Danish Ministry of the Environment
Environmental Protection Agency

Survey of benzyl chloride (CAS no. 100-44-7)

Part of the LOUS-review

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Consultation draft

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Survey of benzyl chloride (CAS no. 100-44-7)

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Preface

Preface

Background and objectives
The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 (Danish EPA, 2011), includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tonnes per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, alternatives, existing regulation, monitoring and exposure, as well as information regarding ongoing activities under REACH.

Based of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns benzyl chloride (CAS 100-44-7). This substance was neither included in the first list in 1998 nor the second list in 2000, but was included in the third list in 2004 and has remained on the list since then (i.e. also included in the fourth list in 2009). The main reason for the inclusion in LOUS is due to the classification as Carc. 1B, H350 "May cause cancer".

The main objective of this study is, as mentioned, to provide background information for the Danish EPA's consideration regarding the need for further risk management measures.

The process
The survey has been undertaken by FORCE Technology during the period September 2013 to May 2014. The project team included:

- Maria Strandesen, FORCE Technology, Project Manager
- Pia Brunn Poulsen, FORCE Technology, contributor
- Anders Schmidt, FORCE Technology, quality assessment
- Ole Schleicher, FORCE Technology, contributor

The work has been followed by an advisory group consisting of:

- Louise Grave Larsen, Danish EPA
- Shima Dobel, Danish EPA
- Nikolai Nilsen, DI

Data collection
The survey and review are based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from HELCOM, OSPAR, the Stockholm Convention, the PIC Convention, and the Basel Convention.
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on ecolabels from the Danish ecolabel secretariat (Nordic Swan and EU Flower) and the German Angel;
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Export of dangerous substances from the Edexim database;
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Data on production, import and export of substances from the Nordic Product Registers as registered in the SPIN database;
- Information from Circa on risk management options (confidential, for internal use only, not searched via the Internet);
- Monitoring data from the National Centre for Environment and Energy (DCE), the Geological Survey for Denmark and Greenland (GEUS), the Danish Veterinary and Food Administration, the European Food Safety Authority (EFSA), and the INIRIS database;
- Waste statistics from the Danish EPA;
- Chemical information from the ICIS database;
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD, IARC, IPCS, WHO, OSPAR, HELCOM, and the Basel Convention;
  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature;
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.
- PubMed and Toxnet databases for identification of relevant scientific literature.

Besides, direct enquiries were sent to Danish and European trade organisations and a few key market actors in Denmark.

Summary and conclusions

Classification and most important regulatory aspects
Benzyl chloride has a harmonised classification of

- Acute Tox. 4, H302 (Harmful if swallowed)
- Skin Irrit. 2, H315 (Causes skin irritation)
- Eye Dam. 1, H318 (Causes serious eye damage)
- Acute Tox. 3, H331 (Toxic if inhaled)
- STOT SE 3, H335 (May cause respiratory irritation)
- Carc. 1B, H350 (May cause cancer)
- STOT RE 2, H373 (May cause damage to organs through prolonged or repeated exposure)

As a consequence of the carcinogenic properties of benzyl chloride, the substance is restricted as a substance or in mixtures for supply to the general public in concentrations above 0.1% and is prohibited for use in cosmetic products.

A threshold limit value of 1 ppm or 5 mg/m^3 is set for the working environment regarding benzyl chloride in the EU[1]. This threshold limit value may not at any time be exceeded. Furthermore, specific precautions regarding work with benzyl chloride are implemented, as benzyl chloride is carcinogenic. A limit value of 0.0008 mg/m^3 for concentrations of benzyl chloride in the air, measured at the property line of the companies, has been set for companies in Denmark.

As a hazardous substance benzyl chloride is subject to specific regulation regarding transportation of dangerous goods[2].

Benzyl chloride has been registered under REACH in a tonnage band of 10 – 100 tonnes per annum, but is neither on the Candidate list of substances of very high concern nor on any of ECHA's Registry of intentions - including the CoRAP list of substances for the period of 2013-2015. Benzyl chloride is, however, on the SIN List because it fulfils the criteria for Substances of Very High Concern.

The Swedish Chemicals Agency has included benzyl chloride in their PRIO database as a "phase-out substance", which means that the use of benzyl chloride "shall cease to the extent possible".

Benzyl chloride is not mentioned directly in any eco-labelling criteria, but will automatically be restricted in any eco-labelling scheme as no carcinogenic substances are allowed in eco-labelled products.

Manufacture and use
Manufacturing sites
Production of benzyl chloride takes place all over the world, among others, in Western Europe, Japan and the United States. Six companies within EU produce (or import from outside the EU) benzyl chloride. They are located in Germany and Belgium. No producers are located in Denmark.

[1] Directive 91/332/EEC
[2] Directive 2008/68/EC

Production volumes
It has not been possible to retrieve information regarding the total volume of benzyl chloride produced worldwide today. However in 1989 approximately 93,000 tons were produced in the western countries, including USA. According to REACH the production (and/or import) of benzyl chloride in EU lies between 10 and 100 tons.

It should be noted, that non-isolated intermediates (i.e. intermediates which are produced but shortly after (by the same company) converted to another substance) are not included in the tonnage band. Since benzyl chloride is such an intermediate, there may be a large production of benzyl chloride in EU, however this is not registered.

Import and export
Only one company in Denmark imports benzyl chloride. The company informs that they import in average 25 tonnes per year; however, it may vary from year to year with up to 10-15 tonnes. No export of benzyl chloride takes places in Denmark, as all imported benzyl chloride is used in the manufacturing of other chemicals.

