remaining 2 pcs., the country of origin was unknown.

The following screening analyses of the 16 bicycle helmets were performed:
- Element determination (SEM-EDS) on the foam material in the helmet
- Element determination (SEM-EDS) on the bicycle strap
- Fluorine determination on the bicycle strap

Among interesting results, the screening analyses showed a small content of both chlorine and phosphorus in a single bicycle helmet (C10). Bromine above the detection limit of 1000 ppm was not identified. A content of fluorine just above the detection limit of 5 ppm was identified in C6 and C10 as well as a high fluorine content of 92 ppm in C4.

Quantitative analyses
Quantitative analyses of certain chlorinated phosphorus-based flame retardants in the pad material in C10 were performed as well as of certain perfluoroalkyl and polyfluoroalkyl substances (PFASs) in bicycle straps on C4, C6 and C10. The results showed that in the pad material in C10, the flame retardants TCPP and TDCP were identified in large amounts (19,550 ppm (2%) and 7,170 ppm (0.7%) respectively) and that TIBP, TCEP and TPHP were identified in small amounts (approx. 2 ppm (0.0002%), 1 ppm (0.0001%) and 60 ppm (0.006%) respectively). A few PFASs were identified in the strap in C4 in small amounts (maximum 0.012 ppm) but no PFASs above the detection limit were identified in the straps from C6 and C10.

Migration analyses
Due to identification of chlorinated phosphorus-based flame retardants in the pad material in C10 and PFASs in the strap on C4, a migration analysis to water was subsequently performed for both the pad material in C10 and the strap on C4.

The results of the migration analyses on the pads inside the bicycle helmet showed that the same chlorinated phosphorus-based flame retardants were identified in the migration liquid as identified at the content analysis carried out on C10. TCPP and TDCP were identified in the largest amounts in the migration liquid, 440 ppm (0.044%) and 10 ppm (0.001%) respectively, for migration for 1 hour. TIBP, TCEP and TPHP were identified in small amounts in the migration liquid (approx. 0.025 ppm, 0.0140 and 0.014 ppm respectively) for 1 hour of migration).

The results of the migration analyses on the bicycle strap on C4 showed that no PFASs migrates above the detection limit of between 0.3 and 0.7 µg/kg/hour of bicycle strap dependent on the individual PFAS.

Risk assessment
Based on the results of the migration analyses, exposure calculations and a subsequent risk assessment of the following exposure scenarios were performed:
- Skin contact with the pads inside C10 for 1 hour every day.
- Skin contact with bicycle straps on C4 for 1 hour every day.
- Oral exposure (if the child sucks the strap) for the bicycle strap on C4 for 10 minutes every day. Here a shorter exposure time was applied as the part of the strap where the PFASs were identified cannot be put into the mouth during normal use of the bicycle helmet. The strap is only situated around the ears.

It must be noted that for the last two exposure scenarios for C4, the detection limit of the PFASs is applied as no migration of the PFASs above the detection limit was identified. The conclusion of the risk assessment of PFAS illustrates that there is no health risk when a child wears the bicycle helmet C4 or when a child sucks the strap of C4 each day for a long period. The total RCR-value for both dermal and oral exposure for all PFASs is well below 1 for the chemical substances investigated in this report.

The conclusion of the risk assessment is from an isolated point of view that even if flame retardants are identified inside in the pads in a single bicycle helmet (out of 16) and that these problematic substances migrate from the bicycle helmet (C10) and thus can be absorbed through the skin of the young children who wear these bicycle helmets, the amounts in question do not constitute a health risk of liver damages which is the critical effect of the flame retardant TCPP (which has the most significant risk in the risk assessment). The flame retardants do neither constitute a health risk, when the amount of the individual flame retardants with the same effects is added. However, even if the calculated RCR values are below 1 for the bicycle helmet C10 which is examined in this project, the values contribute to the total exposure of these flame retardants in different children's products which children use on a daily basis.

Looking only at the bicycle helmets, none of the investigated helmets constitutes a health problem with regard to the chemical substances investigated in this report. Moreover, it should be emphasised that it was only in two bicycle helmets out of 16 analysed helmets where either flame retardants were identified in the pads or where PFASs were identified in the strap. Most of the examined bicycle helmets investigated in this project do not contain neither the investigated chlorine phosphorus-based flame retardants nor PFASs.

1. Introduction

Today, most children use bicycle helmets and according to "the Danish Council for Traffic Safety" and the Danish foundation TrygFonden, in total 89% of the 6 to 9 age group used bicycle helmets on their way to school in 2015. The tendency has been increasing from 52% in 2004 to the 89% in 2015 (The Danish Council for Traffic Safety).

Parts of the bicycle helmet have direct skin contact with for instance the forehead and especially the strap under the chin. It can also be expected that young children put some parts of the bicycle helmet into the mouth, for instance the straps and the closing mechanism. With this project, the Danish Environmental Protection Agency wishes to obtain knowledge about substances in those parts of the bicycle helmets which have direct contact with the skin or parts which children can be expected to put into the mouth.

1.1 Purpose

The project aims to provide an overview of which materials bike helmets typically consist of and whether problematic substances are present in the parts of the bicycle helmets which have direct contact with skin or the parts which children can be expected to put into the mouth. Furthermore, the project aims to examine whether the content of the possibly problematic chemical substances in bicycle helmets can be harmful to health for children.

In this project, focus will be on the youngest children who use bicycle helmets, i.e. from the time when children start sitting in the child's seat on the bicycle as this group is regarded to be the most sensitive to chemical substances. This is partly due to the lower weight of this age group compared to the size of the body and thus a higher total exposure, and partly the fact that the body is still under development. At the same time, these young children are the group of children who have the largest tendency to put parts of the bicycle helmet into the mouth.

1.2 Delimitation

The project is delimited to focus on bicycle helmets for young children, i.e. primarily children at the age under 3 years.

According to WHO, girls in the 1 to 3 age group have cranial circumference between 42 and 51 cm and boys between 43 and 52 cm (WHO). On their home page with bicycle helmets for children, eCykelhjelm.dk writes that suggested sizes of bicycle helmets for children under 1 year are up to 48 cm, that the size for children between 1 and 2 years is 50 cm, and that the size for children between 2 and 5 years is 52 cm (eCykelhjelm.dk, 2016). This means that it is primarily bicycle helmets intended for a cranial circumference of between 42 and 52 cm which are included in this survey.

The project is exclusively limited to focus on bicycle helmets. Ski helmets which some use as bicycle helmets (for instance in the winter period) are not included in the project. Neither the new type of bicycle helmet called bicycle airbag, inflatable bicycle helmet nor invisible bicycle helmet is included in this survey. This type of bicycle helmet is in-stead worn as a collar which is only released/inflated in case of an accident. This new type of bicycle helmet has become incredibly popular in Sweden but according to the producer, it is only approved for children from 15 years and upwards as it is designed for adult movement pattern[1].

[1] http://cykelairbag.dk/; http://ecykelhjelm.dk/hovding-usynlig-cykelhjelm-airbag.html; http://www.hovding.com/faq?_ga=2.231964959.1485808113.1494403325-1433767112.1494403325;

2. Standards and legislation

In this chapter, a short description states the standards and legislation in which bicycle helmets are included.

2.1 Standards

For bicycle helmets, the following standards apply:

- DS/EN 1078 + A1:2012 ”Helmets for pedal cyclists and for users of skateboards and roller skates”
- DS/EN 1080:2013 ”Impact protection helmets for young children”

The common fact for them is that none of them deals with requirements to chemical substances but exclusively safety requirements. Therefore, the standards are not mentioned further in this survey.

2.2 Legislation regarding content of chemical substances

For bicycle helmets, the following legislation applies regarding content of chemical substances:

- Produktsikkerhedsloven (the Danish Product Safety Act based on EU Product Safety Directive)
- REACH Annex XVII: Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles (different specific chemicals)
- Danish legislation regarding heavy metals in products (Pb, Cd and Hg)
- The POP Regulation (PFOS-like substances)

REACH is an EU regulation which regulates chemical substances in compounds and articles, for instance through requirements on registration and approval. An EU regulation is directly valid in Denmark. Annex XVII of the REACH regulation is a list of restrictions for the content of chemical substances in different chemical mixtures, materials and products. Similarly, the POP regulation is European legislation which has implemented the Stockholm convention on persistent organic pollutants (POP). The Product Safety Act is a European directive regarding the safety of consumer products in general. The Product Safety Act is implemented in Denmark through “Act on product safety” (Produktsikkerhedsloven). Finally, separate Danish legislation regarding heavy metals in consumer products exists.

Phthalates are not restricted in bicycle helmets as bicycle helmets are not considered as neither toy nor articles for toddlers.

Below, the legislation is described shortly including the chemical substances which are restricted. Chemical substances which are restricted in bicycle helmets are summarised in Table 1.

2.2.1 The Product Safety Act

According to Act no. 1262 of 16.12.2009 the “product safety act”, producers are only allowed to sell products on the market if these are safe for the consumer. When assessing whether a product is safe, the composition of the product, including its chemical composition, is taken into consideration and whether the product is used under normal or reasonably foreseeable conditions of use (Act no. 1262, 2009).

There is no clear requirement concerning chemical substances in consumer products in the product safety act but with legal basis in the product safety act, the products can be withdrawn from the market if a risk assessment shows that a possible content of a hazardous substance might constitute a health risk for the consumers.

2.2.2 REACH Annex XVII restrictions

The following restrictions in the REACH regulation No. 1907/2006 are relevant for bicycle helmets:

- TRIS (No. 4) – is not allowed to be used in textiles intended to come into contact with skin
- TEPA (No. 7) – is not allowed to be used in textiles intended to come into contact with skin
- Polybrominated biphenyls (PBB) (No. 8) – are not allowed to be used in textiles
- Organic tin compounds (No. 20) – are not allowed to be used in articles
- Cadmium (No. 23) – is not allowed to be used in plastic materials
- Nickel (No. 27) – for buckles of metal, if any, in direct and prolonged contact with the skin
- Azo colourants (No. 43) – limited in textiles in contact direct and prolonged contact with skin
- Octabromo diphenylether (No. 45) – is not allowed to be used in articles
- Nonylphenol ethoxylates (No. 46a) – are not allowed to be used in textiles which reasonably can be expected to be washed in water (however, not until 3 February 2021)
- PAH (No. 50) – limited in plastic and rubber parts which come into direct as well as prolonged or short-term repetitive contact with skin or oral cavity
- DMFu (No. 61) – is not allowed to be used in articles
- Lead (No. 63) – is not allowed to be used in articles which can be placed in the mouth by children
- Decabromo diphenylether (No. 67) – is not allowed to be used in articles (however, from 2 March 2019)

2.2.3 Danish legislation regarding heavy metals

The following Danish legislation regarding heavy metals is relevant for bicycle helmets.

- Statutory order No. 856 of 5.9.2009 regarding ban on import and sale of products containing lead – applies to articles containing chemical lead (with certain exemptions), and is not valid for products regulated through other legislation
- Statutory order No. 858 of 5.9.2009 regarding ban on import, sale and production of cadmium-containing goods – applies to the use of cadmium as colour pigment, plastic inhibitor or surface treatment
- Statutory order No. 73 of 25.1.2016 regarding ban on import, sale and export of mercury-containing products – applies for all articles

2.2.4 The POP regulation

The POP regulation No. 850/2004 sets the following restrictions which are relevant for bicycle helmets:

- Tetrabromo diphenylether – is not allowed in articles
- Pentabromo diphenylether – is not allowed in articles
- Hexabromo diphenylether – is not allowed in articles
- Heptabromo diphenylether – is not allowed in articles
- PFOS and PFOS derivates – are not allowed in articles
- Hexabromo cyclododecane – is not allowed in articles (however, only valid from March 2016) and there is an excep-tion for use in EPS (expanded polystyrene) until 26 November 2019

It should be noted that it is exclusively PFOS and PFOS-like substances which are limited through the POP regulation and not the alternative polyfluoroalkyl substances e.g. with shorter chain length.

2.2.5 Overall overview of legislation regarding chemical substances

Table 1 below shows an overall overview of which chemical substances that are limited in bicycle helmets through legislation.

Table 1: Overview of legislation regarding content of chemical substances in bicycle helmets

Name of substance/ group of substance	CAS no	Legislation	Applies for	Limit value
Heavy metals				
Cadmium	7440-43-9	REACH Annex XVII, No. 23	Certain types of plastic	100 ppm
		DK-BEK 858, 2009	Plastic which is not included in REACH and as colour inhibitor	75 ppm
Nickel	7440-02-0	REACH Annex XVII, No. 27	In articles intended for prolong contact with the skin	0.2 µg/cm^2 /week (migration)
Lead	7439-92-1	REACH Annex XVII, No. 63	In articles which can be placed in the mouth (< 5 cm)	500 ppm
		DK-BEK 856, 2009	All articles	100 ppm
Mercury	7439-97-6	DK-BEK 73, 2016	All articles	100 ppm
Impregnation agents				
TRIS (Triphosphate (2,3-dibromopropyl))	126-72-7	REACH Annex XVII, No. 4	Textiles intended for contact with the skin	Not stated
TEPA (Tris(aziridinyl)phosphinoxide)	545-55-1	REACH Annex XVII, No. 7	Textiles intended for contact with the skin	Not stated
PFOS and derivates	-	POP	All articles	1000 ppm (textiles 1 µg/m^2)
Flame retardants				
PBB (Polybrominated biphenyles)	-	REACH Annex XVII, No. 8	Textiles intended for contact with the skin	Not stated
BDE's (polybrominated biphenylethers)				
tetraBDE		POP	All articles	10 ppm
pentaBDE		POP	All articles	10 ppm
hexaBDE		POP	All articles	10 ppm
heptaBDE		POP	All articles	10 ppm
octaBDE		REACH Annex XVII, No. 45	All articles	1000 ppm
decaBDE		REACH Annex XVII, No. 67	All articles, however, not until 2 March 2019	1000 ppm
HBCDD (Hexabromcyclododecan)	25637-99-4 et al..	POP	All articles	100 ppm

Organic tin compounds				
TBT and TPT		REACH Annex XVII, No. 20	All articles	1000 ppm
DBT		REACH Annex XVII, No. 20	Articles for private use	1000 ppm
DOT		REACH Annex XVII, No. 20	Textiles intended for contact with the skin	1000 ppm
Biocides				
DMFu (dimethylfumerat)		REACH Annex XVII, No. 61	All articles	0.1 ppm
Colourants				
Azo colourants	-	REACH Annex XVII, No. 43	Textiles and leather intended for contact with the skin	30 ppm (release of of carcinogenic, aromatic amines)
Other substances				
PAHs (polycyclic aromatic hydrocarbons)	8 different substances	REACH Annex XVII, No. 50	Rubber and plastic parts in contact with the skin	1 ppm
Nonylphenol ethoxylates (NPE)*	-	REACH Annex XVII, No. 46a	Textiles which are expected to be washed in water, however, not until 3 February 2021	100 ppm

* Legislation regarding NPE only applies for textiles which ”can reasonably be expected to be washed in water during their normal lifecycle”. Whether the future legislation will be applicable for bicycle helmets will depend on the design of the bicycle helmets as some bicycle helmets have detachable inside pads (mounted with Velcro) which might be taken off and washed. In other bicycle helmets, however, the pads are firmly fixed and thus cannot be expected to be washed.

3. Collection of information

In the first phase of this project, information on bicycle helmets for young children was collected. The following methods were used for the collection:

- Contact to the trade, for instance trade association and selected suppliers of bicycle helmets
- Internet search
- Shop visits
- Use of the Danish Consumer Council's and the Danish Environmental Protection Agency's app "Check the Chemistry"
- Literature search, for instance previous consumer projects from the Danish EPA and foreign tests of bicycle helmets for children

Initially, contact to the trade association and selected suppliers of bicycle helmets on the Danish market. The purpose was partly to get information about materials used in bicycle helmets, partly to get information about where bicycle helmets are produced as well as which brands of bicycle helmets for children that are available on the Danish market.

This information was supplemented with an internet search for bicycle helmets for children as well as shop visits in a few bicycle shops and large supermarkets. At the shop visits, the Danish Consumer Council's and the Danish EPA's app "Check the Chemistry" was used, when possible.

