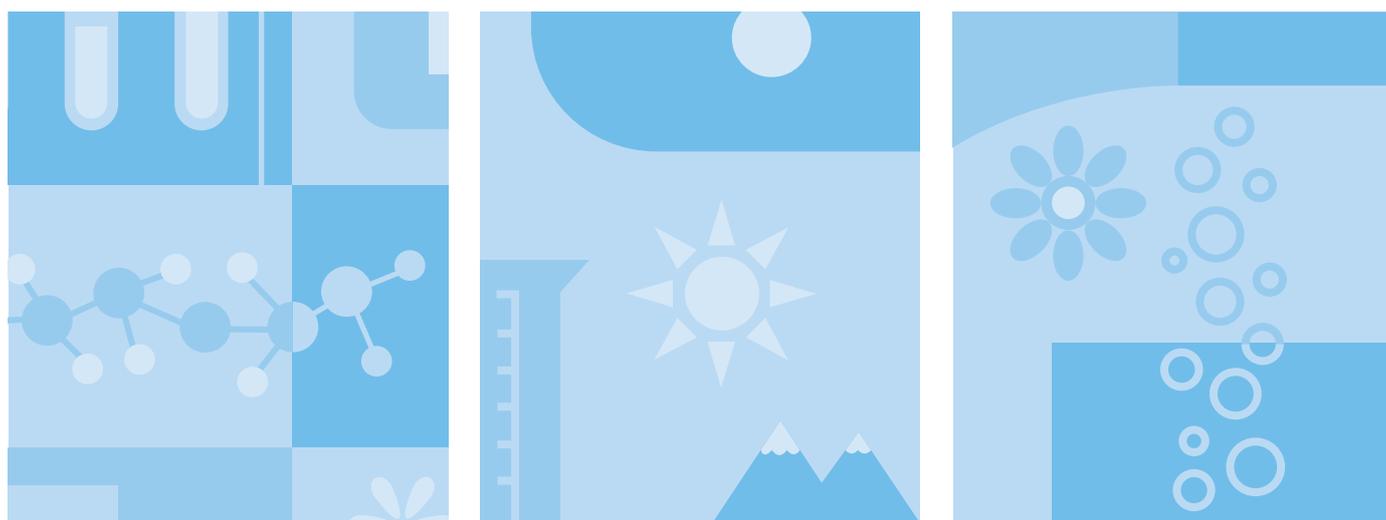


Antibacterial substances leaking out with the washing water

–analyses of silver, triclosan and triclocarban in textiles before and after washing



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Foreword

The Swedish Chemicals Agency has developed an action plan for a non-toxic everyday environment on behalf of the Swedish Government. Reducing the chemical risks in the everyday environment is a step along the way to attaining the Swedish Parliament's environmental quality objective A Non-Toxic Environment. As part of its work on the action plan, the Swedish Chemicals Agency has commissioned the analysis of 30 textile articles, principally clothing, with respect to levels of three antibacterial substances (biocides): silver, triclosan and triclocarban. These chemicals are marketed in most cases as being treated against unpleasant odour. The overarching purpose of the study is to increase knowledge in the area and to highlight the problems that may be associated with the use of biocides in clothing. With this memorandum, the Swedish Chemicals Agency wishes to draw the attention of manufacturers, importers, authorities and the general public to the use of antibacterial substances in textiles and to the fact that these leak out of the articles on washing. The use of antibacterial substances may be associated with health and environmental risks. The Swedish Chemicals Agency has not, however, conducted any risk assessment based on the results of the studies but presents here the problems and fears that have been identified on the basis of the properties of the substances posing a hazard to the environment and health. Anne-Marie Johansson, at the Strategies and Incentives Secretariat, was responsible for implementation of the project.

Swedish Chemicals Agency, 12 December 2011.

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1 English summary

The Swedish Chemicals Agency has been tasked by the Swedish Government with developing an action plan for a toxic-free everyday environment. Reducing chemical risks in the everyday environment is a step towards reaching the Swedish Parliament's environmental quality objective A Non-Toxic Environment. In the context of the action plan, the Swedish Chemicals Agency analysed 30 textile articles with respect to their levels of three antibacterial agents (biocides): silver, triclosan and triclocarban. The antibacterial treatment is usually marketed with the function of preventing odours in textiles. This memorandum describes the purpose of the study, provides background to antibacterial treatment of textiles and the environmental and health hazards posed by the studied biocides, presents results and discusses the conclusions to be drawn from this study.

Substances leaking out with the washing water

Chemical analyses were performed on all samples before washing and after three and ten washes. Silver was found in sixteen of the thirty product samples before washing. A combination of triclosan and triclocarban was found in two samples.

Concentrations of biocides in fabrics fell after washing of those that had been treated with one of the three investigated substances. In the case of triclosan and triclocarban, about half or more of the original level was washed out after ten washes. In the case of silver, the original concentration and washed-out level varied greatly. The original concentration of silver ranged between 0.4 mg/kg textile and 1,360 mg/kg textile. After ten washes 10-98 per cent of the silver had been washed out of the textiles. But half of the silver had already been washed out after three washes in several textiles. Antibacterial treatment is not only used for synthetic materials but also for cotton garments for young children, as well as synthetic, wool and silk mixtures. There are, of course, many manufacturers using biocidal treatment of their articles in addition to those who were included in the present study.

These substances are toxic and may pollute the environment

The Swedish Chemicals Agency is concerned about the increasing use of biocidal products in general. Biocides are often toxic and designed to prevent or control different organisms. Such substances must be used with caution and with good control so they do not spread out of control, harming human health or the environment. It is notable that such a large proportion of added biocides are washed out of textiles and thus enter treatment plants and the environment. The three analysed biocides are not degraded at all (silver) or are degraded slowly (triclocarban and triclosan) in the environment. Silver in ionic form, triclosan and triclocarban are very toxic to aquatic organisms. Triclocarban has demonstrated toxic effects on reproduction in studies, and triclosan has shown endocrine-disrupting properties.

Silver, triclosan and triclocarban leaking from textiles contaminate the sludge from treatment plants. Concentrations of silver are no longer declining in sewage sludge from sewage treatment plants, which had been the case since the photographic industry was digitalised. Sludge might be spread on farmland as soil fertiliser. The substances contained in the sludge can be taken up by cultivated plants, finally ending up in animal feed and food. These substances can also affect water and soil organisms.

Direct health aspects and development of resistant bacteria

In addition to the environmental aspects, there is also concern over direct exposure of children who might suck on biocide-treated clothing. The risk of direct exposure should be evaluated by the companies that manufacture or import the biocide-treated clothing/textiles.

There are also concerns that biocidal use may contribute to the development of resistant bacteria and the development of cross-resistance to antibiotics, which in turn can lead to intractable diseases. Resistance to antibiotics is a serious problem and increasing attention is being paid to this issue by authorities around the world.

Massive lack of knowledge

Humans and the environment are exposed to large numbers of chemicals used in most people's everyday lives. Newborn babies have more than 100 contaminants in their blood when they are born. These are substances that naturally should not be there, transferred from the mother, who, in turn, has been exposed through substances used and dispersed in society and occurring in food, beverages and in the air we breathe and on our skin. Antibacterial substances in textiles are one of many sources of the total chemical load. For many of the chemical elements, we have insufficient knowledge of how they can affect humans and the environment in the long run. We know even less about how different substances can interact with one another. This is a major challenge in efforts to achieve the environmental quality objective A Non-Toxic Environment.

Do we need antibacterial substances in textiles?

Further efforts are needed to reduce the risks associated with chemicals we use in present-day society, and particularly hazardous substances need to be phased out of newly produced articles. It is particularly important to give priority to consumer articles and articles which may expose children to hazardous substances.

According to the Biocidal Products Directive, use of biocidal products must be limited to a minimum. Therefore, there is reason to question whether the function of antibacterial treatment of clothing and other textiles is necessary, and weigh this against the risks that may arise.

It is difficult, as a consumer, to be informed about what biocides are contained in clothes. It is seldom explicitly declared that the clothes are treated with antibacterial agents. If the garment is marketed under labels such as “anti-odour”, “treated against bad smell”, “for lasting freshness”, “hygienic protection”, “antimicrobial” etc., there is reason to suspect that they have been treated with an antibacterial substance.

Companies placing these kinds of products on the market need to consider whether the substances can be phased out. How great is the need for antibacterial agents in clothing? If there are reasons why clothes contain antibacterial agents, companies should clearly inform their customers so that purchasers and consumers can make their own informed choices.