Within the EU it is not possible to retrieve import/export data on benzyl chloride alone since the substance in EUROSTAT is grouped with 'other halogenated derivates of aromatic hydrocarbons'.

Uses
Benzyl chloride is only used as an intermediate, i.e. as a substrate for the production of other chemicals. These other chemicals cover:

- Benzyl alcohol (largest application) (used as solvent for inks, paints, etc.)
- Benzyl quaternary ammonium compounds (used as biocide)
- Benzyl cyanide (used as a precursor for penicillin G)
- Phthalates (especially butyl benzyl phthalate (BBP))
- Certain dyes
- Flavour products
- Pharmaceutical products
- Benzyl magnesium compounds
- Benzyl lithium compounds (used as for instance in nerve medicine (sedatives))
- Chemicals used in the detergent/cleaning agent industry

Furthermore, benzyl chloride is used as a photographic developer and has formerly been used as an irritant gas in chemical warfare (ECD SIDS, 1998; US EPA, 2000a).

Benzyl chloride is not intentionally used in consumer products, but may be present at impurity levels (i.e. in small concentrations – typically well below 0.1%) in some consumer products, like e.g. cosmetic products, modelling clay, car care products, pharmaceutical products and other similar products. Benzyl chloride will, however, react with water in the products and form benzyl alcohol with the harmonised classification Acute Tox. 4 (H302 "Harmful if swallowed" and H332 "Harmful if inhaled"). It is therefore expected that the content of benzyl chloride in cosmetic products in general is insignificant, whereas the impurity of benzyl chloride may be higher in products like modelling clay that do not contain water. However, it is not expected that these impurities of benzyl chloride will result in any health impacts.

The amount of benzyl chloride used in Europe (2000) lies between 100,000 and 500,000 tonnes (IUCLID, 2000). In 2009, China became the largest market for benzyl chloride (35% of total consumption), followed by Western Europe (34%), North America (14%), and India (11%). Overall, Asia accounted for 48% of the global demand.

Trends
The overall worldwide consumption of benzyl chloride is expected to grow at an annual rate of approx. 4% in the period 2009 – 2014. Highest growth rates are expected in China and India, partly due to a greater use of benzyl chloride in solvent applications and partly due to increased export to the US and a use of benzyl chloride as a precursor for benzyl esters. This trend also applies to Western Europe to a certain extent. Despite a rise in feedstock costs, benzyl alcohol will thus be the main cause for benzyl chloride consumption in these regions (IHS Chemicals, 2010).

Waste management
Waste from manufacturing and use
Waste from manufacturing of benzyl chloride is expected to be minor due to the fact that the economically most feasible solution is to ship and sell all manufactured amounts. Waste from manufacturing of benzyl chloride is therefore only expected to be in the form of residues, e.g. in the form of minor leftovers in 'empty' containers. Waste from manufacturing is expected to be treated as chemical waste according to the EU regulation.

Waste from use of benzyl chloride is expected to be in the form of handling 'empty' packaging and is therefore considered to be minor. Emptied packaging has to be treated as hazardous waste and will in Denmark be incinerated at a special incineration site for handling of chemical waste (Nord).

Waste from products containing impurities of benzyl chloride
The content of benzyl chloride in private household waste and in chemical waste is regarded to be insignificant due to the fact that benzyl chloride is not intentionally added to chemical mixtures or consumer products. Benzyl chloride is only expected to be present as an impurity in products that do not contain water, such as car care products and modelling clay. If waste should contain small amounts of benzyl chloride, the waste is expected to be incinerated (for regular household waste) or treated as hazardous waste.

Environmental effects and fate
Benzyl chloride does not have a harmonised classification with respect to environmental effects, but a classification of Aquatic Chronic 2, H411 "Toxic to aquatic life with long lasting effects" has been suggested by several notifiers. This is also the environmental classification that benzyl chloride should have according to the CLP classification.

Benzyl chloride is regarded as readily biodegradable and not bioaccumulating, thus non-persistent in the environment. If benzyl chloride is released into air, water or soil, it will reside predominantly in the compartment to which it is released, but will fairly quickly ('days or weeks') be degraded through hydrolysis to benzyl alcohol, which is also readily biodegradable and non-toxic in the environment. Overall, benzyl chloride cannot be considered as being a PBT substance.

As benzyl chloride is used in closed systems and is not present in consumer products beyond impurity levels, its release to the environment may occur only from production sites, when transported or stored, or when waste is treated in waste incineration facilities. Environment Canada predicts that benzyl chloride would be released in relatively small quantities, mainly to air, but also to some extent to water. Release to soil seems only to be relevant in the case of accidents during transportation.

Other sources to release of benzyl chloride to the environment may be burning of fossil fuels (coal), wildfires, and emissions from municipal solid waste landfills. However, these sources of releases seem to be of minor importance.

Available monitoring data concerning the levels of benzyl chloride in the environment is very limited. This may be due to the fact that benzyl chloride is readily biodegradable, undergoes rapid hydrolysis to benzyl alcohol and the fact that benzyl chloride is not expected to bioaccumulate in organisms. Monitoring data has only been identified from Canada and the USA. The few monitoring data for benzyl chloride in air illustrates that benzyl chloride is found in small concentrations (µg/m^3 to ng/m^3) in air.

To conclude: Based on the current usage pattern of benzyl chloride, the substance cannot be expected to enter the environment in a quantity or concentration that has an immediate or long-term harmful effect on the environment.