Finally, a literature search for previous studies of bicycle helmets for children was made.

3.1 Contact to the trade

3.1.1 Contact to the trade association "Danish Bicycle Dealers"

The trade association "Danish Bicycle Dealers"[2] was contacted. The "Danish Bicycle Dealers" is a trade association which according to their home page has approx. 400 bicycle and moped shops as members, including dealers of bicycle helmets.

The trade association was asked about the materials of the bicycle helmets but they referred to the Danish suppliers of bicycle helmets who are members in their association, i.e.:

- ABUS (German company with sales office in Denmark)
- Bjarne Egedesø (dealer of the American brands GIRO and BELL)
- AGU (Dutch company with sales office in Denmark)

3.1.2 Contact to suppliers of bicycle helmets

Subsequently, contact was taken to selected suppliers of bicycle helmets on the Danish market to get further information about which materials the bicycle helmets are made of and about the suppliers/dealers of bicycle helmets and brands of bicycle helmets who are available on the Danish market. The following suppliers/dealers were contacted:

- ABUS-Gruppen Nordic A/S
- Bjarne Egedesø A/S
- AGU Denmark
- C. Reinhardt as
- COOP

[2] http://www.danskecykelhandlere.dk/

- Dansk Supermarked (Danish Supermarket)

Among other things, the suppliers/dealers were asked which suppliers/dealers of bicycle helmets are available on the Danish market and besides the above suppliers/dealers, the contacted suppliers/dealers informed that the following dealers might be relevant to include in the collection of information:

- thansen
- Silvan
- Harald Nyborg
- Biltema

The contacted suppliers/dealers were generally asked about suppliers/dealers who might be relevant to contact as well as which brands that are the most dominant on the Danish market. The below brands were mentioned by the suppliers/dealers (or it could be found on their home pages). However, it ought to be mentioned that some brands do not necessarily produce bicycle helmets for children but for juniors and/or adults.

- GIRO
- BELL
- Lazer
- MET
- Limar
- ABUS
- Crazy Safety
- CSI
- Puky
- Bluegrass (but the size seems only to be size 51-55 cm and above

The general information from the contacted suppliers/dealers was that the main part of the bicycle helmets is produced in the East where China is mentioned as a specific production place by several suppliers/dealers. Only a few brands are produced in Europe (Germany is mentioned as a specific production place).

Generally, there was not much knowledge about the materials in the bicycle helmets at the contacted suppliers/dealers as in many cases they are only sales offices in Denmark. However, in some cases, the inquiry was forwarded to the main company abroad. Of the returned answers (the number is stated in brackets) regarding materials in bicycle helmets, it is seen that bicycle helmets consist of:

- Outer shell of PC (polycarbonate) (2)
- Inner shell/'skeleton' of EPS (expanded polystyrene) (2)
- Pads/foam of PES textile (polyester) outside and PU (polyurethane) foam (1) or unknown material (1) – a supplier states that pad material in the chin and inside is of the same material.
- Buckle of plastic with no further specification (1) or of the plastic type POM (1) which is a thermoplastic consisting of polyoxymethylene
- Strap of textile - nylon (1) or PES textile (polyester) (1)

From the answers (number stated in brackets) from the contacted suppliers/producers, it could furthermore be concluded that their bicycle helmets neither contain phthalates (3), fluorinated substances (2) nor other substances from the REACH candidate list (2) in concentrations above 0.1% which is the limit that applies for the obligation to provide information regarding candidate list substances in REACH.

3.2 Internet search

An internet search for bicycle helmets for children below 3 years (i.e. up to size 52 cm) was conducted. The search was for various brands and producers of bicycle helmets as well as various types of bicycle helmets, for instance skater bicycle helmets, common bicycle helmets and bicycle helmets with LED light at the back. The search was used to find examples of bicycle helmets which were to be purchased for analyses in phase 2 of the project. Examples of different bicycle helmets are listed in Table 2. At the internet search, information regarding possible materials in the bicycle helmet was noted. This information is also stated in **Fejl! Henvisningskilde ikke fundet.** and summarised in Table 3. A total overview of the identified brands of bicycle helmets is listed in Table 4.

Furthermore, an internet search for information regarding choice of material on the home pages of selected bicycle helmet producers was conducted. This search showed[3] that four helmets are produced with pads/padding of EPS foam (expanded polystyrene). Regarding the outer shell, one helmet in PS (polystyrene), two in ABS (acrylonitrile-butadiene-styrene), one in PVC (polyvinylchloride) were identified. Additionally, one inner shell in EPS (expanded polystyrene) was identified.

During the searches for bicycle helmets on the internet, the term “in-mold technique” was observed. This technique means that the outer and inner part of the bicycle helmets (outer shell and the core) are moulded together which makes the shell solid and thus the helmet stronger and lighter[4]. However, this has no influence on the choice of materials. This “in-mold technique” can be used to mould different materials together.

During the internet search, a so-called ”environmental” bicycle helmet was identified[5] in one single case. The “environmental” issue is that the inner shell is produced of reused EPS foam (expanded polystyrene) and an outer shell in ABS (acrylonitrile-butadiene-styrene) combined with PLA (PolyLactic Acid). PLA is a bioplastic, i.e. it is produced of starch from crops like for instance corn.

3.3 Visits in shops

The selection of bicycle helmets in seven different shops was studied. Three of these were special bicycle shops or shops which exclusively sell bicycle helmets. The remaining shops were supermarkets, DIY centres or shops with auto accessories/bicycles.

The purpose of the shop visits was to supplement the information from the internet search and to get a feeling of the shop personnel’s knowledge about the materials in the bicycle helmets. Furthermore, the inner side of the helmets was examined to see which materials that are in contact with the skin when the helmet is worn.

The general picture of the shop visits was that there is no knowledge about the materials in the bicycle helmets, no knowledge about ingredients (candidate list substances) and no knowledge about where the bicycle helmets are produced. The shops referred to the suppliers

[3] Links: https://nutcasehelmets.com/collections/baby-nutty/products/petal-power?variant=1265688652, (https://nutcasehelmets.com/collections/youth/products/black-zone?variant=25582449477, http://www.crazy-safety.com/index.asp?secid=333, http://www.urbanwinner.dk/om-vores-cykelhjelm, https://www.silvan.dk/rawlink-cykelhjelm-sort-m-54-58-cm?id=7400-1732201, https://www.cykelhjelm.com/shop/melon-cykelhjelm-156c1.html

[4] http://www.harald-nyborg.dk/p12176/boernehjelm-groen-s; http://www.aldi.dk/aldi_skater_cykelhjelm_til_born_48_5_5128_25864.html

[5] https://www.webike.dk/cykeltoej/cykelhjelm/kali-saha-mat-bl-cykelhjelm.html

for more information. Some bicycle helmets had the country of production printed on the helmet or the information was enclosed in the helmets. In all these cases (for approx. five helmets with this information), the production had taken place in China. However, in one of the bicycle shops, the message was that generally all bicycle helmets are produced in China and that they only had knowledge of a German brand which is produced in Germany.

3.4 Use of the app ”Check the Chemistry”

The Danish Consumer Council and the Danish Environmental Protection Agency have developed an app “Check the Chemistry” (“Tjek Kemien”) which has the purpose to send an inquiry about candidate list substances (referring to article 33 in the REACH regulation) in consumer products to the dealer/producer. The function of the app is that the bar code on the product is scanned and in this way a standard email is sent to the dealer/producer.

As far as possible, this app was used on bicycle helmets identified at the shop visits. However, it turned out that in many cases it was not possible to use the app. Among other things, this is because some of the bar codes were not recognised in the app. Furthermore, the bicycle helmets were often shown without the packaging (where the bar code was situated) which in some cases made it impossible to use the app at the shop visits.

At the shop visits, in total four inquiries were made via the “Check the Chemistry” app. Information from the producer/supplier via the “Check the Chemistry” app was received in all four cases. For all the four inquiries, the answer was that the bicycle helmet does not contain any substances from the candidate list in a concentration above 0.1%. In the only case where documentation was attached, it appeared that the test was made in February 2015. Thus, the documentation does not contain information about substances on the candidate list for the last two years.

3.5 Literature search

A literature search was made for tests or reports which describe materials or content of chemical substances in bicycle helmets.

3.5.1 Consumer test of bicycle helmets

Several consumer organisations and other institutions have tested bicycle helmets in relation to different parameters such as safety, comfort etc. There are identified three test programmes where the content of harmful substances was one of the test parameters. The test programmes and results are described below.

ADAC, the German sister club of FDM (the Motor Touring Club of Denmark), has carried out tests on bicycle helmets in 2010, 2013 and again in 2016 in co-operation with Stiftung Warentest. On a general level, the test in 2016 (ADAC, 2016) included 6 categories, including the content of harmful substances which was weighted with 5%. The included substances were PAH (polyaromatic hydrocarbons) and a number of non-specified plasticisers. Of the 19 tested bicycle helmets, 3 bicycle helmets got the worst grade “insufficient” in the category harmful substances, 1 helmet got the grade “sufficient”, 1 got the grade “satisfactory”, 5 got the grade “good”, and the remaining 10 helmets got the grade “very good”. It has not been possible to identify the detailed criteria for the marking and the specific concentrations of the ingredients but it seems primarily to be the content of PAH (polyaromatic hydrocarbons) which has contributed to the bad grades in relation to harmful ingredients.

In 2012, the Danish Consumer Council magazine ”Tænk” tested 18 bicycle helmets against 12 overall test categories, including the category “harmful chemicals” which was weighted with 5%. Within the category “harmful chemicals”, the test examined selected parts of the helmets

such as padding, chin straps and buckles for content of a number of harmful chemicals such as phthalates, PAHs (polyaromatic hydrocarbons), organic tin compounds, azo colourants and the flame retardant TCEP. 16 of the tested bicycle helmets got the best grade “very good”, and the two remaining helmets got the grade “medium” and the grade “bad” respectively.
The specific occurrences of harmful chemicals are not published in the “Tænk” magazine but in the helmet with the worst grade, phthalates were found in the padding of the chin strap in amounts which exceed the limit values for toys, i.e. above 0.1% (Tænk, 2012).

As a part of an overall test programme with several parameters, the German OEKO TEST (2013), which tests various consumer products, has in 2013 also tested 13 helmets for the following selected problematic ingredients:

- Aromatic amines (azo colourants which may release carcinogenic aromatic amines)
- Aniline
- Xylidine
- Dispersion colourants
- Optical brighteners
- Halogenated flame retardants in printed circuit boards (for helmets with LED light)
- Organic phosphorus compounds
- Phthalates
- Other plasticisers
- Phenol compounds (in solution sample of pads and chin strap – attachment pieces made of plastic)

The test of the 13 helmets showed that 3 of 13 helmets contained problematic substances in the form of phthalates (2 helmets) and organic phosphorus compounds. The phthalates (DEHP and DINP) were identified in levels of > 10,000 ppm and > 1,000 ppm respectively in the inner pads in the two helmets. Furthermore, other plasticisers (DEHT) were identified in two helmets.

In 2014, the German OEKO TEST (2014) describes in an article about bicycle helmets that the protecting pads are made of PU foam (polyurethane). However, no test for content of chemical substances is made in this OEKO test.

3.5.2 Information about materials in bicycle helmets

A few home pages were identified describing which materials bicycle helmets are made of. A description of these home pages is presented below.

The home page Design Life-Cycle[6] is an American home page where students after having studied a specific product have described the life cycle for the product in question. However, their knowledge is primarily based on the home page Helmets.org which is described below. According to this home page, American bicycle helmets consist of the following materials:

- Outer shell of PET plastic (polyethylene terephthalate)
- Inner shell of EPS foam (expanded polystyrene)
- Straps of nylon or PP (polypropylene)
- Pads can be made of EPU (expanded polyurethane), EPP (expanded polypropylene), E-PLA (expanded polylactic acid) or “cellufoam” which is a porous material with low density made of nanocellulose[7])

The American home page Helmets.org[8] is a non-profit consumer-supported organisation which gives information about helmets in general. According to their description of bicycle helmets,

[6] http://www.designlife-cycle.com/bicycle-helmets/

[7] http://www.cellutech.se/cellufoam.html

the below materials are generally used (on the American market). The home page also describes that more than the half of the bicycle helmets which are produced worldwide are produced in China or other Asiatic countries. But some helmets are still assembled in the USA and in Europe.

- Outer shell of PET (polyethylene terephthalate) or similar types of plastic but PC (polycarbonate) or ABS (acrylonitrile-butadiene-styrene) is typically used in somewhat more expensive helmets.
- Inner shell is typically made in EPS foam (expanded polystyrene) but in some helmets, the use of EPP (expanded polypropylene) or EPU (expanded polyurethane) has started instead.
- Straps are normally made of either nylon or PP (polypropylene).
- The buckle is normally of plastic (the type is not specified).
- Protective pads are normally used inside in the helmets but it is not stated which material they are made of. However, it is stated that use of antibacterial pads seems to gain ground on the expensive models of bicycle helmets. According to Helmets.org, it is primarily (nano)silver that is used but other chemical substances are also used.

In a case regarding use of their CES Selector tool (a tool for the use of materials selection), the American company Granta Design has described[9] that for bicycle helmets it is exclusively EPS (expanded polystyrene), cork or balsa wood which can be used and give satisfactorily shock-absorbing properties. It is probably the reason why EPS is the most used material for the inner shell in bicycle helmets as it is the cheapest material and has satisfactorily shock-absorbing properties.

3.6 Results of the information collection

The result of the collection of the information about bicycle helmets for young children below 3 years are given in Table 2. In total, approx. 65 different examples of bicycle helmets for children of various brands are given. This list is used as basis for the selection of bicycle helmets for the analyses in phase 2 and covers bicycle helmets identified at shop visits and via the internet search.

For most of the brands, a few different examples of bicycle helmets have been inserted as the bicycle helmets are partly in different price ranges and partly in different shapes (for instances skater helmet, designer helmets (for in-stance helmets shaped like animals) and the more common bicycle helmets (racer helmets with holes for ventilation).

A summery and analysis of the information identified through the internet search and the shop visits are described in section 3.7 “Analysis of information”.