New legislation tightens the requirements

Under the Environmental Code, the EU's, chemicals legislation REACH and the Product Safety Directive, companies placing products on the market have a responsibility to ensure that the products are safe and do not present risks to humans and the environment. Under the

new EU Biocidal Products Regulation, which comes into force in September 2013, it is no longer permitted to place biocidal products on the EU market unless the active ingredients are approved for the intended application. For example, different silver compounds must be approved for use in protection against odour in textile fibres. This requirement will also apply to articles that are imported from countries outside the EU. If a manufacturer claims that an article containing a biocidal product is antibacterial, the article has to be labelled with information to this effect and the name of the active substance must be used. The effectiveness of biocidal treatment has to be documented. The new regulation on biocides will result in considerable changes and improved opportunities for authorities to restrict the use of biocides involving risks.

2. Sammanfattning

Kemikalieinspektionen har på uppdrag av regeringen tagit fram en handlingsplan för en giftfri vardag. Att minska de kemiska riskerna i vardagen är ett steg på vägen att nå riksdagens miljö kvalitetsmål Giftfri miljö. Kemikalieinspektionen har inom ramen för arbetet med handlingsplanen låtit analysera 30 textila varor, främst kläder, med avseende på innehåll av tre antibakteriella ämnen (biocider) silver, triklosan och triklokarban. Det övergripande syftet med studien är att öka kunskapen inom området och belysa de problem som kan vara förknippade med användning av biocider i kläder. Den antibakteriella behandlingen marknadsförs vanligtvis ha som syfte att förhindra dålig lukt i textilierna. Denna PM beskriver bl.a. en bakgrund om biocidbehandling av textilier och de studerade biocidernas miljö- och hälsoegenskaper, resultatet av de analyser som gjorts samt vilka slutsatser Kemikalieinspektionen drar utifrån denna studie.

Ämnena läcker ut med tvättvattnet

Kemiska analyser utfördes på samtliga varuprover innan tvätt och efter tre och tio tvättar. Silver återfanns i sexton av de trettio varuproverna innan tvätt. En kombination av triklosan och triklokarban hittades i två varuprover. De övriga plaggen var sannolikt, med några undantag, behandlade med någon annan biocid som inte ingick i undersökningen.

Biocidhalterna sjönk efter tvätt i alla textilier som var behandlade med någon av de tre undersökta ämnena. För triklosan och triklokarban tvättades kring hälften eller mer av den ursprungliga halten ur efter tio tvättar. När det gäller silver varierade ursprungshalt och urtvättad andel stort. Ursprungshalten av silver varierade mellan 0,4 mg/kg textil till 1360 mg/kg textil. Efter tio tvättar hade 10-98 procent av silvret tvättats ur textilierna. Men redan efter tre tvättar hade hälften av silvret släppt i flera plagg. Antibakteriell behandling sker inte bara av syntetmaterial utan också av bomullsplagg för små barn, samt av syntet-, ull-, och silkesblandningar. Det finns naturligtvis fler tillverkare som biocidbehandlar sina varor än de som kom med i studien.

Ämnena är giftiga och kan förorena miljön

Kemikalieinspektionen ser generellt allvarligt på den ökande användningen av biocidbehandlade varor. Biocider är ofta giftiga och framtagna för att ta död på eller motverka olika organismer. Sådana ämnen måste användas med försiktighet och med god kontroll så att de inte sprids okontrollerat och skadar människors hälsa eller miljö. Det är anmärkningsvärt att så stor andel av tillsatta biocider tvättas ur textilier och därmed kommer ut i reningsverk och i miljön. De tre analyserade biociderna bryts inte ned (silver) eller bryts ner långsamt (triklokarban och triklosan) i miljön. Silver i jonform, triklosan och triklokarban är mycket giftiga för vattenlevande organismer. Triklokarban och triklosan har i studier visats ha fortplantnings- respektive hormonstörande egenskaper.

Silver, triklosan och triklokarban som läcker från textilier förorenar det slam som kommer från reningsverken. Silverhalten minskar inte längre i rötslam från reningsverk, vilket varit en trend sedan fotoindustrin digitaliserades. Rötslammet kan spridas på åkrarna som jordförbättringsmedel. Ämnena som finns i slammet kan då tas upp av de odlade växterna och genom det hamna i djurfoder och i livsmedel. Ämnena kan också påverka vatten- och jordlevande organismer.

Direkta hälsoaspekter och utveckling av resistenta bakterier

Utöver miljöaspekterna finns också oro för direkt exponering av bl.a. barn som kanske suger på biocidbehandlade kläder. Vi känner inte till om hudens normalflora påverkas när man bär biocidbehandlade kläder nära kroppen. Det är tillverkare och importörer som ska bedöma risker vid exponering från de biocidbehandlade kläder som sätts på marknaden.

Det finns dessutom farhågor om att biocidanvändningen kan bidra till utvecklingen av resistenta bakterier och utveckling av korsresistens mot antibiotika som i sin tur kan innebära svårbehandlade sjukdomar. Resistens mot antibiotika är ett allvarligt problem vilket alltmer uppmärksammas av myndigheter i hela världen.

Okunskapen är stor

Människor och miljö exponeras för en stor mängd kemikalier som används i de flesta människors vardagliga liv. Nyfödda barn har 100-tals främmande ämnen i sitt blod när de föds. Det är ämnen som naturligt inte borde finnas där, som förts över från modern och som hon i sin tur har fått i sig genom att ämnen används och sprids i samhället och hamnar i mat, dryck, i luften som vi andas och på huden. Antibakteriella ämnen i textilier är en av många källor till den totala kemikaliebelastningen.

För många av de kemiska ämnena har vi inte tillräcklig kunskap om hur de kan påverka människa och miljö på sikt. Än mindre känner vi till hur olika ämnen kan samverka med varandra. Detta är en stor utmaning i arbetet för att nå miljökvalitetsmålet Giftfri miljö.

Behövs antibakteriella ämnen i textilier?

Ytterligare insatser behövs för att minska riskerna med de kemikalier som vi använder i samhället och särskilt farliga ämnen behöver fasas ut ur nyproducerade varor. Särskilt angeläget är att prioritera konsumentvaror och varor där barn kan exponeras för farliga ämnen.

Enligt biociddirektivet ska användning av biocidprodukter begränsas till det absolut nödvändiga. Det finns därför anledning att fundera över när funktionen av antibakteriellt behandlade kläder och andra textilier är nödvändig och väga detta mot de risker som kan uppstå.

Det är idag svårt som konsument att få information om vilka biocider kläderna innehåller. Det står sällan uttryckligen att kläderna är behandlade med antibakteriella medel. Om plaggen marknadsförs under beteckningar som "Behandlad mot dålig lukt", "For lasting freshness", "anti-odour", "Hygienic protection", "antimicrobial" etc. finns det skäl att misstänka att de är behandlade med något antibakteriellt ämne.

De företag som sätter ut sådana här produkter på marknaden behöver fundera över om ämnena kan fasas ut. Hur stort är behovet av antibakteriella ämnen i kläder? Om det finns skäl till att kläder innehåller antibakteriella ämnen bör företagen på ett tydligt sätt informera sina kunder om detta så att inköpare och konsumenterna kan göra egna val. Vi bedömer dessutom att konsumenterna generellt sett har en låg kunskap om de hälso- och miljörisker som är förknippade med antibakteriella ämnen i kläder.

3. Background

The Swedish Chemicals Agency has developed an “Action Plan for a Toxic-Free Everyday Environment 2011-2014 Protecting Children Better”¹ on behalf of the Swedish Government”. Part of the action plan is concerned with obtaining better knowledge on the use of hazardous substances in articles, for example in clothing, building materials and toys, as well as pursuing the phase-out of hazardous substances. Further efforts are needed to reduce the risks posed by hazardous substances, particularly with a view to protecting our children. An American study, for example, found 273 foreign and toxic substances in the umbilical blood of a newborn baby.²

Leakage of antibacterial substances can pollute the environment

One of the tasks contained in the action plan is to examine which textiles are treated with biocides and what happens to the biocidal substances when the textiles are washed. Earlier studies have shown that biocides are washed out of clothing relatively quickly. The Gothenburg Environmental Administration conducted a noted study in which it was found that the four washed garments leaked silver to differing degrees³. An American study showed that the amounts leaking out of different articles vary widely: three socks lost almost 100 per cent of the silver after four washes, while others leaked less than 1 per cent of their silver⁴.