Human health effects

Toxicokinetics, absorption, distribution, metabolism, and excretion

Most of the benzyl chloride inhaled or ingested can be found in the heart, stomach, lungs, fat, muscle, and the bloodstream. There is no information about dermal absorption of benzyl chloride. Benzyl chloride is rapidly distributed in the body and rapidly excreted from the body via urine (with a $T_{1/2}$ of approximately 6 hours). The stomach can be considered a target organ for the toxic effects of benzyl chloride. Benzyl chloride does not accumulate in the body (OECD SIDS, 1998; ECHAs Registered Substances Database, 2013).

Human health hazard

Benzyl chloride has a moderate oral acute toxicity (Acute Tox. 4, H302 “Harmful if swallowed”), but a higher dermal toxicity and toxicity by inhalation (Acute Tox. 3, H331 “Toxic if inhaled”). Benzyl chloride is regarded as irritating for skin, eyes and respiratory system. Benzyl chloride has the harmonised classification Skin Irrit.2, H315 “Causes skin irritation”, Eye Dam. 1, H318 “Causes serious eye damage”, and STOT SE 3, H335 “May cause respiratory irritation”. However, data regarding toxicity by inhalation and dermal exposure indicate that an Acute Tox. 2 classification (according to EU Regulation no. 286, 2011) would be relevant as well. Furthermore, information indicates, that benzyl chloride should be classified as skin sensitiser (Category 1) and labelled as H317: “May cause an allergic skin reaction” according to the Regulation (EC) No 1272/2008. However, the current harmonised classification of benzyl chloride does not include a classification as skin sensitiser.

Benzyl chloride is considered to be carcinogenic and is classified as Carc. 1B, H350 “May cause cancer”. Furthermore, benzyl chloride is suspected of being weakly genotoxic (evidence of genotoxic potential *in vitro*, but evidence *in vivo* is more limited). Long-term studies show that benzyl chloride may cause damage to organs through prolonged or repeated exposure (STOT RE2, H373).

Exposure to benzyl chloride has also induced non-cancer effects in a range of target tissues, including the liver, forestomach, and lungs, in experimental animals. Effects on the liver have been seen at both oral studies and inhalation studies, whereas effects in the stomach are observed at oral studies. Effects on the lungs have been seen in inhalation studies.

Reproductive studies are limited and a single neurological study with insufficient documentation indicates that benzyl chloride has a neurotoxic effect.

Exposure sources

The human exposure sources are considered to be:

- Consumers: Inhalation and dermal exposure through low levels of impurities in consumer products like cosmetic products, modelling clay, PVC flooring.
- Occupational exposure:
  - In workplaces where benzyl chloride is manufactured
  - In workplaces where benzyl chloride is used as an intermediate chemical to produce other chemicals

- Indirect exposure via the environment: Mainly via air as benzyl chloride is rapidly hydrolysed in the aquatic environment.

Human health impact
Concentrations of benzyl chloride in drinking water, food, or soil are likely to be negligible and the human health impact therefore low or insignificant. The exposure due to the use of consumer products containing residual quantities of benzyl chloride is not expected to produce health impacts.

Risk assessments carried out by Environment Canada (2009a) and OECD SIDS (1998) illustrate that the most important human health impact from benzyl chloride is occupational exposure. However, none of the identified studies reporting measured values of benzyl chloride in the working environment exceeds the Danish occupational threshold limit, thus the risk related to occupational exposure is assessed to be low.

Risk assessments (worst case scenarios) related to the use of products containing impurities of benzyl chloride, inhalation of indoor air with measured content of benzyl chloride, and intake of benzyl chloride by food, generally all result in large safety margins (from 13,000 to 850.000).

For workers, however, a worst case scenario – in which workers did not wear masks and where the measurements were only done during filling operations (where the benzyl chloride concentrations are high) resulted in a margin of exposure below 100 (67). However, it is not expected under normal working conditions, where the exposure is lower, that the exposure of benzyl chloride will constitute a health risk.

Alternatives
As benzyl chloride exclusively is used as a chemical intermediate in the manufacturing of other chemicals, it is necessary to look at the possibility of producing these other chemicals in an alternative way in order to find alternatives to benzyl chloride. This has been carried out for the major chemicals that are produced with benzyl chloride.

The only production where use of an alternative production process takes place is for the production of benzyl alcohol, where the US already uses a hydrogenation process of benzaldehyde instead. This alternative seems to be a better alternative concerning health impacts as benzaldehyde has a less severe harmonised classification than benzyl chloride.

For other uses, no information on alternatives is available (it has neither been identified by RMO (2010) or Environment Canada (2009a)), and the searches performed in this project have only resulted in alternative processes that are not suitable for commercial production or are more energy consuming and thereby more expensive. Furthermore, these alternatives are not safer alternatives than benzyl chloride, as the alternatives are classified as toxic and carcinogenic or reprotoxic.

Sammenfatning og konklusion

Klassificering og vigtige aspekter i relation til regulering
Benzylchlorid har en harmoniseret klassificering på:

- Acute Tox. 4, H302 (Farlig ved indtagelse.)
- Skin Irrit. 2, H315 (Forårsager hudirritation)
- Eye Dam. 1, H318 (Forårsager alvorlig øjenskade)
- Acute Tox. 3, H331 (Giftig ved indånding)
- STOT SE 3, H335 (Kan forårsage irritation af luftvejene)
- Carc. 1B, H350 (Kan fremkalde kræft)
- STOT RE 2, H373 (Kan forårsage organskader ved længerevarende eller gentagen eksponering)

Som en konsekvens af benzylchlorids kræftfremkaldende egenskaber er stoffet begrænset både som enkeltstående kemikalie og i blandinger til offentligheden i en koncentration over 0,1 %. Derudover er det forbudt at anvende i kosmetiske produkter.