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[8] http://www.bhsi.org/howmade.htm; http://www.helmets.org/helmet16.htm

[9] http://www.grantadesign.com/resources/materials/casestudies/helmet.htm

Table 2: Bicycle helmets for young children identified in the project

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Princess Smiley Child helmet from Abus, 45-50 cm	Abus (model Smiley)	Ecykelhjelm.dk	ABUS	Germany	289 DKK	Pink helmet with princess motif.	Unknown	
Nutcase Bumblebee Gen3 Children, 48-52 cm	Nutcase	Ecykelhjelm.dk	Nutcase	USA	489 DKK	Black and yellow striped skater helmet.	Unknown	
Spiderman Bicycle helmet Crazy Safety, 46-52 cm	Crazy Safety	Ecykelhjelm.dk	Crazy	Denmark	299 DKK	Black with spiderman 3D figure upon helmet.	Shock-padding of EPS foam (inner shell), nylon straps	
White Snoopy Scraper Kid v.2 child helmet, 51-55 cm	Abus	Ecykelhjelm.dk	ABUS	Germany	345 DKK	White skater helmet with pink Snoopy motif.	ABS shell	
Limar 242 wave bicycle helmet children w/light, 46-51 cm	Limar	Ecykelhjelm.dk	Limar	Italy	399 DKK	Blue helmet with yellow octopus and red starfishes.	Antibacterial pads. LED light with flash function.	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Giro Scamp Mips, youth extra small, 45-49 cm	Giro	Pauli Cykler	Giro	USA	549 DKK	Pink helmet with white ”giro” sticker and orange flowers. White buckle	Unknown	
Cannondale, approx. 48-51 cm	Cannondale	Pauli Cykler	Cannondale	USA	299 DKK	White helmet with green and purple small squares in random pattern.	Unknown	
Sparkling Blue Youn-I Junior helmet from ABUS, 48-54 cm	ABUS	Ecykelhjelm.dk	ABUS	Germany	389 DKK	Blue helmet with white ABUS logo, orange straps. With red LED light and reflectors on the back.	Unknown	
Maori Purple MountX Child helmet from ABUS, 48-54 cm	ABUS	Ecykelhjelm.dk	ABUS	Germany	449 DKK	Purple and black helmet with gold pattern.	Unknown	
Green tiger bicycle helmet Craxy Safety, 49-55 cm	Crazy Safety	Ecykelhjelm.dk	Crazy	Denmark	299 DKK	Green, white, yellow and black bicycle helmet designed as a tiger head. LED light in the buckle at the back of the neck. With chin cup of unknown material.	Soft pads consist of EPS foam.	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Dull blue GIRO Scamp child helmet, 45-49 cm	GIRO	Ecykelhjelm.dk	GIRO	USA	349 DKK	Blue bicycle helmet with green GIRO logo.	Unknown	
BELL Sidetrack bicycle helmet for children, mint, 47-54 cm	BELL Sidetrack	Ecykelhjelm.dk	BELL	USA	399 DKK	Mint coloured bicycle helmet with yellow/mint flower at the side.	PC shell. PinchGuard lock buckle.	
BELL Zipper Puffer children, 47-54 cm	BELL Zipper	Ecykelhjelm.dk	BELL	USA	339 DKK	Blue helmet with yellow animals on.	PC shell. PinchGuard lock buckle.	
BELL Fraction children blue, 48-53 cm	BELL Fraction	Ecykelhjelm.dk	BELL	USA	399 DKK	Blue helmet with boy on a motor cycle, American colours and stars.	Unknown	
BELL Bellino bicycle helmet, children, blue safari, 48-52 cm	BELL Bellino	Ecykelhjelm.dk	BELL	USA	399 DKK	Blue helmets with white rhinoceros.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Urbanwinner bicycle helmet with light, blue, 48-54 cm	Urban Winner	Ecykelhjelm.dk	UrbanWinner	Denmark	599 DKK	Light blue skater helmet with LED light at the back of the neck.	Unknown. Magnetic catch.	
Casco, Mini Gen-eration Racoon, 44-50 cm	Casco	Ecykelhjelm.dk	Casco	Germany. Is produced in the EU.	599 DKK	White helmet with brim. Grey stripes and drawing of a raccoon.	Unknown	
Nutcase Moo Baby Nutty, 47-50 cm	Nutcase	Ecykelhjelm.dk	Nutcase	USA	499 DKK	White skater helmet with black cow blotches.	Unknown	
Thansen Child bicycle helmet white/pink, size 48-52 cm	Unknown, own brand?	Thansen.dk	Unknown	Unknown	99.95 DKK	White helmet with pink flowers on.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Rawlink Bicycle/skater helmet, junior, 48-52 cm	Rawlink	Silvan.dk	Unknown	Unknown	159.95 DKK	Turquoise skater helmet.	Unknown	
Rawlink Bicycle helmet boy junior, 48-54 cm	Rawlink	Silvan.dk	Unknown	Unknown	129.95 DKK	Blue, white and black with body stripes.	EPS and PVC shell.	
Biltema Child helmet, size 48-52 cm	Unknown	Biltema.dk	Zhao Qing Bo Han Sports Company Ltd. Da Wang Industrial Zone	China	89.90 DKK	Black and pink, looks like a ladybird.	Unknown	
Aldi Skater-/bicycle helmet for children, size 49-54 cm	Unknown	Aldi.dk	Unknown	Unknown	149 DKK	Green and black. With detachable LED light.	Shell of PC, PU foam and inner velvet padding.	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Harald Nyborg Child helmet Green S, 48-52 cm	Busetto	Harald-nyborg.dk	Busetto, imported by City Light	Unknown	99 DKK	Green and black.	Unknown	
On Gear Skate Style Bicycle and skater helmet, matt black, 48-54 cm	On Gear	Cykelpartner.dk	On Gear	Denmark	149 DKK	Black skater helmet.	Unknown	
Lazer BOB Racer black bicycle helmet, 45-51 cm	Lazer	Cykelpartner.dk	Lazer	Belgium	199 DKK	Black skater helmet with check white racer pattern in squares.	Unknown	
Levior Primo Licens bicycle helmet with diode light red/black, 46-51 cm	Levior Primo Licens	Cykelparnter.dk	Levior Helmet-system	Unknown	299 DKK	Black and red with drawing of sabres and shark on the side. With diode light at the back.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
PUKY CH1 with LED flashing light pink, size 46-51 cm	PUKY PH1	Cykelpartner.dk	PUKY	Germany	329 DKK	Pink helmet with blue, purple and white flowers. LED flashing light at the back.	Unknown	
MET Buddy white/pink bicycle helmet with but-terflies, size 46-53 cm	MET Buddy	Cykelpartner.dk	MET	Italy	199 DKK	White/pink helmet with butterflies.	Unknown	
BELL Segment Junior bicycle and skater helmet, Blue Nitro, 48-53 cm	BELL Segment	Cykelpartner.dk	BELL	USA	299 DKK	Blue skater helmet with drawing of ex-haust pipe in flames.	Unknown	
BELL Charger Bicycle helmet, blue, 50-57 cm	BELL Charger	Cykelpartner.dk	BELL	USA	349 DKK	Blue bicycle helmet with light blue BELL label on the side.	PC shell	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
ABUS Super Chili pink, size 46-52 cm	ABUS Super Chili	Cykelpartner.dk	ABUS	Germany	339 DKK	Pink with white pattern.	Unknown	
MET Genio/Elfo blue cheetah bicycle helmet, size 46-53 cm	MET Genio	Cykelpartner.dk	MET	USA	299 DKK	Blue with drawing of a cheetah on.	Unknown	
Mango Scatter Matt black, bicycle and ski helmet, size 49-52 cm	Mango Scatter	Cykelpartner.dk	Mango Sport System	Italy	429 DKK	Completely black.	Unknown	
ABUS Hubble with LED light blue pirate, size 46-52 cm	ABUS Hubble	Cykelpartner.dk	ABUS	Germany	439 DKK	Blue with pirate motif.	Unknown	
GIRO Rascal child bicycle helmet, pink leopard, size 46-50 cm	GIRO Rascal	Cykelpartner.dk	GIRO	USA	279 DKK	Pink with pattern. With LED rear lamp.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Mango Piuma PI-W161 white with print, size 45-48 cm	Mango Piuma	Cykelpartner.dk	Mango Sport System	Italy	459 DKK	White skater helmet with print.	Unknown	
Nutcase Little Nutty Gen3 – Watermelon, size XS 48-52 cm	Nutcase, Little Nutty	Cykelpartner.dk	Nutcase	USA	499 DKK	Green skater helmet which looks like a watermelon.	Unknown	
CSI Bicycle helmet for children, Blue dots, 44-50 cm	CSI	Bilka	CSI, Cycling Supply International (produced in China)	Denmark	189 DKK	Dark blue with dots in white, light blue and green.	Unknown	
CSI Bicycle helmet skater kids, mint, 48-53 cm	CSI	Bilka	CSI, Cycling Supply International (produced in China)	Denmark	299 DKK	Mint skater helmet with pink stripe.	Unknown	
Disney Frost bicycle helmet size XS, 46-53 cm	Disney	Bilka	Stamp, SGS UK (produced in China)	UK	199 DKK	White bicycle helmet with the Frost girls in light blue/pink colours.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Melon "Pure collection" Greeneon, XXS-S, 46-52 cm	Melon	Cykelexperten	Melon Helmets	Germany	549 DKK	Green skater helmet.	Outer shell of PC. The pads of hygienic Coolmax material (soft foam). EPS inner shell. Plastic print on pads inside.	
Scott Sports bicycle helmet, 46-52 cm	Scott	Cykelexperten	Scott-Sports	USA	449 DKK	Blue bicycle helmet with pink and purple stripe. With LED light at the back.	Unknown	
ABUS Smiley 2.0 Helmet, Turquoise Sailor, 45-50 cm	ABUS	Cykelexperten	ABUS	Germany	339 DKK	Light blue bicycle helmets with sailing motifs (anchor, life ring).	Unknown	
Bontrager Solstice MIPS Child helmets, 48-55 cm	Bontrager	Fri Bike Shop	Bontrager	USA	649 DKK	Pink bicycle helmet with pink pattern.	Unknown	
Innergy bicycle helmet Esther, S, 48-54 cm	Innergy	Fri Bike Shop	Innergy	Denmark	299 DKK	White bicycle helmet with multicoloured stars. With LED light at the back.	EPS material. Magnetic buckle.	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Lazer Nut'z Light Blue Mips, 50-56 cm	Lazer	Cykelhjelm.com	Lazer	Belgium	399 DKK	Blue bicycle helmet.	Unknown	
Casco Fun Generation Urban White Mat, 50-55 cm	Casco	Cykelhjelm.com	Casco	Germany	599 DKK	White skater bicycle helmet with pink stripe and Casco logo.	Unknown	
Alpina Carapax Flash helmet pink, 51-55 cm	Alpina	Bikester.com	Alpina	Italy	569 DKK	Pink helmet with white brim.	PC outer shell and EPS inner shell.	
Appina Ximo Flash helmet blue, 47-51 cm	Alpina	Bikester.com	Alpina	Italy	339 DKK	Blue helmet with red car on.	PC outer shell and EPS inner shell.	
Axant Rider Boy Helmet green, 48-55 cm	Axant	Bikester.com	Axant	Germany	189 DKK	Black and green helmet with brim.	EPS foam	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Bern Nina helmet incl. flip visor, white/colourful, 48-51,5 cm	Bern	Bikester.com	Bern Unlimited	USA	339 DKK	White skater helmet with hat brim and colourful flowers.	PC outer shell	
Cube Skull helmet black, 48-52 cm	Cube	Bikester.com	Cube	Germany	109 DKK	Black helmet with skull on.	EPS foam	
C-Preme Raskullz Kitty Tiara helmet pink, 50-54 cm	C-Preme	Bikester.com	C-Preme Limited LLC	USA	229 DKK	Pink helmet with cat's eyes and tiara.	EPS	
Kali Chakra Helmet violet, 48-54 cm	Kali	Bikester.com	Kali Protectives	USA	259 DKK	Violet helmet with mermaids and starfishes on.	Outer shell of PC, inner shell of EPS.	
KED Meggy Trend helmet green/turquoise, 44-49 cm	KED	Bikester.com	KED Germany	Germany	259 DKK	Green and blue helmet, looks like an animal. LED at the back.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
O'Neal Dirt Lid Helmet Rainbow black, 47-48 cm	O'Neal	Bikester.com	O'Neal	USA?	299 DKK	Black skater helmet with rainbow colours on.	100% ABS	
POC POCito Crane Helmet Orange, 51-54 cm	POC	Bikester.com	POC Sports	Sweden	769 DKK	Orange skater helmet.	EPS	
UVEX kid 2 helmet green/white, 46-52 cm	UVEX	Bikester.com	UVEX	Germany	229 DKK	White helmet with grass and sheep.	EPS foam	
Polisport Red bicycle helmet with racer motif, XS, 46-53 cm	Polisport	COOP.dk	Polisport	Portugal	199.95 DKK	Red helmet with racer motif (black/white check pattern).	EPS outer shell.	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Limar bicycle helmet for children, black with yellow flames, S, 46-51 cm	Limar	COOP.dk	Limar	Italy	349.95 DKK	Black bicycle helmet with yellow/orange flames. LED light at the back.	Outer shell of PC and inner shell of EPS foam.	
Mustang bicycle helmet for children – blue with dinosaurs, XS, 45-51 cm	Mustang	COOP.dk	Mustang	Switzerland	149.95 DKK	Green helmet with dinosaurs on.	Outer shell of PC and inner shell of EPS foam.	
Mustang skater helmet for children, matt turquoise, S, 48-52 cm	Mustang	COOP.dk	Mustang	Switzerland	199.95 DKK	Turquoise skater helmet.	Outer shell of PC and inner shell of EPS foam.	
Specialized Mio Pink, child bicycle helmet for the youngest, 44-52 cm	Specialized	Webike.dk	Specialized	USA?	329 DKK	Pink, with white, green and pink pattern/figures.	Unknown	
Specialized Covert Kids Hyper Crackle, 47-53 cm	Specialized	Webike.dk	Specialized	USA?	239 DKK	Black skater helmet with yellow and grey cracks.	Unknown	

Product name	Brand	Dealer	Name of producer	Head office of producer – country*	Price	Appearance	Materials	Pictures
Kiddimoto helmet multi-dotted, 48-52 cm	Kiddimoto	Br.dk	Kiddimoto	UK	349 DKK	White skater helmet with different coloured dots.	Outer shell of ABS plastic.	

* ”Head office of producer – country” indicates the country in which the headquarters of the producer is situated. The production does not necessarily take place in the same country. Next to some country names a question mark is written. The question mark means that it was not possible to identify the country of the headquarters of the producer, but it is assumed to be the country listed (based on information on their web site).

3.7 Analysis of information

In this section, various information from the collection of information is gathered, processed and summarised. The following is examined:

- Identified prices of bicycle helmets
- Identified materials used in bicycle helmets
- Identified producers and brands of bicycle helmets
- Which materials are in contact with the skin when the cyclists wear bicycle helmets

3.7.1 Prices of bicycle helmets

The prices of the identified bicycle helmets for children are between 89.90 DKK for a bicycle helmet in Biltema to 769 DKK for a bicycle helmet of the brand POC (found in a web shop). During the shop visits, prices of bicycle helmets up to 1,999 DKK were observed but these were for adults and seemed to be for more professional sportsmen.

3.7.2 Materials

According to the search on the internet and the shop visits, the collection of information about bicycle helmets shows that the helmets consist of the following parts:

- Outer shell
- Inner shell
- Protective pads which are typically built-up in two different ways:
    - Foam material which is fully encircled by a layer of textile (a pocket of textile)
    - Foam material with a thin layer of textile at the top (towards the user)
- Potential plastic strap inside which has the purpose to create a better fit as it can be tightened/opened by turning a wheel rearmost in the helmet
- Strap
- Chin buckle (in different designs)
- Potential chin pad (probably of the same material as the pads on the inside of the helmet)
- Potential LED lamp at the back of the helmet
- Potential reflectors at the back of the helmet

These parts are made of different materials as described in **Fejl! Henvisningskilde ikke fundet.** below. It should be noted that information about the materials do not solely come from the helmets which are included in **Fejl! Henvisningskilde ikke fundet.** but also include information about helmets for older children (above 3 years) even if they are not shown as examples in Table 2.

An observation of various home pages with specification of the materials is that the outer shell of the skater helmets seems to be made of ABS (acrylonitrile-butadiene-styrene) whereas the more common bicycle helmets (sports bicycle helmets) are made of PC (polycarbonate). However, exceptions were also found.

A literature search on the home pages[10] of the bicycle helmet producers has identified four helmets with pads/padding of EPS foam (expanded polystyrene), and for the outer shell, one helmet in PS (polystyrene), two in ABS (acrylonitrile-butadiene-styrene) and one in PVC (polyvinyl chloride) were identified. Furthermore, an inner shell of EPS (expanded polystyrene) was identified. Other information from the literature search shows that the foam material is PU (polyurethane) foam (Oeko-Test, 2014).

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[10] Links: https://nutcasehelmets.com/collections/baby-nutty/products/petal-power?variant=1265688652, https://nutcasehelmets.com/collections/youth/products/black-zone?variant=25582449477, http://www.crazy-safety.com/index.asp?secid=333, http://www.urbanwinner.dk/om-vores-cykelhjelm/

Table 3: Overview of materials in bicycle helmets for children at the age below 3 years based on information from web shops (the number of home pages with the mentioned material is stated in brackets)

Part of the bicycle helmet	Materials	Comments
Outer shell	ABS-shell (5) Polycarbonate shell (13) PVC (1) PS (1) EPS (1)	LED light at the back (8) PS shell is seen on a bicycle helmet for older children or adults and therefore it is not included in **Fejl! Henvisningskilde ikke fundet.**
Inner shell	EPS (17)	
Pads/paddings and possible chin pad	EPS foam (1) PU foam (1) Antibacterial pads (1)	EPS is a hard material and it is possibly an error that it is stated as used in pads. PU foam with velvet padding. The applied biocide is not stated
Plastic strap inside	Hard plastic of unknown material	
Strap	Nylon (1)	
Chin buckle	Hard plastic of unknown material	Magnetic catch (2) or click buckle of plastic

The information from the contacted suppliers (2) shows that the outer shell is made of PC (polycarbonate) (2), the inner shell is made of EPS (expanded polystyrene) (2), the strap of nylon (1) or PES (polyester) (2), and the protective pads can consist of an outside polyester textile layer with PU (polyurethane) and with foam inside (1). The plastic buckle is made of the thermoplastic type POM (polyoxymethylene) (1).

