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Survey and health and environmental assessments of biocidal active substances in clothing

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Survey and health and environmental assessments of biocidal active substances in clothing Survey and health and environmental assessments of biocidal active substances in clothing

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Foreword

The objective of the project "Survey and health and environmental assessment of biocidal active substances in clothing" was to identify and assess the occurrence and potential risk of biocidal active substances in textiles (clothing) on the Danish market with the emphasis on biocides used to protect textiles during transport from non-EU countries.

The project was carried out from June 2012 - August 2013 in collaboration between COWI (mapping, health and environmental assessments) and the Danish Technological Institute, DTI (laboratory tests). From COWI Jesper Kjølholt (project manager), Carsten Lassen and Sonja Hagen Mikkelsen participated, and from the DTI,Torsten Due Bryld, Eva Jacobsen and Niels Bernth were part of the team.

The advisory group for the project consisted of Lærke Ambo Nielsen, Dorthe Bjerregaard Lerche, Annette Gondolf and Magnus Løfstedt, all from the Danish Environmental Protection Agency (DEPA).

Summary and Conclusion

The overall objectives of this study have been i) to survey the use and occurrence of biocidal active substances applied to protect textiles (clothing) against pests and microbial degradation during transport from manufacturer to consumer, and ii) to assess the possible risks to consumers and the environment from such use, focusing on clothes imported from countries outside the EU.

About two thirds of the clothes on the Danish market originate from countries outside the EU, in particular from Asia. The clothes are stored temporarily in transport containers in the countries of origin and are afterwards transported over long distances before reaching the consumer in Denmark. It is known that biocidal products have been used in these situations to protect the clothes against deterioration by microorganisms or pests and, therefore, there is a risk that residues of the active substances may still be present in the clothes upon reaching the consumer.

During the project period the scope of the study was expanded to include residues of biocides used for protection of the fabric during the production process, i.e. all relevant types of biocides with the exception of those having a designated biocidal function in the use phase of the clothes.

The study encompassed the following main components: Survey of the use of biocides in clothes, chemical analyses and laboratory tests (migration and wash tests), consumer health risk assessment and environmental risk assessment.

Survey
The survey component of the study encompassed three categories of biocidal products:

- Biocidal products intended for protection of clothes against damage by microorganisms during transportation and storage;
- Biocidal gases used for disinfection/protection of the clothes against insect damage during transportation and storage, and
- Biocidal products used to prevent microbial growth in the liquids used in the production of the clothes.

As part of the study, direct enquiries have been made to a number of large international manufacturers of biocidal products and their websites have been consulted. In their marketing, none of the manufacturers specifically mention use of biocides for protection against microorganisms or insects during transport and storage of clothes. The dominant Danish importers of clothes all have policies restricting or banning the use and occurrence of certain biocides in the clothes they import. Other biocides may occur but the companies state that they have no information on active use of biocides for preservation of clothes. Typically the clothes are protected mainly by keeping them dry.

Thus, no verifiable information on the actual use of biocides for this purpose has been identified. Based on literature information on antimicrobial biocides that could possibly be used in this context, a gross list of candidate active substances has been produced. Similarly, a list has been developed of biocides possibly used as “in-can-preservatives” to protect liquids used in the production of clothes; these residues may be present in the clothes even when they reach the consumer.

Disinfection of transport containers by use of biocidal gases to protect the contents against insect pests is widespread. Thus, containers used to transport wood from tropical areas are routinely disinfected and it is also common to treat empty containers to avoid occurrence of insects that could pose a problem to the next cargo to be transported, e.g. clothes. Gases are rarely used to treat containers already filled with clothes. Containers arriving in Denmark and suspected of retaining residues of toxic gases are tested prior to being opened. The most frequently used gases are methyl bromide, sulfuryl difluoride and phosphine. These gases occur in concentrations above the Danish threshold limits in 1-3 % of the containers; however, they typically exceed the limits only slightly.

Laboratory investigations
Based on the outcome of the survey, a programme for chemical analysis and testing of clothes samples was established and conducted within the framework of the study. It was ascertained that biocidal products were most likely to have been applied to clothes made of natural fibres such as cotton (primarily), wool or silk. As the highest risk of exposure of consumers to biocides in clothes was considered to occur through skin contact, products involving direct skin contact during use (underwear, shirts, t-shirts, trousers, pyjamas and scarves) were prioritized in the selection of samples. Initially, the samples were screened by GC-MS for a wide range of substances to identify possible residues of relevant chemicals.

A total of 34 samples were analysed chemically, of which the majority was made of cotton; however, samples of clothes made of wool and silk were also included. In cases that positive identification of biocides occurred, the samples were tested for biocide migration to artificial sweat and release to wash water during textile washing.

Only two biocidal active substances were identified in the samples: formaldehyde (bactericide) and permethrin (insecticide). Formaldehyde was found in 7 samples at rather low concentrations (3-23 mg/kg clothes) while permethrin was only detected in 2 samples; however, the permethrin occurrences were at concentrations of 367-407 mg/kg clothes. Both samples containing permethrin also contained fomaldehyde. Formaldehyde was detected in all types of materials (cotton, wool and silk) while permethrin was only detected in clothes made of wool.

In the migration tests, formaldehyde occurred in the artificial sweat in amounts corresponding to 0.2-1.42 mg/kg and permethrin in amounts corresponding to 1.94 mg/kg. In the wash tests, the release of formaldehyde was generally higher than 50 % of the total (however, in one sample release was measured at only 9 %) while the release of permethrin (only one test) was 30% (111 mg/kg). It was expected that the release of formaldehyde during textile washing would be higher.

Human health assessment
Dermal contact is the most significant exposure route for humans from biocide-containing clothes in the use phase. In relation to the assessment of exposure and risk undertaken in this project, it is assumed that inhalation and oral ingestion have limited relevance. Consequently, these exposure routes are not specifically addressed or accounted for in the laboratory analyses.

Exposure to biocides by skin contact is assessed for the two active ingredients, formaldehyde and permethrin, based on the measured concentrations in clothing for adults and children, and the measured or calculated concentrations in artificial sweat.

Based on the measured concentrations in the clothes and the migration to sweat, the daily external dermal dose of formaldehyde associated with the use of clothes for 24 hours was calculated to a maximum of 0.035 mg kg bw/day for a man's shirt and 0.0057 mg/kg bw/day for a child's undershirt. For permethrin, the daily external dermal dose associated with the use of a child's undershirt for 24 hours was calculated to a maximum of 0.14 mg/kg bw/day.

The maximum concentration of formaldehyde in the sweat was calculated to be 1.42 mg/kg (1.42 ppm), which was more than a factor of 20 below the estimated threshold for elicitation of skin allergies of 30 ppm (0.0030%) and more than 100 times smaller than the threshold for sensitisation. The risk of local effects is therefore considered to be insignificant.

Additionally, the worst-case inhalatory exposure has been calculated. The result does not raise concern regarding risk for health effects.

For permethrin the DNEL was calculated at 0.14 mg/kg bw/day, based on a NOAEL of 5 mg/kg bw/day established in an oral test with dogs where damage to the adrenal glands was observed. The risk characterisation ratio was thus 0.25 without correction for dermal absorption and 0.014 with correction, assuming 100 % uptake following oral administration. This indicates that neither the content of formaldehyde nor the content of permethrin measured in the clothes alone would pose a risk to children or adults.

Environmental assessment

Release to surface water of treated sewage including wastewater from textile washing in private homes appears to be the main pathway of potential environmental exposure to biocides used in clothes. The environmental risk from this exposure pathway was assessed for the two biocidal active substances identified by the chemical analyses, formaldehyde and permethrin, using both the measured concentrations and frequencies of occurrence, and model release scenarios and environmental hazard profiles of the two substances. The latter were primarily extracted from risk assessment reports carried out under the EU evaluation programme for biocides.

Regarding formaldehyde, a scenario where 20 % of all clothes were assumed to contain formaldehyde (as in the investigated samples) at the median of the measured concentrations resulted in a risk quotient (PEC/PNEC ratio) of 0.29, i.e. less than 1. A risk quotient of less than 1 indicates an acceptably low risk for impacts from formaldehyde in clothes released to wastewater during textile washing. A risk quotient equal to 1 will be obtained if 68 % of all clothes contain formaldehyde, which is not considered realistic. No impacts from application of formaldehyde-containing sewage sludge to soil are expected.

Permethrin is found to be highly toxic to aquatic organisms, in particular to insects and crustaceans, which results in a low predicted no-effect level (PNEC) for this substance. In a moderately conservative scenario for permethrin released to urban sewage during textile washing, a risk quotient of approx. 14 was estimated at the border of a mixing zone (where sewage effluent is discharged into a surface another water body), outside of which the risk quotient should be less than 1. Therefore, with the present available level of information, the risk for impact in the aquatic environment related to the use of permethrin in clothes cannot be excluded.

This finding is in line with the conclusion in the EU risk assessment of permethrin used as biocide (insecticide) to preserve various textiles (e.g. carpets). Monitoring data collected by the International Office of Water, INERIS, also show that permethrin concentrations of the same order of magnitude occur in European rivers and streams. The application of sewage sludge containing permethrin released during washing of textiles is ascertained not to pose any unacceptable risk for impact on organisms in the soil environment.

The impact of gaseous biocidal active substances used for disinfection of transport containers (e.g. methyl bromide) on the tropospheric ozone layer or on global warming (greenhouse effect) is assessed to be marginal.

1. Background and introductio

1.1 Objectives of the project

About two thirds of the clothes on the Danish market originate from countries outside the EU, in particular from Asia. The clothes are stored temporarily in transport containers in the countries of origin and are afterwards transported over long distances before reaching the consumer in Denmark, during which there is a risk for damage by insect pests and/or microorganisms.
There is evidence from the literature that biocides have been used to protect clothing against damage by microorganisms (mainly fungi) and insects during storage and transport; as a result, the clothing sold on the Danish market might contain residues of biocidal active substances.

This project has focused primarily on biocidal active substances used to protect textiles during storage and transport from non-EU countries. The project has been extended to include residues of biocidal active substances used for the protection of the liquids used during the production of textiles. The project thus involves all groups of biocidal active substances in clothing which do not have an intended effect relating to the usage of the clothing.

Biocides are classified under the Biocide Directive in 23 different product types (PT), including disinfectants, preservatives (including wood preservatives and slimicides), pesticides (including rat poisons, insecticides) and antifouling agents. The three product types as far as this project is concerned are:

- PT 6: Preservatives for use in containers.
- PT 9: Fibre, leather, rubber and polymerised materials.
- PT 18: Insecticides, acaricides and products to control other arthropods.

The project objectives are:

- to establish an overview of the biocidal active substances used to protect clothing during storage and transport from non-EU countries;
- to establish an overview of which biocidal active substances are used for protection of liquids and used during the production of the fabrics, and
- to measure the extent of residues of these substances in clothes on the Danish market, and to assess whether the detected content of residues in clothing may pose a health and/or an environmental risk.

1.2 Regulation of biocides

Biocides must be approved before they may be used for the treatment of textiles in the EU. The active ingredients in the biocides (called biocidal active substances) have to be assessed by the EU Member States according to the Biocide Directive[1]. Biocidal substances must be approved by each EU Member State. In Denmark, biocides are approved by the Environmental Protection Agency.

During the preparation of the Biocides Directive, a list of existing biocidal active substances in the EU was established. The list is set out in Appendix I to Commission Regulation (EC) No 1451/2007. In addition, a list of biocidal active substances in biocidal products was compiled, which shall be

[1] European Parliament and Council Directive 98/8/EC of 16 February 1998 concerning the placing of biocidal products.

assessed as a part of the EU's 10-year work program for the study of active substances in biocidal products. Each of the substances is assessed in relation to its application in a number of specified product types. The list is set out in Appendix II to Commission Regulation (EC) No 1451/2007. Biocides containing biocidal active substances that are not discussed in the programme must be withdrawn from the market by 1 September 2006 according to the Biocide Directive. They are therefore no longer legal to use.

Biocidal active substances will be included in the lists of approved biocidal active substances for the evaluated combinations of biocidal active substances/product types (Annex I, IA of the Biocidal Products), or placed on a list of substances which must not be used for such purposes. The EU list of banned biocidal active substances "*Existing Active Substances for which a decision of non-inclusion into Annex I or Ia of Directive 98/8/EC is adopted* " contains substances which must not be used in biocidal products. For some of the active substances, the decision that they must not be used is limited to certain types of product.

Until the EU has assessed all biocidal active substances, some biocides will not be covered by the approval requirement. It depends on whether the active substance in the biocidal product is approved, disapproved or under approval. During the transition period, some biocides will still be subject to the existing national Danish approval rules.

Biocides which are used for protecting textiles outside the EU, and whose active substances may be contained in the articles exported to the EU, have not been subject to applicable restrictions under the Biocide Directive and the Danish biocide policy. This means that textiles already imported could contain biocidal active substances, even though they are not approved for manufacture, storage and transport of textiles in the EU. Some biocidal active substances are covered by more general restrictions under the REACH Regulation or other regulation that includes the presence of substances in the prepared articles. This applies, for example, to pentachlorophenol (PCP) and dimethyl fumarate (DMF).

With the Biocides Regulation[2] , which replaces the Biocides Directive and has been implemented in Europe as of September 2013, textiles treated with biocides will be considered to be biocidally treated articles, which are covered by the regulation (some confusion as to meaning here). This means that textiles are only permitted to contain biocidal active substances approved in the EU.

However, the Biocides regulation does not apply to treated articles where treatment has been restricted to fumigation or disinfection of premises or containers used for storage or transport, and where residues after such treatment are unlikely.

[2] European Parliament and Council Regulation (EU) No 528/2012 of 22 May 2012 available on the market and use of biocidal products.

2. Mapping

2.1 Mapping of biocidal active substances used for storage and transport of clothes

2.1.1 Previous evaluations of chemicals in clothing

In a previous study of chemical substances in textile products (Larsen et al., 2000), 11 textile products were tested for occurrence of the following biocidal active substances (CAS numbers are added here, as for many of the substances they are not listed in the report):

- Naphthalene (CAS No. 91-20-3)
- o-, m-and p-chlorophenol (CAS No. 95-57-8, 108-43-0, 106-48-9, respectively)
- 2,4-dichlorophenol (CAS No. 120-83-2)
- 2,4,6-Trichlorophenol (CAS No. 88-06-2)
- Tetrachlorphenols (CAS No. 4901-51-3, 58-90-2, 935-95-5, 25167833)
- Pentachlorophenol (PCP) (CAS No. 87-86-5)

Of these, only naphthalene and o-chlorophenol have been found in the clothes.

Naphthalene was found in two textile samples in concentrations of 0.9 and 1 mg/kg textile sample. The two fabrics in which naphthalene was found consisted of polyester or polyester/cotton blend. It is therefore suggested by the authors that naphthalene has been used as an adjuvant for dyeing (carrier) and not as a biocide in the mentioned cases. Another possibility is that the measured naphthalene originates from naphthol-dyeing agents, or from oils or anti-foaming agents used for dyeing, according to the authors of the report.

o-Chlorophenol was found in four textile samples of wool and cotton, at concentrations of 3.6-3.9 mg/kg textile sample. Textile samples have been imported, but the country of origin is not known.

As a part of the EPA surveys of chemical substances in consumer products, Poulsen et al. (2011) have reviewed the literature about the chemical substances in textiles. Under "anti-molding agents", dimethyl fumarate (DMF) is the only chemical found on the list. In the past, DMF has been widely used as an anti-molding agent. However, since the Statutory Order (No. 325 of 28/04/2009) from 2009 prohibiting the importation and sale of products containing DMF, it has not been allowed to import and sell textiles containing DMF in concentrations above 0.1 mg/kg.

Despite the ban, there have been a few examples of jeans with DMF sold in Sweden in 2009 (reported in Poulsen et al., 2011). On behalf of the Danish EPA, in 2010, Aarhus University checked the contents of DMF in 302 pieces of footwear sampled on the Danish market (Krongaard et al., 2011). Out of the 302 examined pieces of footwear, only 1 contained DMF in concentrations above the exposure limit of 0.1 mg/kg. The sample contained 0.10 to 0.17 mg DMF per kg.

2.1.2 Industry guidance on chemicals in textiles

A new guidance on chemicals in textiles for textile companies, published in cooperation between the Danish Chamber of Commerce, Danish Retail, National Sports Outfitters Association and Danish Fashion and Textile, contains data relating to the use of biocidal active substances in textiles (Danish Chamber of Commerce, 2011).

The guidance indicates that the most commonly used chemicals for the fumigation of containers are:

- Methyl bromide (CAS No. 74-83-9);
- Phosphine (CAS No. 7803-51-2);
- Hydrogen cyanide (CAS No. 74-90-8);
- Formaldehyde (CAS No. 50-00-0);
- Sulfur sulfide [presumably sulfonyl difluoride, CAS No. 2699-79-8];
- Carbonyl sulfide (CAS No. 463-58-1).