En grænseværdi på 1 ppm eller 5 mg/m^3 er fastsat for arbejdsmiljøet med hensyn til benzylchlorid i EU[3]. Denne grænseværdi må ikke overskrides på noget tidspunkt. Desuden er der implementeret specifikke forhåndsregler vedrørende arbejde med benzylchlorid, da benzylchlorid er kræftfremkaldende. En grænseværdi på 0,0008 mg/m^3 for koncentrationer af benzylchlorid i luften, målt ved skellet til firmaerne, er blevet fastsat for virksomheder i Danmark.

Som et sundhedsfarligt stof er benzylchlorid underlagt en specifik regulering vedrørende transport af farligt gods[4].

Benzylchlorid er registreret i REACH med et tonnagebånd på 10 – 100 tons pr. år. Det er hverken på Kandidatlisten over særligt problematiske stoffer eller på andre af ECHA's Registre – deriblandt CoRAP-listen over stoffer for perioden 2013-2015. Benzylchlorid er dog på SIN-listen, fordi det opfylder kriterierne for særligt problematiske stoffer pga. den kræftfremkaldende effekt.

Den svenske kemikalieinspektion har inkluderet benzylchlorid i deres PRIO-database som et "udfasningsstof", hvilket betyder, at brugen af benzylchlorid "skal så vidt muligt ophøre".

Benzylchlorid nævnes ikke direkte i nogen miljømærkekriterier, men vil automatisk blive underlagt alle miljømærkeordninger, da kræftfremkaldende stoffer ikke er tilladt i miljømærkede produkter.

Produktion og brug
Produktionssteder
Produktion af benzylchlorid finder sted over alt i verden, bl.a. i Vesteuropa, Japan og USA. Seks firmaer indenfor EU producerer benzylchlorid (eller importerer fra lande udenfor EU). De er placeret i Tyskland og Belgien. Ingen producenter er placeret i Danmark.

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[3] Directive 91/332/EEC
[4] Directive 2008/68/EC

Produktionsmængder
Det har ikke været muligt at finde oplysninger om den totale mængde benzylchlorid produceret world-wide idag. Men i 1989 blev der produceret ca. 93.000 tons i de vestlige lande, herunder USA. Ifølge REACH ligger produktion (og/eller importen) af benzylchlorid i EU mellem 10 og 100 tons.

Det skal her bemærkes, at ikke-isolerede mellemprodukter (dvs. mellemprodukter, som produceres, men kort efter (af samme virksomhed) omdannes til et andet produkt/stof)) ikke er inkluderet i tonnagebåndet. Siden benzylchlorid er et sådant mellemprodukt, kan der således være en stor produktion af stoffet i EU, men dette er ikke registreret.

Import og eksport
Kun et firma i Danmark importerer benzylchlorid. Firmaet oplyser, at de importerer i gennemsnit 25 tons pr. år. Det kan dog variere fra år til år med op til 10-15 tons. Der finder ikke nogen eksport af benzylchlorid sted i Danmark, da alt importeret benzylchlorid bruges til fremstillingen af andre kemikalier.

Indenfor EU er det ikke muligt at finde import/eksportdata på benzylchlorid alene, da stoffet i EUROSTAT er grupperet med 'andre halogenerede derivater fra aromatiske kulbrinter'.

Brug
Benzylchlorid bruges kun som et mellemstof, dvs. som et substrat til produktion af andre kemikalier. Disse andre kemikalier inkluderer:

- Benzylalkohol (største anvendelse) (bruges som opløsningsmiddel til blæk, maling, mv.)
- Benzyl kvartenær ammonium forbindelser (bruges som biocid)
- Benzylcyanid (bruges som precursor for penicillin G)
- Ftalater (især butyl benzyl ftalat (BBP))
- Visse farver
- Aromaprodukter
- Farmaceutiske produkter
- Benzylmagnesium forbindelser
- Benzyllitium forbindelser (bruges fx i nervemedicin (sedative))
- Kemikalier der bruges i vaske/rengøringsmiddelindustrien

Benzylchlorid bruges desuden som fotografisk fremkalder og er tidligere blevet brugt som en irritationsgas i kemisk krigsførelse (ECD SIDS, 1998; US EPA, 2000a).

Benzylchlorid bruges ikke bevidst i forbrugerprodukter, men kan være til stede som urenhed (dvs. i små koncentrationer – typisk et godt stykke under 0,1 %) i nogle forbrugerprodukter, som fx kosmetiske produkter, modellervoks, bilplejeprodukter, farmaceutiske produkter og andre lignende produkter. Benzylchlorid vil dog reagere med vand i produkterne og danne benzylalkohol med den harmoniserede klassifikation Acute Tox. 4 (H302 " Farlig ved indtagelse" og H332 " Farlig ved indånding"). Det forventes derfor, at indholdet af benzylchlorid i kosmetiske produkter generelt er ubetydelig, hvorimod urenhed fra benzylchlorid kan være højere i produkter som modellervoks, der ikke indeholder vand. Det forventes imidlertid ikke, at disse urenheder af benzylalkohol i forbrugerprodukter vil medføresundhedsmæssige risici.
Mængden af benzylchlorid, anvendt i Europa (2000), ligger mellem 100.000 og 500.000 tons (IUCLID, 2000). I 2009 blev Kina det største marked for benzylchlorid (35 % af det samlede forbrug), efterfulgt af Vesteuropa (34 %), Nordamerika (14 %) og Indien (11 %). Alt i alt stod Asien for 48 % af den globale efterspørgsel.