A more general literature search shows that bicycle helmets are typically made in the following materials:

- Outer shell of PET (polyethylene terephthalate) or similar types of plastic but PC (polycarbonate) or ABS (acrylonitrile-butadiene-styrene) is typically used in somewhat more expensive helmets
- Inner shell is typically made of EPS foam (expanded polystyrene) but in some helmets, the use of EPP (expanded polypropylene) or EPU (expanded polyurethane) has been initiated instead
- Straps are normally made of either nylon or PP (polypropylene)
- The buckle is normally made of plastic (the type is not specified)
- Protective pads are normally used inside the helmet but the material in question is not stated

The information on typical material use can be summarized as:

- Outer shell – primarily PC (polycarbonate) and then ABS (acrylonitrile-butadiene-styrene) but it is also observed in PVC (polyvinylchloride), PS (polystyrene), EPS (expanded polystyrene) etc.
- Inner shell – to a great extent of EPS (expanded polystyrene)
- Straps – in nylon, PES (polyester) or PP (polypropylene)
- Buckle – normally in hard plastic (unknown material) – in one single case it is stated to be of the plastic type POM (polyoxymethylene)
- Protective pads – not much information but they seem to be made of PU foam (polyurethane) either with a textile layer PES (polyester) or fully encircled by a layer of textile (a pocket of textile)

3.7.3 Producers and brands

According to the search on the internet and the shop visits, the collection of the information about bicycle helmets shows that the following 39 brands and producers of bicycle helmets have been identified. These are presented in the table below.

Table 4: Overview of identified producers and brands of bicycle helmets

Brands	Name of producer	Head office of producer – country	Produced in
ABUS	ABUS	Germany	
Alpina	Alpina	Italy	Italy
Axant	Axant	Germany	
BELL	BELL	USA	China
Bern	Bern Unlimited	USA	
Biltema	Zhao Qing Bo Han Sports Company Ltd	China	China
Bontrager	Bontrager	USA	
Busetto (Harald Ny-borg)			
Cannondale	Cannondale	USA	
Casco	Casco	Germany	EU
C-Preme	C-Preme Limited LLC	USA	
Crazy Safety	Crazy	Denmark	China
CSI	CSI (Cycling Supply Interna-tional)	Denmark (part of ABUS, is behind Crazy Safety)	China
Cube	Cube	Germany	
GIRO	GIRO	USA	China
Innergy	Innergy	Denmark	
Kali	Kali Protectives	USA	
KED	KED Germany	Germany	Germany
Kiddimoto	Kiddimoto	UK	
Lazer	Lazer	Belgium	China
Levior	Levior Helmetsystem	Germany	Germany
Limar	Limar	Italy	China
Mango	Mango Sport System	Italy	Italy
Melon	Melon Helmets	Germany	China
MET	MET	Italy	China
Mustang	Mustang	Switzerland	
Nutcase	Nutcase	USA	China
O'neal	O'neal	USA?	
On Gear	On Gear	Denmark	
Outtrek (Thansen)	Outtrek		China
Polisport	Polisport	Portugal	
POC	POC Sports	Sweden	
PUKY	PUKY	Germany	Germany
Rawlink (Silvan)			
Scott	Scott-Sports	USA	
Specialized	Specialized	USA?	

Brands	Name of producer	Head office of producer – country	Produced in
Stamp	Stamp	France	China
Urbanwinner	UrbanWinner	Denmark	
UVEX	UVEX	Germany	Europe, mainly Germany

Empty fields mean that the identification of the producer, producer country and/or place of production has failed.

3.7.4 Materials in contact with the skin

In connection with the shop visits, the inner side of the bicycle helmets were closely examined to identify the materials which are in contact with the skin when the consumers (in this report, children) wear the bicycle helmet. On some home pages, photos of the inner side of the bicycle helmets could be examined as well.

3.7.4.1 The inner side of the bicycle helmet

The inner side appearance of the various brands of bicycle helmets is very different and the type of the used pad material as well. However, common to all helmets is that the consumer is not in contact with neither outer shell nor inner shell but only with the pad material. Some bicycle helmets might have a piece of plastic around the inner shell which is covered with pad material almost the whole way around but in some cases, direct contact with plastic, typically in the back of the head, might occur where the helmet (the plastic material) can be tightened by turning a button. However, it is relatively hard plastic which means that the probability of use of plasticisers here is very small.

Typically, the pad material is a layer of foam covered with a thin layer of textile. In many cases, the pad material, however, consists of a sewed "pocket" of textile filled with unknown "cotton-like" material. Often the pad material is fastened to the inner side of the helmet by use of Velcro but the consumers have solely skin contact with the textile pad.

The information from one of the bicycle shops was that more and more of the brands start to produce pads consisting of a textile pocket with padding. This is a question of quality as a layer of foam covered with a thin layer of textile can quickly fray at the edge. According to one of the bicycle helmet shops, only a few bicycle helmets use pads of foam material covered with a thin layer of textile today (see picture of white/pink bicycle helmet in fact box). Different types of bicycle helmets are shown in the fact box on the next page.

The inner side of different bicycle helmets

Bicycle helmets with foam material covered with a thin layer of textile (white helmet, white foam material with pink textile and black helmet with black foam material with black textile)

Bicycle helmets with a ”pocket” of textile filled with ”cotton-like” unknown foam material. Some bicycle helmets have padding material all around the head while some only have in the top, at the side and in the front (see red lining).

Some bicycle helmets contain pads with plastic print (helmet with “melon” print below)

3.7.4.2 Straps and buckle

When the bicycle helmet is tightened, there will be skin contact with the strap at the ears/cheeks and under the chin for all bicycle helmets. Furthermore, there will be contact with the buckle (made of hard plastic) unless, in some cases, this buckle is hidden behind a chin pad of the same type of material like the pad material inside the helmet.

3.7.4.3 Conclusion of materials in contact with the skin

Therefore, the material types in contact with the skin are:

- Textile (upon or around the foam material) in the inner side of the helmet or at a possible chin pad. Largest and direct skin contact is in the forehead. At the top of the head and in the sides, the user's hair is typically between the bicycle helmet and the skin. There might be skin contact with textile on bicycle helmets which have chin pads in front of the buckle.
- Straps of textile have contact with the skin under the ears, at the cheeks and under the chin.
- Plastic buckles under the chin (if no chin pad is used) or possible plastic holders to collect the straps at the ears.

As described in Table 1 in the section about standards and legislation (see chapter 2), a number of limitations for chemical substances are restricted by legislation. These limitations also apply to textiles used in bicycle helmets due to the skin contact with the textiles in the pad material inside the bicycle helmets. Even if these substances (for instance azo colourants) have been identified in previous tests of bicycle helmets, they are restricted by legislation and thus not relevant to examine in detail in this project as it is not a control project.

During the information collection, a single brand of bicycle helmet with plastic print on top of the pad material was seen. This plastic print might contain phthalates but the use of plastic print on the pad material is not common according to the survey carried out in this project. Furthermore, during the information collection, one single bicycle helmet was identified where it was stated that the pad material was "antibacterial treated". The chemical substance in question used for the antibacterial treatment is not known but the impression from the information collection is that this is not a common phenomenon. Thus, it is considered to be irrelevant to examine the textile for the content of these chemical substances.

Certain fluorinated compounds are applied for impregnation of textile, i.e. to make textile or straps dirt- and water/sweat-repelling. However, only PFOS or PFOS-like compounds are restricted by legislation – other applied fluorinated compounds like perfluoroalkyl and polyfluoroalkyl substances (PFASs) are not. Therefore, it was decided to examine the straps in the bicycle helmets for the content of fluorine to get an indication of a possible use of PFASs, although two dealers of bicycle helmets gave information that fluorinated compounds are not applied in their bicycle helmets.

According to a former survey, the foam material has turned out to contain phthalates in small amounts (described as > 1% and > 0,1% respectively) in some cases (2 out of 13 bicycle helmets). These results indicate that they are impurities and not phthalates which are added to get a softening function. Therefore, it is considered to be irrelevant to analyse the foam material for content of phthalates in this project.

In previous survey projects[11] from the Danish Environmental Protection Agency, foam material has turned out to contain flame retardants – primarily Cl/P-based flame retardants. Therefore, it was decided to examine whether the foam material in bicycle helmets for young children might also contain flame retardants.

It is considered irrelevant to examine the content of chemical substances in the buckle which is made of hard plastic in nearly all cases. It is not expected that these buckles contain problematic chemical substances which can migrate in amounts that might constitute a risk for the user's health. In the meantime, undesirable substances like PAH (polyaromatic hydrocarbons), which have been identified in previous tests of bicycle helmets, have been restricted in plastic and rubber parts which come into direct long or repeated short contact with skin.

[11] Kortlægning nr. 135 "Kemiske stoffer i autostole og andre produkter med tekstil til børn", 2015 (http://mst.dk/service/publikationer/publikationsarkiv/2015/apr/kemiske-stoffer-i-autostole/). Kortlægning nr. 126 "Kortlægning, sundheds- og miljøvurdering af flammehæmmere i tekstiler", 2014 (http://mst.dk/service/publikationer/publikationsarkiv/2014/mar/kortlaegning,-sundheds--og-miljoevurdering-af-flammehaemmere-i-tekstiler/).

4. Selection of products for analysis

Based on the information gathered through the information collection in this project, it was decided to carry out the following analyses of 16 different bicycle helmets for children:

- Determination of fluorine on the straps to get an indication of a possible use of perfluoroalkyl and polyfluoroalkyl substances (PFAS) (for impregnation of the straps).
- Screening analyses (analyses of elements) of both straps and foam material (not the textile in the pad material) to get an indication of possible use of flame retardants.
- Potential quantitative analyses of selected flame retardants if the screening analyses show an increased content of for instance chlorine, phosphorus or bromine.

It was not possible within the allocated budget to investigate both strap and textile in the padding material inside the bicycle helmet. The focus was therefore on the bicycle strap for several reasons:

- PFAS chemicals are relatively expensive chemicals and are therefore presumably used in more expensive products.
- The bicycle strap has direct contact with the skin for a large part of the strap, whereas the pads inside the helmet often do not have direct contact with the skin (hair will be in between) – except for the forehead.
- A young child may be further exposed by chewing/sucking on the bicycle strap. This is not considered to be possible for the pads, which are situated inside the helmet.

4.1 Purchase of products for analysis

For the above-mentioned analyses, in total 16 different bicycle helmets for children were purchased, based on the following guidelines (in prioritised order):

1. Bicycle helmets in various brands are purchased.
2. Bicycle helmets with different types of pad material are purchased – however, it seems that most bicycle helmets today are with textile “pockets” with padding. The aim is to purchase several different types (appearance) of pad material.
3. Bicycle helmets in different price ranges are purchased (the cheap bicycle helmets below DKK 200, the expensive bicycle helmets from approx. DKK 400 and up as well as bicycle helmets in the intermediate price range). However, most bicycle helmets in the cheapest price range and the intermediate price range are bought.
4. Bicycle helmets of various types (skater helmets, common bicycle helmets, special bicycle helmets designed as animals) are bought.

Regarding item 1 on purchase of different brands, it must be noted that the list of the most common brands, which suppliers of bicycle helmets gave (see section 3.1.2 “Contact to suppliers of bicycle helmets”), as well as the most used brands and models found on different home pages through the internet search were taken into consideration.

The purchased 16 bicycle helmets for children are distributed as described below in Table 5. All the purchased models are in the sizes starting with 44-49 cm in head size, i.e. for the quite young children from 0-3 years. Some helmets have sizes up to 52-55 cm, i.e. some helmet can also be used by children above 3 years.

Table 5: Overview of the 16 bicycle helmets purchased for analysis

Brands	Price	Produced in	Type of helmet	Type of pad material
16 various brands were purchased	Cheapest: 90 DKK Most expensive: 599 DKK Average: 320 DKK < 200 DKK: 5 pcs. 200 - 400 DKK: 7 pcs. > 400 DKK.: 4 pcs.	China: 11 pcs. Germany: 1 pc. Italy: 1 pc. EU: 1 pc. Unknown: 2 pcs.	Common: 10 pcs. Skater: 5 pcs. Special: 1 pc.	Foam material with top layer of textile: 5 pcs. Textile pocket with foam padding: 11 pcs.

4.2 Use of the app ”Check the Chemistry”

The Danish Consumer Council’s and the Danish Environmental Protection Agency’s app “Check the chemistry” was used on all the 16 bicycle helmets purchased for analyses. For 7 bicycle helmets, the result was that the app could not be used because the bar code could not be recognised. For the 9 bicycle helmets where an inquiry on candidate list substances was sent, in total 2 answers were returned stating that the bicycle helmets do not contain candidate list substances in concentrations above 0.1%. For the remaining 7 bicycle helmets, no information was received about content of candidate list substances within the deadline of the 45 days.

5. Screening analyses

First screening analyses were performed in the form of SEM-EDS (Scanning Electron Microscope – Energy Dispersive x-ray Spectroscopy) for determination of certain elements, partly in the foam in the pad material inside in the bicycle helmet, partly in the straps. Furthermore, the content of fluorine in the straps was determined by means of a calorimeter bomb method to reach a lower detection limit than by SEM-EDS.

5.1 Analysis methods

Analysis methods for SEM-EDS (determination of elements) and determination of fluorine are described in detail below. These analyses were performed by FORCE Technology.

5.1.1 SEM-EDS

The surface of the selected samples (both straps and foam from the pads in the bicycle helmets) was screened for content of elements in Scanning Electron Microscope (SEM). The selected areas were analysed by use of Energy Dispersive x-ray Spectroscopy (EDS) which can determine elements with atom number higher than 5.

The detection limit of elements analysed by SEM-EDS depends on among other things the homogeneity and other element composition of the sample material. In general, the detection limit is typically approx. 0.1%.

The uncertainty of measurements also depends on a number of parameters where the most important issue is the concentration of the element. Typical relative uncertainties for this semi-quantitative analysis method are:

- 2-3% for content of elements from 20-100%
- 4-6% for content of elements from 5-20%
- 10-20% for content of elements from 1-5%
- 50-100% for content of elements from 0.1-1%

5.1.2 Determination of fluorine

A representative partial sample of the straps (approx. 1 g) was burnt in a calorimeter bomb with 30 atmospheric oxygen. At the oxidation, the contained fluorine compounds are transformed to hydrogen fluorine which is absorbed in the calorimeter bomb solution. The liquid collected was analysed for fluorine by ion chromatography. The content of fluorine was determined by use of calibration curve.

The analysis was conducted as real duplicate determination.

The detection limit of the applied method is 5 mg/kg (5 ppm). The uncertainty of the analysis is approx. 20-30%.

5.2 Analysis results

The analysis results for the determination of elements and the determination of fluorine are stated below.

5.2.1 Analysis results – determination of elements (SEM-EDS)

The analysis results for the determination of elements (SEM-EDS) are stated in Table 6 and Table 7 below. Table 6 contains determination of elements for straps and Table 7 contains results of the determination of elements for the padding/foam material in the pads inside in the bicycle helmets.

In general, for the straps, the selected material is the material with the largest amount contained in the bicycle helmet or the material with the largest contact with the skin (i.e. primarily at the cheeks). One single bicycle helmet had two types of strap material. In this case, the material with the largest amount was analysed, i.e. the part of the strap which goes from the helmet, around the ears and down along the cheeks where it is gathered in one different type of strap under the chin.

In general, regarding the pad material, the selected foam material is the material with contact to the forehead. In the few cases, where this was impossible or the pad material was thinner here, foam material was taken from the pads in the top of the bicycle helmet.