According to the guidance, chlorophenols are used as biocidal active substances in the production of textiles. They may be used for the treatment of natural fibres and leather against mildew and rot. Moreover, chlorophenols can occur as preservatives in other ancillary products used in the production process. Textiles must not contain pentachlorophenol (PCP), which is covered by Annex XVII of REACH with a limit value of 5 mg/kg. Furthermore, the guidance indicates that textiles must not contain tetrachlorophenol, its salts nor tetrachlorophenol compounds (listed as CAS No. 25167833, 935955). However, there is generally no prohibition of articles containing tetrachlorophenol, but the substance is part of many companies' negative lists and negative lists of several ecolabels.

Today it is forbidden to market articles containing DMF above the limit value, but according to the guidance, DMF has previously been used to protect shoes against mold during transport. DMF can occur in small bags, but can also be sprayed on, so it is not directly recognizable if the product is treated. The substance impregnates textiles through vapours which penetrate the textile and thereby protects it from fungal damage.

Formaldehyde is specified in the manual to be present in textiles in small quantities. Danish legislation does not ban formaldehyde, but the substance is listed on the negative lists in relation to a number of eco-labels: Flower, Swan, OekoTex 100, and Global Organic Textile Standard.

2.1.3 Result of contact with industry

In the survey, a number of companies and organizations have been contacted. The Danish trade organization Danish Fashion and Textile was consulted in order to identify the major importers of clothing from countries outside the EU. In addition, two of the main players in the market, the manufacturer Bestseller and the importer COOP, were contacted to gain knowledge about the use of biocides in the industry. Additionally, internet searches were conducted for identification of business requirements. Furthermore, the Danish shipping company Prime Cargo, which transports clothes to Denmark, the EWS Scandinavia (Eco Worldwide Services) which perform gas measurements on import containers for a number of major importers of clothing and the Bureau Veritas, which performs control measurements of chemical substances in (amongst others) textiles, were contacted.

The trade organization Danish Fashion and Textile does not affirm that biocidal active substances can be found in clothes on the Danish market. The organization has not been able to assist with information about their use in clothing. The trade organization has identified the current largest clothing companies in Denmark, which are probably also the biggest importers of clothing from countries outside the EU. In Table 1, for the purpose of illustrating their relative size (based on revenue), the 11 largest companies are listed with their position in the top 1000 companies in Denmark. The position on the list does not necessarily correspond to the companies' relative market shares of imported clothing.

In addition to the clothing companies listed below, the retailers COOP and Danish Supermarket are also large importers.

TABLE 1.
THE 11 LARGEST IMPORTERS OF GARMENTS IN DENMARK IN 2012 (SOURCE: INDUSTRY ORGANIZATION DANISH FASHION & TEXTILE).

Company Name	Region of head-quarters	Top 1000 DK (company)
Bestseller	Central Jutland	43
IC Companys	Capital Region	124
BTX Group	Central Jutland	167
H & M	Abroad (Sweden)	199
Esprit	Abroad (Germany)	590
Triumph	Abroad (Germany)	627
Noa Noa	Nothern Zealand	741
Bon A 'Parte	Central Jutland	767
Mascot	Central Jutland	827
Trevira Neckelmann	Central Jutland	871
Kwintet Kansas	Funen	997

Source: Trade organization Danish Fashion & Textile.

There is also a large group of smaller importers who also import from Asian countries. It has therefore not been possible to get a full overview of the industry. The latest analysis by the Competition Authority of the clothing market is from 2002 and, at that time, it was considered to be a market with many small businesses and widespread competition.

Denmark's largest clothing company, Bestseller, imports large quantities of clothing to Denmark from countries outside the EU. The company has a chemicals policy (Bestsellers Chemical Restrictions) prohibiting the use and presence of about 25 drug groups and a testing program to detect whether their suppliers meet the Bestsellers requirements (Bestseller, 2010).

The major importers of clothes, according to available information, all require information on the presence of hazardous substances in the clothes. The following biocidal active substances are prohibited in clothes delivered to Bestseller and H & M (Bestseller, 2010, H & M, 2009):

- Formaldehyde (CAS No. 50-00-0) - not allowed more than 16 mg/kg in clothing and leather goods for children under 3 years. For other clothing the limit value is 75 mg/kg, while it is 150 mg/kg for leather goods. Formaldehyde may also have different functions apart from biocidal, relating to the manufacturing of clothes.
- Pentachlorophenol (PCP) (CAS No. 87-86-5) - not allowed more than 0,05 mg/kg.
- Tetrachlorophenol (TeCP) (CAS No. 935-95-5, 58-90-2, 4901-51-3) - not allowed more than 0,05 mg/kg.
- Orthophenylphenol (PPP, o-phenyl phenol) (CAS No. 90-43-7) - not allowed more than 50 mg/kg of clothes for children under 3 years and 100 mg/kg in other clothes.

These requirements correspond to Oeko-Tex ® 100 standard criteria (Oeko-Tex, 2012), although requirements for formaldehyde are slightly more stringent.

In addition, there is a list of more than 50 crop protection agents, which must not be present in a concentration above the detection limit of 0.1 mg/kg (including PCP and TeCP).

Compliance with the requirements is typically carried out in the exporting countries following the importers' demand by independent laboratories that typically belong to large international laboratory companies, such as SGS. Textiles in Denmark are controlled only to a minor extent.

2.1.3.1 Fumigation of containers

EWS Scandinavia conducts gas measurements in imported containers of clothes for several large Danish companies in the clothing industry. In Denmark, they perform about 12,000 gas measurements and related services annually. In Northern Europe as a whole, it is several hundred thousand measurements per year.

Gas measurements are performed on demand from importers. Not all containers are tested. Criteria derived from experience are followed to assess which containers should be tested. In this manner, only containers suspected to contain gases in concentrations above the limit are tested.

The gas meters can identify three types of sources for elevated concentrations in the air in the containers:

1. Primary gas contamination originating from direct gassing of the container, rarely seen in the containers imported by the major clothing companies.
2. Secondary contamination, resulting from textile production chemicals (also includes substances other than biocidal active substances).
3. Tertiary contamination, which consists of remnants of gases resulting from earlier transports. The chemical residues are usually in the wooden flooring of the containers. Tertiary contamination is the most frequently occurring contamination type in textile containers.

EWS reports that the biocidal substances found most frequently in containers with imported clothing are the following:

- Methyl bromide, CH_3Br (CAS No. 74-83-9);
- Sulfuryl difluoride, SO_2F_2 (CAS No. 2699-79-8), and
- Phosphine, PH_3, hydrogen phosphide (CAS No. 7803-51-2).

EWS reports that these substances are found in about 1-3% of the textile containers, which are tested upon arrival in Denmark. It is primarily methyl bromide which is found in textile containers, but there is a tendency among manufacturers towards using sulfuryl fluoride as a substitute for methyl bromide. The concentration is typically only slightly above the limit in the containers in which the limit is exceeded.

According to a Swedish guide, 15% of the 8 million containers handled annually in the Port of Rotterdam are gassed in order prevent insect damage (TYA, 2009).

There has previously been a high usage of methyl bromide as biocidal substance in the EU, but the substance is now subject to restrictions on the use of ozone-depleting substances, and therefore the use of methyl bromide, with certain exceptions, is banned in Denmark (Statutory Order No. 243 of 19/04/2002). According to EWS, methyl bromide and phosphine, however, are still widely used in Asia. According to EWS, all major and significant importers of textiles to Denmark are under strict chemical requirements not to allow gassed containers into Denmark.

Apart from biocidal gases, EWS noted the following substances in the air in containers with imported clothes and shoes:

- Formaldehyde (CAS No. 50-00-0), and
- Benzene (CAS No. 71-43-2).

Containers that test positive for the presence of benzene and formaldehyde constitute 1-3% of all imported containers of clothes and shoes. The concentrations in these containers may in some cases exhibit 100 to 1,000 times the limit (discussed further in Section 2.2). In these cases, products would typically be tested subsequently.

However, it is unknown whether benzene has been used as biocidal active substance or used as a solvent in the production process. In the above lists of substances which must not occur in the clothes from Bestseller and H&M, benzene is also indicated as a solvent. According to information from trade organisations, some producers may dip their products, especially shoes and leather goods, into benzene to protect them against fungal damage during transport. However, this information is not verified.

It should be emphasized that there are also elevated levels of a number of chemicals which are not biocidal active substances. Containers with biocidal gases (see section 2.2) represent only a small part of the total number of limit value exceedances. In particular, containers with shoes exceed limit values; about 40% of the containers contain other substances in concentrations above the limits.

In Denmark, the Danish Working Environment Authority (Arbejdstilsynet, AT) enforces the rules on health and safety, and has produced a guide on clearing containers fumigated with methyl bromide (AT, 2007a). The occupational exposure guidance on clearing containers fumigated with methyl bromide indicates that there are examples of containers containing shoes, slippers, pillows, mattresses, bags, photo albums, and pistachios have been gassed in countries outside the EU. According to the instructions, containers must be tested with a gas meter before discharge if it is suspected that the container may be gassed (AT, 2007a). If a certificate of fumigation of the container is included, the container has certainly been gassed. According to the instructions, the following signs raise suspicion of methyl bromide fumigation: the container is labelled as "dangerous goods" or vent valves on the container are duct-taped. Occupational exposure limits are discussed in more detail in section 2.2. In recent years, there has been an increased focus on the health and safety problems with gas in containers.

Shipping company Prime Cargo informed the authors that in addition to fumigating containers in relation to loading with clothes, fumigation of containers prior to loading may take place. This occurs so the shipping company can provide a ready-to-use container for the new customer, ensuring that there are no pests in the container from the most recent product carriage that can damage the new product to be placed in the container. The shipping company estimates that between 10% and 20% of all containers arriving in Denmark have been gassed before they are filled. The shipping company is notified every time they get a container from a company which has been gassed, so that they have the opportunity to let it degas before they go in and work in them. They do this by leaving it open for a while.

There will also be a release of gases during transport, but the containers are typically stacked so densely that it only a fraction will escape into the environment during transport.

It is considered unlikely to find remaining biocidal gases used for transportation in the finished products in retail, since the gases are highly volatile and quickly evaporate when the product is unpacked.

If a container with concentrations of biocidal gases which exceed the acceptable limits of the importer's test programs is found in a control test, it is typically ensured that the container and products are left for degassing for a few weeks. This is typically done in large warehouses.

The substances which appear on the ban lists of the larger importers and which are not covered by general legislation may be present in the clothes from importers who do not have corresponding requirements.

An inquiry was made to two companies which perform testing of textiles in relation to the specified requirements. The intention was to get an idea of the extent to which these requirements are not complied with. It may be identified whether it is probable that the substances will occur in textiles imported by importers who do not make these claims. It was found that companies have no statistics on how often the requirements are not met.

According to a major importer, there are generally no problems with non-compliance with the requirements. Checks are carried out, however, primarily in the exporting countries.

In addition to these biocidal active substances, substances could occur from any importer which are not on the companies' negative lists, as no check is made for these. There is no requirement that biocidal active substances must not be used at all. Furthermore, there is no information about which chemical substances manufacturers use as alternatives to substances in the negative list.

2.2 Other information on the use of biocides for transport

In the search on biocide producers' and suppliers' websites, it has proven difficult to find information about biocidal active substances or biocides whereby the etiquette specifically states that these can be used to protect textiles and leather during transport.

2-phenylphenol (o-phenylphenol, CAS No. 90-43-7) is marketed under the name Preventol ® o Lanxess to prevent the growth of microorganisms during storage and transport of the hide or leather (Lanxess, 2012).

The international supplier of biocides, THOR Chemicals, was contacted and has indicated that a number of biocides, which are generally used to control microorganisms, can also be used to protect fabrics against microorganisms associated with transport. The received data sheets do not indicate that the chemicals are used for textiles for transport, but rather that they are used for protecting textiles during use. One of the means used more broadly to protect against microorganisms is Acticide ® TC 10, which contains octyl-isothiazolinone (26530-20-1).

Arch Lonza, which is also a major international supplier of biocides with offices in many parts of Asia, was contacted but has not been able to indicate biocides used specifically for the storage and transport.

The EU ecolabel ("Flower") for textile products relates directly to biocidal active substances used for transportation. The criteria include a requirement that chlorophenols (their salts and esters), PCBs and organotin compounds shall not be used for the transport and storage of products and semi-finished products (EC, 2009). There is a background document describing in detail the reasons for this requirement.

An article from Satra Technology (Satra, 2012), with departments in UK, USA and China, provides instructions on how to avoid microbial growth on textiles and leather during storage and transport. Among the advice given, it is recommended to provide appropriate biocidal active substances in the production of raw materials (specific chemical substances not mentioned). Use of drying agents during transport can help to reduce the growth of microorganisms, but, according to the article, this measure is not adequate. It is therefore recommended to use small packets which release chlorine during transport to protect against the growth of microorganisms (specific substances are not mentioned). None of the contacted individuals in the industry has been aware of the existence of such packages. DMF has been used in the form of small packets to a certain extent, but these do not emit chlorine.

Occupational exposure limits
The WEA has set limits to be observed in connection with the unloading of containers. The following limits are set for biocidal gasses and other substances that could be used as biocidal active substances (AT, 2007b).

- Methyl bromide, CH_3Br: 20 mg/m^3
- Formaldehyde: 0.4 mg/m^3
- Benzene: 1.6 mg/m^3
- Sulfuryl difluoride, SO_2F_2: 20 mg/m^3
- Phosphine, PH_3: 0.15 mg/m^3

2.3 The use of biocidal active substances throughout the life cycle of the fabric

Use of biocidal active substances in the different life cycle stages of textiles are described in an emission scenario document for biocidal active substances in textiles, which was prepared in connection with the development of the Biocides Directive (Tissier et al., 2001).

Use of biocidal active substances in various forms may be carried out at different stages in the life cycle of the textile:

- The production and processing of fibres:
  - Biocidal active substances in liquids used during the processing of cotton or wool;
  - Biocidal active substances, as incorporated into textile fibres (such as disclosed in Rastogi et al., 2003).
- The production of textiles in the form of biocidal active substances in liquids used in relation to the pre-treatment (for example, removal of chemicals used in the spinning of fibres), as well as dyeing and/or printing.
- The chemical finishing of the textiles, including:
  - Biocides, which are added to prevent odors caused by microorganisms such as sportswear (described in e.g. Rastogi et al., 2003).
  - Biocides added to prevent the occurrence of mites in bedding such as described in Lassen et al., 1999, among others;
  - Biocidal agents added to prevent the growth of fungi and other micro-organisms in the fabrics for outdoor use (described in Lassen et al., 1999, among others).
- The storage and transport of fibres (e.g. bales of cotton or wool), fabric or finished garments including:
  - Biocides to limit insects which can attack the fibres;
  - Biocidal agents to reduce fungus and other microorganisms.
- By finishing of textiles in use to maintain protective properties.

2.3.1.1 Textile Production

The biocidal active substances which are reported in the emission scenario document (Tissier et al., 2001) to be used in the production of textiles are (no CAS numbers are given in the document):

- Pyrethroids;
- Pyrimidine derivatives (eg. chlorophenylid, permethrin or ammonium fluorosilicate);
- Thiazole derivatives and chlorinated hydroxyphenyl ethers, and
- Organocopper compounds such as copper naphthalene and copper hydroxydiphenyl ethers.

It has not been possible to identify biocidal agents specifically marketed for use in liquids used in textile production, but the patent literature mentions the same substances often for this use with other applications in aqueous media. In the survey of biocidal products in Denmark (Lassen et al., 1999), biocides were used for preservation of liquids in textile production, accompanied by a variety of other uses for product type 6 "preservatives for use in containers". In principle, all the listed substances could be used in liquids for the production of textiles.

The chemicals listed were:

- Formaldehyde (CAS No. 50-00-0);
- 1,3-propanediol, 2-bromo-2-nitro-(Bronopol, BNPD) (CAS No. 52-51-7);
- Benzoic acid, sodium salt (sodium benzoate) (CAS No. 532-32-1);
- 1,2-benzisothiazol-3 (2H)-one (BIT) (CAS No. 2634-33-5);
- 2-Methyl-3 (2H)-isothiazolone (MIT) (CAS No. 2682-20-4);
- Carbamic acid, 1H-benzimidazol-2-yl, methyl ester (Carbendazim) (CAS No. 10605-21-7);
- 5-Chloro-2-methyl-3 (2H)-isothiazolone (CIT) (CAS No. 26172-55-4);
- 2-octyl-3 (2H)-isothiazolone, (CAS No. 26530-20-1), and
- 4,4-Dimethyl-oxazolidine (CAS No. 51200-87-4).