Whether the substances are washed out is significant from several points of view. Firstly toxic substances in the washing water cause an increased load on sewage treatment plants, and secondly aquatic organisms may be affected when the substances reach the environment. In an American study, silver used as an antibacterial substance in clothing has been found to harm necessary bacteria in the treatment process because the ability of the bacteria to reproduce is inhibited.⁵ There are studies showing that biocides (triclosan) are found in fish downstream of sewage treatment plants, which suggests that the treatment processes are not adequate for this type of pollution.⁶ A problem that has been highlighted is that certain biocides, for example silver⁷, triclosan^{8,9} and triclocarban¹⁰ are present in sludge from sewage treatment plants, which means that the sludge may have unsuitable properties for use as a fertiliser or in landscaping.

The level of silver in sewage and sludge has fallen in the 21st century as a result of the digitalisation of the photographic industry. This trend has been interrupted in the last few years (see Figure 1 for silver levels in sludge from two sewage treatment plants in

¹ <http://www.kemi.se/Start/Handlingsplan-for-en-giftfri-vardag/>.

² <http://www.ewg.org/news/study-unborn-babies-exposed-toxic-chemicals>

³ Environmental Administration (2009). Analyser av kemikalier i varor. Rapport 2009:8. City of Gothenburg.

⁴ Troy, M Benn and Paul Westerhoff (2008). Nanoparticle silver release into water from commercially available sock fabrics. Environ. Sci. Tech. 2008, 42, 4133-4139.

⁵ Hu Zhiqiang and Choi Okkyoung (2008) Silver nanoparticles may be killing beneficial bacteria in wastewater. TreatmentScienceDaily (Apr 30, 2008).

⁶ Adolfsson-Erici M, Pettersson M, Parkkonen J and J Sturve (2000). Triclosan, a commonly used bactericide found in human milk and in the aquatic environment. Dioxine Conference 2000, Monterey, USA. Chemosphere 2002;46:1485-89

⁷ Stockholm Water. Silver i slam år 2000-2010. Miljörapport 2010.

⁸ Länsstyrelsen, Västra Götaland (2009) Miljögifter i inkommande avloppsvatten och slam- omfattande 8 reningsverk i Västra Götaland. Rapport 2009:8

⁹ Nordic Council of Ministers (2011). Using sludge on arable land- effect based levels and longterm accumulation for certain organic pollutants. TemaNord 2011:506

¹⁰ Adolfsson-Erici, Margaretha och Allmyr, Mats (2007). Antibakteriellt behandlade konsumentprodukter- källa till exponering av människa och miljö? Miljöförvaltningen. Stockholm Stad. Nya gifter- nya verktyg.

Stockholm). The fact that levels of silver are no longer declining in the sludge is assumed to be due to increased use of silver as a biocide in various articles. The use of biocides has increased in a number of consumer products, and in addition to textiles now occurs for example in shoes, refrigerators, toothbrushes, plastic bottles, vacuum cleaner filters, shower curtains, kitchen worktops, mattresses and chopping boards. Biocides are also used in cosmetics, medical supplies and cooling systems and for the disinfection of drinking water.

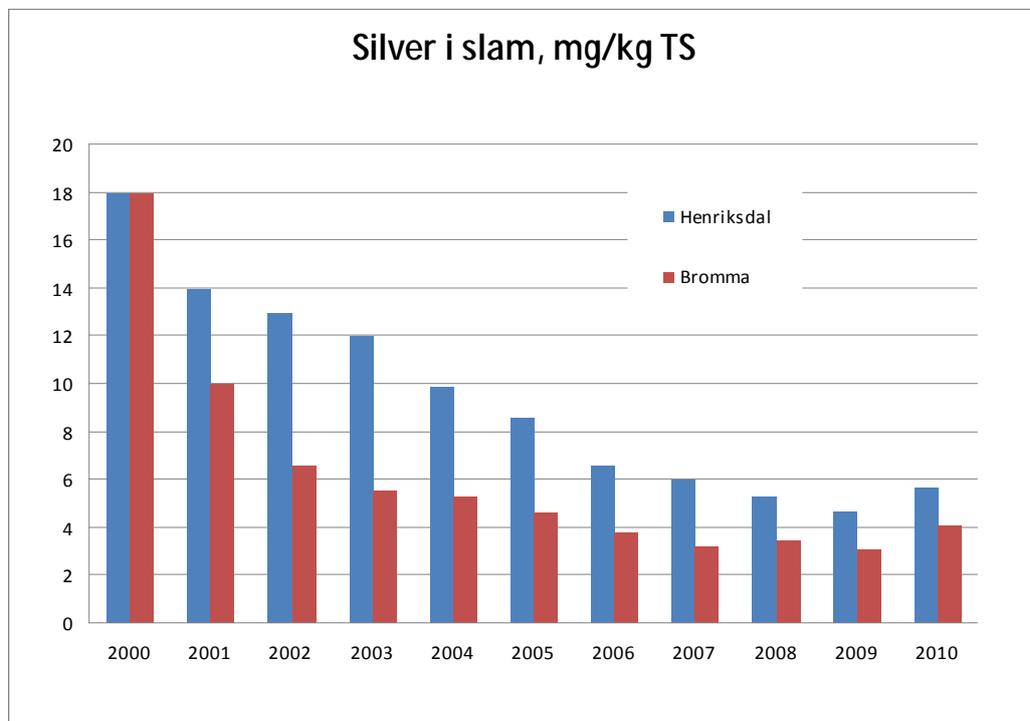


Figure 1. Silver level in sludge (mg/kg dry matter (DM)) from two sewage treatment plants in Stockholm, Henriksdal and Bromma, time series between 2000 and 2010. Source: Stockholm Vatten annual report 2010.

It has been shown in an American study that plants (soya) take up triclosan and triclocarban that was present in sludge with which the soil has been treated.¹¹

Concern also over health risks

As the substances are toxic, various soil organisms can also be inhibited and harmed. In addition to the environmental aspects, there is also concern over the direct exposure of children who may perhaps suck on textiles treated with biocides. We do not know whether the normal flora of skin is affected when biocide-treated clothing is worn close to the body. Antibacterial agents additionally lead to concern over the possibility of cross-resistance arising with antibiotics. One of the EU's scientific committees (SCENIHR) has reviewed mechanisms of action and found that there are many similarities between antibiotics and antibacterial substances¹².

¹¹ Wu, C, AL Sponberg, JD Witter, M Fang and KP Czajkowski.(2010). Uptake of pharmaceuticals and personal care products by soybean plants from soils applied with biosolids and irrigated with contaminated water.

¹² Assessment of the Antibiotic Resistance Effects of Biocides
http://ec.europa.eu/health/archive/ph_risk/committees/04_scenihr/docs/scenihr_o_021.pdf

A further problem is that the marketing may be misleading if the biocides are washed out and the effect fails to occur.

The purpose of the study

Knowledge of in which textiles biocides are used is limited. In addition there is contradictory information on whether biocides in textiles are washed out or not and if so to what extent this happens. The Swedish Chemicals Agency has therefore commissioned a laboratory to analyse three biocides that occur in textiles. The purpose of the study is to:

- Increase knowledge on whether and, if so, to what extent the biocide content disappears on washing. The study is also to provide certain knowledge on whether the material or the way of incorporating the biocide into the material influences leaching.
- Contribute to increased knowledge among businesses, authorities and consumers about examples of types of clothing that may be treated with biocides
- Draw the attention of companies, for instance in the sports and outdoor activity industries, and consumers to the fact that biocides with properties hazardous to health and the environment are used in textiles and the problems that may be associated with them.

The results of the study are additionally to contribute to increased knowledge, provide a basis for developing the work on articles treated with biocides in the biocide regulations, provide a basis for dialogue with manufacturers and other possible measures.

Materials and methods

Internet searches and visits to sports and outdoor activity shops were made to select the textiles that were studied. By conducting Internet searches it was possible to identify garments and brands where claims such as “anti-odour”, “hygienic”, “counteracts odour” etc. were made. We also looked for similar statements on garment labels in shops. We also made use of earlier studies in which clothing containing antibacterial substances was identified. Silver-treated textiles are often marketed with labelling concerning the silver treatment in the product information on the textile itself. But in many cases it is not stated on the textiles what biocide has been used or what substance the article has been treated with. On the other hand, all the articles had some claim about the material counteracting unpleasant odour or that it had been given anti-odour treatment. We selected three common biocides where there was some previous knowledge concerning their presence and where it was possible to commission a laboratory to perform analyses.

The primary focus was on sports and leisure wear which is assumed to be washed relatively often. We looked for clothing that is used by both adults and children.

A total of 30 articles were purchased and sent to a laboratory for analysis. The purchased articles comprised nine pairs of socks, seven items of underwear, six jerseys, two buffs, a balaclava, a sweatband, a pair of ice-hockey shorts, a body and a pair of pyjamas for young children. A wipe was also among the material analysed.