It should be noted that only results for the elements which are identified above the detection limit of 0.1% are stated. From the results, it can be seen that no content of bromine has been identified in any of the samples, i.e. a possible content of bromine will be found in concentrations below 0.1% which indicates no use of brominated flame retardants.

Table 6: Analysis results – Determination of elements (SEM-EDS) in the strap on the purchased bicycle helmets

	Content of element in %								
Strap on bicycle helmet	**Carbon**	**Nitrogen**	**Oxygen**	**Aluminium**	**Silicon**	**Calcium**	**Sulphur**	**Titanium**	**Sum**
C1	64.33		35.67						100.00
C2	89.98		9.84					0.18	100.00
C3	63.73		35.92	0.11				0.24	100.00
C4	69.70	9.62	19.76		0.81		0.11		100.00
C5	72.51	9.40	17.95				0.14		100.00
C6	64.29		35.71						100.00
C7	64.68		35.14					0.18	100.00
C8	74.78		25.04					0.18	100.00
C9	67.88	11.09	21.03						100.00
C10	90.22		9.17			0.17		0.44	100.00
C11	64.54		35.46						100.00
C12	89.74		10.26						100.00
C13	85.25		14.75						100.00
C14	69.59	10.80	19.48				0.13		100.00
C15	91.68		8.32						100.00
C16	92.89		7.11						100.00

Table 7. Analysis results – Determination of elements (SEM-EDS) in the padding/foam material inside the purchased bicycle helmets

	Content of elements in %											
Foam in pad in bicycle helmet	**Carbon**	**Nitrogen**	**Oxygen**	**Aluminium**	**Silicon**	**Calcium**	**Sulphur**	**Phosphorus**	**Chlorine**	**Barium**	**Magnesium**	**Sum***
C1	69.29	5.49	25.05		0.17							100.00
C2	68.95	5.33	25.58		0.14							100.00
C3	61.93	4.20	33.88									100.01
C4	61.19	5.41	33.22	0.17								99.99
C5	70.62		28.58	0.11	0.13	0.38					0.17	99.99
C6	69.05	5.55	24.68		0.22	0.50						100.00
C7	67.23	5.05	26.81	0.11	0.23	0.57						100.00
C8	68.33	5.15	25.56		0.22	0.16	0.14			0.44		100.00
C9	64.55	5.78	29.20	0.20	0.16	0.11						100.00
C10	66.57	3.14	29.22		0.19			0.29	0.60			100.01
C11	60.83	5.57	33.60									100.00
C12	67.20	3.85	28.95									100.00
C13	67.38	5.97	26.52		0.13							100.00
C14	69.40	4.48	25.15	0.35	0.18	0.44						100.00
C15	67.29	5.92	26.03	0.18	0.38	0.20						100.00
C16	62.72	4.87	32.41									100.00

* A sum higher or smaller than 100 is due to round-off.

5.2.2 Analysis results – Determination of fluorine

The analysis results for the determination of fluorine of the straps are stated in Table 8 below. The analysis results are stated as the average of the two results from the duplicate determination.

Table 8: Analysis results for determination of fluorine

Bicycle helmet	Content of fluorine in straps mg F/kg strap (ppm)
C1	< 5
C2	5
C3	< 5
C4	92
C5	< 5
C6	6.3
C7	< 5
C8	< 5
C9	< 5
C10	7.7
C11	< 5
C12	< 5
C13	< 5
C14	< 5
C15	< 5
C16	< 5

5.2.3 Discussion of analysis results

From the results in both Table 6 and Table 7, it is seen that more than 99% of the elements in both straps and pad material consist of the elements carbon (C), oxygen (O) and nitrogen (N). In section 3.5.2 "Information about materials in bicycle helmets", it is stated that straps typically consist of nylon (contains C, O and N) or PP (polypropylene) (contains only C and O, but not N) and that pad material typically consists of PU foam (polyurethane) (contains C, O and N) or EPP (expanded polypropylene) (contains C and O). Based on this information, the screening results together with visual observations could thus indicate that 4 out of 16 straps are of nylon and the remaining of PP (polypropylene) whereas 15 out of 16 helmets probably have pad material which consists of PU foam (polyurethane) and one single bicycle helmet has foam material consisting of for instance EPP (expanded polypropylene). However, other analyses which have not been carried out in this project must be performed to confirm the material composition in the purchased bicycle helmets.

As described, no content of bromine above the detection limit of 0.1% was identified in any of the samples. According to Janssen (2005), a content of brominated flame retardants in flame retarded products will typically be between 5-30% and other sources state that concentration of brominated flame retardants in plastic is typically in concentrations between 0.1-28%. This means that concentrations of bromine under 0.1% does not indicate use of brominated flame retardants.

Chlorine and phosphorus were only identified in amounts above 0.1% in one product (C10). It concerns relatively small amounts of 0.6 and 0.29% respectively. In a previous survey report from the Danish EPA (Nørgaard Andersen et al., 2014), a content of both chlorine and phosphorus at the screening is identified as a content of the flame retardants TDCP and TCPP in foam material in furniture. Therefore, the identified content of chlorine and phosphorus respectively might indicate a content of chlorinated phosphorus-based flame retardants such as TDCP and/or TCPP in bicycle helmet C10. For that reason, bicycle helmet C10 was selected for quantitative analysis for a content of chlorinated phosphorus-based flame retardants. The result of the quantitative analysis is stated in chapter 6.

The results of the fluorine determination in the straps show that fluorine was identified in four of the bicycle helmets (C2, C4, C6 and C10). However, concerning C2, the duplicate determination only identified a content of fluorine above the detection limit in one of the two samples. The results of the two samples are thus 5.2 ppm fluorine and < 5 ppm respectively. The content of fluorine in C6 and C10 is just above the detection limit with 6.3 and 7.7 ppm fluorine respectively whereas the value of the content of fluorine in C4 is somewhat higher at 92 ppm. The content of fluorine in C4 (and possibly C6 and C10) could thus indicate a content of potential polyfluoroalkyl substances (PFASs) whereas the content of fluorine is so low in the other products that they either contain no fluorinated compounds or have a very low content of potential PFASs.

Regarding other elements, small amounts of aluminium (Al), silicon (Si), calcium (Ca), sulphur (S) and titan (Ti) were identified in the straps. Identification of titanium is most likely due to use of titanium dioxide (white colourant) whereas identification of the other elements might be due to use of filler, such as for instance aluminium oxide, calcium carbonate and silicon oxide. However, other analyses, not carried out in this project, must be made to confirm the type of potential fillers.

In the foam material, aluminium (Al), silicon (Si), calcium (Ca), sulphur (S), barium (Ba) and magnesium (Mg) were also identified in small amounts. Here the finding is probably also due to use of fillers, such as aluminium oxide, calcium carbonate, silicon oxide and barium sulphate or possible use of (residues of) the flame retardant aluminium hydroxide. However, other analyses, not carried out in this project, must be made to confirm the type of various other potential substances.

However, common to these elements is that they are identified in small amounts (< 1%).

6. Quantitative analyses

A quantitative analysis of the foam material in the pads in bicycle helmet C10 was performed to examine whether the identified content of chlorine and phosphorus is due to a content of chlorinated phosphorus-based flame retardants. Furthermore, quantitative content analyses in the straps of C4, C6 and C10 for content of PFASs were performed.

6.1 Analysis methods

Analysis methods for quantification of chlorinated phosphorus-based flame retardants in the pad material and quantification of PFASs in bicycle helmet straps are described further below. These analyses were performed by Eurofins.

6.1.1 Quantitative analysis of chlorinated phosphorus-based flame retardants

Quantitative analysis of chlorinated phosphorus-based flame retardants on bicycle helmet C10 was undertaken at Eurofins (Eurofins, Germany). The specific chlorinated phosphorus-based flame retardants which were a part of the analyses are listed in Table 9.

As the foam material weighs very little in a bicycle helmet in relation to the sample amount which is needed for the analysis, an extra identical bicycle helmet (with the same batch number and production date) was purchased for the use of the duplicate determination. The bicycle helmet which was used for screening analyses is named C10A and the identical new bicycle helmet is named C10B. Thus, quantitative analysis of chlorinated phosphorus-based flame retardants is made on the foam material in the two identical bicycle helmets C10A and C10B. The results are stated in Table 9.

The quantitative analysis of chlorinated phosphorus-based flame retardants was carried out in the following way: The sample was added quantification standards and prepared by ultrasonic extraction with ethyl acetate. The extract was evaporated, cleaned-up by column chromatography and recovery standards were added. The measurements were performed by gas chromatography with mass selective detection (GC/MS/MS-EI) on a 60-meter column. The quantification was performed by the method of isotope dilution/method of internal standard using 5 isotope-labelled standards.

6.1.2 Quantitative analysis of PFASs

Quantitative analysis of PFASs on bicycle helmet C4, C6 and C10 was performed at Eurofins. The analyses were for two groups of PFASs. Each group of PFASs requires its own analysis method.

1. Perfluorinated compounds (PFC) – in total 22 different compounds
2. Neutral fluorinated compounds (NPFC), also called neutral PFOA-based substances – in total 11 compounds

As the bicycle helmet strap material weighs very little in a bicycle helmet in relation to the sample amount which must be used for the analysis, two extra identical bicycle helmets (with the same batch number and production date) were purchased to perform the duplicate determination.

The bicycle helmets on which screening analysis was performed are named C4A, C6A and C10A and the identical new bicycle helmets are described with B and C respectively. For bicycle helmet C4 it was not possible to provide two extra bicycle helmets with the same batch number and production date like the helmet from the screening analysis. Therefore, three new helmets with another production date were purchased (but all three with the same batch number and production date). These helmets were named C4newA, C4newB and C4newC respectively.

In order to have material enough for a possible subsequent migration analysis, it was decided to prepare a mixture sample of the three identical bicycle helmets A, B and C for each type of bicycle helmet C4new, C6 and C10. For each mixture sample, material was selected to perform duplicate determination (described with 1 and 2 respectively). The in total six quantitative analyses which were performed for content of PFASs were therefore performed on C4newABC-1, C4newABC-2, C6ABC-1, C6ABC-2, C10ABC-1 and C10ABC-2. The results are stated in Table 9.

The fundamental analysis steps are as follows:
- Addition of internal isotope-labelled standards
- Ultrasonic extraction of the homogenised sample material with matrix-dependent solvents (multi)-step-sample clean-up (depending on matrix; e.g. SPE)
- Analysis by liquid chromatography coupled with mass spectrometry (LC/MS-MS)
- Identification via retention time and molecule or fragment ions
- Quantification of the native PFC components via internal isotope-labelled standards
- LOQ: 1-5 µg/kg dry mass dependent of the matrix
- Reference method: DIN 38414-S14 modified to the matrix

6.2 Results of the quantitative analyses

The analysis results of the quantitative content analyses for chlorinated phosphorus-based flame retardants and PFASs are stated below.

6.2.1 Analysis results for chlorinated phosphorus-based flame retardants

The analysis results for the quantitative determination of the content of chlorinated phosphorus-based flame retardants of the foam material in C10 are stated in Table 9 below. The analysis results are stated separately for the two helmets C10A and C10B and as the average of the two results from the duplicate determination. As previously mentioned, the two analyses in the duplicate determination are performed on two bicycle helmets with identical batch number and production date.

Table 9: Analysis results (content) for chlorinated phosphorus-based flame retardants in foam material

Flame retardant	C10A (mg/kg)	C10B (mg/kg)	Average (mg/kg)
Tri-o-cresyl phosphate	< 0.1	< 0.1	< 0.1
Tricresyl phosphate	< 0.4	< 0.4	< 0.4
Tris(2-chloroisopropyl) phosphate (TCPP)	20,400	18,700	19,550
Tris(1,3-dichloroisopropyl) phosphate (TDCP)	6,320	8,020	7,170
Tris(2-butoxyethyl) phosphate (TBEP)	< 0.2	< 0.2	< 0.2
Tributyl phosphate (TBP)	< 0.2	< 0.2	< 0.2
Triisobutyl phosphate (TIBP)	2.6	2.4	2.5
(2-Ethylhexyl)-Diphenyl phosphate	< 0.5	< 0.39	< 0.5

Flame retardant	C10A (mg/kg)	C10B (mg/kg)	Average (mg/kg)
(EHDP)			
Tris(2-chloroethyl) phosphate (TCEP)	1.1	1.0	1.1
Tris(2-ethylhexyl) phosphate	< 0.52	< 0.63	< 0.63
Triphenyl phosphate (TPHP)	60	58	59

LOD (Limit of detection) = 0.1 – 0.5 mg/kg

< x = less than x, corresponding to LOD

From Table 9 it is seen that TCP and TDCP are identified in large amounts (19,550 ppm (2%) and 7,170 ppm (0.7%) respectively) and that TIBP, TCEP and TPHP are identified in small amounts (approx. 2 ppm (0.0002%), 1 ppm (0.0001%) and 60 ppm (0.006%) respectively).

By comparison, a limit value of 5 mg/kg (5 ppm) has been determined for TCPP, TDCP and TCEP respectively (EU Directive 2014/79/EU, 2014) for toys intended for children below the age of 3 years and toys intended to be put into the mouth. However, these limits do not apply to bicycle helmets.

6.2.2 Analysis results for PFASs

The analysis results for the quantitative analysis of the content of PFASs in bicycle straps in C4new, C6 and C10 are stated in Table 10 below. The analysis results are stated one by one for each of the two analyses (duplicate determination) for each of the three helmets C4new, C6 and C10. Furthermore, an average value for C4new is stated. It is the only helmet where PFASs above the detection limit are identified. As mentioned earlier, the two analyses in the duplicate determination are performed on a mixture sample of three bicycle helmets A, B and C with identical batch number and production date.

From Table 10 it is seen that only a few PFASs are identified in C4 but no PFASs are identified in C6 and C10. This is consistent with the fact that according to the fluorine determination, C4 had a far higher content of fluorine (approx. 92 ppm) in comparison with C6 and C10 where the content was just above the detection limit of the 5 ppm (approx. 6-7 ppm).

The identified PFASs in C4 are perfluorooctanoic acid (PFOA), perfluorohexane sulphonate (PFHxS) and perfluorohexanoic acid (PFHxA). PFHxS is identified in the highest concentration of 11.6 ppb (µg/kg) in one of the two single determinations.

However, it must be noted that PFOA and PFHxA are only identified in one of the two single determinations and that the concentration of PFHxS in the two single determinations has a factor 10 of difference. This can partly be due to the general uncertainties at the analyses and partly the fact that the measured values are close to the detection limit. Another uncertain factor is that C4newABC is produced as a mixture sample of three different bicycle helmets. Even if these “identical” bicycle helmets have the same production number and batch number they are not necessarily identical. Finally, the proportion of the mixture between strap from helmet A, B and C can be a little different in the two single determinations.

In Table 11 the values which are above the detection limit are converted to µg/m^2 based on the measurements which were made of weight and area of the analysed samples. It must be noted that especially for C4 which consists of round ropes as bicycle strap the calculation is uncertain. Here the calculation of the surface area is performed by calculating the area of a cylinder. In the calculations, an average of the values for weight per area unit, which were measured for the two duplicate determinations for each bicycle helmet, was used.

The identified concentrations of PFASs in C4 are converted to $\mu g/m^2$ thus 1.02 $\mu g/m^2$ for perfluorooctanoic acid (PFOA), 6.26 $\mu g/m^2$ for perfluorohexane sulphonate (PFHxS), and 0.98 $\mu g/m^2$ for perfluorohexanoic acid (PFHxA).

By comparison, the limit value for PFOS and PFOS derivates in articles is 0.1% (1000 ppm) or 1 $\mu g/m^2$ for textiles. None of the detected PFASs falls under the description PFOS derivates.