A leading supplier of biocides, Arch Lonza (Arch, 2010), markets the following active substances for preserving liquids in cans/containers (not specifically indicated for liquids used in textile production):

- 1,2-benzisothiazol-3 (2H)-one (BIT) (CAS No. 2634-33-5);
- 1,3-Propanediol, 2-bromo-2-nitro-(Bronopol, BNPD) (CAS No. 52-51-7);
- 2-methyl-3 (2H)-isothiazolone (MIT) (CAS No. 2682-20-4);
- Zinc pyrithione (ZPT) (CAS No. 13463-41-7);
- Poly (hexamethylene biguanide) hydrochloride (PHMB) (CAS No. 27083-27-8);
- Hexahydro-1 ,3,5-tris (2-hydroxyethyl)-s-triazine (HST) (CAS No. 4719-04-4).

Formaldehyde, sodium benzoate and carbendazim are currently not approved for use in products of product type 6.

Leading producers of biocides are currently marketing a series of formaldehyde donors based on, for example, ethylene dioxydimethanol (EDDM, CAS No. 3586-55-8) (including Schülke, 2012).

2.3.1.2 Chemical finishing

There is a large variety of biocidal agents used to control the growth of microorganisms on fabrics in the use phase.

According to the survey of biocidal products in Denmark, the active ingredients used to protect finished fabrics used for outdoor purposes were (Lassen et al., 1999):

- o-Phenylphenol (CAS No. 90-43-7);
- Carbendazim (CAS No. 10605-21-7);
- Zinc pyrithione (CAS No. 13463-41-7);
- Ethyl ziram (CAS No. 14324-55-1), and
- Thiocyanic acid, (2-benzothiazolylthio) methyl ester (TCMTB) (CAS No. 21564-17-0).

For leather the following were used:

- Tetrahydro-3 ,5-dimethyl-2H-1 ,3,5-thiadiazine-2-thione (dazomet) (CAS No. 533-74-4);
- TCMTB (CAS No. 21564-17-0).

A leading supplier of biocides, Arch Lonza, has a guidance indicating which biocides can be used for various purposes in textiles (ARCH, 2012). None of the biocides are directly indicated to be useful in the storage and transport of textiles. Biocidal agents used for the control of micro-organisms in the use of fabrics (control of odours and the growth of microorganisms), in particular for industrial fabrics and ropes.

The following active substances were included in the range of biocidal products:

- 3-Iodopropynyl butyl carbamate (CAS No. 55440-53-6);
- Poly-hexamethylene biguanide hydroxychloride (CAS No. 27083-27-8, 32289-58-0);
- Sodium pyrithione (CAS No. 3811-73-2), and
- Zinc pyrithione (CAS No. 13463-41-7 8-10).

The biocidal agents are used in amounts of 0.1-4% by weight of the fabric, depending on the fabric's purpose and active substance.

Another leading supplier of biocides for textiles, Thor, uses synthetic pyrethroids (CAS number not specified) for protection against insect damage (Thor, 2012). There are no biocidal agents in the range of products specifically indicated to be used for such protection during transport and storage.

For protection against microorganisms, the following biocidal active substances are used (CAS No. not available for all active substances):

- 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) (CAS No. 64359-81-5) - known as SeaNine;
- 2-n-octyl-4-isothiazolin-3-one (OIT) (CAS No. 26530-20-1);
- Isothiazolinone in combination with a benzimidazole derivative;
- Octylisothiazolinone with a triazine derivative or benzisothiazolinone compound;
- Zinc pyrithione with carbendazim, and
- Cationic zirconium paraffin emulsions with fungicides.

For leather, Thor has biocides based on phenols: TCMTB and carbendazim.

The substances used at the end of the 1990s for these purposes appear to be the dominant ones used at present.

Antibacterial agents used in clothing to reduce odour have previously been described in the Survey of Chemical Substances in Consumer Products, No. 24 (Rastogi et al., 2003). Antibacterial agents are used in clothing to avoid odour problems associated with bacterial breakdown of perspiration; in this manner, the clothes can be free from odour for a long periods of time. In 17 products bought on the Danish retail market in 2003, triclosan was found in 5 of the tested products at concentrations of 0.0007 to 0.0195%, while none of the products contained the other biocidal active substances/mixtures they were tested for: triclosan, dichlorophen, Kathon 893, hexachlorophene, triclocarban and Kathon CG (Rastogi et al., 2003).

Currently, there are a number of silver-based biocides on the market aimed to reduce odour in fabrics. A new Swedish study mentions silver-based biocides as follows: Agiene ®, Balsan Silver Care ®, Polygiene ®, Sanitized ®, Silpure ® and X-Static ® (KemI, 2012a). A Swedish study on leaching of active substances from textiles from 2012 found silver in 16 of 30 examined samples, while in two samples, a combination of triclosan and triclocarban was found (KemI, 2012). In the other samples, these three active substances could not be detected (they was not analysed for other active substances). The product samples were selected from clothes advertised by terms such as "odour", "hygienic", "silver", "counteracts odours" and the like.

2.4 Other transportation techniques that permit the transport of clothes without using biocidal active substances

A screening exercise has been carried out in order to identify transportation techniques that permit the transport of clothing without the use of biocides. To protect clothes from pests during transport, importers have begun to optimize the integrity of the garment instead of using biocidal active substances. A sealed packing is as good a protection as fumigation according to EWS, and it is not considered to be more costly. However, it is not always possible to pack clothes in sealed package before shipment from factories in Asia, because this can only be done in a dry atmosphere. In humid periods in China, India and Bangladesh, it is difficult to achieve a dry package.

2.5 Biocidal active substances for analysis and test program

This project includes, as mentioned, only the biocidal active substances that do not have an intended function during the use phase.

Table 2 below contains biocidal active substances for which it is known that they are used or have been used for the protection of textiles or during storage or transport. The table indicates, for each identified active substance, whether it is on the EU list of prohibited active substances or is slated for the EU review program of active substances under the Biocides Directive. It is also indicated whether the substance is on the EU list of existing active substances (see reference in the note to the table).

In the table it is stated which PT the prohibitions and assessment program, respectively, relate to.

According to the Biocide Directive, the two types of products that are relevant in relation to the use of biocides to protect textiles during storage and transport are:

- PT 9: Fibre, leather, rubber and polymerised materials, and
- PT 18: Insecticides, acaricides and products to control other arthropods.

Pentachlorophenol (CAS No. 87-86-5) is not listed because there is a general ban on the import of articles containing the substance according to Statutory Order 854 of 5 September 2009 banning the import, sale, use and export of products containing pentachlorophenol (PCP). DMF is also not mentioned, as the substance is limited by Annex XVII of the REACH Regulation.

TABLE 2.
BIOCIDAL ACTIVE SUBSTANCES KNOWN TO BE USED OR HAVING BEEN USED TO PROTECT TEXTILES DURING STORAGE AND TRANSPORT.

Chemical name	CAS No	On the EU list of existing active substances *2	On the EU list of banned active ingredients, product types *1	On EU review programme of active substances under the Biocide product types *2
Methyl bromide	74-83-9	Yes	Yes * 3	No
Sulfuryl difluoride	2699-79-8	Yes	No	Yes, 8, 18
Phosphine	7803-51-2	No	No	No
Hydrogen cyanide	74-90-8	Yes	No	Yes, 8, 14, 18
Carbonyl sulfide	Sulfide 463-58-1	No	No	No
2,3,5,6-Tetrachlorophenol	935-95-5	No	No	No
2,3,4,6-Tetrachlorophenol	58-90-2	No	No	No
2,3,4,5-Tetrachlorophenol	4901-51-3	No	No	No
Tetrachlorophenol	25167 833	No	No	No
Biphenyl-2-ol (o-phenylphenol)	90-43-7	Yes	No	Yes, 1,2,3,4,6,7,9,10,13
o-chlorophenol	95-57-8	No	No	No
m-chlorophenol	108-43-0	No	No	No
p-chlorophenol	106-48-9	No	No	No
2,4-dichlorophenol	120-83-2	No	No	No
2,4,6-Trichlorophenol	88-06-2	Yes	No	No
Formaldehyde	50-00-0	Yes	Yes, 1, 2,4,6, 9, 11, 12, 13, 18, 21, 23 * 3	Yes, 1, 2, 3, 4, 5, 6, 9, 11, 12, 13, 20, 22, 23
Benzene	71-43-2	No	No	No
Naphthalene	91-20-3	Yes	Yes, 19	Yes, 19
2-octyl-2H-isothiazol-3-one	26530-20-1	Yes	No	Yes, 4,6,7,9,10,11,12,13

* 1 "Existing Active Substances for which decision on non-inclusion into Annex I or Ia of Directive 98/8/EC has been made". Consolidated list of 22/02/2012. http://ec.europa.eu/environment/biocides/pdf/list_dates_product_2.pdf
* 2 "Commission Regulation (EC) No 1451/2007 of 4 December 2007 on the second phase of the ten-year work program referred to in Article 16. 2, the European Parliament and Council Directive 98/8/EC concerning the placing of biocidal products ".
* 3 For other types of products covered by the assessment program, which received no complete dossier within the allotted timeframe.

Textiles can also contain active substances that have been used as preservatives in the liquids that are used during the production. These will typically be covered by PT 6: "preservatives for use in cans/containers" according to the Biocides Directive. Use of biocides in production could also have an impact on the protection of textiles during storage and transport by limiting the presence of germs, which could later develop into bacterial or fungal infestations.

It has been difficult to obtain specific information confirming the use of biocides to protect clothing during storage and transport. There has been a choice, therefore, to screen for the presence of a number of active substances which may have been used for the protection of liquids in the production of clothing.

TABLE 3.
EXAMPLES OF BIOCIDAL ACTIVE SUBSTANCES THAT MAY BE USED AS PRESERVATIVES IN LIQUIDS IN THE PRODUCTION OF TEXTILES

Chemical name according to *2	CAS No	On the EU list of existing active substances *2	On the EU list of banned active ingredients, product types *1	On EU review programme of active substances under the Biocide product types *2
Bronopol	52-51-7	Yes	Yes, 1, 3, 4, 7, 10, 13	Yes, 1,2, 3, 4, 6, 7, 9, 10, 11, 12, 13, 22
1,2-benzisothiazol-3 (2H)-one (BIT)	2634-33-5	Yes	Yes, 7.10, 22	Yes, 2, 6, 7, 9, 10, 11, 12, 13, 22
2-methyl-(2H)-isothiazole-3-one (MIT)	2682-20-4	Yes	Yes, 2, 4, 7, 9, 10, 22	Yes, 2, 6, 7, 9, 10, 11, 12, 13, 22
Carbendazim	10605-21-7	Yes	Yes, 6, 11, 12,13	Yes, 6, 7, 9, 10, 11, 12,13
5-Chloro-2-methyl-2H-isothiazol-2-one (CIT)	26172-55-4	Yes	No	No
2-octyl-2H-isothiazol-3-one	26530-20-1	Yes	Yes, 4, 8, 12	Yes, 4, 6, 7, 9, 10, 11, 12, 13
4,4-dimethyl-oxazolidine	51200-87-4	Yes	Yes, 11	Yes, 6, 11, 12, 13
(Ethylene dioxy) dimethanol	3586-55-8	Yes	Yes, 3, 4, 9	Yes, 2, 3, 4, 6, 9, 11, 12, 13

* 1 "Existing Active Substances for which decision on non-inclusion into Annex I or Ia of Directive 98/8/EC has been made". Consolidated list of 22/02/2012. http://ec.europa.eu/environment/biocides/pdf/list_dates_product_2.pdf
* 2 "Commission Regulation (EC) No 1451/2007 of 4 December 2007 on the second phase of the ten-year work program referred to in Article 16. 2, the European Parliament and Council Directive 98/8/EC concerning the placing of biocidal products ".

Since, from the survey, substances cannot be identified that obviously would be present in imported clothing, the programme of chemical analyses in this project was initiated with screening analyses covering a broad group of potentially relevant biocidal active substances such as chlorophenols, isothiazolinones, naphthalenes and a variety of other hazardous substances including some insecticides. The purpose of the screening was to identify as many unknown substances as possible. Furthermore, in this phase the samples were analysed specifically for formaldehyde, which cannot be detected with the screening method applied.

It should be noted that the five top substances listed in Table 2 are gases. These gases are vented in connection with the emptying of the transport containers and the residues in textiles are ascertained to have evaporated before the textiles reach the consumers. It was therefore concluded that it is not relevant to include these substances in the analysis and testing programme.

2.6 Products for analysis and testing program

There is no information suggesting that biocidal active substances, which have been used to preserve liquids during production or to protect during storage and transport, will be particularly frequent in certain products.

Biocidal active substances could in principle be found in small concentrations in all types of fabrics, as a result of the use of preservatives in the liquids used in production. Moreover, it must be expected that biocidal active substances used for protection during storage and transport, in particular, could be used on textiles of natural fibres like cotton, wool and silk, since these are vulnerable to microorganisms that can break down the fibres (Lacasse and Baumann, 2004). There is therefore a focus on clothes based on these fibres in this study.

The most significant exposure is likely to be associated with clothing that is worn directly on the body, such as underwear, sleepwear, t-shirts, pants and shirts.

The screening program includes a total of 34 pieces of clothing in different categories as shown in Table 4 .

For all products are produced in South, East or Southeast Asia, which account for a large part of textile import from outside the EU, chemical legislation usually does not follow EU principles and specific requirements.

The purchase of the clothes was made based on the above criteria of material origin, variation in quality and partly the price. This resulted in a comprehensive shopping effort, as many stores choose to simply brand clothes with "Import" and several of the products were hard to find in these materials. About 60-70 shops were visited in the Aarhus and Lyngby areas, ranging from large chains to small specialty shops.

The clothes were purchased in a variety of stores, including department stores, supermarkets, some of the most dominant clothing chains and a few special boutiques. Undershirts of wool caused particular difficulties, as most woolen underclothes and wool socks are either produced in Europe or simply labelled "Import". This has resulted in two sets of special pieces imported from China, as well as an undershirt from a supermarket labelled "Import" with no further information. Moreover, the country of origin of two of the cotton products is unknown. There is a varied selection of children's, men's and women's clothing from both budget and premium brands.

TABLE 4. PURCHASED PRODUCTS BY MATERIAL.

No	Product	Country of Origin	Fibre type	Sex/Age	Type of store
B1	Sleepwear	Cambodia	Cotton	Baby	Chain
B2	Sleepwear	China	Cotton	Child	Department store
B3	Sleepwear	China	Cotton	Child	Department store
B18	Sleepwear	China	Cotton	Child	Chain
B19	Sleepwear	Unknown	Cotton	Child	Supermarket

No	Product	Country of Origin	Fibre type	Sex/Age	Type of store
B4	Undershirt	India	Cotton	Baby	Supermarket
B5	Undershirt	Bangladesh	Cotton	Child	Chain
B17	Undershirt	China	Cotton	Men	Department store
B20	Undershirt	India	Cotton	Child	Special Boutique
B21	Undershirt	China	Cotton/silk (30/70)	Women	Chain
B6	Pants	Bangladesh	Cotton	Child	Chain
B7	Pants	India	Cotton	Women	Chain
B8	Pants	China	Cotton	Men	Department store
B22	Pants	China	Cotton	Men	Chain
B23	Pants	China	Cotton	Women	Chain
B9	T-shirt	Bangladesh	Cotton	Men	Supermarket
B10	T-shirt	Bangladesh	Cotton	Men	Chain
B11	T-shirt	Bangladesh	Cotton	Men	Department store
B12	T-shirt	Bangladesh	Cotton	Women	Chain
B24	T-shirt	China	Cotton	Men	Chain
B13	Shirt	Bangladesh	Cotton	Men	Chain
B14	Shirt	China	Cotton	Men	Department store
B15	Shirt	China	Cotton	Men	Department store
B16	Shirt	China	Cotton	Men	Chain
B25	Shirt	China	Cotton	Men	Chain
B26	Shirt	China	Cotton	Men	Chain
U1	Undershirt	China	Wool	Child	Special Boutique
U2	Undershirt	Unknown	Wool	Women	Supermarket
U3	Undershirt	China	Wool/silk (70/30)	Women	Chain
U4	Panties	China	Wool (94)	Women	Special Boutique
U5	Undershirt	China	Wool	Women	Special Boutique
B27	Scarf	Bangladesh	Silk	Women	Special Boutique
B28	Undergarment	Unknown	Silk	Women	Special Boutique
B29	Scarf	India	Silk	Women	Chain

3. Analysis and testing programme

3.1 Introduction

The mapping in Chapter 2 has shown that, with the exception of a number of gases for disinfection of containers, active substances specifically used for the protection of textiles (garments) during transport (and temporary storage) from manufacturer to the consumer could not be identified. Since these gases are not expected to be present in the textiles in a retail store or at the consumers' homes, they are not included in the analysis and testing program, but evaluated only from a theoretical standpoint.

However, it is believed that a number of active substances used to protect clothing primarily against microorganisms in the production phase may also be protective during transportation or at least present as residues, possibly at relevant concentrations, if they are not removed/washed out before the transport phase. Such active substances have therefore only been entered into the test program if they have been detected in the initial screening assays in the relevant concentrations.