The textiles were analysed with respect to their content of the biocidal substances silver, triclosan and triclocarban.

The analyses were performed before washing, after three washes and after ten washes. The method of analysis used cannot distinguish between different silver-containing chemical compounds. The different silver compounds are regarded as separate biocidal substances in the legislation on biocides.

For a description of how washing and analyses were performed, see *Annex I*.

4. Results

To summarise, the results of the analyses were as follows:

The biocide concentrations fell after washing in all the textiles that were treated with any of the three biocides studied, silver, triclosan and triclocarban.

Two of the garments contained a combination of triclosan and triclocarban.

The original concentration of triclosan in the two garments was 50.7 and 48.9 mg/kg textile. After ten washes, 64 and 84 per cent respectively had leaked out compared with the original concentration of triclosan.

The original concentration of triclocarban in the two garments was 3.5 and 4.5 mg/kg textile. After ten washes, 46 and 58 per cent respectively had leaked out compared with the original concentration of triclocarban.

Sixteen of the 30 samples contained silver. The original concentration of silver ranged between 0.4 and 1360 mg/kg textile. However, most of the silver-treated items of clothing had an original concentration between 8 and 49 mg/kg. Some garments originally contained small quantities of silver compared with most other samples (0.4-0.5 mg silver/kg textile). After ten washes, 10-98 per cent of silver had leaked out of the textiles. Half or more had already escaped after three washes in many of the analysed samples.

A sports sock contained substantially higher levels of silver than the other samples (1360 mg/kg). After ten washes 25 per cent had been washed out, which means that 340 mg per kg textile had disappeared.

A silver-treated wipe was analysed for which the manufacturer had stated that nanosilver is used. The original concentration of silver was nevertheless high (154 mg/kg textile). After ten washes 19 per cent had been washed out, equivalent to 30 mg silver/kg textile.

Some garments contained silver without the manufacturer marketing this fact. The other twelve garments in which there was neither triclosan, triclocarban nor silver may have been treated with other biocides, to judge from the marketing of the garments. The alternative is possibly exaggerated or false marketing.

There are various ways of applying biocides to textiles. The results suggest that the methodology for adding the biocides to the textile or fibre is significant when it comes to deciding how the substances leak out. The results further show that biocidal treatment is not just done in synthetic materials but also in cotton and mixtures of synthetics, wool and silk.

For the full analytical results, see *Annex 1*.

5. Rules on biocides and other hazardous substances

Biocidal products are pesticides and are used to kill or control harmful organisms. Biocides for the treatment of articles occur for example in timber treated with wood preservative, textiles and leather products treated against mould and in sports equipment, chopping boards, kitchen worktops, shoes etc. given an antibacterial treatment.

What rules are applicable?

Biocides normally have to be approved for them to be allowed to be used under the Biocidal Products Directive (98/8/EEC). For it to be possible for a biocidal product to be approved, the active substance must be evaluated and included in Annex I to the Directive. During the time it takes to evaluate the substances, EU Member States are allowed to retain their national rules. There is an exemption from approval in Sweden for substances that are used to protect clothing, as in the relevant uses in the study. The active substance must be notified to the EU's evaluation programme for the exemption to apply.

In addition to the biocides legislation there are several sets of rules that regulate responsibility for eliminating environmental and health risks. Under the Swedish Environmental Code (1998:808) and also in the EU's chemicals legislation REACH (1907/2006/EC) the principal responsibility for chemical products and articles being safe for health and the environment is

borne by the companies that place the products on the market. Chapter 2 of the Environmental Code contains general rules of consideration, with requirements to be met by operators in relation to knowledge, precautions and choice of less hazardous products and articles. Section 2 requires everyone to acquire the knowledge needed to protect human health and the environment against damage or detriment. The precautionary principle in Section 3 requires all operators to take precautions that are necessary in order to prevent, hinder or combat damage to human health or the environment. The 'product choice principle' (Section 4) stipulates that chemical products and articles that may be feared to cause harm to human health or the environment must be avoided if they can be replaced by less hazardous products.

The Product Safety Act (SFS 2004:451) is based on the European Community Product Safety Directive¹³, which is intended to prevent damage by ensuring that unsafe products are not placed on the market. The Directive applies to products intended for consumers and takes account of health risks.

Labelling requirements on the way

Under the new Biocidal Products Regulation that comes into force in September 2013, however, articles treated with biocides may no longer be placed on the EU market unless the active substances are approved for the envisaged use. For example, the various silver compounds must be approved for them to be allowed to be used to protect against odour in textile fibres. This requirement will also apply to imported textiles. There will also be a requirement for labelling on the article stating that it has been treated with biocides and with what active substance, if a claim is made for antibacterial effect. The effectiveness of the biocidal treatment must be documented.

Sweden is evaluating silver

Silver and triclosan have been notified to the EU evaluation programme and are currently being evaluated by competent authorities in the EU. Triclocarban has already been evaluated and is no longer permitted in biocidal products in the EU. On the other hand, the articles may be treated outside the EU and then imported. Articles treated with triclocarban cannot at present be prevented from being imported into the EU.

Sweden (the Swedish Chemicals Agency) is responsible for the evaluation of silver. Further information concerning the Biocidal Products Directive and the forthcoming Biocidal Products Regulation can be found on the Swedish Chemicals Agency website¹⁴

6. Antibacterial treatment of textiles

A large number of different biocides are reported to be used to protect textiles from odour. As well as various silver compounds, triclosan and triclocarban, which are highlighted in this study, substances reported to be present include, for example, zinc pyrithione, polyhexamethyl biguanide, tributyl tin, isothiazolines, cyclodextrin, permethrin, chitosan and quaternary ammonium compounds. It is usually synthetic material that is treated with

¹³ Europaparlamentets och rådets direktiv 2001/95/EG om allmän produktsäkerhet

¹⁴ <http://www.kemi.se/sv/Innehall/Bekampningsmedel/Biocidprodukter/>

antibacterial substances. Certain materials, such as wool, are usually marketed as naturally antimicrobial because the water-repellent structure of the wool fibre does not form the same breeding ground for microorganisms.

Silver can be added in various chemical forms (metallic, salts etc.) that can release silver ions. Silver is also reported to be used in nanof orm. The definition of nanoparticles is a subject for discussion, but generally refers to structures that are one to a few hundred nanometres (i.e. less than a millionth of a metre) and are consequently capable of giving the material special properties. Knowledge of how nanoparticles are taken up in humans and animals is incomplete and consequently so too is knowledge of what risks these small particles pose. It can be noted, however, that nanoparticles are so small that they can cross barriers in the body's tissues, for example the blood-brain barrier.¹⁵

The Textile Importers Association in Sweden (a trade association) recommends in its chemicals guide that certain named biocides must not be present in textiles and shoes, including triclosan and silver complexes at nanosize¹⁶.

Is the antibacterial treatment effective?

There are divided opinions on how effective it is to add antibacterial substances to textiles to protect them against odour. Odour arises through various substances present in sweat being converted by bacteria. This can take place both on the body and in the fabric. In functional garments, the moisture has to be transported out through the fabric. The unpleasant-smelling breakdown products may, however, remain in the garment. Many people find that the odour problems disappear on washing, but that they return as soon as the garment becomes damp again. The microorganisms need a moist environment to thrive. Microorganisms largely disappear on washing at 60 degrees for ten minutes¹⁷.

In a study carried out at the Swedish School of Textiles in Borås it was not possible to identify any substantial difference in reduced odour when a panel was asked to compare (smell) antibacterially treated with untreated training tops when two halves of each top were sewn together.¹⁸

Manufacturers of antibacterially treated clothing claim that there is demand from customers for this function. As such a great proportion of the original concentration of the biocides was found to be washed out in many of the analysed garments, the question arises at what concentration the biocidal treatment in that case is still effective. The added quantity in some clothing was very low. As the silver ion is highly toxic, the silver concentration in textiles may be as low as 0.0005 per cent (weight/weight) and yet be effective. The crucial factor for the effect on bacteria is, however, that the substance continues to be released from the textiles and consequently comes into contact with the microorganisms.

Manufacturers of antibacterially treated clothing argue that treated clothing does not have to be washed as often and consequently saves water and energy. In a survey conducted in the same study mentioned above, no change in behaviour was found and consumers washed

¹⁵ KemI (2007). Nanoteknik- stora risker med små partiklar. KemI Rapport 6/07.