Tendenser
Det samlede forbrug af benzylchlorid i verden forventes at vokse med en årlig rate på ca. 4% i perioden 2009 – 2014. Højeste vækstrater forventes i Kina og Indien, dels pga. en større anvendelse af benzylchlorid i opløsninger, og dels pga. stigende eksport til USA og et forbrug af benzylchlorid som precursor for benzylestere. Denne tendens gælder også i et vist omfang for Vesteuropa. Benzylalkohol forventes at blive hovedårsagen til forbruget af benzylchlorid i disse regioner (IHS Chemicals, 2010).

Håndtering af affald
Affald fra produktion og brug
Affald fra produktion af benzylchlorid forventes at være lille, idet det økonomisk set er mest fordelagtigt at få solgt alt hvad man har produceret. Affald fra produktion af benzylchlorid forventes derfor kun at være i form af rester, fx mindre rester i 'tomme' beholdere. Affald fra produktionen forventes at blive behandlet som kemisk affald i henhold til EU-forordningen.

Affald fra brugen af benzylchlorid forventes at være i form af håndtering af 'tom' emballage og anses derfor at være ubetydelig. Tom emballage skal behandles som sundhedsfarligt affald og vil i Danmark blive brændt i et specielt forbrændingsanlæg til håndtering af kemisk affald (Nord).

Affald fra produkter, der indeholder urenheder fra benzylchlorid
Indholdet af benzylchlorid i privat husholdningsaffald og i kemisk affald betragtes som værende ubetydelig på grund af, at benzylchlorid ikke tilsættes bevidst til kemiske blandinger eller forbrugerprodukter. Benzylchlorid forventes kun at være til stede som en urenhed i produkter, som ikke indeholder vand, som fx bilplejeprodukter og modellervoks. Hvis affaldet skulle indeholde små mængder benzylchlorid, forventes det, at affaldet bliver brændt (som almindeligt husholdningsaffald) eller behandlet som kemisk affald.

Miljømæssige effekter og skæbne
Benzylchlorid har ikke en harmoniseret klassifikation med hensyn til miljømæssige effekter, men en klassifikation som Aquatic Chronic 2, H411 "Giftig for vandlevende organismer, med langvarige virkninger" er blevet foreslået af adskillige anmeldere. Det er også den miljømæssige klassifikation, som benzylchlorid burde have ifølge CLP-klassificeringen.

Benzylchlorid betragtes som let bionedbrydeligt og ikke bioakkumulerende, og er således flygtig i miljøet. Hvis benzylchlorid frigives til luft, vand eller jord, vil det primært blive i det medie, hvortil det blev frigivet, men vil rimelig hurtigt ('dage eller uger') nedbrydes via hydrolyse til benzylalkohol, som også er let bionedbrydeligt og ikke-giftigt i miljøet. Alt i alt kan benzylchlorid ikke betragtes som værende et PBT-stof.

Da benzylchlorid anvendes i lukkede systemer og ikke er til stede i forbrugerprodukter over forureningsniveauet, kan det kun frigives til miljøet fra produktionsstederne, når det transporteres eller lagres, eller når affaldet behandles i affaldsforbrændingsanlæg. Environment Canada forudsiger, at benzylchlorid vil blive frigjort i relativt små mængder, primært til luft, men også i et vist omfang til vand. Frigivelse til jord ser kun ud til at være relevant i tilfælde af ulykker under transport.

Andre kilder til frigivelse af benzylchlorid til miljøet kan være afbrænding af fossile brændsler (kul), skovbrande og emissioner fra kommunale affaldsdepoter for fast affald. Disse frigivelseskilder ser dog ud til at være af mindre betydning.

Tilgængelige overvågningsdata vedrørende niveauer af benzylchlorid i miljøet er meget begrænsede. Dette kan skyldes, at benzylchlorid er let bionedbrydelig, gennemgår hurtig hydrolyse til benzylalkohol, og at benzylchlorid ikke forventes at bioakkumulere i organismer. Overvågningsdata er kun fundet i kilder fra Canada og USA. De få overvågningsdata for benzylchlorid i luft illustrerer, at benzylchlorid findes i små koncentrationer (µg/m^3 til ng/m^3) i luft.

Det kan således konkluderes at det aktuelle brugsmønster for benzylchlorid ikke medfører at stoffet frigives til miljøet i en kvantitet eller koncentration, som har en øjeblikkelig eller langsigtet sundhedsskadelig effekt på miljøet.

Sundhedseffekter på mennesker
Toksikokinetik, absorbering, udbredelse, metabolisme og udskillelse
Hovedparten af det benzylchlorid, der indåndes eller indtages, findes i hjertet, mave, lunger, fedt, muskler og blodbaner. Der er ikke nogen oplysninger om dermal absorbering af benzylchlorid. Benzylchlorid fordeles hurtigt i kroppen og udskilles hurtigt fra kroppen via urinen (med en $T_{1/2}$ på ca. 6 timer). Maven kan betragtes som det primære organ i relation til giftige effekter af benzylchlorid. Benzylchlorid akkumulerer ikke i kroppen (OECD SIDS, 1998; ECHAs Registered Substances Database, 2013).