Screening for organic compounds and PCP are left out of the program when the survey gave no indication that such compounds were relevant in the current context. In addition, according to the survey, benzene may occur in imported clothing left out of the analysis program as this substance is not a biocide.

3.2 Overview of analyses and tests

Therefore, as there was still some uncertainty as to what can be expected to be found in the purchased textiles following the survey, the analysis and test program was conducted step-wise according to the following general procedure:

1. Step 1: Screening analysis of all purchased products by GC-MS (qualitative analysis). In such analyses, a large number of organic substances (including substances as biocides) in the clothes may be identified. The analysis can, for instance, detect chlorophenols, pyrethrins, fumarates, isothiazolinones and a number of other biocidal active substances with a detection limit of between 5 and 10 ppm. As well, the determination of formaldehyde is given by a separate, quantitative method in the analysis program in step 1.[3]
2. Step 2: Quantitative analyses of specific substances identified in step 1 and considered to be essential for either health or environmental assessment.
3. Step 3: Migration and wash test of selected products in the various categories of purchased clothes (where relevant from the results of steps 1 and 2). The migration test is performed only with artificial sweat (migration in contact with skin). Exposure by inhalation is ascertained in this context not to be critical; therefore, release by degassing is not tested.

Initially, a well-defined subsample of each purchased article, which is measured to know the exact surface area and weighed to determine the weight per unit area is produced. In addition, the weight of the total clothing article is determined.

[3] Screening by GC-MS is not suitable for the detection of highly water-soluble substances, but it is estimated that among biocides, this may be relevant for the treatment of clothes. It is really only formaldehyde which falls into this category. For this substance, determination is carried out by a separate analytical method.

3.3 Screening analyses

With the purchased products, a screening analysis by GC-MS for polar and non-polar biocides was performed; the biocides being screened included chlorophenols, fumarates, pyrethrins and naphthalenes. The active ingredients are extracted from the textile samples with acetone, to which selected deuterated internal standards have been added. The identification of the various components was made on the basis of the NIST directory (American database of standard mass spectra for a very large number of substances, the National Institute of Standards and Technology).

In addition, all products were analysed quantitatively for the content of formaldehyde in accordance with the accredited method specified in the Oeko-Tex ® (Japanese Law 112), where the identification and quantification is done using UV-VIS.

Table 5 provides a number of specific examples of biocidal active substances which may be identified by GC-MS screening. In addition, groups of substances such as isothiazolones and -zolinones may be determined by the screening.

TABLE 5.
KNOWN ORGANIC ACTIVE AS BIOCIDES THAT CAN BE SCREENED IN A SINGLE GC-MS-ANALYSIS.

Group	Name	CAS-No.
OEKO-TEX ® Standard 100	Pentachlorophenol	87-86-5
	2,3,5,6-Tetrachlorophenol	935-93-5
	2,3,4,6-Tetrachlorophenol	58-90-2
	2,3,4,5-Tetrachlorophenol	4901-51-3
	Deltamethrin	52918-63-5
	Cypermethrin	52315-07-8
	Cyhalothrin	91465-08-6
Other wellknown active substances	2,4-Dichlorophenol	91-20-3
	2,4,6-Trichlorophenol	88-06-2
	o-Chlorophenol	95-57-8
	m-Chlorophenol	108-43-0
	p-Chlorophenol	106-48-9
	Naphthalene	91-20-3
	Dimethyl fumarate	624-49-7
	Bis-(2-ethylhexyl) fumarate	141-02-6
	Permethrin	52645-53-1

3.3.1 Methods for screening

The biocides are pulled out of a subset of clothes with a highly effective extraction method called ASE (accelerated solvent extraction). This method uses an organic solvent (acetone in this case) and an elevated temperature (120 ^{0} C) and pressure (2000 psi) for 6 minutes. This treatment results in an extract containing the biocides. The amount and nature of the biocides can then be determined using chemical analysis with reference substances among the biocides to be analysed for. This project used gas chromatographic separation followed by mass spectrometric detection (GC-MS analysis) that provides a high sensitivity and identification security. The analytical method is an

Oeko-Tex ® standard, which is currently performed routinely at the Danish Technological Institute. The active substances extracted from the clothes can have both polar and non-polar characteristics.

The non-polar biocides may, without further processing, be identified by GC-MS, which uses the following conditions: Column: Varian CP5871, CP-Sil 8 CB-MS - 30m x 0.25 mm x 0.50 µm, 80 ° C (0.5 min) to 250 ° C, rate of 8 ° C/min, then rate 15 ° C/min to 320 ° C for 13 min. Run time: 39.4 min. Carrier: He, 15 psi, inj. temp: 280 ° C.

The detection limit is 1-5 mg/kg (depending on the biocide).

The polar pesticides require derivatization before analysis on GC-MS is possible. The derivatization takes place through treatment with diazomethane, as is a process of converting carboxylic acids to methyl esters.

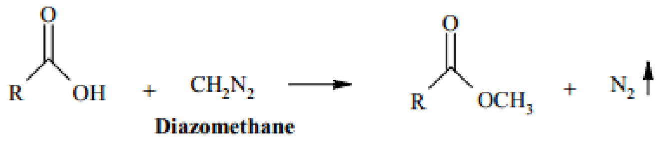

FIGURE 1.
REACTION OF POLAR BIOCIDES WITH DIAZOMETHANE.

The derivatization procedure for a subsample (100 ul) is transferred to a vial, to which a diazomethane solution is added (100 uL). It is then possible to analyse the sample by GC-MS: Column: Varian CP5871, CP-Sil 8 CB-MS - 30m x 0.25 mm x 0.50 µm, 50 ° C (0.75 min.) to 320 °C, rate 20 °C/min for 15 min. Run time: 29.3 min. Carrier: He, 15 psi, inj. temp: 280 ° C).

The detection limit is 1-5 mg/kg (depending on the biocide).

For each product two screens are carried out: one for the polar and the non-polar biocide, but using only a single extraction.

3.3.2 Formaldehyde

Formaldehyde is determined by the accredited method of Japanese Law 112 (also used for certification to textiles Oeko-Tex ® Standard 100), where the samples are extracted in an aqueous solution at 40° C and the formaldehyde content is determined using the acetyl acetone method and subsequent spectrophotometric analysis (UV-VIS). This method exploits the fact that formaldehyde reacts with pentane (see Figure 2) to form a closed ring compound (3,5-diacetyl-1 ,4-dihydrotlutidin), which has a characteristic UV-signal and therefore able to quantify the initial content of formaldehyde from the UV signal of this compound.

The detection limit is 2 mg/kg.

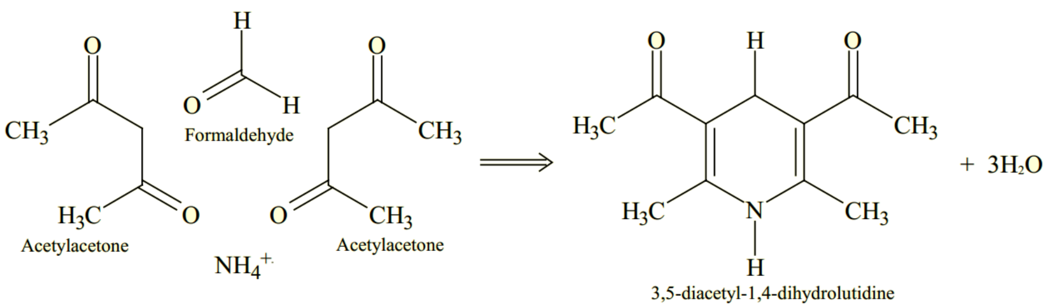

FIGURE 2.
THE REACTION OF FORMALDEHYDE WITH ACETYLACETONE

3.3.3 Results for the screening

The following table indicates the biocides that are identified in the different products.

TABLE 6.
RESULTS OF SCREENING FOR THE PRESENCE OF BIOCIDES (SEE TABLE 4 FOR DETAILED PRODUCT INFORMATION.)

Samples no.	Product	Biocide found	Sample no.	Product	Biocide found
B1	Sleepwear	No	**B18**	Sleepwear	No
B2	Sleepwear	No	**B19**	Sleepwear	No
B3	Sleepwear	No	**B20**	Undershirt	No
B4	Undershirt	No	**B21**	Undershirt	Formaldehyde
B5	Undershirt	No	**B22**	Pants	No
B6	Pants	No	**B23**	Pants	No
B7	Pants	No	**B24**	T-shirt	No
B8	Pants	No	**B25**	Shirt	No
B9	T-shirt	No	**B26**	Shirt	No
B10	T-shirt	No	**B27**	Scarf	No
B11	T-shirt	No	**B28**	Slip	Formaldehyde
B12	T-shirt	No	**B29**	Scarf	No
B13	Shirt	No	**U1**	Undershirt	Permethrin Formaldehyde
B14	Shirt	No	**U2**	Undershirt	No
B15	Shirt	Formaldehyde	**U3**	Undershirt	Formaldehyde
B16	Shirt	Formaldehyde	**U4**	Panties	Permethrin
B17	Undershirt	No	**U5**	Undershirt	Formaldehyde

It should be added that in the three products B28, B29, and U5, MCPA (2-methyl-4-chlorophenoxy acetic acid) was detected, which is an herbicide used in agriculture. MCPA is therefore not a biocide, and, hence, no further investigation of this substance was made.

3.3.4 Discussion of screenings

It can be seen that only two different biocides, formaldehyde and permethrin, were identified in the products. The screening analysis would have identified whether other relevant biocides had been present in concentrations above 5 mg/kg.

The herbicide MCPA was found in a few products, which is unusual. It is not possible to determine from the results whether there is a connection between the fabric type or country of origin and the presence of biocide.

3.4 Quantitative analyses

Through screening only two different biocides were identifed. One, formaldehyde, was quantified immediately by means of the method described. The second biocide identified by screening, permethrin, was quantified against external standards according to the Danish Environmental Protection Agency guidelines. The products in which permethrin were detected in the initial screening were subjected to a quantitative analysis of this substance.

3.4.1 Methods of quantitative analysis

The quantitative analysis of formaldehyde was carried out as described under screenings, above.

The analysis of permethrin was conducted to meet the Danish EPA requirements for analytical methods described in Annex 1 of the tender specifications: "Chemical analysis, requirements documentation of method of analysis" (section 3a/3b). The method is thus verified in terms of detection limit, measurement range, blank and recovery/correctness for published methods from scientific articles. A 6-point calibration curve, recovery experiments, and detections limit experiments were carried out. The quantitative analysis was performed as described in non-polar biocides and quantified against external standards.

3.4.2 The results of the quantitative analyses

The results of the quantitative chemical analysis are given below.

TABLE 7.
QUANTITATIVE DETERMINATION OF BIOCIDES IN CLOTHES.

Samples no.	Formaldehyde (mg/kg)	Permethrin (mg/kg)
B15	14	
B16	23	
U1	4	367
B21	7	
B28	22	
U3	21	
U4		407
U5	3	

3.4.3 Discussion of the results of quantitative analyses

It appears that in those products where formaldehyde is detected (7 out of 34, or 20% of the samples), the concentration of the substance is moderate and below the limit of what is acceptable according to the Oeko-Tex ® Standard. Formaldehyde is detected in products made of cotton, wool and silk. Six out of the seven products come from China, while the country of origin of the final product is unknown.

It can be seen that in the two products containing permethrin (2 out of 34, or 6% of the samples), this biocide is found in rather high concentrations, i.e. more than 350 mg/kg. Both cases involve woollen underwear that originated in China.

3.5 Migration analyses

Migration analysis was performed on the products which contained permethrin and formaldehyde.

3.5.1.1 Method for migration analyses

The products are subjected to migration assays with artificial sweat for 24 hours at 37 ° C, as this simulates the situation of a person that, for example, wears the underwear. A volume of 20 mL of artificial sweat is used, which is produced according to ISO 105-E04 for 1 g of product.

The quantification of permethrin in the artificial sweat is carried out by adding an internal standard (hexachlorobenzene-$^{13}C_6$) to the sweat. The sweat is then extracted with an organic solvent (DCM). Permethrin is then found in the organic phase with the internal standard; it can thus be verified that extraction is complete. It is then possible to quantify the amount of permethrin in the artificial sweat by GC-MS, as described in quantitative analyses. This is done since it is not possible to analyse the artificial sweat directly.

With respect to formaldehyde, the product was analysed for the remaining amount of formaldehyde in clothing after having been exposed to the migration test. The method used here is identical to the one that was used in quantitative analyses. This method was used since it was not possible to measure the formaldehyde in artificial sweat with the given method.

3.5.2 Results of the migration analysis

The results of the migration analysis are given below.

TABLE 8.
RESULTS OF MIGRATON ANALYSES OF BIOCIDES.
THE LIMIT OF DETECTION FOR FORMALDEHYDE IS 2 MG/KG AND FOR PERMETHRIN 5 MG/KG.

Samples no.	Concentration in fabric before migration (mg/kg)	Concentration in fabric after migration (mg/kg)	Concentration in artificial sweat (mg/kg)	Area of the sample (cm²)	Migration (mg/dm²)
B15	Formaldehyde 14	Formaldehyde <2	Formaldehyde 0.7 *	114.6	0, 010
B16	Formaldehyde 23	Formaldehyde <2	Formaldehyde 1.42 *	67.3	0, 031
U1	Permethrin 367	Permethrin 328 **	Permethrin 1.94	51.9	0, 075
U1	Formaldehyde 4	Formaldehyde <2	Formaldehyde 0.2 *	61.1	0.0 03
B28	Formaldehyde 22	Formaldehyde <2	Formaldehyde 1.1 *	89.6	0, 023
U3	Formaldehyde 21	Formaldehyde <2	Formaldehyde 1.0 *	123.4	0, 016

* Calculated from the concentration in the clothes after migration
** Calculated from concentration in artificial sweat

It was not possible to perform a migration test on sample no. U4 because an insufficient amount of sample material was available.

3.5.3 Discussion of the results of the migration tests

The migration analyses reveal that formaldehyde readily migrates from the product and in the sweat, indicating that a person wearing a garment containing formaldehyde will be exposed to formaldehyde in the product. It is seen that permethrin (see Figure 2) does not migrate to the same extent under the given conditions; this is not surprising given the non-polar nature of permethrin.

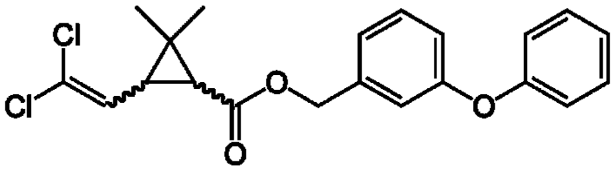

FIGURE 2.
STRUCTURE OF PERMETHRIN.

3.6 Washing Tests

For the laundry experiments, DTI's accredited wash laboratory, which has 5 identical Miele Novotronic W 375th washing machines, was used. The machines can wash 5 kg/cycle and have a variety of washing programmes.

3.6.1 Method for washing test

The laundry is done according to ISO 6330 in accredited washing machines and dryers. Certified soap ISO 6330 and a washing program according to ISO 6330 are applied. The water temperature was 40° C and dryer temperature was 60° C. The clothes were dried to a moisture content of approx. 3% according to ISO 6330.

For the washing test, a subsample was measured and weighed, and subsequently quantitatively analysed for the presence of permethrin and formaldehyde. The subsample was then washed and subsequently dried at room temperature. The primary sample is then analysed again for the quantitative determination of residues in the fabric after washing.

The selected subsamples were washed separately in one of the laboratory washing machines. Washing Ballast (pillow covers) and detergent are as specified in EN 60 456. Washing/rinsing water from the municipal water supply was adjusted down to the hardness of 2.5 mmol/liter using reverse osmosis water. Subsamples are sewn along one edge of a pillowcase to achieve typical washing effect. The washing temperature is measured with a temperature data logger sewn into ballast clothes. Residual moisture after spinning is determined for the ballast garment.

Application/determination of detergent, water hardness, water volume, washing time and residual moisture is accredited by DANAK, reg. No. 300. Temperature provisions are not covered by the accreditation.

3.6.2 Results of the washing test

TABLE 9.
RESULTS OF THE WASH TEST.

Samples no.	Concentration in fabric before washing (mg/kg)	Concentration in fabric after washing (mg/kg)	Leaching (mg/kg)
B15	Formaldehyde 14	Formaldehyde 7	7 (50%)
B16	Formaldehyde 23	Formaldehyde 21	2 (9%)
U1	Permethrin 367	Permethrin 256	111 (30%)
U1	Formaldehyde 4	Formaldehyde <2	> 2 (> 50%)
B21	Formaldehyde 7	Formaldehyde <2	> 5 (> 71%)

Samples no.	Concentration in fabric before washing (mg/kg)	Concentration in fabric after washing (mg/kg)	Leaching (mg/kg)
B28	Formaldehyde 22	Formaldehyde 5	17 (77%)
U3	Formaldehyde 21	Formaldehyde 5	16 (76%)
U5	Formaldehyde 3	Formaldehyde <2	> 1 (> 33%)

It was not possible to perform the washing tests on test No U4 due to an insufficient amount of test material.