¹⁶ Textilimportörernas kemikalieguide. "Guide to buying terms for the chemical content in textiles, clothing, leather goods and shoes", edition 4, September 2011

¹⁷ http://www.svd.se/nyheter/inrikes/bakterier-trivs-i-tvatt_3843421.svd

¹⁸ Damm, Josefin (2011). Silver i "luktfria" kläder - en stinkande lösning. Kandidatexamen i Textil produktutveckling med entreprenörs- & affärsinriktning. Textilhögskolan i Borås. Rapport nr: 2011.14.6.

treated clothing just as often as untreated garments. Nor had there been demand for the antibacterial treatment from the consumers.

The three analysed biocides are described a little more closely below.

Silver

Silver is a metal that is best known for its traditional use as a precious metal, for example in jewellery, and in photography. In recent years the use of silver has instead increased in other areas, for instance in consumer products such as textiles, shoes, refrigerators, toothbrushes, plastic bottles, vacuum cleaner filters, mattresses and chopping boards. Silver is also used in cosmetics, medical supplies and cooling systems and for the disinfection of drinking water.

Silver in ionic form has bactericidal properties.

How different silver compounds are applied

Silver ions can be formed from various forms of silver and silver compounds. One way of generating ions is using a silver electrode. However, it is more common to use silver salts such as silver nitrate, silver chloride or silver citrate. Other silver compounds such as silver zeolites or various kinds of silver glass in powdered form are mostly used in articles. Metallic silver in the form of small particles (micro or nano size) is also used in articles. However, an antimicrobial effect is always dependent on the silver compounds or the silver coming into contact with water or some other fluid and forming ions.

Silver and silver salts are solid and highly temperature-tolerant. Silver can be added during the manufacturing of a material either directly or in the form of a liquid coating that contains silver and that may form a surface covering on a fibre, fabric or other material, see Figure 2. There are many different ways of adding the silver.

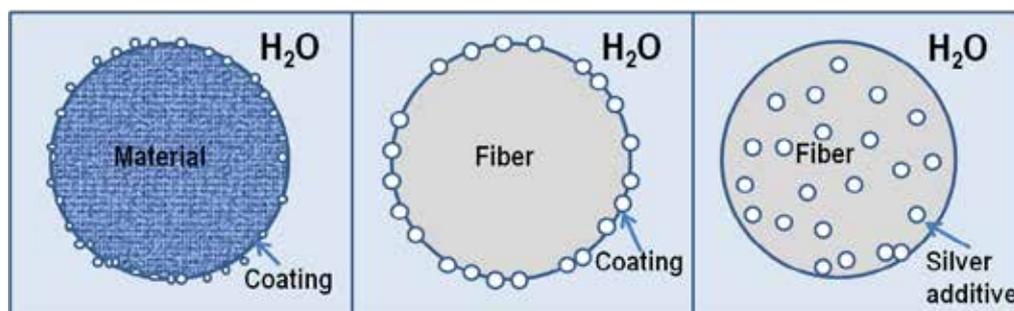


Figure 2. Silver can be added to the textiles in various ways. In the first box it is the surface of the textile that is covered. In the second box it is the surface of the fibres that is treated, while the third box illustrates how silver may have been added to the polymer.

Properties and risks

Silver ions are very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Fish and small crustaceans (for example water fleas) are particularly sensitive. Growth and reproduction are adversely affected at silver ion concentrations as low as less than 1 µg/l. Silver is persistent, which means that once silver has been released into the environment it will remain there.

The use of silver ions in various types of consumer products contributes to diffuse spread to the environment through wastewater and sewage sludge. Silver ions are not, however, particularly stable in wastewater and in sewage treatment plants. They react quickly with inorganic sulphur or with organic matter, so that they are no longer dissolved. The bound silver then gradually sinks down into sediment or ends up on arable land through digestion sludge. Here silver can accumulate and have adverse effects on sediment and soil organisms.

Despite silver being an antimicrobial agent with a long tradition, it is not certain that it is entirely unproblematic for humans. Particularly with silver-treated textiles, exposure in some cases may be quite high, for example if a child sucks on a garment treated with silver. In addition, there are fears that extensive use of silver can lead to the development of silver-resistant bacteria. If so, targeted use of silver in important areas (e.g. in the treatment of wounds) may be threatened. In addition, it is feared that it will no longer be possible to treat and cure common diseases such as pneumonia with antibiotics because of cross-resistance.

Triclocarban

Triclocarban (CAS No 101-20-2) has bactericidal properties. It is widely used in the United States in products such as soaps. In a study conducted by the Stockholm Environmental Administration, triclocarban was found in an insole, two T-shirts, a sports sock and a pair of cycling shorts. In the same study triclocarban was measured in digestion sludge from one of the city's sewage treatment plants.¹⁹

Triclocarban has already been evaluated and has not been permitted in biocidal products in the EU since 2006.

Triclocarban is permitted as a preservative in cosmetics and hygiene products in the EU with a maximum permitted concentration of 0.2 per cent.

Triclocarban is not included in the EU's official classification list. According to safety data sheets from manufacturers, the substance is classified as R50/53: very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

The substance may be released in use of the articles, for example in washing, and end up in the environment through sewage treatment plants. The greater part of the triclocarban that reaches the sewage treatment plants will resist breakdown and mostly be stored in the sludge²⁰. Measured concentrations in nature downstream of sewage treatment plants have additionally pointed to high levels in sediments and have been found in snails in the United States. The substance is persistent and appears to be capable of bioaccumulation. Concentrations of triclocarban in the environment in the United States are of the same order of magnitude as those found to be toxic in laboratory studies on crustaceans and algae²¹. Triclocarban has also been found to be toxic to mammals, with effects on reproductive capacity²².

¹⁹ Adolfson-Erici, Margaretha och Allmyr, Mats (2007). Antibakteriellt behandlade konsumentprodukter- källa till exponering av människa och miljö? Miljöförvaltningen. Stockholm Stad. Nya gifter- nya verktyg.

²⁰ Heidler, J., Sapkota, A. och Halden, R.U., 2006. Partitioning, Persistence, and Accumulation in Digested Sludge of the Topical Antiseptic Triclocarban during Wastewater Treatment. *Environ. Sci. Technol.*, 40 (11), 3634–3639.

²¹ Talia E.A. Chalew, Rolf U. Halden, (2009). Environmental exposure of Aquatic and Terrestrial Biota to Triclosan and Triclocarban. *Journal of the American water resources association* 45 (1) 4-13.

²² Rolf U. Halden, Daniel H. Paull (2005). *Co-occurrence of triclocarban and triclosan in U.S. Water Resources*. *Environ. Sci. Technol.* 39, 1420-1426

Triclocarban is broken down among other things to 3,4-dichloroaniline, which is persistent in the environment. The half-life of 3,4-dichloroaniline in soil is estimated to be around 1000 days. This means that the substance can accumulate in arable soil if it is spread with sludge. The breakdown product 3,4-dichloroaniline has been found to be toxic to reproduction in fish. The substance has been found to be sensitising (allergenic) in a standard test for skin allergy.²³

Triclosan

Triclosan (CAS 3380-34-5) is a fat-soluble substance with bactericidal properties. The substance occurs in toothpaste and deodorants and in other articles used by consumers. Triclosan is permitted to be included as a preservative in cosmetic products at a maximum concentration of 0.3 per cent. The Environmental Administration in Stockholm carried out a study in 2007 and found triclosan in several insoles, a pair of leggings, a T-shirt, earplugs, a travel pouch and a wrist support. There are reports of use in many different types of articles such as flooring, plastic in spa facilities, air filters in air-conditioning systems, shower curtains, chopping boards and deodorants for shoes. The Swedish Environmental Protection Agency has commissioned a preliminary study in which it is found that there are kitchen worktops of plastic composite containing triclosan (Microban). Based on available information on the composition of the composite worktops (0.1-5 per cent in patents for Microban) they may constitute hazardous waste when they become waste, if the higher concentrations are used.

The turnover (use and importing into Sweden) of triclosan has been between 2 and 3 tonnes in the past five years according to the Products Register. Use in articles manufactured outside Sweden does not appear in the Products Register statistics. The use of triclosan, for instance in toothpaste, increased in the early 2000s. One study showed that triclosan was present in breastmilk²⁴. This contributed to there being a debate in the media, which in addition was reinforced by a press release²⁵ in March 2000 when five government agencies, including the Swedish Chemicals Agency, jointly dissociated themselves from antibacterial substances that were not sufficiently investigated. The Swedish Society for Nature Conservation published a noted report²⁶. Several of the large grocery retailers then cleared antibacterial articles from their shelves.