Table 10: Analyses results (content) of PFASs in bicycle straps – unit: µg/kg (ppb)

PFAS compound	C4newABC-1 µg/kg (ppb)	C4newABC-2 µg/kg (ppb)	C4newABC Average µg/kg (ppb)	C6ABC-1 µg/kg (ppb)	C6ABC-2 µg/kg (ppb)	C10ABC-1 µg/kg (ppb)	C10ABC-2 µg/kg (ppb)
NPFC, neutral PFOA derivatives (*, #1)							
4:2 Fluorotelomer alcohol (4:2 FTOH)	< 485	< 463	< 474	< 289	< 265	< 493	< 513
6:2 Fluorotelomer alcohol (6:2 FTOH)	< 485	< 463	< 474	< 289	< 265	< 493	< 513
8:2 Fluorotelomer alcohol (8:2 FTOH)	< 485	< 463	< 474	< 289	< 265	< 493	< 513
10:2 Fluorotelomer alcohol (10:2 FTOH)	< 485	< 463	< 474	< 289	< 265	< 493	< 513
6:2 Fluorotelomer acrylate (6:2 FTAc)	< 194	< 185	< 190	< 116	< 106	< 197	< 205
8:2 Fluorotelomer acrylate (8:2 FTAc)	< 194	< 185	< 190	< 116	< 106	< 197	< 205
10:2 Fluorotelomer acrylate (10:2 FTAc)	< 194	< 185	< 190	< 116	< 106	< 197	< 205
N-methylperfluorooctane sulfonamide (MeFOSA)	< 97.1	< 92.6	< 94.9	< 57.8	< 53.1	< 98.5	< 103
N-ethylperfluorooctane sulfonamide (EtFOSA)	< 97.1	< 92.6	< 94.9	< 57.8	< 53.1	< 98.5	< 103
N-methylperfluorooctane sulfonamide-ethanol (MeFOSE)	< 97.1	< 92.6	< 94.9	< 57.8	< 53.1	< 98.5	< 103
N-ethyl-perfluorooctansulfonamide-ethanol (EtFOSE)	< 97.1	< 92.6	< 94.9	< 57.8	< 53.1	< 98.5	< 103
PFC. perfluorinated substances (*. #2)							
Perfluorooctane sulfonate (PFOS)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorooctanic acid (PFOA)	**1.60**	< 0.543	**1.07**	< 0.498	< 0.518	< 0.459	< 0.513
Total PFOS/PFOA excl. LOQ	**1.60**	ND	**1.07**	ND	ND	ND	ND
Total PFOS/PFOA incl. LOQ	2.10	1.09	1.60	0.995	1.04	0.917	1.03
Perfluorobutane sulphonate (PFBS)	<0.758	< 0.815	< 0.787	< 0.746	< 0.777	< 0.688	< 0.769
Perfluorobutanoic acid (PFBA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluoropentane acid (PFPeA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorohexane sulphonate (PFHxS)	**11.6**	1.60	**6.60**	< 0.746	< 0.777	< 0.688	< 0.769
Perfluorohexanoic acid (PFHxA)	**1.52**	< 0.543	**1.03**	< 0.498	< 0.518	< 0.459	< 0.513
Perfluoroheptan sulphonate (PFHpS)	<0.758	< 0.815	< 0.787	< 0.746	< 0.777	< 0.688	< 0.769
Perfluoroheptanoic acid (PFHpA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorooctane sulfonamide (PFOSA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorononanoic acid (PFNA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513

PFAS compound	**C4newABC-1** **µg/kg (ppb)**	**C4newABC-2** **µg/kg (ppb)**	**C4newABC Average** **µg/kg (ppb)**	**C6ABC-1** **µg/kg (ppb)**	**C6ABC-2** **µg/kg (ppb)**	**C10ABC-1** **µg/kg (ppb)**	**C10ABC-2** **µg/kg (ppb)**
Perfluorodecane sulphonate (PFDS)	<0.758	< 0.815	< 0.79	< 0.746	< 0.777	< 0.688	< 0.769
Perfluorodecanoic acid (PFDA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluoroundecanoic acid (PFUnA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorododecane acid (PFDoA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorotridecane acid (PFTrA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluorotetradecane acid (PFTA)	< 0.505	< 0.543	< 0.524	< 0.498	< 0.518	< 0.459	< 0.513
Perfluor-3.7-dimethyloctane acid (PF-3.7-DMOA)	< 1.01	< 1.09	< 1.05	< 0.995	< 1.04	< 0.917	< 1.03
7H-Dodecafluoroheptanoic acid (HPFHpA)	< 1.01	< 1.09	< 1.05	< 0.995	< 1.04	< 0.917	< 1.03
6:2 Fluorotelomer sulphonate (6:2 FTS) (H4PFOS)	< 0.758	< 0.815	< 0.787	< 0.746	< 0.777	< 0.688	< 0.769
4:2 Fluorotelomer sulphonate (4:2 FTS) (H4PFHxS)	< 1.01	< 1.09	< 1.05	< 0.995	< 1.04	< 0.917	< 1.03
8:2 Fluorotelomer sulphonate (8:2 FTS) (H4PFDS)	< 1.01	< 1.09	< 1.05	< 0.995	< 1.04	< 0.917	< 1.03
Total PFC excl. LOQ	**14.7**	1.60	**8.15**	ND	ND	ND	ND
Total PFC incl. LOQ	27.3	16.3	21.80	14.2	14.8	13.1	14.6

* = not accredited

#1 = Internal test method GC-MS

#2 = Internal testmethod GLS OC 400, LC-MS/MS

LOQ (Limit of quantification) for the individual substances is listed with < x, for the substances

ND = not detected

Table 11: Analysis results (content) for PFASs in bicycle straps

PFASs	C4newABC Average µg/kg (ppb)	C4newABC Average µg/m^2
Perfluorooctanoic acid (PFOA)	1.07	1.02
Perfluorohexane sulphonate (PFHxS)	6.6	6.26
Perfluorohexanoic acid (PFHxA)	1.03	0.98
Total PFC excl. LOQ	**8.15**	**7.73**

6.2.3 Summary of analysis results

The results from the screening showed a content of chlorine and phosphorus in the pad material in C10 (which might indicate a content of chlorinated phosphorus-based flame retardants) as well as a content of fluorine in the straps in C4, C6 and C10 (which might indicate a content of fluorinated compounds). Therefore, pad material in C10 was analysed quantitatively for a content of chlorinated phosphorus-based flame retardants and the straps in C4, C6 and C10 were analysed quantitatively for a content of fluorinated compounds.

The result was that TCPP and TDCP were identified in the pad material in C10 in large amounts (19,550 ppm (2%) and 7,170 ppm (0.7%) respectively) and TIBP, TCEP and TPHP were identified in small amounts (approx. 2 ppm (0.0002%), 1 ppm (0.0001%) and 60 ppm (0.006%) respectively).

A few PFASs were identified in the strap in C4 but no PFASs above the detection limit in the straps in C6 and C10. This corresponds with the fact that according to the fluorine determination C4 had a far higher content of fluorine in comparison with C6 and C10. The identified PFASs in C4 are perfluorooctanoic acid (PFOA), perfluorohexane sulphonate (PFHxS) and perfluorohexanoic acid (PFHxA). PFHxS is identified in the highest concentration of 6.6 ppb (µg/kg) as an average of the two single determinations.

Due to identification of chlorinated phosphorus-based flame retardants in the pad material in C10 and PFASs in the strap in C4, migration analysis to water for both the pad material in C10 and the strap in C4 was subsequently performed.

7. Migration analyses

Based on findings of chlorinated phosphorus-based flame retardants in the foam material in the bicycle helmet C10 and PFASs in the bicycle strap in bicycle helmet C4, migration analyses were performed for these substances in the two bicycle helmets where these substances were identified at the quantitative analyses.

7.1 Migration conditions

The following migration conditions were applied:
- 1 hour
- 37 °C
- Static conditions, i.e. no stirring
- Migration to water

The exposure time for a child below 3 years was set to 1 hour per day as worst-case corresponding to 30 minutes of transport each way. A temperature of 37 °C corresponding to a general body temperature was used. No stirring was used at the migration but static conditions in order to simulate the practical use as far as possible.

For the chlorinated phosphorus-based flame retardants, the special condition was that these were identified in the foam material inside the pads on the inner side of the bicycle helmet. In most of the bicycle helmets (and also in C10), the foam material was encircled by a layer of textile on all sides, i.e. no direct contact between skin and the foam material takes place. Therefore, the entire pads were put into the migration liquid to simulate the real situation when the bicycle helmet is worn.

Regarding the migration analyses, the migration was performed to water and not to artificial sweat for two reasons: According EN 71-10:2005 it is stated that analytical tests have shown that for the organic substances for which analyses are performed in EN 71-10 and EN 71-11 (i.e. among other things these chlorinated phosphorus-based flame retardants), water is as good a simulant as other typically used simulants, such as artificial sweat. In addition to this, the analysis results for migration to water can be used for both the calculation of the theoretical dermal and oral exposure.

7.2 Analysis methods

Analysis methods for migration of chlorinated phosphorus-based flame retardants in pad material and migration of PFASs in bicycle strap are described closer below. These analyses were performed by Eurofins.

7.2.1 Migration analysis for chlorinated phosphorus-based flame retardants

Migration analysis for chlorinated phosphorus-based flame retardants was performed for the foam material in the bicycle helmet C10. As the foam material weighs very little in a bicycle helmet in relation to the sample amount which is needed for the analysis, the duplicate determination was carried out by means of purchase of an extra identical bicycle helmet (with the same batch number and production date). The bicycle helmet on which screening analyses were performed is named C10A and the identical new bicycle helmet is named C10B. Thus, both quantitative analysis and migration analysis of chlorinated phosphorus-based flame retardants are performed on the foam material in the two identical bicycle helmets C10A and C10B.

The migration analysis for chlorinated phosphorus-based flame retardants in C10 was performed in the following way:

- Addition of quantification standards.
- Ultrasonic extraction with ethylacetate, evaporation of the extract, addition of recovery standard.
- Measurement: GC/MS/MS-EI on 60 m VFXms.
- Quantification by method of isotope dilution/method of internal standard using 5 isotope-labelled standards.
- 3.7 g sample material and 75 mL simulant (water) for the migration analysis were applied.
- The migration was performed at 37 °C for 1 hour.

The results are stated in Table 12 below.
The 3.7 g sample material corresponded to approx. half of the pad material which was in the bicycle helmet.

7.2.2 Migration analysis of PFASs

Migration analysis for PFASs was performed for the strap in bicycle helmet C4, however, not on the very same bicycle helmet on which the screening analyses were performed but on three new helmets (C4new) with another production date as it was impossible to buy more bicycle helmets with the same production date.

The strap material from the three new bicycle helmets, named C4newA, C4newB and C4newC respectively, was mixed to two mixture samples C4newABC-1 and C4newABC-2 which constituted the duplicate determination as the strap weighs very little in a bicycle helmet compared to the sample amount which is needed for the analysis. Thus, both quantitative determination of content of PFASs as well as migration of PFASs on sample material from the same bicycle helmets (mixture sample of material from three identical bicycle helmets) were performed.

The migration analysis for PFASs in C4newABC was performed in the following way:

- Addition of internal isotope-labelled standards and ultrasonic extraction of the homogenised sample material with matrix-dependent solvents (multi)-step-sample clean-up (depending on matrix; e.g. SPE).
- The analysis is performed by liquid chromatography coupled with mass spectrometry (LC/MS-MS) with identification via retention time and molecule or fragment ions. The quantification of the native PFC components is performed via internal isotope-labelled standards.
- The quantification limit LOQ is 50-100 ng/L simulant or 0.3-0.7 µg/kg bicycle strap dependent of the substance.
- Reference method: DIN 38414-S14 modified to the matrix.
- 12.4 and 11.9 g sample material respectively was used and 75 mL simulant (water) for the migration analysis. The migration was performed at 37 °C for 1 hour.

The results are stated in Table 13.

7.3 Results of the migration analyses

The analysis results of the migration analyses for chlorinated phosphorus-based flame retardants and PFASs are stated below.

7.3.1 Analysis results for chlorinated phosphorus-based flame retardants

The analysis results for the migration analysis for chlorinated phosphorus-based flame retardants of the foam material in C10 are stated in **Fejl! Henvisningskilde ikke fundet.** below. The analysis results are stated individually for the two helmets C10A and C10B and as the average of the two results from the duplicate determination. As earlier mentioned, the two analyses in the duplicate determination are performed on two bicycle helmets with identical batch number and production date. Differences in the analysis result can thus be due to both common measurement uncertainty and individual differences in two bicycle helmets from the same production date.

The analysis results are stated both as amount of substance per litre of simulant (µg/l) and amount of substance per amount of sample material (µg/kg). The migration analysis was performed for one hour so the real units are µg/l/hour and µg/kg/hour respectively.

Table 12: Analysis results (migration) for chlorinated phosphorus-based flame retardants in foam material

Flame retardants	C10A (µg/l/ hour)	C10A (µg/kg/ hour)	C10B (µg/l/ hour)	C10B (µg/kg/ hour)	Average (µg/l/ hour)	Average (µg/kg/ hour)
Tri-o-cresyl phosphate	< 0.2	< 4	< 0.2	<4	< 0.2	<4
Tricresyl phosphate	< 0.8	<16	< 0.8	<16	< 0.8	<16
Tris(2-chloroisopropyl) phosphate (TCPP)	26,000	530,000	17,500	350,000	21,750	440,000
Tris(1,3-dichloroisopropyl) phosphate (TDCP)	545	11,000	450	9,100	498	10,050
Tris(2-butoxyethyl) phosphate (TBEP)	< 0.4	<8	< 0.4	<8	< 0.4	<8
Tributyl phosphate (TBP)	< 0.4	<8	< 0.4	<8	< 0.4	<8
Triisobutyl phosphate (TIBP)	1.26	26	1.19	24	1.23	25
(2-Ethylhexyl)-Diphenyl phosphate (EHDP)	< 0.4	<8	< 0.4	<8	< 0.4	<8
Tris(2-chloroethyl) phosphate (TCEP)	7.79	160	6.11	120	6.95	140
Tris(2-ethylhexyl) phosphate	< 1.1	<23	< 0.518	<11	<0.81	<17
Triphenyl phosphate (TPHP)	0.659	14	0.663	13	0.661	14

< x = less than x, corresponding to the detection limit. As the detection limit depends on the amount of sample material the detection limit can vary for the same substance in different samples.

From Table 12 it is seen that in the migration liquid the same chlorinated phosphorus-based flame retardants are identified as those which were identified in the analysis with regard to content (Table 9), i.e. TCPP, TDCP, TIBP, TCEP and TPHP.

TCPP and TDCP are identified in the largest amounts in the migration liquid 440,000 and 10,050 µg/kg/hour respectively, corresponding to 440 µg/g/hour and 10 µg/g/hour respectively. TIBP, TCEP and TPHP are identified in smaller amounts in the migration liquid (approx. 0.025 µg/g/hour, 0.140 µg/g/hour and 0.014 µg/g/hour respectively).

7.3.2 Analysis results for PFASs

The analysis results for the migration analysis for PFASs in the bicycle helmet in C4new are stated in Table 13 below. The analysis results are stated individually for the two samples C4newABC-1 and C4newABC-2 and as the average of the two results from the duplicate determination. As earlier mentioned, the two analyses in the duplicate determination are performed on a mixture sample of three different bicycle helmets with identical batch number and production date.

The analysis results are stated as both amount of substance per litre of simulant (ng/l) and amount of substance per amount of sample material (µg/kg). The migration analysis was performed for one hour so the real units are ng/l/hour and µg/kg/hour respectively.

In general, no PFASs are identified above the detection limit of between 0.3-0.7 µg/kg/hour of bicycle strap. In Table 13, only the analysis results for the three PFASs which were identified at the quantitative analysis are stated.

Table 13: Analysis results (migration) for PFASs in bicycle strap

PFASs	C4newABC-1 (ng/l/hour)	C4newABC-1 (µg/kg/hour)	C4newABC-2 (ng/l/hour)	C4newABC-2 (µg/kg/hour)
Perfluorooctanoic acid (PFOA)	< 50	< 0.3	< 50	< 0.4
Perfluorohexane sulphonate (PFHxS)	< 75	< 0.5	< 75	< 0.5
Perfluorohexanoic acid (PFHxA)	< 50	< 0.3	< 50	< 0.4

< x = less than end x, corresponding to the detection limit. As the detection limit depends on the amount of sample material the detection limit can vary for the same substance in different samples.