3.6.3 Discussion of the results of the washing tests

The washing tests show that neither permethrin nor formaldehyde leach very easily. It is a surprising result that the highly polar chemical formaldehyde is not washed out to a greater extent than documented by the results. Especially for one single product (B16) the leaching is low, while for others it is more significant (B28 and U3). The strong absorption of formaldehyde to the product might be the reason that formaldehyde is found at all in the product. The manufacturer may have washed either product or fabric before shipping, but the leaching of formaldehyde has not been complete. It is less surprising that permethrin only leaches to a limited extent, since this substance is much less soluble in water.

4. Health Assessment

4.1 Introduction

The health risk assessment below is based on the results of the survey, the conducted chemical content analysis of the purchased fabric samples and subsequent migration tests performed on the fabric samples.

Two biocidal active substances were revealed by the chemical analyses and migration tests were performed with a total of six fabric samples.

4.2 Toxicity of the found biocides

The following are the main health properties associated with the two identified biocidal active substances, formaldehyde and permethrin.

4.2.1 Formaldehyde

Formaldehyde is classified for acute toxicity by any exposure route for burns, skin sensitization and possible carcinogenic effects: Acute Tox. 3 (H301) Acute Tox. 3 (H311) Skin Corr. 1B (H314) Skin Sens. 1 (H317) Acute Tox. 3 (H331), Carc. 2 (H351). The European Chemicals Agency's Committee for Risk Assessment (RAC) endorsed a proposal by France in December 2012 to update the current harmonized classification of formaldehyde and add mutagenicity category 2 (substances suspected to cause genetic defects). With regard to France's proposal to upgrade the substance to be carcinogenic in the top category 1A, which includes substances that are known to have carcinogenic potential for humans, the RAC recommended a lower category, 1B, which includes substances suspected of having carcinogenic potential in humans. The final decision was taken by the Commission.

There are a number of animal experiments with varying results for the investigation of acute toxicity. The following acute toxicity data are commonly reported and reproduced in the registration dossier available on the ECHA website:

LD50, oral, rat:	640/800 mg/kg bw	(ECHA, 2013)
LC50, inhalation, rat (4 h)	(12 -) 588 mg/m^3 (490 ppm)	(ECHA, 2013)

As for acute dermal toxicity, data is missing (data waiving) in the registration on the ECHA website. IUCLID data sheet (IUCLID, 2000) and most other sources that refer a dermal LD50 value indicate a value of 270 mg/kg bw with reference to Lewis et al., 1980[4] . There are no further details about the study or other studies in support of the results that are reflected in formaldehyde classification as toxic by skin contact.

Formaldehyde has been shown to cause irritation of eyes, skin and mucous membranes in clinical and epidemiological studies and has acrid properties if swallowed. Solutions of formaldehyde up to 37% are considered mild to moderate skin irritating (NIOSH, 2011). The odour threshold for the most part lies between 0.5 and 1 ppm and eye irritation is observed at concentrations in the air

[4] LEWIS, R.J., Sr & TATKEN, R.L. (1980) Registry of toxic effects of chemical substances, Cincinnati, Ohio, National Institute for Occupational Safety and Health, Vol. 1, p. 695.

starting at 0.3 to 0.5 ppm, but only becomes more pronounced at 1 ppm. More severe eye irritation is seen at 2 to 3 ppm, which also causes irritation of the nose and throat.

Direct effects on the skin in non-sensitized people are studied in a standard patch test. Application of formaldehyde in amounts from 0.57 to 1.12 mg/cm² resulted in irritation (NIOSH, 2011). Trials comparing irritation and allergic reactions with 1% and 2% formaldehyde in patch tests showed no statistical difference with regard to allergies, but significantly more irritative reactions (Trattner et al., 1998). Results are used as the basis for proposing a concentration of 1% formaldehyde in a standard patch test.

Absorption through the skin is generally assumed to be less than 10% based on *in vivo* toxico-kinetics studies in animals (NIOSH, 2011). Systemic absorption of formaldehyde through the skin is assumed to be limited and there are no available data that show elevated levels in blood after dermal exposure. In experiments with monkeys exposed to 0.4-0.9 ug ^{14}C-formaldehyd/cm² on the skin, the percutaneous penetration of the skin was calculated to max. 0.5% of the applied dose and 0.2% were found upon necropsy. In most of the other animals with dermal absorption, the absorption is estimated on the basis of measurements of radio-labelled formaldehyde applied to the skin and the remaining amount after the exposure period. These studies give no information about the systemic absorption. It is considered likely that formaldehyde reacts with macromolecules in the skin surface or is metabolized in the penetration of the skin layer (Larsen, 1999).

There is no discussion of the individual results for acute dermal toxicity compared with data, suggesting that the results (very limited systemic absorption) and study quality can probably be questioned. In their *Skin Notation Profile* (NIOSH, 2011), NIOSH omitted this study for formaldehyde and did not assign the notation indicating that the substance may cause systemic effects in contact with skin. In the review process (NIOSH, 2010), it was pointed out by a reviewer that the study was not mentioned in the profile, and it must be assumed that there is a deliberate omission in the final version.

Both animal and human experience demonstrates that formaldehyde is a moderate to strong skin sensitizer. A lower limit for the induction of allergies is not fixed, but is estimated to be less than 5% in an aqueous solution. The limit for elicitation of an allergic reaction in sensitized individuals ranges from 30 to 60 ppm (w/w) in an aqueous solution, using a patch test for products containing formaldehyde (OECD, 2002). In cosmetics, it has been shown that the free formaldehyde can induce skin allergies at levels of 200 - 300 ppm (Groot et al, 2009).

Mixtures containing formaldehyde are classified as skin sensitising if the mixture contains ≥ 0,2% of a substance, according to both the CLP Regulation and the old classification rules, which apply during the transitional period for CLP implementation until 1 June 2015. If the content of formaldehyde ≥ 0.1% but ≤ 0.2%, a label has to be supplied declaring the name and the possibility that an allergic reaction can be triggered. This is primarily to protect already sensitized individuals.

There are studies on formaldehyde's ability to induce asthma, but clinical assessments suggest that it happens only rarely, if at all. Asthmatics appear do not to be particularly sensitive to formaldehyde (OECD, 2002).

Repeated exposure to formaldehyde only causes effects in the form of local tissue destruction, where there has been direct contact by respectively inhalation, oral or dermal exposure. The effects on tissue depend on the concentration more than the cumulative dose and do not follow a linear relationship. Typical lesions after inhalation are seen in the nose, in the stomach after oral intake and skin after dermal exposure (OECD, 2002). In mouse studies with repeated exposure to formaldehyde, 3 hours per week for 26 weeks, showed only minimal skin irritation at concentrations of 0.5 to 1% (OECD, 2002).

The most sensitive "no observed effect concentration" (NOAEC) for morphological lesions that are found in the referenced literature is determined to be between 1 and 2 ppm by inhalation (IRIS, 2011). In a 24-month drinking water study in rats in which formaldehyde was administered in drinking water, NOAEC was found to be 260 mg/l (equivalent to the NOAEL of 15 and 21 mg/kg bw/day for male and female rats), based on a reduction in weight gain, histopathologic changes in the gastrointestinal tract and kidneys, as well as lesions in the gastric mucosa (IRIS, 2011). The U.S. EPA has established an oral reference dose (RfD) of 0.2 mg/kg/day, based on this study and using a safety factor of 100 for intra-and interspecies differences and no modifying factor (IRIS, 2011).

In the registrations dossier for formaldehyde (ECHA, 2012) an additional 24-month drinking water study in rats (1989) is given, where the NOAEC for local lesions in the stomach was determined to be 0.02% in drinking water, corresponding to a NOAEL of 10 mg/kg bw/day.

In dermal studies, no systemic toxicity at concentrations up to 1% have been found (1% was the highest test concentration) and NOAEC for local irritation in mice was 1% (OECD, 2002).

Formaldehyde is found to be slightly genotoxic in various *in vitro* systems and is generally described as a topical but weak mutagen, which primarily results in the genotoxic effects on the directly exposed tissue. *In vitro* studies support the conclusion that the genotoxic effects are restricted to cells in direct contact with the substance and that no effects can be seen in the tissue far from the site of exposure. This is consistent with formaldehyde having high reactivity with nucleophiles in the cells and a rapid metabolic degradation (OECD, 2002).

There are numerous studies of formaldehyde's carcinogenicity in humans and animals, indicating that it is carcinogenic by inhalation. Cancer development is seen locally where the substance comes into contact with tissue. Species-related differences in the development of cancer are thought to be attributable to different disposition of the nasal tissue due to anatomical differences, among other factors. In rats, inhalation of concentrations of 10 ppm (12 mg/m^3) leads to an increase in the number of tumours in the nose. Studies of people exposed to social environmental exposure show a limited correlation between exposure to formaldehyde and the development of tumours in the nose. Formaldehyde is not considered to be carcinogenic to humans by exposure conditions that do not lead to cytotoxicity, and is therefore not considered a potent human carcinogen at low concentrations. "The Carcinogenic Potency Database" (CPDB)[5] reports a TD50[6] of 1.35 mg/kg bw/day in rats.

There is no evidence that inhalation of formaldehyde causes birth defects or damage to reproduction (Wibowo, 2003). IARC concludes the same for all routes of exposure (IARC, 1995).

The critical effects in the risk characterization of formaldehyde in clothing are mainly skin sensitization and local effects associated with repeated exposure to the substance, where the level of concentration is essential. In light of the limited absorption and distribution of the substance via dermal exposure and significantly higher doses associated with systemic toxicity via oral or dermal exposure, sensitization is considered the most sensitive "endpoint" of dermal exposure.

4.2.2 Permethrin

Permethrin is rapidly absorbed and metabolized after oral absorption and does not appear to accumulate to a significant degree. Only 3-6% of the administered dose is excreted unchanged in the faeces. Absorption after both inhalation and ingestion is assumed to be 100%. Dermal absorption is set to 3% based on a human study with dermal penetration submitted for evaluation

[5] http://toxnet.nlm.nih.gov/cpdb/pdfs/ChemicalTable.pdf (latest opdate 2010)
[6] Tumourigenic dose rate 50 (mg/kg bw/day), i.e. the dose that induces tumours in 50 percent of test animals otherwise free of tumours

of permethrin as an active substance for Product type 18 of the Biocide Directive (Ireland, 2012). The U.S. EPA in connection with their registration for the substance reported that human dermal absorption is in the range of 1.4 to 5.7% and as "worst case" added absorption to 5.7%.

Permethrin is classified for acute toxicity by inhalation and ingestion, and skin sensitization: Acute Tox. 4 (H302), Skin Sens. 1 (H317), and Acute Tox. 4 (H332). LD50 values for acute oral toxicity are found in the range of 480 to 1623 mg/kg bw/day. Studies to elucidate inhalation toxicity give varying results and one study in particular has given rise to the classification of the substance. There are no reported signs of systemic toxicity via dermal exposure (Ireland, 2012).

There are no reports on eye or skin irritant effects in tests on rabbits. Results from experiments with mice show no or only transient mild irritation (U.S. EPA, 2009).

Results of sensitization studies do not all support the classification, but positive results are reported from two studies from 1989 and 1995 (Ireland, 2012). In the literature, permethrin is often described as non-sensitizing.

Permethrin exhibits low toxicity after repeated exposure and observed effects are transient. The critical effect in rats is an increase in absolute and relative liver weight (the liver is the target organ). At the same time hepatocellular hypertrophy was observed. Based on the 90-day oral rat studies, a NOAEL of about 175 mg/kg bw/day based on reversible liver effects was established. Dermal LOAEL and NOAEL values were 2000 and 1000 mg/kg bw/day based on effects such as tremors, spiky fur, statistically significant decrease in body weight and food intake, and increased liver weight in males. A NOAEL of 5 mg/kg bw/day is established on the basis of an oral one-year study in dogs on the basis of histopathological changes in the adrenal glands, reduced body weight gain in females, and an increase in liver weight (Ireland, 2012). The U.S. EPA (2009) has identified a NOAEL for systemic toxicity at 500 mg/kg bw/day for risk assessment.

Based on the results of a number of genotoxicity studies, it was concluded that permethrin does not exhibit a genotoxic potential (Ireland, 2012).

Chronic toxicity/carcinogenicity studies in rats and mice show no treatment-related effects. A NOAEL of 50 mg/kg bw/day was established on the basis of rat studies, while a NOAEL was established at 150 mg kg bw/day in mice. A recent study from 2007 (the species is not listed) gave rise to a NOAEL of 75 mg/kg bw/day (Ireland, 2012). It has not been possible to obtain more details on this test.

There is no evidence that permethrin causes birth defects or damage to reproduction. A NOAEL of 180 mg/kg bw/day established for effects on maternal and fertility on the basis of a two-generation study in rats. A NOAEL of 400 mg/kg bw/day (highest dose) was established on the basis of a study in rabbits (Ireland, 2012).

The LOAEL for neurotoxicity by the U.S. EPA (2009) is proposed as 75 mg/kg bw/day.

Human data evaluated by WHO showed that soldiers who have used clothing impregnated with 0.2% w/v permethrin showed no signs of irritation or other effects (Ireland, 2012).

Histopathological changes in the adrenal glands and reduced body weight gain in dogs in a 12-month study were considered the critical effects. A NOAEL of 5 mg/kg bw/day will be used in the risk assessment.

4.3 Exposure of humans

The exposure assessment focuses on consumer exposure associated with the use of clothing as the pieces are purchased and tested in the project. Purchased and tested products are all clothing believed to be worn in a snug fit (t-shirts, underwear, nightwear, shirts, pants), so that there is maximum contact between skin and clothing.

It is also considered as the "worst case" that the clothes would be worn for a full day at a time; migration analyses are also based on 24 hours of migration.

4.3.1 Dermal exposure

Consumer exposure shall be estimated on the basis of the formulas in section 15.3.2 of ECHA IR & CSA guidance (dermal Scenario B).

In order to calculate the dermal impacts caused by skin exposure to consumers (i.e. the amount allocated to the skin), values for total migration to the skin per unit area and unit time, exposed surface, exposure time per event, as well as the number of incidents, are used.

For use as a "Tier 1" calculation (a rough initial assessment) the present study uses the average migration to artificial sweat per unit time.

For a realistic "worst case" scenario, in this case the measured migration in the sweat of 0.031 mg/cm/24 hours and an exposed area (A_{skin}) are based on values specified in the Nordic Council (2012) "Existing Default Values and Recommendations for Exposure Assessment "and U.S. EPA (2011):" Child-specific Exposures Handbook ".

A worst-case scenario is illustrated by exposure to formaldehyde in a men's shirt with the highest level of the substance, and where there is found the largest migration of the substance.

The formula for the calculation of the external dermal dose D is indicated below.
According to the instructions, the dermal load is calculated as follows:

$$L_{der} = \frac{Q_{prod} \cdot Fc_{prod} \cdot Fc_{migr} \cdot F_{contact} \cdot T_{contact}}{A_{skin}}$$

When the migration of formaldehyde from the textile to the sweat simulant (Migr.) per unit area is measured over a period corresponding to the contact period, the formula for the dermal load is given as follows:

$$L_{der} = Migr \cdot F_{contact} \cdot T_{contact}$$

where the measured Migr. is equivalent to:

$$Migr \cong \frac{Q_{prod} \cdot Fc_{prod} \cdot Fc_{migr}}{A_{skin}}$$

The external dermal dose is calculated as:

$$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{BW},$$

wherein A_{skin} is the skin surface in contact with the garment, $F_{contact}$ is the proportion of the clothes in contact with the skin (= 1), n is the number of contacts with the garment per. day (= 1), $T_{contact}$ is the contact time per contact (24h), and BW is the body weight of the person using the clothing.

An explanation of the parameters is given in Table 10, along with units of the given parameters.

TABLE 10.
EXPLANATION OF THE INPUT PARAMETERS FOR DERMAL EXPOSURE SCENARIOS.

Input parameter	Description	Unit
Q_{prod}	Volume of product	mg
Fc_{prod}	Weight fraction of substance in product	mg/mg of product
Fc_{migr}	Rate (percentage) of the substance that migrates to the skin per unit time	mg/mg/h/day
Migr.	Volume of the substance that migrates to the skin per unit area and unit time	mg/cm²/hour/day
$F_{contact}$	Share in contact with skin (Default = 1)	cm²/cm²
$T_{contact}$	Duration of contact	hrs/day
A_{skin}	Area of the contact area between the product and the skin	cm²
C_{der}	Dermal concentration of the substance on the skin	mg/cm ³
BW	Body weight	kg
n	Average number of incidences per day	d-1
Output parameter	Description	Unit
L_{der} (dermal load)	Expected dermal problems for the skin based on the migration	mg/cm²
D_{der} (dermal dose)	External dermal dose per day and body weight	mg /kg bw/d

Exposure is calculated for one scenario for children 2-3 years (12.3 kg) and for an adult male (70 kg). The area of exposed skin is calculated based on the figures in Table 11.