It is suspected that the substance can contribute to increased resistance in bacteria, which has been demonstrated in the laboratory environment.²⁷ Triclosan is an organochlorine compound with an eye and skin irritant effect. The substance has high toxicity for aquatic organisms, which can cause long-term effects in the environment. Triclosan has shown endocrine-disrupting properties in experiments on frogs²⁸ and on rats²⁹.

²³ European Chemicals Bureau (2006). European Union Risk Assessment Report 3,4-dichloroaniline (3,4-DCA).

²⁴ Adolfsson-Erici M. Pettersson, M., Parkkonens J., Sturve J., Triclosan a commonly used bactericide found in human milk and in the aquatic environment in Sweden. *Chemosphere*, 46 (2002).

²⁵ Initiativ mot antibakteriella substanser i konsumentprodukter. Rapport om samverkan mellan Kemikalieinspektionen, Konsumentverket, Livsmedelsverket, Läkemedelsverket och Smittskyddsinstitutet. Mars 2001.

²⁶ Naturskyddsföreningen (2007). Triclosan i tandkräm – konsumenter borstar ofrivilligt tänderna med miljögift

²⁷ Scientific Committee on Consumer Safety (SCCS) Opinion on triclosan. Antimicrobial Resistance. SCCP/1251/09. Approved 22 June 2010.

²⁸ Veldhoen et al. (2006). *Aquat. Toxicol.* 2006, 80(3), 217-227.

²⁹ Zorrilla, L.M. m.fl., 2009. The Effects of Triclosan on Puberty and Thyroid Hormones in Male Wistar Rats. *Toxicological Sciences*, 107(1), ss.56 -64.

Triclosan is not readily degradable and can consequently accumulate in the environment³⁰. Triclosan is found in 48 sludge samples analysed in a study from 2010, at a mean concentration of 4.5 mg/kg sludge.³¹

In a new study performed in Germany, researchers measured triclosan at 802 places in the catchment area of the Elbe between 2006 and 2008. They subsequently compared measured values with the concentration (PNEC – Predicted No Effect Concentration) at which it has been judged that the substance does not have any harmful effects on aquatic organisms. The results show that the concentrations exceeded the PNEC for algae at more than 75 per cent of the sampling points. The researchers consider that previous risk assessments have underestimated the risks posed by triclosan and propose that the substance should be introduced as a priority substance into the Water Directive.³²

The International Chemical Secretariat (ChemSec) includes triclosan in its list of substances of very high concern (SIN list, Substitute It Now list) on the grounds that it is very toxic to aquatic organisms and potentially bioaccumulative and that endocrine-disrupting effects have been reported³³. Triclosan is a prioritised risk reduction substance in the Swedish Chemicals Agency's PRIO guide based on the fact that the substance can cause harmful long-term effects in the aquatic environment.

Triclosan is officially classified in the EU with the risk phrases R36/38: Irritating to eyes and skin and R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

7. Are antibacterially treated textiles a problem for a toxic-free everyday environment?

Under the EU's Biocidal Products Directive (98/8/EEC), use of biocidal products is to be restricted to what is absolutely necessary. It is worrying that an increase appears to be taking place in the use of biocides in more and more consumer products. Biocides are often toxic and are produced to prevent or deter various organisms. Such substances must be used with caution and good control so that they do not end up in undesirable places and are consequently capable of harming human health or the environment. There is reason to consider whether the function of antibacterially treated clothing and other textiles is necessary and to weigh this against the risks that may arise. Children's clothing being treated against sweat odour can be seriously questioned.

We have obtained confirmation through this study that biocides in clothing leak out on washing. The Swedish Chemicals Agency takes a serious view of the fact that such a large proportion of such toxic substances is washed out so quickly in many of the analysed textiles. The three biocides analysed are highly problematic in the aquatic environment and for sewage treatment plants, which makes it particularly important that they do not leach from the

³⁰ OECD SIAP, 2010. SIDS Initial Assessment Profile, Triclosan

³¹ WSP (2010). RAPPORT. Miljöövervakning av miljögifter i urbana områden - sammanställning och analys. Uppdrag av Naturvårdsverket.

³² von der Ohe, P.C., Schmitt-Jansen, M., Slobodnik, J. & Brack, W. (2011). Triclosan – the forgotten priority substance? *Environmental Science and Pollution Research*. DOI: 10.1007/s11356-011-0580-7.

³³ <http://www.sinlist.org/> (2011-12-07)

garments in washing. There are evident risks of the substances reaching watercourses and accompanying the sludge that is spread on arable land.

Some manufacturers claim that the treatment does not leak or leaks very little in washing. This study indicates the opposite. On the other hand, the study indicates that different ways of applying silver, such as differing original concentrations, cause differing levels of leakage. A question that arises when such a large proportion of the original biocidal content is washed out is what concentration of the biocides needs to remain in the clothing to attain the marketed antibacterial effect.

The Swedish Chemicals Agency considers that it ought to be apparent from the product information that the clothing has been treated with antibacterial substances so that purchasers and consumers have an opportunity to choose whether they consider themselves to need this function or not.

New legislation tightens the requirements

Under the Environmental Code, the EU's chemicals legislation REACH and the Product Safety Directive, the companies that place products on the market bear the main responsibility for ensuring that the products are safe and do not pose risks to humans and the environment.

Under the EU's new Biocidal Products Regulation that comes into force in September 2013, articles treated with biocides are no longer permitted to be placed on the EU market unless the active substances are approved for the envisaged use. For example, the various silver compounds must be approved for them to be allowed to be used to protect against odour in textile fibres. This requirement will also apply to textiles imported from countries outside the EU. There will also be a requirement for labelling on the article stating that it has been treated with biocides and if so with what active substance, if a claim is made for antibacterial effect. The effectiveness of the biocidal treatment must be documented.

The Biocidal Products Regulation will signify great changes and better opportunities for the authorities to limit the use of biocides that pose risks.

Inadequate knowledge of health risks

We have inadequate knowledge of any direct health risks in the use of antibacterially treated clothing. We do not know, for example, whether the normal flora of the skin can be affected. Risks of children sucking on treated garments can be feared. Nanoparticles, for example, are so small that they can cross the body's natural barriers to a greater degree, for example the blood-brain barrier. Silver is also used in nanoform for the treatment of textiles.

Fears that increased and extensive use of biocides can contribute to the development of resistant bacteria and the development of cross-resistance to antibiotics must be taken very seriously as the effects of the increasingly widespread antibiotic resistance can have severe consequences. There is therefore reason to apply the precautionary principle and avoid using biocides in articles or only to use them with great caution.

Triclocarban and triclosan have been found in studies to interfere with reproduction (triclocarban) and have endocrine disrupting properties (triclosan). Substances that disrupt reproduction or the endocrine system are counted as being substances of very high concern and, under the Swedish Parliament decision on the environmental objective of A Non-Toxic Environment, have to be phased out on the basis of their inherent properties. Endocrine-

disrupting substances disturb the body's signalling systems, and it is a matter for particular concern if these substances are present during pregnancy and in children and adolescents as children's organs are still developing.

Many chemical substances in our everyday environment

Knowledge is still lacking on the ways in which many of the substances we use in consumer products can affect humans and the environment.

There are obviously more manufacturers and importers who treat articles with biocides or import articles treated with biocides than those covered by this study. Overall, the Swedish Chemicals Agency considers there to be reason to draw attention to the increasing use of biocides in people's everyday environment. There are also other biocides used in clothing that have not been analysed in this study that may also pose risks to humans and the environment. It is very difficult for consumers to obtain information on what biocides the clothing contains. In addition, biocides are just some of the many different sources for the dispersal of hazardous substances.

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Uppdragsgivare KEMI Box 2 172 13 Sundbyberg	Uppdragsgivarens ref. nr. 240-H11-00923
	Kontaktperson Anne-Marie Johansson
	Vårt ref. nr. 5110737

Intention: Investigation of how washing leaches the biocides silver, triclosan and triclocarban from antibacterially treated textiles.

Sample material: Thirty different sample materials for which there was a claim in most cases that the material counteracts unpleasant odour or has anti-odour treatment.

See Annex 3 for a detailed description of sample materials.

The sample materials were received from the client on 26 September.2011. The assignment was carried out from 7 October 2011 to 9 November 2011

Summary: Silver, triclosan and triclocarban were analysed in the garments before washing, after three washes and after ten washes. Washing took place at 40 degrees using common household detergents without TAED or bleach. In all cases where any of the three biocides was detected before washing a decrease in biocide concentrations was measured, which suggests that they leach from the garments and enter the washing water. The possibility of some of the textiles being treated with biocidal substances other than the three analysed in this study cannot be ruled out.