Sundhedsrisiko for mennesker
Benzylchlorid har en moderat oral akut toksicitet (Acute Tox. 4, H302 ”Farlig ved indtagelse”), men en højere dermal toksicitet og er også toksisk ved indånding (Acute Tox. 3, H331 ”Giftig ved indånding”). Benzylchlorid betragtes som irriterende for hud, øjne og åndedrættet. Benzylchlorid har den harmoniserede klassifikation Skin Irrit.2, H315 “Forårsager hudirritation”, Eye Dam. 1, H318 “ Forårsager alvorlig øjenskade” og STOT SE 3, H335 “ Kan forårsage irritation af luftvejene”. Data omhandlende toksicitet ved indånding og dermal eksponering indikerer, at en Acute Tox. 2 klassifikation (ifølge EU Regulation no. 286, 2011) også ville være relevant. Desuden indikerer oplysningerne, at benzylchlorid burde klassificeres som hudallergent (Kategori 1) og mærket som H317: “Kan forårsage allergisk hudreaktion” ifølge Regulation (EC) No 1272/2008. Den nuværende harmoniserede klassifikation af benzylchlorid inkluderer dog ikke en klassifikation som hudallergent.

Benzylchlorid anses for at være kræftfremkaldende og er klassificeret som Carc. 1B, H350 “Kan fremkalde kræft”. Desuden mistænkes benzylchlorid for at være svagt genotoksisk (bevis for genotoksisk potentiale *in vitro*, men bevis *in vivo* er mere begrænset). Langtidsstudier viser, at benzylchlorid kan forårsage skade på organer gennem langvarig eller gentaget eksponering (STOT RE2, H373).

Eksponering for benzylchlorid har også medført effekter (ikke relateret til kræft) i et område dækkende leveren, formaven og lunger, i forsøgsdyr. Effekter på leveren er blevet set ved både orale studier og indåndingsstudier, hvorimod effekter i maven er observeret ved orale studier. Effekter på lungerne er set i indåndingsstudier.

Reproduktive studier er begrænsede. Et enkelt neurologisk studie med utilstrækkelig dokumentation indikerer, at benzylchlorid har en neurotoksisk effekt.

Eksponeringskilder
Kilder til human eksponering anses for at være:
- Forbrugere: Inhalation og dermal eksponering gennem små niveauer af urenheder i forbrugerprodukter som fx kosmetiske produkter, modellervoks, PVC-gulve.
- Eksponering via arbejde:
  - På arbejdspladser hvor benzylchlorid fremstilles
  - På arbejdspladser hvor benzylchlorid bruges som et kemisk mellemstof til at fremstille andre kemikalier
- Indirekte eksponering via miljøet: Hovedsageligt via luften da benzylchlorid hurtigt hydrolyseres i vandmiljøet.

Sundhedseffekter på mennesker
Koncentrationer af benzylchlorid i drikkevand, mad eller jord vil sandsynligvis være ubetydelige og indvirkningen på menneskers sundhed derfor lille eller ubetydelig. Eksponering på grund af brugen af forbrugerprodukter, der indeholder restmængder af benzylchlorid, forventes ikke at have sundhedsmæssige risici.

Risikovurderinger udført af Environment Canada (2009a) og OECD SIDS (1998) viser, at den vigtigste indvirkning på menneskers sundhed fra benzylchlorid er eksponering i forbindelse med arbejde. Ingen af de identificerede studier, der rapporterer om målte værdier af benzylchlorid i arbejdsmiljøet, overskrider dog den danske arbejdshygiejniske grænseværdi . Derfor vurderes risikoen, relateret til eksponering i forbindelse med arbejde, at være lav.

Risikovurderinger (worst-case scenarier), der er relateret til brugen af produkter, som indeholder urenheder af benzylchlorid, inhalering af indendørsluft med målt indhold af benzylchlorid og indtagelse af benzylchlorid via mad, resulterer alle generelt i store sikkerhedsmarginer (fra 13.000 til 850.000).

For arbejdere resulterede en worst-case situation – hvor arbejderne ikke bar masker, og hvor målingerne kun blev udført under påfyldningerne (hvor koncentrationerne af benzylchlorid er høje) - i en eksponeringsmargin under 100 (67). Det forventes dog ikke under normale arbejdsforhold, hvor eksponeringen er lavere, at eksponeringen af benzylchlorid vil udgøre en sundhedsrisiko.

Alternativer
Da benzylchlorid udelukkende anvendes som et kemisk mellemstof ved fremstillingen af andre kemikalier, er det nødvendigt at se på muligheden for at producere disse andre kemikalier på en alternativ måde for at finde alternativer til benzylchlorid. Muligheden for dette er blevet undersøgt for de fleste kemikalier, som er fremstillet med benzylchlorid.

Den eneste produktion, hvor brugen af en alternativ produktionsproces finder sted, er ved produktionen af benzylalkohol, hvor USA allerede anvender en hydrogenisationsproces af benzaldehyd i stedet. Dette alternativ ser ud til at være et bedre alternativ, hvad angår sundhedspåvirkninger, da benzaldehyd har en mindre alvorlig harmoniseret klassifikation end benzylchlorid.

I relation til de andre anvendelser er der ikke fundet information om alternativer (hverken RMO (2010) eller Environment Canada (2009a) har identificeret viden relateret hertil). Søgninger, der er udført i dette projekt, har kun resulteret i alternative processer, som ikke er egnede til kommerciel produktion eller er mere energikrævende og dermed dyrere. Desuden er disse alternativer ikke mere sikre end benzylchlorid, da alternativerne er klassificeret som giftig og kræftfremkaldende eller skadelig for forplantningen.