TABLE 11.
ASSUMPTIONS CONCERNING. EXPOSED SKIN AREA (A_{SKIN}) AND DURATION OF SKIN CONTACT ($T_{CONTACT}$).

Tøjkategori	Material	Age group	Body Part	A_{skin} * cm²	$T_{contact}$ hrs
Shirt, men	*Cotton*	Adult	Upper body and arms	7,970	24
Undershirt, child	*Wool*	Child, 2-3 y r	Upper Body	2,350	24
Slip dress, lady	*Silk*	Adult	Upper body and thighs	6,680	24
Undershirt, lady	*Wool/silk*	Adult	Upper Body	4,957	24

* Based on the Nordic Council (2012) "Existing Default Values and Recommendations for Exposure Assessment". TemaNord 2012:505. ISBN 978-92-893-2316-1. Child: U.S. EPA (2011): Child-specific Exposures handbook.

Parameters used in the calculation are shown in Table 12.

TABLE 12. PARAMETERS USED TO CALCULATE DERMAL EXPOSURE SCENARIOS.

Parameter		Value Men's shirt Formaldehyde	Value Undershirt, child Formaldehyde	Value Undershirt, child Permethrin	Source
Total amount migrating to sweat mg/cm² per 24 hours	$Migr_{Total}$	0, 00031	0, 00003	0.00075	Based on the measurement of migration f over 24 hours
Migration to sweat, mg/cm²	Migr.	0, 13 × 10^{-4}	0, 13 × 10^{-5}	0.31 × 10^{-4}	Calculated on the basis of the total migration divided by 24 hours
Concentration in sweat, mg/kg	$Conc_{Sweat}$	1.42 *	0.2 *	1.94	Calculated or measured concentration in sweat
Contact duration, t	$T_{contact}$	24 hours	24 hours	24 hours	Estimated Exposure time
Fraction of the surface in contact with skin, cm²/cm²	$F_{contact}$	1	1	1	Default - 1 cm² skin affects 1 cm² of the clothes
Surface of exposed skin, cm²	A_{skin}	7,970	2,350	2,350	Nordic Council, 2012
Body weight, kg	BW	70	12.3	12.3	Body weight of a 2-3 year old child
Incidents per day	n	1	1	1	Assumption: 1 incident per day (24 hours)

* Calculated from the concentration in the clothes after migration

On the basis of the figures in Table 12, the external dermal dose is calculated as shown in the following.

Formaldehyde:

Exposure to formaldehyde in shirt, adult male:

$$D_{der} = \frac{Migr \cdot T_{contact} \cdot F_{contact} \cdot A_{skin} \cdot n}{BW} = \frac{0{,}000013 \frac{mg}{cm2 \times t} \cdot \times 24\, t \quad \cdot \times 1 \times \cdot\, 7970\, cm2 \times 1}{70\, kg} = 0{,}035 \frac{mg}{kg} lgv/d$$

Exposure to formaldehyde in undershirt, child:

$$D_{der} = \frac{Migr \cdot T_{contact} \cdot F_{contact} \cdot A_{skin} \cdot n}{BW} = \frac{0,0000013 \frac{mg}{cm2 \times t} \cdot \times 24\ t \quad \cdot \times 1 \times \cdot\ 2350\ cm2 \times 1}{12,3\ kg}$$
$$= 0,0060 \frac{mg}{kg} lgv/d$$

Permethrin:

Exposure to permethrin in undershirt, child:

$$D_{der} = \frac{Migr \cdot T_{contact} \cdot F_{contact} \cdot A_{skin} \cdot n}{BW} = \frac{0,000031 \frac{mg}{cm2 \times t} \cdot \times 24\ t \quad \cdot \times 1 \times \cdot\ 2350\ cm2 \times 1}{12,3\ kg}$$
$$= 0,14 \frac{mg}{kg} bw/d$$

4.3.2 Other exposure

Dermal exposure is considered to be the main route of exposure in relation to the use phase of biocide-containing clothes. Oral exposure is likely to occur with certain garments for children under 3 years, but is not included here because the clothes were fitting and not immediately available for oral exposure. Therefore no migration test to artificial saliva was carried out. The amount of biocide that can be expected to evaporate from the clothes depends on binding to the textile fibres as well as on other conditions such as temperature and humidity. The evaporation is expected to be limited and it has therefore not been prioritized to perform an evaporation test within the scope of this project. Instead, a worst case estimate of the risk associated with inhalation of formaldehyde vapours from an undershirt for children was carried out.

4.4 Health risk assessment

The health risk assessment was carried out by comparing the calculated exposure in a realistic "worst case" scenario with the derived no-effect level, DNEL (Derived No Effect Level), which indicates the exposure level below which no health effects are expected.

In the case of contact allergy, a comparison is made between the measured concentration in artificial sweat with the knowledge levels of induction and elicitation of allergy in humans.

For other endpoints, the risk assessment in this project is based on the NOAEL (C) (No Observed Adverse Effect Level), derived from the critical effect.

The DNEL value is determined on the basis of the NOAEL adjusted with a variety of correction factors. The correction factors to be used depend on the quality and relevance of the study from which the NOAEL is derived. From this the endpoint-specific DNEL value is calculated (ECHA November 2012 - R8).

The endpoint-specific DNEL (i.e. the value is determined in relation to specific organs affected) is determined using the following formula:

$$Endpoint - specific\ DNEL \quad = \frac{NOAEL_{corr}}{AF_1\ x\ AF_2\ x \ldots AF_n} = \frac{NOAEL_{corr}}{Overall\ AF}$$

$NOAEL_{corr}$ is the corrected NOAEL, i.e. the carefully selected NOAEL from which the DNEL is calculated (NOAEL corrected, R8).

The applied correction factors are shown in the table below. The correction factors are determined in accordance with the principles of default factors in the REACH guidelines.

A correction is also provided if the intake path of the selected NOAEL differs from the exposure scenario.

TABLE 13.
DEFAULT CORRECTION FACTORS USED IN DETERMINING THE DNEL

Parameter	Value	Correction factor
Between species (interspecies)	Allometric scaling. Correction for differences in metabolic rate per. kg kropsvæ weight.	AF: 1.4 for dogs
Between species (interspecies)	Remaining differences between species	2.5
Within the species (intraspecies)	Differences between individuals	10

4.4.1 Formaldehyde

4.4.1.1 Contact allergy

The health assessment of formaldehyde is based on the detected levels of 200 - 300 ppm in cosmetics associated with the induction of skin allergies upon exposure to formaldehyde. With respect to elicitation, levels between 30 ppm (w/w) in aqueous solution to 60 ppm (w/w) for products containing formaldehyde are proposed using a patch test.

As shown in the analysis results, formaldehyde was found in concentrations of up to 23 mg/kg in the products tested. The highest concentration was found in a product for children of 4 mg/kg in an undershirt.

Migration rates of formaldehyde measured for the five selected product types ranged from 0.13×10^{-5} and 0.13×10^{-4} mg/cm^2/hour, corresponding to total doses between 0.0001 and 0.00031 mg/cm^2 during 24 hours of exposure. Analyses showing how the migration rate change over time and whether the rate and thereby also the risk of allergy will be decreasing have not been carried out.

The highest migration rate of 0.13×10^{-4} mg/cm^2/hour has been found in tests of a men's shirt. The corresponding concentration in sweat calculated on the basis of concentration of the clothes after migration was 1.42 mg/kg (1.42 ppm). Comparing this concentration with the estimated levels of induction and elicitation of, respectively, 200-300 ppm formaldehyde, it is seen that the calculated concentration in sweat is more than a factor of 20 below the limit of 30 ppm (0.0030%) believed to potentially trigger an allergic reaction from a sensitized person. The calculated concentration is also more than a factor of 100 below the limit likely to cause allergies in non-sensitized individuals. Thus it must be assumed that the content of formaldehyde and migration from the analyzed clothing alone does not constitute a risk associated with the induction of allergies or allergic reactions.

4.4.1.2 Local effects

In the registration dossier on the ECHA website a DNEL of 0.012 mg/cm^2 (AF = 3) for local effects by dermal exposure over a long time is given. However, the value is not further justified.

The risk ratio calculated on this basis is 0.06, indicating that the risk of the local effects from long-term exposure is negligible.

$$RCR = \frac{Eksponering}{DNEL} = \frac{0{,}0003\ mg/cm^2}{0{,}012\ mg/cm^2} = 0{,}0025 < 1$$

4.4.1.3 Other exposure

Calculated concentration in the air from a worst-case scenario where all formaldehyde evaporates from the child's undershirt with the highest level of the substance (Fc_{prod}) and evaporation takes place to a room of 20 m³ (V_{room}), the following concentration in the breathing air for an undershirt with a weight of 200 g (Q_{prod}) is obtained:

$$C_{inh} = \frac{Q_{prod} \cdot Fc_{prod}}{V_{room}} = \frac{200\, g \cdot 23 \frac{mg}{1000}g}{20\, m^3} = 0{,}0023 \frac{mg}{m^3}$$

The calculated risk ratio on the basis of this concentration and the lowest DNEL specified in the registration of formaldehyde for the general population if inhaled over a long period (local effects) of 0.1 mg/m³ gives the following result:

$$RCR = \frac{Eksponering}{DNEL} = \frac{0{,}0023 \frac{mg}{m^3}}{0{,}1 \frac{mg}{m^3}} = 0{,}023 < 1$$

This result indicates that there is a no risk associated with exposure to formaldehyde from an undershirt alone. It should be emphasized that any evaporation from formaldehyde-containing clothes will contribute to the overall exposure to the substance in the indoor environment.

4.4.2 Permethrin

4.4.2.1 Systemic effects

The results of the analysis show that the permethrin has been found in a single sample, an undershirt for children, in a concentration of 367 mg/kg, and the concentration in sweat was measured to be 1.94 mg/kg.

The DNEL is calculated based on a NOAEL of 5 mg/kg bw/day based on effects on the adrenal glands seen by oral intake of permethrin in dogs.

The total correction factor is set to 35 on the basis of a factor of 2.5 for general interspecies differences, 1.4 for allometric scaling between dog and man and 10 for intra-species differences.

Thus the DNEL for permethrin is estimated at 0.14 mg/kg bw/day (NOAEL/AF) without correction for dermal absorption. This value is compared with the highest estimated dermal dose of:

$$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{\mathrm{BW}} = 0{,}035 \frac{\mathrm{mg}}{\mathrm{kg}}\, bw/dag$$

$$RCR = \frac{Eksponering}{DNEL} = \frac{0{,}035 \text{ mg/kg bw/dag}}{0{,}14 \text{ mg/kg bw/dag}} = 0{,}25 < 1$$

If a correction for dermal absorption is 5.7% assuming 100% absorption through oral consumption (NOAEL based on an oral study) is made, the corrected NOAEL of 87.7 is obtained. The derived DNEL is therefore 2.5. This results in a RCR of 0.014. The content of permethrin and migration from the analyzed garments alone do not therefore constitute a risk associated with the induction of allergies or allergic reactions in either children or adults.

5. Environmental Assessment

5.1 Introduction

The environmental assessment described below is carried out based on the results of the mapping of biocidal active substances used for the transport and storage of clothing and the subsequent chemical characterization and testing of purchased fabric samples in different categories.

The detailed assessment includes only the two biocidal active substances identified by the chemical analysis. A more general environmental assessment is made for the biocidal gases used for the disinfection of transport containers. These were not included in the analysis program because it was ascertained that they would have evaporated before the clothes would reach the consumers.

5.2 Environmental properties of the identified biocides

This section outlines the key environmental characteristics of the biocidal active substances identified in the purchased fabric samples (formaldehyde and permethrin), and the main active substances known to be used for fumigation of containers for the transport of clothing from country of production to country of consumption (methyl bromide , sulfuryl difluoride and phosphine).

5.2.1 Formaldehyde

5.2.1.1 Environmental fate and behaviour

At room temperature, formaldehyde is a colourless gas with a pungent odour, which freezes at -19 to -21 degrees (Environment Canada, 2001). The vapour pressure is high, 516 kPa at 25 ° C, but it also has a high solubility in water of between 400 and 550 g/l at 25 ° C. Henry's Law constant, H, can be estimated at 0.022 to 0.034 Pa m^3/mol, indicating a moderate tendency to evaporation from water. This also implies that the formaldehyde in the aqueous solution, for example in wastewater discharges, will largely remain in the aqueous phase (NICNAS, 2006).

Formaldehyde has a bactericidal effect, but at low concentrations in water, the substance is readily biodegradable as shown by e.g. 90% degradation within 28 days in a standard OECD closed bottle test and between 57-99% removal in biological wastewater treatment plants. In contrast, the substance is not degraded abiotically by hydrolysis. The estimated half-life in surface water is 1-7 days and in groundwater 2-14 days. The half-life both in non-acclimated sludge and soil (aerobic) is estimated to be 1-7 days (NICNAS, 2006).

Bioaccumulation of formaldehyde is not considered to be probable as the maximum octanol-water partition coefficient is 0.35 (Environment Canada, 2001).

In the atmosphere, the most significant transformation of formaldehyde is photochemical degradation. Formaldehyde absorbs radiation in the UV band of less than 290 nm to 340 nm and produces, at its cleavage, molecular hydrogen and carbon monoxide. The half-life of direct photodegradation in the atmosphere is about 4 hours. There is also a secondary pathway, where formaldehyde is converted to hydroperoxyl radicals and carbon monoxide (NICNAS, 2006). Formaldehyde is an important precursor to smog formation in cities. Due to its high solubility in water, formaldehyde is leached from the atmosphere by rain, mainly in the form of formic acid and hydrogen peroxide (NICNAS, 2006).

5.2.1.2 Effects in the environment

The effect of formaldehyde on aquatic organisms is almost exclusively examined in short-term studies, presumas ably due to the fact that the substance undergoes rapid degradation in aquatic environments. Neither IPCS/INCHEM (1989), OECD (2002) nor Environment Canada (2001) reports on long-term efficacy studies, but only presents results of acute or short-term studies.

NICNAS (2006) has summarized the most sensitive endpoints for a range of taxonomic groups and trophic levels of aquatic organisms (Table 14).

NICNAS also refers to two chronic tests (7 days) with the water flea *Cerodaphnia dubia* resulting in a lowest NOEC = 1 mg/l, but the results were not used by NICNAS in the further risk characterization, probably because the original study has not been available, but only been discussed in a review paper. The study is also referred to in the registration dossier for formaldehyde on the European Chemicals Agency ECHA website[7], which concluded: "*Overall, there is no reliable test available on the chronic toxicity to invertebrates with formaldehyde as test substance*".

TABLE 14.
LOWEST EFFECT CONCENTRATIONS OF FORMALDEHYDE TO A NUMBER OF GROUPS OF AQUATIC ORGANISMS (FROM NICNAS, 2006).

Organism group	Species	Endpoint	Concentration (mg/l)
Fish	*Morone saxatilis*	96 h LC50	16.9
Invertebrates	*Daphnia pulex*	96 h EC50	5.8
Algae	Green alga, freshwater	*	-
Amphibians	*Rania pipiens*	72 h LC50	8.7
Molluscs	*Corbicula* sp.	96 h EC50	35

*) No reliable data.

The lowest reported acute EC50/LC50-værdi in aquatic organisms is an EC50 = 5.8 mg/l for the freshwater flea *Daphnia pulex*.

There is no identified ecological effect data for relevant soil organisms, but formaldehyde is used as a disinfectant with an effect on microorganisms and nematodes at relatively high concentrations. An exposure level of 2 ppm gaseous fomaldehyde was effective against a number of soil-borne fungi, while 66 mg/dm^3 in aqueous solution effectively controlled nematodes in peat moss (Environment Canada, 2001).

Formaldehyde has no environmental classification, but Statutory Order No. 1022 (2010)[8] set a national Danish environmental quality standards for discharge into surface water of 9.2 g/L (added the natural background concentration) and an associated requirement for short-term exposures at 46 ug/L.