7.3.3 Summary of results for the migration analyses

The following migration analyses were performed:

- Migration of chlorinated phosphorus-based flame retardants in bicycle helmet C10
- Migration of PFASs in bicycle helmet C4

The results of the migration analyses on the pads inside the bicycle helmet show that the same chlorinated phosphorus-based flame retardants are identified in the migration liquid as those which were identified in the analysis with regard to content in C10. TCPP and TDCP are identified in the largest amounts in the migration liquid, 0.044% and 0.001% respectively for migration for 1 hour, corresponding to 440 ppm and 10 ppm respectively for one hour of migration. TIBP, TCEP and TPHP are identified in smaller amounts in the migration liquid (approx. 0.025 ppm, 0.140 ppm and 0.014 ppm respectively for one hour of migration).

The results from the migration analyses of the bicycle strap on C4new show that no PFASs migrate above the detection limit of between 0.3 and 0.7 µg/kg/hour of bicycle strap dependent on the individual PFAS.

8. Hazard assessment

A summary (in the form of a table) of the most important data for use in the risk assessment for the substances which migrate from the bicycle helmets for the two types of migration analysis in this project (i.e. chlorinated phosphorus-based flame retardants and PFAS compounds) has been prepared.

Data identified for the substances which migrate from the bicycle helmets is summarised in Table 14. The reference for the data is stated in the outermost right column and is briefly described below. The identified data, i.e. DNEL value (Derived No Effect Level), and values for skin and oral absorption are used directly in the risk assessment.

It should be noticed that risk assessments have formerly been performed in one or more of the 'chemicals in consumer products' surveys carried out for the Danish EPA for the flame retardants TCPP, TDCP and TCEP. The DNEL values and values for skin and oral absorption used in these projects are used directly in this project. Both Nørgaard Andersen et al. (2014) and Kjølholt et al. (2015) list dermal and oral absorption values for TCPP of 40% and 80% respectively, and values for TDCP of 30% and 100% for dermal and oral absorption respectively. Kjølholt et al. (2015) uses an absorption of 100% for TCEP for both dermal and oral absorption. These values are listed in an EU risk assessment of the substance (EU RAR, 2009). The former projects used as references are from 2014 and 2015 respectively. For this reason, it is assumed that the used DNEL values not necessarily have been changed since then.

For the flame retardants TIBP and TPHP, the DNEL values as listed in the ECHA database of registered substances are used well aware that these values are assessed by the producers and are not validated by impartial experts. In general, the DNEL values for skin and oral absorption for the general population are used. As no data for skin and oral absorption is listed for these two substances, an absorption of 100% is used as a worst-case.

For the PFASs, risk assessments have also been performed in a couple of the former 'chemicals in consumer products' surveys carried out for the Danish EPA. Furthermore, an environmental project (Larsen & Giovalle, 2015) has been prepared. In this former project, a health assessment of PFOA, PFOS and PFOSA has been carried out. This health assessment was used as a basis of determination of limit values for these substances in drinking water amongst other things. The survey project Klinke et al. (2016) uses DNEL values from this environmental project whereas a former survey project (Lassen et al., 2015) states DNEL values from other literature as the environmental project was prepared simultaneously.

The used DNEL values for PFOA from the different projects are more or less at the same level. However, the DNEL value for serum (blood fluid), which is stated by RAC in an opinion on PFOA (ECHA, 2016a), cannot be used directly in the calculations in this project as we do not have information about serum values when using bicycle helmets with PFASs in the bicycle straps. Larsen & Giovalle (2015) calculates a TDI value (Tolerable Daily Intake) of 0.1 µg/kg bw/day for PFOA. This value is listed as a DNEL value for PFOA in Klinke et al. (2016) whereas Lassen et al. (2015) lists a DNEL value of 0.08-0.17 µg/kg bw/day based on earlier literature.

The information available on DNEL values for other PFASs is limited. These are therefore often assumed on the basis of knowledge of PFOA and PFOS. In Larsen & Giovalle (2015), they calculate a TDI value of 0.03 µg/kg bw/day for PFOS. In Klinke et al. (2016), they describe that the Danish EPA decided to use this TDI value for PFOS as a worst-case limit value for a total sum of 12 PFASs, including PFOA, PFHxS and PFHxA, which have been identified in a bicycle strap in this project. This DNEL value of 0.03 µg/kg bw/day is therefore used as DNEL value for the total sum of PFASs in Klinke et al. (2016).

The same choice has been made in this project on bicycle helmets. This means that the DNEL value of 0.03 µg/kg bw/day is used as the worst-case value for the sum of PFOA, PFHxS and PFHxA. It is a worst-case value as PFHxS and PFHxA probably are far less toxic than PFOA (based on knowledge of NOAEL values (No Observed Adverse Effect Level) for PFHxA of 100,000 µg/kg bw/day (Iwai & Hoberman, 2014), for PFHxS of 20,000 µg/kg bw/day (Loveless et al, 2009) and for PFOA of 60 µg/kg bw/day (Lassen & Giovalle, 2015)).

A value for skin absorption of 2% is used for all PFASs as stated in Lassen et al. (2015). In Lassen et al. (2015), it is stated that the skin absorption of PFASs is < 2%. A value for oral absorption of 90% is used as stated in Lassen et al. (2015).

Values used in the risk assessment are marked in bold in Table 14.

Table 14: Data hazard assessment of identified substances by migration analysis

Name of substance	CAS no.	Harmonised classification	DNEL dermal (µg/kg bw/day)	DNEL oral (µg/kg bw/day)	Critical effect	Skin / oral absorption	Reference
Tris(2-chloroisopropyl) phosphate (TCPP)	13674-84-5	Harmonised classification: None Notified classification: Acute Tox. 4 H302 (568) Aquatic Chronic 3 H412 (35) Eye Irrit. 2 H319 (4) Skin Irrit. 2 H315 (1)	720* **70**	No data 70	Liver damage	**40%** (derm) 80% (oral)	ECHA registration dossier Nørgaard Andersen et al., 2014 Kjølholt et al., 2015
Tris(1,3-dichloroisopropyl) phosphate (TDCP)	13674-87-8	Harmonised classification: Carc. 2 H351	17 **5**	17 5	Kidney damage	**30%** (derm) 100% (oral)	ECHA registration dossier Nørgaard Andersen et al., 2014 Kjølholt et al., 2015
Triisobutyl phosphate (TIBP)	126-71-6	Harmonised classification: None Notified classification: Skin Sens. 1 H317 (244) Aquatic Chronic 3 H412 (134) Eye Irrit. 2 H319 (30) Skin Irrit. 2 H315 (39) Resp. Sens. 1 H334 (23)	**2,130**	2,130	-	-	ECHA registration dossier
Tris(2-chloroethyl) phosphate (TCEP)	115-96-8	Harmonised classification: Acute Tox. 4 H302 Carc. 2 H351 Aquatic Chronic 2 H411 Repr. 1B H360F	No data **13**	No data 13	Kidney damage	**100%** (derm) 100% (oral)	ECHA registration dossier Kjølholt et al., 2015 EU RAR, 2009
Triphenyl phosphate (TPHP)	115-86-6	-	**1,980**	500	Liver damage	-	ECHA registration dosier

Name of substance	**CAS no.**	**Harmonised classification**	**DNEL dermal (µg/kg bw/day)**	**DNEL oral** (µg/kg bw/day)	**Critical effect**	**Skin / oral absorption**	**Reference**
Perfluorooctanoic acid (PFOA)	335-67-1	Harmonised classification: Acute Tox. 4 H302 Eye Dam. 1 H318 Acute Tox. 4 H332 Carc. 2 H351 Lact. H362 STOT RE 1 H372 Repr. 1B H360D	0.08 – 0.17 0.1 **0.03** (total PFAS) 0.8 µg/ml serum	0.08 – 0.17 0.1 **0.03** (samlet PFAS) 0.8 µg/ml serum	Liver damage Reprotoxic effects	**2%** (derm) **90%** (oral)	Lassen et al., 2015 Larsen & Giovalle, 2015 Klinke et al., 2016 RAC opinion, 2016
Perfluorohexane sulfonate (PFHxS)	355-46-4	Harmonised classification: None Notified classification: None	0.08 – 0.17 **0.03** (total PFAS)	0.08 – 0.17 **0.03** (total PFAS)	Liver damage	**2%** (derm) **90%** (oral)	Lassen et al., 2015 Klinke et al., 2016 Larsen & Giovalle, 2015
Perfluorohexane sulfonic acid (PFHxA)	307-24-4	Harmonised classification: None Notified classification: Skin Corr. 1B H314 (29) Resp. Sens. 2 H335 (3) Met. Corr. 1 H290 (1) Eye Dam. 1 H318 (1) Acute Tox. 3 H301 (1) Acute Tox. 3 H311 (1) Acute Tox. 2 H330 (1)	0.08 – 0.17 **0.03** (total PFAS)	0.08 – 0.17 **0.03** (total PFAS)	Liver damage	**2%** (derm) **90%** (oral)	Lassen et al., 2015 Klinke et al., 2016 Larsen & Giovalle, 2015

* No DNEL value is listed. The value is a DMEL value (Derived Minimum Effect Level). The listed value is for workers and not for the general population.

Values in bold are used in the risk assessment.

9. Exposure calculations

In this chapter exposure calculations are carried out, i.e. calculation of the amount of chlorine phosphorus-based flame retardants and PFASs which children below the age of 3 years will be exposed to during use of bicycle helmet C4 and C10 respectively. Exposure calculations are carried out for the following scenarios:

- Dermal exposure for chlorine phosphorus-based flame retardants in pad materials in C10
- Dermal exposure for PFASs in bicycle straps in C4
- Oral exposure for PFASs in bicycle straps in C4 (if the child sucks on a piece of the strap)

Even though no migration of PFASs from the strap in the bicycle helmet C4 was identified in the migration analysis to water, an exposure calculation has been performed and the detection limit has been used as the value for the amount migrating.

It is not considered to be likely that a child will suck on the pads fastened inside the bicycle helmet. The pads must be taken out of the helmet for this scenario to be possible as the pads are fastened with Velcro. At normal use of the bicycle helmet C4, it is not possible to get a piece of the strap which has been analysed in this project into the mouth. This part of the bicycle helmet is two pieces of rope which are situated around both ears and not under the chin. On these two pieces of robe around the ears, a strap is attached and this strap is fastened under the chin. The strap which goes under the chin (it looks like the straps from other bicycle helmets) has not been analysed in this project.
A worst-case scenario for oral exposure for the PFASs which migrate from the rope is calculated if a child should suck on this part of the strap, e.g. if the child sits with the bicycle helmet in its hand before departure/transport by bicycle with the bicycle helmet on the head.

9.1 Method for calculation of dermal exposure

As a basis for calculation of the dermal exposure, which young children will be exposed to by use of bicycle helmets, the model for calculation of dermal exposure stated by ECHA is used. According to the REACH Guidance on consumer exposure assessment (ECHA, 2016b), the exposure for a substance migrating from a product can be described by the formula below (appendix R.15.5).

$$D_{der} = \frac{Q_{prod} \times F_{prod} \times F_{migr} \times F_{contact} \times T_{contact} \times 1000\, mg/g \times n}{BW}$$

where

D_{der}	Dermal dose, i.e. the amount of substance, which potentially can be absorbed per kg body weight. Later in the calculations the dermal absorption rate of the substance is considered	mg/kg bw/day
Q_{prod}	Amount of product used	g
F_{prod}	Weight fraction of substance in the product	g/g product
F_{migr}	Rate (fraction) of substance migrating to skin per unit time (hours)	g/g/hours
$F_{contact}$	Fraction of contact area for skin, to account for the fact that the product is only partially in contact with the skin (default value = 1)	cm^2/cm^2
$T_{contact}$	Contact duration between product and skin	hours
n	Mean number of events per day	/day
BW	Body weight	kg

In this project, where migration analyses have been carried out, the result from the migration analyses can be used directly instead of the weight fraction of the substances in the product (F_{prod}). In this case, this means that the analysis result from the migration (migrated substance per g product per time) multiplied with the total weight of the pad material in C10 (Q_{prod}) corresponds to the total amount of substance that can migrate from the pads in the bicycle helmet. Furthermore, it is not the entire amount of the migrated chlorine phosphorus-based flame retardants that are absorbed through the skin. In the calculations, the actual possible fraction which can be absorbed is accounted for. The modified formula used for calculation of the exposure in this report is therefore:

$$D_{der} = \frac{Q_{prod} \times MG_{prod} \times F_{contact} \times T_{contact} \times F_{abs} \times n}{BW}$$

where

D_{der}	Dermal dose, i.e. the amount of substance, which potentially can be absorbed per kg body weight. By use of F_{abs} the dermal absorption rate of the substance is considered	µg/kg bw/day
Q_{prod}	Amount of product used	g
MG_{prod}	Amount of substance, which migrates per amount of product per unit time (here: migration time is 1 hour)	µg/g/hours
$F_{contact}$	Fraction of contact area for skin, to account for the fact that the product is only partially in contact with the skin (default value = 1)	-
$T_{contact}$	Contact duration between product and skin	hours
F_{abs}	Fraction of substance absorbed through skin	-
n	Mean number of events per day	/day
BW	Body weight	kg

As the point of departure, the calculations are carried out for a worst-case scenario, which afterwards can be refined, if the calculations result in a risk. As part of this worst-case scenario it is assumed that e.g. the measured migrations are constant over the used exposure time.

9.2 Method for calculation of oral exposure

As the point of departure, for the calculation of the oral exposure, which young children will be exposed to by use of bicycle helmets, the formula as listed above for dermal exposure is used, but modified for oral exposure.

$$D_{oral} = \frac{Q_{prod} \times MG_{prod} \times F_{contact} \times T_{contact} \times F_{abs} \times n}{BW}$$

where

D_{oral}	Oral dose, i.e. the amount of substance, which potentially can be absorbed per kg body weight. By use of F_{abs} the oral absorption rate of the substance is considered	µg/kg bw/day
Q_{prod}	Amount of product used	g
MG_{prod}	Amount of substance, which migrates per amount of product per unit time (here: migration time is 1 hour)	µg/g/hours
$F_{contact}$	Fraction of product in the mouth, to account for the case where the product is only partially in contact with the mouth (default value = 1)	-
$T_{contact}$	Contact duration between product and mouth	hours
F_{abs}	Fraction of substance absorbed orally	-

n	Mean number of events per day	/day
BW	Body weight	kg

9.3 Used exposure values

The following values are used for the exposure calculations in this project:

Dermal (D_{der}) / Oral (D_{oral}) exposure

D_{der} and D_{oral} are the calculated dermal and oral exposure respectively of a specific substance. This exposure is used in the risk assessment. The dermal exposure illustrates the exposure when the bicycle helmet is worn at transport on bike. The oral exposure illustrates the exposure when the child sucks on parts of the bicycle helmet, e.g. right before departure/transport on bike. It is not possible to put the parts, of which a risk assessment is carried out, into the mouth during transport where it is assumed that the bicycle helmet will be worn correctly on the head.

Amount of product (Q_{prod})

Q_{prod} is the total weight of pads inside the bicycle helmet C10 where a migration of chlorine phosphorus-based flame retardants has been identified and the total weight of strap in the bicycle helmet C4 where a migration of PFASs is identified.

For C10 the total weight of all pads in the bicycle helmet of 7.45 g is used even though not all pads in the bicycle helmet are in direct contact with the skin. C10 consists of a total of four pads inside where one pad is situated in the forehead (probably with direct skin contact), two pads are situated in each side of the helmet and the last pad is situated in the top of the helmet. The two pads in the sides of the helmet as well as the pad in the top of the helmet probably do not have any direct skin contact as the hair of the child will be between the pads and the scalp. In the winter where the child carries a knitted hat under the bicycle helmet the skin contact will be even smaller.

Similar for C4, the total weight of in all 2 x 13 cm bicycle strap, i.e. 7.0 g strap corresponding to the strap going from the edge of the helmet and around the ears is used for the calculation of the dermal exposure. C4 is constructed with two different types of straps where fluorine has been identified in the strap (rope) going around the ears. It is the total weight of this rope that is used in the calculations.