Procedure: Water washing and drying were performed in accordance with ISO 6330:2001 (Textiles. Domestic washing and drying procedures for textile testing + A1:2009 (Suspended drying)

Washing machine: Type A, Electrolux Wascator FOM 71 MP-Lab

Water supply: 17 l/min

Water quality: Soft, < 2.8 dH °

Washing programme used: 5A, 40°C Detergent: Via Color, as requested by the client (Not in accordance with ISO 6330:2001)

Dosage: 1 g/l

Number of washes: 10

Total quantity of material (filler material and sample material): 2 kg

Filler material: 100 % Knitted polyester, (310±20) g/m²

Drying: The material was dried after the third and tenth washes.

Drying method A, suspended drying.

All the materials have been washed together.

Sample extraction. Sample material was cut from at least five different places on the garments/textiles in the analyses, based on the mutual distribution of the parts. Extracted sample material was finely divided and mixed before samples from this mixture were weighed

in for analysis. This reduces the influence of uneven distribution of biocide in the garment, but does not entirely eliminate the risk.

Analysis of triclosan and triclocarban was performed by GC-MS (gas chromatography-mass spectrometry) or LC-UV (liquid chromatography with UV detector). 1.00 g of the material was extracted with 10 ml ethyl acetate in an ultrasonic bath for 10 min at room temperature. Benzyl benzoate (4000 mg/l, 30 µl / sample) was used as internal standard. After extraction, the extract was rotation-evaporated to dryness and the samples were redissolved in 1.0 ml methanol. The extract was filtered through 0.45 µm nylon filter before injection onto GCMS for triclosan and HPLC-UV for triclocarban. The analytical limit was set at 1.0 mg/kg. The samples were quantified against a standard curve based on purchased certified pure substance and diluted with controlled pipettes and volumetric vessels. The analyses are not quantified against the same dilution of the standard curve as the analyses of unwashed and washed samples are not performed on the same occasion.

The mean value of the measurements can be seen in the table below, where the concentrations are stated in milligrams of biocide per kilogram of textile.

All the measurements appear in tabular form in Annex 1.

Biocide	Triclosan, CAS 3380-34-5 (mg/kg)	
Sample	Sample 4 Sock, Funq wear	Sample 28 Ice-hockey shorts children's, Bauer
Before washing	50.7	48.9
After 3 washes	60.7	23.6
After 10 washes	18.4 (-64 %)	7.9 (-84 %)

Biocide	Triclocarban, CAS 101-20-2 (mg/kg)	
Sample	Sample 4 Sock, Funq wear	Test 28 Ice-hockey shorts children's
Before washing	3.5	4.5
After 3 washes	5.9	3.8
After 10 washes	1.9 (-46 %)	1.9 (-58 %)

Conclusion: Of the 30 samples analysed, triclosan and triclocarban were only encountered in two samples, sample 4 and sample 28. The analysis was performed twice for unwashed and three and ten times washed samples. The sample material was selected from different areas of

the sample to obtain a wide spread of measured results. It is unclear how the biocides are distributed across the sample material, which may explain why the concentrations increase from unwashed to washed three times in sample 4. In addition, the unwashed garments are analysed on one occasion and the washed ones on another. The biocides are leached on washing in all cases, although at differing rates for the different materials.

Analysis of silver content was performed by ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) after leaching. 1.00 g of the material has leached under slight warming in 22 ml aqua regia (concentrated hydrochloric and concentrated nitric acid in the ratio 1:1) for two days. Before analysis the solution has been diluted to 50 ml with distilled water. Two wavelengths have been utilised in analysis, 328.068 nm and 338.289 nm. The result from 328 nm is presented, while the analysis at 338 nm has verified the absence of spectral interference. Duplicate samples have been analysed and the mean value is presented.

The analytical limit has been set at 0.1 mg/kg. Lower concentrations can be measured, but this concentration is the lowest that has been verified using replacement experiments at known concentrations in real samples.

In the analysis of silver content by ICP-OES the samples before and after washing were analysed in the same run and against the same standard curve. The samples have been analysed material by material in the sequence washed/unwashed/ washed/unwashed to minimise the influence of instrument drift.

The method with leaching in aqua regia does not break the fibres down completely, and is not to be regarded as total decomposition. All the silver that is exposed on the surfaces of the fibres and consequently has biological activity can leach out, but silver that occurs entirely unexposed inside synthetic fibres can have limited exchange in the method.

The methods that exist for total decomposition of textile material are based on substantially smaller sample extracts (0.1-0.2 g) with consequent homogeneity problems. They are additionally based solely on oxidising acid (nitric acid) and to keep silver stable in solution a surplus of chloride ions is required that shifts the balance of silver towards soluble AgCl_2 . The surplus must be so great that AgCl is not formed, a requirement that is met in aqua regia even after dilution as above. This is the background to the choice of methodology in this study.

Only the materials where silver has been detected are presented in the table below, and only the mean value of the measurements is indicated.

All the measurements appear in tabular form in Annex 2.

Silver concentration. All values in mg/kg textile.

Sample No	Unwashed	3 washes	10 washes
1	1360	1180 (- 13 %)	1020 (- 25 %)
2	15.2	15.1(no rel.)	12.2 (- 20 %)
3	8.0	4.4 (- 45 %)	2.1 (- 74 %)
10	36.0	29.3 (- 19 %)	14.0 (- 61 %)
11	49.0	2.6 (- 95 %)	1.2 (- 98 %)
13	0.5	0.3 (- 40 %)	0.2 (- 60 %)
16	23.7	18.7 (- 21 %)	13.8 (- 42 %)
17	9.7	4.7 (- 52 %)	3.9 (- 60 %)
20	16.9	6.9 (- 59 %)	3.3 (- 80 %)
21	38.8	9.3 (- 76 %)	6.7 (- 83 %)
22	0.4	0.2 (- 50 %)	0.1 (- 80 %)
24	9.0	4.2 (- 53 %)	3.3 (- 63 %)
30	154	142 (- 7.8 %)	124 (- 19 %)
31	1.8	1.7 (- 6 %)	1.6 (- 10 %)
32	27.8	6.2 (- 78 %)	3.6 (- 87 %)
33	9.3	5.3 (- 43 %)	1.4 (- 85 %)

All results apply only to the sampled materials.

Comments:

- It is mentioned in the marketing for sample 4 that “Sanitized” is Öko-Tex approved. Sanitized is not an individual product but is present in many different compositions with different active substances. Only certain variants are Öko-Tex approved, and it is not indicated what type of Sanitized product has been used in this case.
- The biocide concentrations fell after washing in all textiles treated with any of the three biocides studied (silver, triclosan (CAS No 3380-34-5) and triclocarban (CAS No 101-20-2)).
- Two of the garments contained both triclosan and triclocarban at concentrations above the analytical limit.
- 16 samples contained silver.
- The original concentration of silver ranged between 0.4 and 1360 mg/kg textile.
- After ten washes 10-98% silver had leaked out of the textiles of measured origin. The original concentration of triclosan in the two garments was 50.7 and 48.9 mg/kg textile.
- After ten washes, 64 and 84 per cent respectively had leaked out compared with the original measured concentration of triclosan.
- The original concentration of triclocarban in the two garments was 3.5 and 4.5 mg textile.
- After ten washes, 46 and 58% respectively had leaked out compared with the original measured concentration of triclocarban. Some garments originally contained small quantities of silver compared with most other samples (0.4-0.5 mg silver/kg textile).
- Most of the silver-treated items of clothing had an original concentration between 8 and 49 mg/kg.
- An sports sock contained substantially higher levels of silver than the other samples, 1360 mg/kg. After 10 washes 25% had been washed out, which means that 340 mg per kg textile had disappeared.
- A silver-treated swatch, which is a sample from a manufacturer, was analysed. The original concentration of silver was 154 mg/kg textile. After ten washes 19% had been washed out, equivalent to 30 mg silver/kg textile.
- There are various ways of applying biocides to textiles. The results suggest that how the biocides are added to the textiles or the fibre is significant for how the substances leak out.
- The results show that biocidal treatment is not just done in synthetic material but also in mixed materials, in wool, cotton and silk mixes.
- The analyses cannot provide an answer regarding the form in which silver is applied to the textiles (for example in nanoform, in various salts, as filaments etc.).
- Some garments contained silver without the manufacturer reporting/marketing this fact.
- The garments may be treated with other and/or further biocides, but this cannot be verified by the analyses performed.
- In many cases it was difficult to ascertain which biocide was used. On the other hand, they all had some claim about the material counteracting unpleasant odour or that it had been given anti-odour treatment. This may suggest that other biocides have been used, the alternative possibly being exaggerated or false marketing.