5.2.2 Permethrin

5.2.2.1 Environmental fate and behaviour

Technical permethrin is a racemic mixture of two optical isomers (cis- and trans-) of the molecule, which have slightly different characteristics. The mixture is a viscous brown liquid with a melting point of 31-35 °C and boiling point of 220 °C (USEPA, 2009). The substance has a low water

[7] http://apps.echa.europa.eu/registered/data/dossiers/DISS-9daa7594-c409-0ed0-e044-00144f67d249/DISS-9daa7594-c409-0ed0-e044-00144f67d249_DISS-9daa7594-c409-0ed0-e044-00144f67d249.html

[8] Statutory Order nr. 1022 of 25.08.2010 on environmental quality standards for surface waters and requirements to releases of pollutants to water courses, lakes and the sea.

solubility of 0,21 mg/l (USEPA 2009) to <0,00495 mg/l ("virtually insoluble") , the latter value stated in the Competent Authority Report for permethrin (EU Commission, 2012). Both values are for a temperature of 20 °C. The low vapour pressure, 2.16 x 10^{-6} Pa ved 20 °C, as well as the Henry's Law constant between 0.46 x 10^{-2} and >4.5 x 10^{-2} Pa m^3 mol^{-1} indicate a very low tendency for evaporation. The substance has a log P_{OW} of 4.67 and thus a relatively high solubility in fatty tissue, indicating a potential for bioaccumulation. However, there are studies that show a fairly rapid excretion of the substance from fish (European Commission, 2012).

Permethrin is not readily biodegradable, but biodegrades over time (inherent biodegradability). Half-lifes (DT50) in aerobic water/sediment systems at 25 ° C are 63.7 days (cis-isomer) and 27.3 days (trans-isomer) (corresponding to approx. 180 and 77 days at 12 ° C, respectively). In another experiment with the water/sediment from a river and a lake much faster degradation times were calculated (first order DT50 values, respectively. approx. 27 and 47 days at 12 ° C). The degradation under anaerobic conditions is somewhat slower. Disappearance from the water phase is rapid, i.e. DT50 between 1.3 to 3.1 days (EU Commission, 2012).

Regarding abiotic degradation in water, the substance is stable to hydrolysis and it is only slowly degradable by photolysis (EU Commision, 2012).

There are reports of a measured BCF (bioconcentration factor) for permethrin in fish of 570 l/kg in a study in which half-life of excretion of the substance was 4-5 days, while more than 80% was excreted within 14 days. Therefore, the substance is not considered to be significantly bioaccumulating (European Commission, 2012).

In soil under aerobic conditions permethrin is found to be transformed with moderate speed; reliable studies reported DT50 values between 77 and 141 days at 12 ° C, with an average of 106 days. The Cis-isomer is broken down more slowly than the trans-isomer (European Commission, 2012).

As previously mentioned, there appears to be no significant evaporation of permethrin to the atmosphere and as the substance is also considered to degrade rather quickly in this environmental compartment, long-range transport is unlikely (EU Commission, 2012).

5.2.2.2 Effects in the environment

The European Commission (2012) indicates the following validated endpoints for toxicity of permethrin to aquatic organisms in acute/short-term tests:

- Fish, acute LC50 = 0.0051 mg/l;
- *Daphnia*, acute EC50 = 0.00127 mg/l, and
- Algae, short-term EC50: not determined with confidence, higher than the water solubility.

Thus, permethrin shows high acute toxicity to aquatic organisms. The toxicity at longer exposure times (chronic toxicity) is also high, demonstrated by the lowest NOEC = 0.0000047 mg/L (4.7 ng/l) in a reproduction test with *Daphnia*. In tests with sediment organisms, LC50 = 2.11 mg/kg and a NOEC = 0.1 mg/kg have been found. The metabolites of permethrin, DCVA and PBA, are much less toxic than the parent compound (EU Commission, 2012).

The British Advisory Committee on the Water Framework Directive (UKTAG) has proposed a long-term EQS for permethrin in fresh water at 0.001 ug/L = 1 ng/L (UKTAG, 2012).

In the terrestrial environment, permethrin is found to be particularly toxic to insects, including bees. It is, however, not highly toxic to terrestrial macro-organisms, such as worms (EC 50 = 371 mg/kg), micro-organisms in the soil or plants. As well, the metabolites DCVA and PBA are found to be less toxic in soil than permethrin itself (EU Commission, 2012).

There is not considered to be a risk for food chain effects (secondary poisoning) regarding permethrin (EU Commission, 2012).

In terms of environmental properties, permethrin is classified as N (dangerous for the environment) with the risk phrases R50/53 (Very toxic to aquatic organisms aquatic organisms, may cause long-term adverse effects in the aquatic environment). The substance is not a PBT (Persistent, Bioaccumulative, Toxic substance) as it does not meet the B criterion; furthermore, it is not considered to be vPvB, since neither the vP criterion or vB criterion are met (EU Commission, 2012).

5.2.3 Biocidal gases

The main biocidal gases which are known to be used for fumigation of containers according to the survey (Chapter 2) are methyl bromide, sulfuryl difluoride, and phosphine (hydrogen phosphide). In particular, use of methyl bromide appears to be widespread. These substances are emitted mainly during the opening/venting of containers to the atmosphere, where they will be rapidly diluted through mixing with air masses to concentrations whereby toxic effects are not deemed to occur. Therefore, in this section the focus is on the fate in the atmosphere and impact-related properties such as ozone depletion potential and global warming.

5.2.3.1 Methyl bromide

Methyl bromide shows high acute toxicity to aquatic organisms and is harmful to the ozone layer. It is classified as N, R50 (very toxic to organisms living in water) and N, R59 (harmful to the ozone layer). Methyl bromide is not considered to be a greenhouse gas.

Methyl bromide is included in the Montreal Protocol list of ozone-depleting substances and is regulated under Protocol Article 2H, which states that the phase-out of the substance began in 2005 and should be fully completed on 1 January 2015. However, the use of methyl bromide for fumigation of containers for disinfecting purposes is exempted from the Protocols phase-out requirements (the QPS Exemption (QPS = Quarantine and Preshipment uses). According to Protocol Annex E, methyl bromide has a ozone-depleting potential of 0.6 (relative to the reference substance CFC-11 = 1) (UNEP, 2013).

5.2.3.2 Sulfuryl difluoride

Sulfuryl difluoride has no environmental classification, but is known to be a greenhouse gas with a Global Warming Potential (GWP) some 4000-5000 times higher than that of carbon dioxide (Wikipedia, 2013). As, however, the quantities of sulfuryl difluoride are considered negligible relative to those of carbon dioxide, the EU Commission (2009) is of the opinion that this GWP has no practical significance. The substance has no ozone-depleting effect.

5.2.3.3 Phosphine

Phosphine (phosphorus trihydride) is classified as N; R50, very toxic to aquatic organisms living in the water. It is neither a greenhouse gas nor an ozone-depleting substance.

5.3 Environmental exposure

The exposure assessment is based on textiles in the form of clothing. For the evaluation of human exposure, the product purchase and analysis focused on clothing with significant direct body contact (t-shirts, underwear, nightwear, shirts, pants), while the environmental exposure includes all garments cleaned by washing (i.e. clothing that is typically sent for cleaning are not included in the assessment). Washing of clothes is considered to be by far the most important source of environmental exposure to biocides in clothing (as a consumer product).

In addition, gaseous biocides used for fumigation of transport containers is identified as fundamentallybeing a source of environmental exposure to biocides (but not in relation to consumers). Therefore, an overall assessment of this type of environmental exposure is made.

5.3.1 Exposure via wastewater

5.3.1.1 Method of calculation

In relation to the use phase of biocides in clothing, the washing of clothes and thus domestic/municipal sewage are identified as the main source and distribution pathway causing environmental exposure. The following describes the method that is used to calculate environmental exposure resulting from the inputs to the wastewater as a basis for the exposure aspect of the environmental risk assessment of biocides in clothes.

when clothes are washed in the households, the grey water containing biocides is mostly discharged to the public sewage system through which it is transported to a wastewater treatment plant, where partly a transformation of the biocidal substance occurs and partly a redistribution of the substance between water phase and solid phase (sludge) takes place. The treated wastewater is discharged into surface water, typically a river or the sea near the coast, while the sludge is incinerated, converted into other products or applied to soil (mostly farmland).

In accordance with the guidelines of the EU for environmental assessment of chemical substances described in the European Chemicals Agency, ECHA's "Guidance on Environmental Exposure Estimation" Guidance (R.16; paragraph R.16.5.5.4), the assessment of environmental exposure from washing uses a standard EU wastewater plant, i.e. a plant with a capacity of 10,000 PE (person equivalent). Each PE contributes 200 liters of water/day and 0.11 kg sludge/day. That gives in total for a wastewater treatment plant of this size, respectively, 2,000,000 liters of water/day and 1.100 kg sludge/day.

In the current context, the 10,000 PE is assumed to be spread over 2,500 households, each consisting of four people.

The daily discharge of biocides with wastewater from a standard household/family is calculated for each biocidal active substance by the following formula:

Daily emission of "Biocide X" from washing of clothes per household =

Number of washing cycles/day * Quantity (weight) of clothing/wash * Proportion (%) of clothing that contains Biocide X * Proportion (%) of Biocide X in the treated clothing * Proportion (%) of Biocide X, emitted/cycle.

The above formula input factors are set according to an initial "worst case" calculation and refined subsequently as necessary (see Section 5.3.1.2):

- Number of washing cycles/day is set = 1 (i.e. in total 2500 washing cycles/day going to a 10.000 PE wastewater treatment plant)
- Quantity (weight) of clothing/wash is set as average = 6 kg
- Proportion (%) of clothing that contains Biocide X is calculated for two scenarios, respectively the absolute "worst case" scenario, where all the clothes (100%) are believed to contain biocide specifically on the basis of the results of the analyses performed.

- Proportion (%) of Biocide X in the treated clothing: Fabric-specific, on the basis of the results of the analyses performed. The calculation uses the median value if possible, since a single extreme value would influence the results too much if simple averages were used.
- Proportion (%) of Biocide X, emitted/wash: It is assumed that in the "worst case" the emission from clothing is the same every time, corresponding to the emissions found in the wash tests. The worst case scenario thus reflects a situation where it is always new clothing that is washed.

Stepwise estimation of exposure
Based on the above specified calculation method, and in line with the general principles of chemical risk assessment ("tiered approach"), a step-wise estimation of environmental exposure is made starting with (Step 1) calculations based on the above conservative assumptions. If the subsequent risk assessment, where the exposure is compared with the toxicity of the substance, shows that the risk under these conditions is unacceptable, repeated exposure calculations with more realistic pre-entries is performed, based on which a new risk assessment is obtained (etc.).

5.3.1.2 Estimation of environmental exposure to formaldehyde and permethrin

The two biocides that were identified in the 34 analysed samples of clothes are the bactericide formaldehyde and the insecticide permethrin.

Below for the two substances, exposure calculations in steps 1 and their results are given, while any more sophisticated calculations (Step 2, etc.) are described in Section 5.4.1 (risk assessment for the discharge of wastewater).

Formaldehyde – Step 1
Formaldehyde was detected in 7 out of 34 samples, corresponding to 20% of the samples. The median concentration in the clothes before washing was 14 mg/kg and after washing 5 mg/kg (if residues in the clothes were less than the detection limit, the "worst case" concentrations were set equal to the detection limit), i.e. the leached amount was 9 mg/kg as the median value.

This gives us the following leached amount of formaldehyde per household per day:

Quantity = 1 x 6 kg load x 0.2 x 9 mg/kg load = 10.8 mg formaldehyde/household/day.

If all clothes, that is 100%, had contained the same amount of formaldehyde, then the amount leached would have been 5 times as high, i.e. 54 mg formaldehyde/household/day.

The total amount of formaldehyde to a wastewater treatment plant (WWTP) of 10.000 PE corresponding to 2500 households may then for the two scenarios (20% and 100%) be calculated respectively as 2500 x 10.8 mg = 27,000 mg/day and 2500 mg x 54 = 135,000 mg/day.

From this result, an inlet concentration is calculated of formaldehyde to the WWTP, respectively: 27.000/2.000.000 mg/L = 0.0135 mg/L and 135.000/2.000.000 mg/L = 0.0675 mg/L.

Assuming a removal of 80% by the WWTP (due to rapid degradation of formaldehyde at concentrations lower than the limit of bactericidal effects) (NICNAS, 2006, p 47), the resulting outlet concentrations are, respectively, 0.0027 mg/L and 0.0135 mg/L.

Permethrin – Trin 1
Permethrin was detected in 2 of 34 samples, corresponding to 6% of the samples. The concentration in the one sample that could be tested before washing was 367 mg/kg, and after washing 256 mg/kg - i.e. the leached amount was 111 mg/kg (30%).

This gives the following leached amount permethrin per household per day:

Quantity = 1 x 6 kg load x 0.06 x 111 mg/kg load = 40 mg permethrin/household/day.

If all the clothes, that is 100%, had contained the same amount of permethrin, the leached amount would have been 666 mg permethrin/household/day.

The total amount of permethrin to a WWTP of 10.000 PE, corresponding to 2500 households, may then be calculated for the two cases (6% and 100%), respectively: 2500 x 40 mg = 100,000 mg/day and 2500 mg x 666 = 1,650,000 mg/day.

From this an inlet concentration of permethrin to the WWTP is calculated, respectively: 100.000/2.000.000 mg/L = 0.05 mg/L and 1.650.000/2.000.000 mg/L = 0,825 mg/L.

Assuming a removal of 80% by the wastewater treatment plant (mainly caused by sorption to sludge phase) (EU Commission, 2012) the resulting outlet concentrations can be calculated, respectively: 0.01 mg/L and 0,165 mg/L.

5.3.2 Exposure via the atmosphere

The potential overall environmental exposure via the atmosphere (i.e. from a global perspective) is the total amount of gaseous biocides supplied to transport containers with a disinfection purpose, since the entire amount is assumed to be released into the atmosphere either in the country of origin, during transport, or through venting in the destination country.

In Denmark the number of containers with clothes is approx. 12,000 per year of which the control measurements find contents above the occupational exposure limit in only approx. 3%, corresponding to approx. 360 containers per year (typically 40 foot containers with a volume of 77 m^3).

Using methyl bromide as a "worst case" example and assuming all 360 containers (of 40 feet) to be treated in this way with a dose of 48 g/m^3, the total annual amount of methyl bromide released into the atmosphere (globally) is approx. 1330 kg[9].

The magnitude of the emission of biocidal gases to the atmosphere in Denmark, again using methyl bromide as an example and the mentioned frequency of findings in the control measurements, is calculated as follows:

- The number of containers with clothing is approx. 12000 per year. Import of clothing from countries outside the EU can be estimated at 145,000 tons/year (Sum of item codes G_61, G_62 and G_63 in trade statistics) and the 12,000 containers weigh approx. 12 tonnes of clothes/container.
- An average container is a 40-feet-container with a volume of 77 m^3.
- 3% of the containers contain a biocidal gas, here assumed to be methyl bromide, above the occupational exposure level.
- The containers contain as a "worst case" 10 times the occupational limit value (see section 2.1.3).

Under these assumptions, the total amount of methyl bromide emitted to the atmosphere in Denmark from containers of clothing imported from outside the EU is calculated at 5.5 kg/year.

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[9] By fumigating containers with methyl bromide in accordance with international maritime requirements (e.g. containers of wood) according to the information, available doses between 32 g/m^3 to 80 g/m^3 are used (India Mart, 2013). The Australian methyl bromide standard prescribes for the fumigation of containers by timber a dose of 48 g/m^3 at 21 ° C for 24 hours (AQUIS, 2013).

This amount represents a small proportion relative to the total emission to the atmosphere of the entire transport operation from country of origin to Denmark (including both).

5.3.3 Other environmental exposure

The disposal phase of used clothing could potentially give rise to environmental exposure with biocides. The performed leaching tests indicate that the vast majority of the biocides will be washed out in the laundry before the disposal phase.

Furthermore, the main methods of disposal for textiles/clothing are incineration and reuse/recycling. In the case of incineration, it is assumed that active substances are completely degraded and are thus not contributing to environmental exposure with biocides. By reusing and recycling (possibly as rags), it is assumed that the fabrics become part of the general household and are therefore included in the laundry scenario, while they ultimately will be disposed of by incineration.

Other potentially relevant environmental routes of exposure to biocides in clothes are not identified, but there are other sources of environmental exposure with biocides such as formaldehyde and permethrin. It is, however, beyond the scope of this project to assess the magnitude and significance of these.

5.4 Environmental risk assessment

5.4.1 Environmental risk from discharge of wastewater

5.4.1.1 Formaldehyde

The review of formaldehyde's effects in the aquatic environment (Section 5.2.1.2) shows that acute effect data exist for the major groups of organisms and that the lowest acute value is EC50 = 5.8 mg/L for *Daphnia pulex*. There is also a 7 day chronic NOEC for *Cerodaphnia dubia* = 1.73 mg/L, which, however, is not considered sufficiently robust to be used in a risk assessment.

As stated in section 5.2.1.2, there is also an official Danish environmental quality standard for formaldehyde in surface water of 9.2 g/l, which is derived based on a larger amount of data (including the above), and it was considered appropriate to use this as the PNEC (Predicted No Effect Concentration) for the substance in the risk assessment.

Formaldehyde is also readily biodegradable at concentrations below the effect concentrations and is not bioaccumulative.