1. Introduction to benzyl chloride

Benzyl chloride also known as α-chlorotoluene is an organic chemical with the molecular formula C_6H_5-CH_2Cl. Benzyl chloride has a strong, unpleasant odour (TOXNET, 2013) and is a colourless liquid at room temperature (ECHA Registered Substances Database, 2013). Furthermore, the substance is moderately flammable and gives off explosive fumes when heated. The liquid is insoluble in water and may in a humid environment act corrosive towards many metals.

Benzyl chloride is manufactured by chlorination of toluene (TOXNET, 2013; Ullmann's, 2006). Benzyl chloride may be structurally the simplest side-chain chlorinated derivate of toluene, but economically it is the most important derivate. Benzyl chloride is the starting material for a large number of industrial syntheses, i.e. it is used as a chemical intermediate for organic synthesis of e.g. plasticisers (e.g. BBP), benzyl alcohol, dyes, flavours, perfumes , quaternary ammonium salts, and phenylacetic acid used in the production of synthetic penicillin (Ullmann's, 2006).

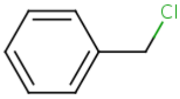
Benzyl chloride is classified as H350 (may cause cancer) and H373 (may cause damage to organs through prolonged or repeated exposure). The substance is placed in Group 2 on the IARC list (International Agency for Research in Cancer) – which means that it is a substance which probably is carcinogenic to humans. The substance also appears on the SIN List, due to its classification as a CMR substance and on the Danish EPA's List of Undesirable Substances, due to its classification as CMR cat. 1 and 2. For further information regarding health aspects, please see section 6.

Physical-chemical properties, etc. of benzyl chloride are given in Table 1 and Table 2 below.

1.1 Definition of the substance

TABLE 1
IDENTIFICATION PARAMETERS OF BENZYL CHLORIDE (OECD SIDS, 1998; ECHA REGISTERED SUBSTANCES DATABASE, 2013; ULLMANN'S, 2006)

	Benzyl chloride
EC Number	202-853-6
CAS Number	100-44-7
Synonyms	Benzyl chloride (OECD name), (chloromethyl)benzene (IUPAC name), alpha-chlorotoluene, α-chlorotoluene (EC name), omega-chlorotoluene, chlorophenylmethane, tolyl chloride
Molecular weight	126.59

Molecular formula and structure	C_7H_7Cl $C_6H_5CH_2Cl$ 
Degree of purity	99.8%
Major impurities	Benzal chloride ($C_6H_5CHCl_2$), chlorotoluene ($C_6H_4ClCH_3$), 2,4-dichlorotoluene ($C_6H_3Cl_2CH_3$), toluene ($C_6H_5CH_3$), chlorobenzene (C_6H_5Cl), hydrogen chloride (HCl)

1.2 Physical and chemical properties

Benzyl chloride is capable of reacting with metals and their salts. For this reason storage of benzyl chloride in enamel, glass or lined vessels is essential (Ullmann's, 2006).

TABLE 2
PHYSICAL-CHEMICAL PROPERTIES OF BENZYL CHLORIDE

Property		Reference
Physical state	Liquid fumes in moist air at 20°C and 1013 hPa	ECHA RSD, 2013
Colour	Colourless	ECHA RSD, 2013
Odour	Pungent	ECHA RSD, 2013
Substance type	Organic	ECHA RSD, 2013
Melting point	-48 to -43 °C	ECHA RSD, 2013
Freezing point	-39.2 °C	ECHA RSD, 2013; Ullmann's, 2006
Boiling point	179.4 °C at 1013 hPa	ECHA RSD, 2013; Ullmann's, 2006
Flash point	67 °C at 1013 hPa 60 °C	ECHA RSD, 2013 Ullmann's, 2006
Autoflammability/ self-ignition temperature	585 °C at 1013 hPa	ECHA RSD, 2013; Ullmann's, 2006
Relative density	1.1 g/cm^3 at 20 °C	ECHA RSD, 2013; Ullmann's, 2006
Viscosity	1.38 mPa s (dynamic) at 20 °C 1.289 mPa s (dynamic) at 25 °C	ECHA RSD, 2013; Ullmann's, 2006

Property		Reference
Vapour pressure	0.16 kPa at 25 °C 0.747 kPa / 0.99 kPa at 50 °C 2.66 kPa at 75 °C 7.83 kPa / 7.96 kPa at 100 °C	ECHA RSD, 2013 /Ullmann's, 2006 /Ullmann's, 2006
Henry's Law constant	41.8 Pa · m^3/mol (modelled)	Environment Canada, 2009a
Surface tension	37.8 mN/m at 20 °C 29.15 mN/m at 88 °C 19.5 mN/m at 179.5 °C	ECHA RSD, 2013; Ullmann's, 2006
Water solubility	Decomposes 0.46 g/L at 30 °C (reported in 1975)	ECHA RSD, 2013
Log P (octanol/water) **Log K_{OW}**	2.69 (calculated by use of CHEMICALC) 2.3 (experimental results) 2.3 and 2.79 (QSAR predictions)	ECHA RSD, 2013

2. Regulatory framework

This chapter gives an overview of how benzyl chloride is addressed in existing and upcoming EU and Danish legislation, international agreements, and eco-label criteria.