Appendix 1, Results from analyses of triclosan and triclocarban:
(mg/kg textile)

Sample	Unwashed -1 Triclosan/Triclocarban	Unwashed -2 Triclosan/Triclocarban	3 washes -1 Triclosan/Triclocarban	3 washes -2 Triclosan/Triclocarban	10 washes -1 Triclosan/Triclocarban	10 washes -2 Triclosan/Triclocarban
1	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
2	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
3	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
4	61,4 / 3,8	40,0 / 2,7	48,8 / 4,9	72,6 / 6,9	15,3 / 1,6	21,5 / 2,2
5	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
6	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
7	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
8	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
9	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
10	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
11	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
13	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
14	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
15	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
16	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
17	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
18	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
19	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
20	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
21	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
22	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
23	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0

Sample	Unwashed -1 Triclosan/Triklokarban	Unwashed -2 Triclosan/Triklokarban	3 washes -1 Triclosan/Triklokarban	3 washes -2 Triclosan/Triklokarban	10 washes -1 Triclosan/Triklokarban	10 washes -2 Triclosan/Triklokarban
24	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
27	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
28	43,5 / 3,9	54,3 / 4,7	24,6 / 4,1	22,5 / 3,6	8,0 / 1,8	7,7 / 2,0
29	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
30	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
31	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
32	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0
33	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0	< 1,0 / < 1,0

Appendix 2, Results from analyses of silver.
(mg/kg textile).

Sample	Unwashed -1	Unwashed -2	3 washes -1	3 washes -2	10 washes -1	10 washes -2
1	1310	1410	1160	1200	1050	990
2	14,9	15,5	15,3	14,9	12,5	11,9
3	8,2	7,8	4,5	4,3	2,1	2,1
4	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
5	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
6	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
7	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
8	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
9	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
10	36,1	35,9	28,9	29,7	13,6	14,4
11	51,0	47,1	2,7	2,5	1,0	1,4
13	0,5	0,5	0,3	0,3	0,1	0,3

Sample	Unwashed -1	Unwashed -2	3 washes -1	3 washes -2	10 washes -1	10 washes -2
14	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
15	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
16	23,7	23,7	18,8	18,6	13,5	14,1
17	9,9	9,5	4,7	4,7	3,7	4,1
18	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
19	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
20	16,8	17,0	6,9	6,8	3,3	3,3
21	38,5	39,1	9,2	9,3	6,4	7,0
22	0,4	0,3	0,2	0,2	0,1	0,1
23	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
24	9,0	8,9	3,8	4,5	3,2	3,3
27	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
28	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
29	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
30	150	158	139	144	116	133
31	1,8	1,8	1,8	1,6	1,5	1,7
32	27,7	27,8	6,4	6,0	3,5	3,6
33	9,6	9,0	5,2	5,3	1,2	1,6

Appendix 3, detailed description of the test material.

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	1	Sock	X-socks.	Run sky run	31/14/18/14/12/11 % SkinNODOR/SilverNODOR/ Nylon/Robur/Mythlan/ Elastodiene	SilverNODOR/ (silver yarn)	250	Runners Store
	2	Sock	Asics	Kayano sock. Women's running	57/20/15/5/2/1 % Polyamid/Polyamid Skinlife/Polypropylen/ Polyamid Nanoglide/Elastan/ Polyester Lumen	"antibacterial yarn"	150	Runners Store
	3	Sock	Falke	Running RU 4 Cushion Women	37/31/24/8 % Polypropylen/Polyamid Silver integrated/Cotton/Wool	Falke silver	190	Runners store

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	4	Sock	Funq wear	Stödstrumpor	55/30/15 % Cotton/Polyamid/Elastan	Santized ”ett ÖkoTex- certiferat medel som motverkar odör”	185	Läns- försäkringar
	5	Sock	BlueWear	Arbetssocka ”antibakteriell” 39/42 4-pk	71/14/10/3/2 % Cotton/Polyester/Nylon/ Elastodien/Elastan	“Purista är en antibakteriell behandling som motverkar dålig lukt”	99	Jula
	6	Sock	SOC	Training allround. Mid cut sock. 2 pack	75/23/2 % Polyester Cottonolmax/Polyamid/ Elastan	Coolmax active	99	Stadium

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	7	Sock	Under Armour	Allsport	88/10/1/1 % Olefin/Nylon/Polyester/ Spandex	ArmourBlock –prevent growth of odor-causing bacteria in the sock	99	Stadium
	8	Sock (children)	Viking	2-pack Comfort Zokks Coolmax	80/15/5 % Cottonolmax/Polyamid/ Elastan	Coolmax	119	Uteungar.se
	9	Sock (children)	Bridgedale	Ullhybridstrumpa Junior Trekker	37/31/31/1 % Polyamid/Wool/Polypropylen /Elastan	-	139	Uteungar.se

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	10	Underwear/ jersey	Craft	Craft Layer 1 Zero. Zero Extreme wmn zip turtleneck	100 % Polyester	“luktresistent”	500	Intersport
	11	Underwear/ longjohns	Craft	Pro Zero. Women PZ Extreme long underpant	100 % Polyester	Coolmax Fresh FX i plaggen förhindrar dålig lukt	400	Intersport
	13	Underwear/ jersey (children)	Isbjörn of Sweden	Ulltröja Thin Kiddie Roundneck	40/57/3 % Wool/Polyester/Elastan	”Odour resistance”	349	Uteungar.se

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	14	Underwear/ jersey, longjohns (children)	The North Face	Tekniskt underställ	100 % Polypropylen	HyActive fabric. "Highly odor resistant"	599	Uteungar.se
	15	Underwear	Patagonia	M's Cap 2 LW Zip Neck	46/54 % Polyester/ Recycled Polyester	Gladiodor odor control	569	Addnature.com
	16	Underwear/ jersey (children)	Peak Performance	Jr base LS T	86/14 % Polyester/Elastan	Polygiene Active Odor Control	400	NK

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	17	Jersey	Haglöfs	Actives Cool Roundneck	100 % Recycled Polyester	Polygiene. Permanent odor control	475	Addnature.com
	18	Jersey	Newline	Ionic carbon shirt w/mns	100 % Polyester	Bamboo charcoal Bacterial resistant, anti-odourization, smell resistant	500	Runners store
	19	Underpants and linen	Kari Traa	W's Butterfly hipster + top	95/5 % Polyamid/Spandex	"inhibit odour formation"	499	Addnature.com

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	20	Buff	Buff	Kukuxumusu. Junior Size (fåret Shaun)	100 % Polyester Microfiber	”Active odor Control” Polygiene (silver)	179	Team Sportia
	21	Buff	Disney Baby Buff	”Winnie the Pooh”	100 % Polyester Microfiber	”Active odor Control” Polygiene (silver)	119	XXL Sport & Vildmark
	22	Jersey (children)	Nike	Nike Miler Running, Boys 152-158 cm	100 % Polyester	Dri-fit	199	XXL Sport & Vildmark

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	23	Jersey (children)	Adidas	RPS SS Tee Y	100 % Polyester	Climalite	179	XXL Sport & Vildmark
	24	Jersey	Crivit sports	Running top/löpartröja	48/47/5 % Polyester/Polyester 4 Chanel/Elastan	Rudolf Silver+ Protection (silverplus-material)	79.90	Liedl
	27	Sweatband	Adidas	Adidas CR Tennis HB, headwear	37/36/17/6/4 % Wool/Acryl/Polyamid/Polyester/Elastodien	“Antimicrobial”	80	Intersport

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	28	A pair of icehockey shorts (children)	Bauer	Core compression Jock short. Junior	KROPP: 83/17 % Polyester/Elastan MASKA: 90/10 % Polyester/Spandex	“Antibacterial”	300	Intersport
	29	Balaclava (children)	Houdini	Balaclava Kids	24/72/4 % Wool/Polyester/Nylon	Sportwool Altiude Jersey	279	Uteungar.se
	30	Wipe	Klin-tec	-	80/20 % Polyester/Polyamid	Silver		Prov från tillverkare

Picture	Sample	Article	Brand name	Article	Material	Biocide/marketing	Price	Place of purchase
	31	Underwear/ jersey	Houdini	Womens's Airborn Crew	75/25 % Wool/Silke	"Naturligt antibakteriell"	899	Naturkompaniet
	32	Body (children)	Eiser trikå	Comfymitt Body with Hood	100 % Cotton	47th Element (silver)	159 kr	Eiser Trikå
	33	A pair of pyjamas (children)	Eiser trikå	PJ Bottoms + Top Sweetheart	100 % Cotton	Silver	149 kr	Eiser Trikå

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