The inlet concentration of formaldehyde to a standard WWPT (10,000 PE) was calculated in section 5.3.1.2 as being 0,0135 mg/L (formaldehyde in 20 % of clothing) and 0,0675 mg/L (formaldehyde in 100 % of clothing), respectively. This led to the calculated outlet concentrations of 0.0027 mg/L and 0.0135 mg/L, respectively (assuming 80% removal in the WWTP) under the very conservative assumption that the textiles deliver the same amount of formaldehyde every time they are washed (the experiments showed that more than half of formaldehyde is washed out by the first wash in most cases).

Under these very conservative assumptions , the PEC/PNEC ratios are 0.29 and 1.5, respectively, for the two scenarios. Therefore, in the case of emission of formaldehyde from 100% of the clothes, the environmental risk ratio in the discharge of wastewater exceeds 1, whereas the ratio for the emission from 20% of the clothes will be below 1. The value of 1 will occur if formaldehyde is emitted to the specified extent (emission corresponding to the first time wash) from 68% of all the clothes by an ordinary wash. This is considered to be a significant overestimation of exposure.

It is assessed on this basis without further calculations that the environmental risk associated with wastewater discharge of formaldehyde from the laundry will be acceptably small.

The risk of effects of formaldehyde resulting from clothes by spreading of sewage sludge on agricultural land is considered to be negligible.

5.4.1.2 Permethrin

For permethrin, the English Advisory Committee on the Water Framework Directive (UKTAG, 2012) proposed an EQS = 1 ng/L for permethrin in fresh water, which is used as PNEC in the risk assessment. This value takes into account both the direct toxicity of permethrin and the degradability and bioaccumulation potential of the substance.

In Step 1 (section 5.3.1.2), the inlet concentration of permethrin resulting from washing clothes in a standard treatment plant (10,000 PE) was calculated to 0.05 mg /L (permethrin in 6% of the clothes) and 0.825 mg/L (permethrin in 100 % of the garment), respectively. Consequently, calculated outlet concentrations correspond to 0.01 mg/L and 0.165 mg/L (80 % removal in the WWTP), respectively. Moreover, it was very conservatively assumed that the clothing delivers the same amount of permethrin as determined in the laboratory test (first wash) every time it is washed.

The PEC/PNEC ratio ("risk quotient") is under these very conservative assumptions 10,000 and 165,000 (in the wastewater discharge), respectively. This means that in the scenario based on the present findings (i.e., 6% of the garments) there must be a dilution of 10,000 times in order to achieve an acceptable concentration in the environment, while in the "absolute worst case" case (permethrin in all the clothes) a dilution of 165,000 times should occur.

In Step 2 the following adjustments are are therefore made to approximate the conditions for exposure assessment in Step 1 (see Section 5.3.1.1) to a more realistic level:

- Number of washes per household is reduced to one every other day = 0.5 /household/day.
- Quantity (weight) of clothes per wash does not change.
- Proportion of clothing containing permethrin should be reduced to 1% for the following reasons: Permethrin was detected in 2 of 34 move fabric samples (6%). However, the substance was detected only in clothes made of wool and only in clothes made in China. It is therefore considered that the sample material probably significantly overestimates clothing with permethrin relative to the average composition of clothes washed in private households.
- Fraction (concentration) of permethrin in the treated clothing is not changed because the available data shows no evidence for a decrease in the value.
- The proportion of permethrin on average emitted per wash (determined in the laboratory at 30% on initial wash (one sample) is reduced in the following way: Instead of using the leached amount determined in the laboratory test, the total concentration (367 mg/kg clothes) will be used. It is assumed that equal shares of this amount are leached per wash, distributed over 20 washing cycles , i.e. yielding approx . 18 mg/kg clothing/cycle. This is considered much more realistic than assuming a level approaching the first time leaching in each wash.

This more realistic scenario gives a total daily amount of permethrin from the laundry of 0.54 mg/household or a total flow to the wastewater treatment plant of 1350 mg, and thus an inlet concentration of 0.007 mg/L and an outlet concentration at 80% removal of 0.00014 mg/L. This leads to a PEC/PNEC ratio (Risk) of 140 and, thus, a corresponding need for dilution in water. For a standard dilution of waste water at 10 times the discharge into surface water, a risk quotient at the edge of the mixing zone 14 is indicated, which indicates a risk of environmental impact.

It is considered likely that the retention in the WWTP of a substance with as high a high Log Pow as permethrin (4.67) may be somewhat higher than the 80% derived from insufficient data that is used here. The risk quotient will then be lower. There is, however, no identified literature documenting removal rates for permethrin in sewage treatment plants based on measurements.

Therefore, on the present basis it cannot be excluded that permethrin, used as a biocide in clothing, may imply a risk for some effects on aquatic organisms. Since the basis for assessment, however, is weak on several points, there is a need for further development of data.

The assessment in this report is supported by the EU risk assessment (EU Commission, 2012) for the use of permethrin as a biocide in carpets, where the estimated risk quotient (= PEC/PNEC) is estimated at approx. 9 for the discharge of sewage effluent during the "service life". This value (based on a presumably lower load than using permethrin as a biocide in clothing) is described as critical in the EU risk assessment.

INERIS (International Office for Water) gathers and processes data, including monitoring data, for chemicals in the aquatic environment and, on the basis of available data from Europe, calculated an average concentration of permethrin in fresh waters (mainly rivers) of approx. 20 µg/l and a median value of approx. 10 µg/l (INERIS, 2013). These are values in the same range as those calculated above for the most realistic scenario.

With regard to the risk of effects of permethrin by spreading of sewage sludge on agricultural land, 20% of the 1350 mg/day that are led to a WWTP will be discharged to the aquatic environment, as calculated in the revised scenario above (1% scenario). Another ten percent is estimated to be degraded in the treatment processes. The remaining 945 mg will be mixed in the 10,000 x 0.11 kg sludge/day = 1100 kg/day produced at the plant, corresponding to a concentration of approx. 0.86 mg/kg dw sludge.

UKTAG (2012) suggests a PNEC for freshwater sediment of 0.004 mg/kg dw, which is proposed to be used as a basis for the soil environment, for which no PNEC exists and only one EC_{50} = 371 mg/kg - for earthworms - is known.

If 1,100 kg sludge are applied on 1 ha (10,000 m^2) and evenly mixed in the top 20 cm of the soil (density 1500 kg/m^3), the concentration of permethrin in the soil is calculated at 945 mg/3000000 kg soil = 0.00032 mg/kg soil dw. This gives a PEC/PNEC = 0.079, indicating that the risk of adverse effects in the soil environment in a reasonable realistic exposure scenario is acceptably low.

5.4.2 Environmental risk of emission to the atmosphere

It is calculated in Section 5.3.2 that emissions of methyl bromide to the atmosphere in Denmark from containers of clothing will be a maximum of 5.5 kg/year. The total emission from treatment in the country of origin to the opening of the container in the receiving country (Denmark) will be approx. 1330 kg. These quantities are considered to be insignificant for the depletion of the ozone layer, which is much more affected by methyl bromide from other countries and other ozone-depleting substances existing in greater quantities than methyl bromide. The same assessment applies to the other biocidal gases known to be used for fumigation of containers, since none of these appear in larger amounts or have properties that are more problematic than methyl bromide with respect to the atmosphere.

5.4.3 Other environmental risks

It is ascertained that there are no other environmental risks of any significance attached to the use of biocides in the transport and storage of clothing.

6. Conclusion

6.1 Mapping

The mapping comprised three categories of biocides:

- Biocides which are used to protect clothing against damage by fungi and other micro-organisms during storage and transport;
- Biocidal gases used to protect clothes from damage by insects during storage and transport;
- Biocides which are used to prevent the growth of microorganisms in liquids used during manufacture of the garment.

This mapping provides only a comprehensive description of the biocides, which are used to protect the clothing and other fabrics during use, or used to prevent the development of odour in clothing.

During the project, major international producers of biocides operating on the global market were contacted and searches were made on their websites. None of the companies that sell biocides specifically market these as textile protection agents against damage by micro-organisms during transport and storage. The large Danish importers of clothing adhere, according to the available information, to all requirements for the presence of certain biocides in clothes. In addition to pentachlorophenol and dimethyl fumarate, both of which are prohibited, the major companies limit the presence of formaldehyde, tetrachlorophenol and orthophenylphenol. Other biocides may occur in the clothes, but the companies are not aware of the biocides actively used to protect clothes from damage by microorganisms. Damage is typically prevented by keeping clothes dry.

No reliable data on biocides actually used for this purpose was found. Based on information from the literature and on biocides marketed to control microorganisms in general, a gross list of substances that could possibly occur in clothes has been prepared.

Fumigation of containers is commonly used to prevent infestations by harmful insects. Containers transporting wood from tropical areas are fumigated routinely, and it is also common to fumigate the empty containers in order to prevent intrusion of insects that can cause damage to the new load, which may consist of clothes. According to the available information, it is rare that containers are fumigated after they are filled with clothes. Containers arriving in Denmark, for which it is assessed that there is a risk of gases existing at concentrations exceeding the Occupational Exposure Level are tested for the presence of toxic substances in the air. In clothing containers arriving in Denmark, biocides gases rarely originate from direct gassing of the container, but are commonly found as residual gases derived from previous transports or fumigation of the empty container. The chemical residues are then typically located in the container's wooden flooring.

The most common gases are methyl bromide, sulfuryl difluoride, and phosphine, which are found in concentrations above the occupational exposure limits in 1-3% of the containers. In the containers in which the limit is exceeded, it is typically only slightly above the limit. Additional to the biocidal gases, elevated levels of benzene and formaldehyde are seen in 1-3% of the containers with clothes and shoes. For these substances, the concentration in some cases may be 100 to 1,000 times the limit.

Based on information from producers of biocides, a list of biocides used for the protection of the liquids used in the manufacture of textiles has been prepared. These biocides are typically the same as used for the protection of other technical liquids in cans/containers ("in-can preservatives"). It is common that such liquids contain biocides, but it is uncertain to what extent the finished textiles will contain residues of biocides.

6.2 Analyses and tests

There were a total of 34 samples of clothes analysed that are assumed to be worn snugly fitting, i.e. underwear, blouses, shirts, trousers, nightwear, etc. Most of the samples were clothes made of cotton, but samples made of wool and silk were also analysed for content of biocidal active substances. In case of positive findings, the samples were subject to additional testing for migration to the skin (migration tests with artificial sweat) and release to wastewater in connection with washing of clothes.

Only two biocidal active substances were identified by the chemical analysis: formaldehyde (bactericidal) and permethrin (insecticidal). Formaldehyde was detected in 7 samples (approximately 20% of samples) in fairly low concentrations (3-23 mg/kg clothes), while permethrin was detected in only 2 samples (corresponding to 6% of the samples) at concentrations of 367 to 407 mg/kg. The two permethrin containing samples also revealed the presence of formaldehyde. It should also be noted that while formaldehyde was detected in samples obtained from samples of cotton, wool and silk, permethrin was only detected in wool. All the samples in which biocides were detected originated from China, with the exception of one sample, where the country of origin was unknown.

In the migration tests with artificial sweat, levels of formaldehyde in the sweat ranged from 0.2 to 1.42 mg/kg while levels of permethrin were determined at 1.94 mg/kg. In the majority of the wash tests, formaldehyde was released at levels of more than 50% (however, one sample only 9%), whereas the leaching rate of permethrin was 30% (111 mg/kg). It was expected that the leaching rate of formaldehyde would be higher.

6.3 Health

The most significant human exposure route from biocides in clothes during the use phase is dermal exposure. Related to the specific assessment of this project, it is assumed that inhalation and ingestion by mouth has limited relevance and, therefore, these exposure pathways were not considered further except for a worst-case scenario involving instant evaporation of the formaldehyde content in a child's undershirt.

The exposure to biocides through skin contact was rated for the two analytically identified active ingredients, formaldehyde and permethrin, based on the measured concentrations in clothing for adults and children, and the measured or calculated concentration in artificial sweat.

Based on the concentrations found in the clothes and migration to sweat, the daily external dermal dose of formaldehyde associated with the use of clothes for 24 hours, was calculated to a maximum of 0.035 mg/kg bw/day for a men's shirt and 0.0057 mg/kg bw/day for a child's undershirt. For permethrin, the daily external dermal dose associated with the use of a child's undershirt for 24 hours, was calculated to a maximum of 0.14 mg/kg bw/day.

The maximum concentration of formaldehyde in the sweat was calculated to be 1.42 mg/kg (1.42 ppm), and was thus more than a factor of 20 below the estimated limit for elicitation of skin allergies of 30 ppm (0.0030%) and more than 100 times less than the threshold for sensitization.

For permethrin, the DNEL was calculated to 0.14 mg/kg bw/day, based on a NOAEL of 5 mg/kg bw/day established in an oral test with dogs where there were effects on the adrenal glands. The risk characterisation ratio was thus 0.25, while after adjustment for dermal absorption, the value was reduced to 0.014. Therefore, neither the content of formaldehyde nor content of permethrin measured in clothes suggests a risk to children and adults.

A worst case scenario involving inhalation of fomaldehyde evaporated from a child's undershirt resulted in a risk characterization ratio of 0.023 and there was thereby no indication of risk from this exposure pathway.

6.4 Environment

The main potential environmental exposure to biocides in clothing during the use phase is considered to be the discharge of wastewater from the washing of clothes. Furthermore, gaseous biocides for disinfection of containers are used to a certain extent. The gases will be released into the atmosphere at some point during the transport (and will therefore have evaporated from the clothes before reaching the consumer). Other potential routes of environmental exposure to biocides in clothing, including in the waste disposal phase, are ascertained to be insignificant.

Exposure and environmental risk from the release of biocides by normal laundry washing is rated for the two identified active ingredients, formaldehyde and permethrin, partly based on the analysed concentrations and frequency of occurrence in the samples examined, and partly based on the model scenarios for wastewater (inlet and fate) derived in accordance with applicable REACH guidelines, and finally partly based on ecotoxicological data for the substances, primarily resulting from recent risk assessments made under the EU review program for biocides.

On the basis of the Danish environmental quality standard for formaldehyde, a PNEC (predicted no-effect concentration) of 0.0092 mg/l was used and an effluent concentration from a wastewater treatment plant (= PEC; predicted environmental concentration) of 0.0027 mg/L as a maximum in the scenario, where 20% of the clothes contained formaldehyde. In this case, the risk quotient (= PEC/PNEC) yielded 0.29, which is less than 1. This indicates an acceptably low risk for environmental effects of formaldehyde in clothing by washing and subsequent release to the aquatic environment with treated wastewater. A risk quotient = 1 is obtained, under otherwise unchanged conditions if 68% of the total washed clothes contain formaldehyde, which is considered unrealistically high. In the case of application of sludge to agricultural land, no effects of formaldehyde are expected.

Permethrin has a very high toxicity to insects and crustaceans in the aquatic environment, which is expressed by a very low PNEC. For the assessment, a PNEC of 1 ng/l = 0.000001 mg/ is applied, as recommended by the national English Advisory Committee on the Water Framework Directive. Since the effluent concentration of permethrin in wastewater under presumably fairly realistic assumptions is 0.00014 mg/l, a risk quotient (= PEC/PNEC) of approx. 140 is calculated for the discharge of wastewater, which implies that the waste water has to be diluted 140 times before the risk of adverse effects in the aquatic environment through long-term exposure (e.g. continuous discharge of wastewater) is acceptable. Generally, a 10-times dilution is assumed to the boundary of the mixing zone, beyond which the risk quotient should be less than 1. In this calculation scenario, however, the ratio will be 14.

Therefore, on the present basis it is not possible to exclude a risk of environmental impact by leaching of permethrin from washing of clothes. This is also concluded in the EU risk assessment of permethrin used as a biocide in product group 18 (insecticides) for impregnating of e.g. carpets. European monitoring data published by the international water office, INERIS, show that concentrations of permethrin of this order occur in European rivers.

Exposure of soil environments to permethrin through the application of sewage sludge on land is ascertained not to pose an unacceptable risk to the soil environment under normal circumstances.

Effects on the ozone layer and greenhouse effects of the biocidal gases used for fumigation of containers (e.g. methyl bromide) are considered to be marginal.

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Survey and health and environmental assessments of biocidal active substances in clothing

About two thirds of the clothes on the Danish market originate from countries outside the EU. The clothes might be treated with biocides to protect clothing against damage by microorganisms and insects pest while stored and transported. The clothes might also contain biocidal active substances used for the protection of the liquid used during the production of textiles. Biocides are designed to kill or control living organisms. Thus the biocides may be harmful towards human and environment.

The Danish Environmental Protection Agency has therefor created an overview on the biocides used for protection of liquids used in the production of the fabrics as well as the biocides used to protect clothing during storage and transport. Additionally the extent of residues of these substances in clothes on the Danish market was investigated. Further it was assessed whether the detected content of residues in clothing may pose a health and/or an environmental risk. [Back Page Text]

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