A calculation of oral exposure is also carried out if a young child should suck on this rope. However, it must be emphasised that it is not possible to put this rope into the mouth, when the child wears the helmet correctly, but only when for example the child sits with the bicycle helmet in its hands or plays with the helmet. Here as worst-case it is decided to use an amount of 4 cm of rope, corresponding to the part of the rope that is possible for the child to get into the mouth because the rope is attached in both ends to the edge of the bicycle helmet.

Migration (MG_{prod})

MG_{prod} is the amount of substance which at chemical analysis has shown to migrate out of the product to water at 37 °C for 1 hour (is equal to the result of the migration analysis).

Fraction of area in contact with skin/mouth ($F_{contact}$)

$F_{contact}$is the fraction of the product which is in contact with the skin or the mouth.

A value of 0.5 is used for skin contact for the pads inside the helmet of C10 and for the strap of C4 because it is only the one side of the pads and the strap which is in contact with the skin.

The pads in C10 are about 0.5 to 1 cm thick and the strap of C4 is a round rope with a diameter of about 1 cm.

A default value of 1 is used for contact with the mouth as it is assumed that the child has the entire piece of strap with a diameter of about 1 cm in the mouth.

Contact time ($T_{contact}$)

$T_{contact}$ is the time in hours which the bicycle helmet is worn by the child. In this project, a contac time of 30 minuttes (0.5 hours) has been used as a worst-case contact time for dermal contact each time the bicycle helmet is worn.

For the situation with oral exposure a contact time of 10 minutes is used corresponding to the time it is assumed the child will have the bicycle helmet in its hands before departure/transport on bike. It is not possible for the child to suck on the part of the strap where PFASs have been identified when the helmet is worn correctly on the head.

Absorption (skin or oral (F_{abs}))

F_{abs} is the fraction of the substance which is absorbed through skin or via the mouth. The fraction is listed in Table 14 and specific values are used if available. Otherwise 100% is used as a worst-case when data is missing.

Events per day (n)

As mentioned earlier, the total exposure time is assumed to be 1 hour corresponding to 30 minutes of transport in each direction (e.g. to and from day care centre). The mean number of events per day, n, where the young children wear the bicycle helmet is assumed to be 2 per day, corresponding to transport to and from e.g. day care centre.

Body weight (BW)

Based on RIVM (2014), the value of 9.8 kg as the body weight of a child under 3 years has been chosen. ECHA (2016b) refers to default values in RIVM (2014). Here it is stated that the average weight for 1-2-year-old Dutch children is 9.8 kg and that the average weight for 2-3-year-old Dutch children is 12.4 kg. As a worst-case value the lowest value, i.e. 9.8 kg is used, which will result in the highest exposure (D_{der}/D_{oral}).

9.4 Exposure calculations

The different parameters and values which are used in the exposure calculation for C10 are summarised in Table 15 where the dermal dose (D_{der}) for the flame retardants also is calculated.

Table 15: Exposure calculation of dermal exposure to C10

Substance	TCPP	TDCP	TIBP	TCEP	TPHP
Q_{prod} (g)	7.45	7.45	7.45	7.45	7.45
MG_{prod} (µg/g/hour)	440	10.05	0.025	0.14	0.014
$F_{contact}$ (-)	0.5	0.5	0.5	0.5	0.5
$T_{contact}$ (hours)	0.5	0.5	0.5	0.5	0.5
F_{abs} (-)	0.40	0.30	1	1	1
n (per day)	2	2	2	2	2
BW (kg)	9.8	9.8	9.8	9.8	9.8
D_{der} (µg/kg bw/day)	**66.898**	**1.146**	**0.010**	**0.053**	**0.005**

Similar the different parameters and values used in the exposure calculation for C4 are summarised in Table 16 and Table 17 where the dermal exposure (D_{der}) for the PFASs is calculated when a child wears the bicycle helmet and the oral exposure (D_{oral}) for the PFASs when a child sucks on the strap of the bicycle helmet before departure/transport on bike. As mentioned earlier, the detection limit has been used as the value for the amount migrating, as no migration of PFASs from the strap in the bicycle helmet C4 was identified in the migration analysis. The calculation has been performed to ensure that no health risk exists from a possible migration below the values for which it is possible to analyse.

Table 16: Exposure calculation of dermal exposure to C4

Substance	PFOA	PFHxS	PFHxA
Q_{prod} (g)	7	7	7
MG_{prod} (µg/g/hour)	0.0004	0.0005	0.0004
$F_{contact}$ (-)	0.5	0.5	0.5
$T_{contact}$ (hours)	0.5	0.5	0.5
F_{abs} (-)	0.02	0.02	0.02
n (per day)	2	2	2
BW (kg)	9.8	9.8	9.8
D_{der} (µg/kg bw/day)	2.9 E-06	3.6 E-06	2.9 E-06

Table 17: Exposure calculation of oral exposure to C4

Substance	PFOA	PFHxS	PFHxA
Q_{prod} (g)	7	7	7
MG_{prod} (µg/g/hour)	0.0004	0.0005	0.0004
$F_{contact}$ (-)*	0.154	0.154	0.154
$T_{contact}$ (hours)**	0.167	0.167	0.167
F_{abs} (-)	0.9	0.9	0.9
n (per day)	1	1	1
BW (kg)	9.8	9.8	9.8
D_{oral} (µg/kg bw/day)	6.6 E-06	8.2 E-06	6.6 E-06

* Here a fraction of 4 cm out of 26 cm has been used

** Here a fraction of 1/6 hours has been used

10. Risk assessment

As described earlier, the purpose of this project has been to investigate whether the content of the identified problematic chemical substances in bicycle helmets can be hazardous to health for children.

The method used for calculating the risk is stated below. As described earlier, no hazard assessment has been performed for the substances investigated in this project and migrating from the bicycle helmets. However, the DNEL values which are used in the reports Nørgaard Andersen et al. (2014), Kjølholt et al. (2015), Lassen et al. (2015) and Klinke et al. (2016) are used in this report as well (see values marked in bold in Table 14).

10.1 Method for calculation of the risk

In principle, exposure to substances in bicycle helmets can happen through the different exposure pathways – dermal, oral and by inhalation. Exposure to substances that evaporate from the bicycle helmets is considered to be negligible and will moreover be considerably diluted in outdoor air. Oral exposure, i.e. if the children sucks on the bicycle helmet, is assumed to be irrelevant in the actual use situation as it is not possible to suck on either the pads inside the helmet of C10 or the part of the strap that has been analysed for PFASs in C4. On the contrary, it will be possible for a child to suck on the examined strap in C4 when the helmet is not worn, but it is not considered to be likely that a child will suck on the pads inside the helmet as these pads in that case will have to be taken out of the helmet first (they are attached with Velcro). Therefore, a calculation of the exposure through skin (the dermal exposure D_{der}) for C10 and C4 as well as a calculation of the oral exposure (D_{oral}) for C4 has been calculated in this project. The oral and dermal exposure to PFASs in C4 are added up in order to get the total exposure.

According to the REACH Guidance document on risk assessment (ECHA, 2016c), it should be assessed in each single case whether a risk of health hazards exists by use of the following formula. The risk is expressed as Risk Characterisation Ratio (RCR), which is calculated as the ratio between the size of the exposure (D_{der} or D_{oral}) and the Derived No Effect Level (DNEL):

$$RCR = \frac{Exposure\ (D_{der})}{DNEL}$$

If RCR > 1 (i.e. the exposure is higher than the DNEL) a risk exists. If RCR < 1, the exposure is not considered to constitute a risk.

Exposure to different substances with the same effect (in this project several different flame retardants or several different PFASs that result in liver damage) can be characterised as cocktail effects. Cocktail effects from several substances with the same effect can be calculated as an additive effect by use of the dose-addition principle, which has also been in several of the former survey projects from the Danish EPA.

Therefore, the total, i.e. additive risk is calculated by adding up the RCR values of the single substances (1 to n):

$$RCR_{total} = RCR_1 + RCR_2 + RCR_3 + \cdots + RCR_n$$

It is only for substances from the same bicycle helmet with the same effects where the RCR values are added up, as it is assumed that no children use more than one bicycle helmet (e.g. C4 and C10) at the same time.

10.2 Risk assessment

In the risk assessment, the calculated exposure (the calculated dermal exposure D_{der} or the calculated oral exposure D_{oral}) is compared with the DNEL value. The used DNEL values for these substances which migrate from the bicycle helmets C4 and C10 in this project are listed in Table 14.

The calculated RCR values for these flame retardants and PFASs are listed below for C10 (Table 18) and C4 (Table 19) respectively. The total sum of the RCR values (RCR total) for TCPP and TPHP respectively, as well as TDCP and TCEP has been calculated as these substances according to Table 14 have the same critical effect, i.e. liver damage and kidney damage. Correspondingly, the sum of the RCR values for PFASs has been calculated, as these substances also have the same critical effect (liver damage).

Table 18: Risk assessment (calculation of RCR-values) for C10

Substance	D_{der} (µg/kg bw/day)	DNEL (µg/kg bw/day)	RCR	RCR total
TCPP	66.898	70	0.96	0.96
TPHP	0.005	1,980	0.000003	
TDCP	1.146	5	0.23	0.23
TCEP	0.053	13	0.004	
TIBP	0.010	2,130	0.000004	-

It is evident from Table 18 that all calculated RCR values are below 1, with the highest RCR value for TCPP of 0.96. The RCR value for TCPP of 0.96 is, however, close to 1 and is the only value which is close to 1. However, several aspects of the calculation cause the calculation to be a worst-case calculation and therefore indicate that the actual exposure will be considerable smaller:

- A total exposure time of 1 hour has been used in the calculations. This is a long transportation time on bike for a little child, and this exposure time will probably be shorter for most young children.
- Moreover, the exposure has been calculated by use of the migration from all four pads in the bicycle helmet, where it primarily is the pad placed in the forehead that will be in direct contact with the skin. For most young children, the hair of the children will be in between the pads inside the helmet and the scalp.
- Finally, different conditions regarding the actual migration analysis are relevant for the calculations and lead to worst-case conditions for the calculations:
    - For the migration analysis, a total amount of migration fluid of 75 ml was used (in order to be able to carry out the analysis in practice) and the intact pads were submerged in the fluid. This means that in practice the pads were soaked with fluid. It is not assumed that in practice a young child who rides on its parents' bike or rides on its own bike will sweat that much so such a large amount of the flame retardant will migrate when the helmet is worn.
    - In C10 a total amount of TCPP of 19,550 µg/g and a migration of 440 µg/g/hour were identified, i.e. in theory the total amount of TCPP will migrate out of the pads in about 44 hours (or 44 days with 1 hour of use/day) provided that the rate of migration is constant and that the pads are soaked with sweat each time.

Therefore, the assessment is that there is no real health risk when a child carries the C10 bicycle helmet each day for a longer period – even though the highest RCR value (for TCPP) is close to 1. Similar, there is no real health risk even though the RCR values for several of the substances with the same critical effect are added up. The total RCR values for the same critical effect are still below 1.

Table 19: Risk assessment (calculation of RCR values) for C4

Product (substance)	D_{der} / D_{oral} (µg/kg bw/day)	DNEL (µg/kg bw/day)	RCR	RCR Total (dermal and oral)
PFOA (dermal)	2.9 E-06	0.03	-	0.001
PFHxS (dermal)	3.6 E-06			
PFHxA (dermal)	2.9 E-06			
Total PFAS (dermal)	**9.3 E-06**	**0.03**	**0.0003**	
PFOA (oral)	6.6 E-06			
PFHxS (oral)	8.2 E-06			
PFHxA (oral)	6.6 E-06			
Total PFAS (oral)	**2.1 E-05**	**0.03**	**0.0007**	

Table 19 illustrates that the total RCR values for the PFASs are well below 1. This means that there is no health risk for a child to wear the bicycle helmet C4 each day for a longer period. Even though a worst-case overall DNEL value has been used for all PFASs, no health risk exists. The total RCR value for both dermal and oral exposure for all PFASs is still significantly below 1 with regard to the chemical substances investigated in this project.

Furthermore, it should be emphasised that the analyses did not result in a migration of PFASs from the strap in C4 but that the detection limit has been used for the calculations. This calculation has been made to ensure that a migration lower than the detection limit could constitute a health risk.

10.3 Conclusion

In this project, chlorine phosphorus-based flame retardants have been identified in pads inside one single bicycle helmet (out of 16) and PFASs have been identified in a strap in one single bicycle helmet (out of 16). The flame retardants migrate from the pads, but no migration of PFASs from the strap was identified.

Based on the risk assessment results calculated in this project, it can be concluded that even though flame retardants have been identified inside the pads in a single bicycle helmet (out of 16) and even though these problematic substances migrate from the bicycle helmet and thereby can be absorbed through the skin of the young children wearing these helmets, the amounts are on a level that seen in isolation does not constitute a health risk for liver damage, which is the critical effect of the flame retardant TCPP (with the highest RCR value). In addition, the amounts do not constitute a health risk even when adding up the amount of the different flame retardants with the same health effect.

However, it should be noted that numerous PFASs exist and chemical analyses were only carried out in this project for 33 selected PFASs. Therefore, it may be possible that other PFASs are present in the bicycle helmets investigated in this project and that these compounds may migrate but these chemical analyses have not been carried out in this project, as they are not a part of the standard analyses for PFASs.

Former studies have shown that children are also exposed to the same flame retardants and the same PFASs from other consumer products. A selection of the results from the latest surveys from the Danish EPA is listed below:

- Furniture (PFAS-compounds), RCR = 0.0026 (Klinke et al., 2016)
- Snowsuit + contribution from indoor environment (PFASs), RCR = 0.008 (Lassen et al., 2015)
- Total contribution from indoor environment (TDCP), RCR = 0.65 (Nørgaard Andersen et al., 2014)
- Total contribution from indoor environment (TCPP), RCR = 0.07 (Nørgaard Andersen et al., 2014)

In the Danish EPA survey about child safety seats and other children products with textiles (Kjølholt et al., 2015), RCR values above 1 (corresponding to a possible health risk) were identified for TDCP in one single child safety seat and baby mattress, and for TCEP and TCPP in one single baby carrier. For the other investigated products, the RCR values were between 0.06 and 0.81. Overall, the flame retardants may constitute a health risk provided that the same child is exposed to the specific investigated products at the same time. However, it should be pointed out that in general worst-case assumptions have been used and that the calculations contain uncertainties.

Even though the calculated RCR values are below 1 for the bicycle helmet C10 investigated in this project, they contribute to the total exposure to these flame retardants in different children products which children use daily.

Looking only at the bicycle helmets, none of the investigated helmets constitutes a health problem with regard to the chemical substances investigated in this project. Moreover, it should be emphasised that it was only in two bicycle helmets out of 16 analysed helmets where either flame retardants were identified in the pads or where PFASs were identified in the strap. Most of the examined bicycle helmets investigated in this project do not contain neither the investigated chlorine phosphorus-based flame retardants nor PFASs.

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Survey and risk assessment of chemical substances in bicycle helmets

The purpose of this project has been to examine whether the content of the possibly problematic chemical substances in bicycle helmets can be hazardous to children's health. In total 16 different bicycle were purchased. The screening analyses showed a small content of both chlorine and phosphorus in a single bicycle helmet (C10). A content of fluorine just above the detection limit of 5 ppm was identified in C6 and C10 as well as a high fluorine con-tent of 92 ppm in C4. Quantitative analyses of certain chlorinated phosphorus-based flame retardants in the pad material in C10 were performed as well as of certain PFASs in bicycle straps on C4, C6 and C10. The results showed that in the pad material in C10, the flame retardants TCPP and TDCP were identified in large amounts and that TIBP, TCEP and TPHP were identified in small amounts. A few PFASs were identified in the strap in C4 in small amounts but no PFASs above the detection limit were identified in the straps from C6 and C10. The results of the migration analyses on the pads inside the bicycle helmet showed that the same chlorinated phosphorus-based flame retardants were identified in the migration liquid as identified at the content analysis carried out on C10 (TCPP TDCP,TIBP, TCEP and TPHP. The results of the migration analyses on the bicycle strap on C4 showed that no PFASs migrate above the detection limit. Looking only at the bicycle helmets, none of the investigated helmets constitutes a health problem with regard to the chemical substances investigated in this report.

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