For readers not accustomed with legislative issues, Appendix 2: provides an overview of the different legislatives instruments in the EU and Denmark. The appendix also gives a brief introduction to the chemicals legislation, it explains the lists referred to in this chapter, and it provides a brief introduction to international agreements and selected eco-label schemes.

2.1 Legislation

This section lists existing legislation addressing benzyl chloride, the classification of benzyl chloride, and finally aspects concerning REACH.

2.1.1 Existing legislation

Table 3 provides an overview of existing legislation addressing benzyl chloride. For each area of legislation, the table lists the relevant legislation ('Legal instrument') – whether this is a Directive, Regulation or Danish Statutory Order. Furthermore, it is noted whether the legislation covers the EU, Denmark or both and a short description of the aspects concerning benzyl chloride is provided in each case. It should be noted that national rules (i.e. Statutory Orders) will only be described in case the Danish rules differ from the related EU Directive.

TABLE 3
EU AND DANISH LEGISLATION ADDRESSING BENZYL CHLORIDE (AS OF NOVEMBER 2013)

Legal instrument	EU/DK	Requirements which concern benzyl chloride
Regulation addressing chemicals		
REGULATION (EC) No 1272/2008 of 16 December 2008 on classification, labelling and packaging of substances and mixtures (CLP)	EU/DK	The CLP Regulation where benzyl chloride is listed in Annex VI of the Regulation with the harmonised classification. See Table 4 in this report. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2008R1272:20110419:EN:PDF
REGULATION (EC) No 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)	EU/DK	Benzyl chloride is listed in Appendix 2 of Annex XVII of REACH: "Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles". Appendix 2 is named: "Entry 28 – Carcinogens: category 1B". Entry 28 in Annex XVII concerns carcinogenic substances. Carcinogenic substances are not to be placed on the market, or used, as substances, as constituents, or in mixtures, for supply to the general public, when the individual concentration in

Legal instrument	EU/DK	Requirements which concern benzyl chloride
		the substances or mixture is equal to or greater than the relevant specific concentration limit. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R1907:20130421:EN:PDF
Regulation addressing products		
REGULATION (EC) No 1223/2009 of 30 November 2009 on cosmetic products	EU/DK	Benzyl chloride is listed as entry no. 650 in Annex II: "List of substances prohibited in cosmetic products". This means that benzyl chloride must not be used as an ingredient in cosmetic products. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2009R1223:20130711:EN:PDF
Regulation addressing waste		
DIRECTIVE 2008/98/EC of 19 November 2008 on waste and repealing certain directives	EU	General legislation on waste and description of the waste hierarchies. Benzyl chloride is not mentioned directly, but it is stated in annex III that waste is considered to be dangerous when it contains carcinogenic substances (thus indirectly covers benzyl chloride). http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:EN:PDF
STATUTORY ORDER No. 1309 of 18.12.2012 on waste	DK	General legislation on waste based on the EU legislation on waste. Benzyl chloride is not mentioned directly, but it is stated in annex 4 that waste is considered to be dangerous if it contains 0.1% or more of a chemical substance considered to be carcinogenic Carc. 1B, H350 as is the case with benzyl chloride. https://www.retsinformation.dk/Forms/R0710.aspx?id=144826#Bil4
Regulation addressing emissions to the environment		
GUIDANCE no. 10702 of 19.11.2008 on B-values (B-værdier)	DK	Benzyl chloride is listed with a B value (contribution value) of 0.0008 mg/m^3. This is the limit value set for companies in Denmark for concentrations of benzyl chloride in the air, measured at the property line of the companies. https://www.retsinformation.dk/Forms/R0710.aspx?id=135894

Legal instrument	EU/DK	Requirements which concern benzyl chloride
STATUTORY ORDER no. 8 of 29.5.2008 of annex to protocol of 2 November 1973 concerning remedial action on the open sea at pollution of the sea of other substances than oil	DK	Benzyl chloride is listed in Appendix 2 of this Danish Statutory order. This means that benzyl chloride is considered as a harmful substance that will pollute the sea and the environment if accidents should happen at sea. Spillage of benzyl chloride at sea therefore results in remedial actions to be taken. https://www.retsinformation.dk/Forms/R0710.aspx?id=114936
Regulation addressing emissions to the working environment		
DIRECTIVE 91/322/EEC of 29 May 1991 on establishing indicative limit values by implementing Council Directive 80/1107/EEC on the protection of workers from the risks related to exposure to chemical, physical and biological agents at work DIRECTIVE 2000/39/EC of 8 June 2000 establishing a first list of indicative occupational exposure limit values in implementing Directive 98/24/EC on the protection of the health and safety of workers from the risks related to chemical agents at work	EU	The threshold limit value for benzyl chloride in the working environment in Denmark is 1 ppm or 5 mg/m^3. Benzyl chloride is marked with L and K which means that the threshold limit value is a ceiling value and may not at any time be exceeded (L) and that the substance is regarded as being carcinogenic (K).
STATUTORY ORDER no. 507 of 17.5.2011 on threshold limit values for substances and materials - and subsequent changes (e.g. 986 of 11.10.2012)	DK	Same as above. https://www.retsinformation.dk/Forms/R0710.aspx?id=143596 https://www.retsinformation.dk/Forms/R0710.aspx?id=136417
DIRECTIVE 2004/37/EC of 29 April 2004 on the protection of workers from the risks related to exposure to carcinogens or mutagens at work DIRECTIVE 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks	EU	Because of the carcinogenic properties of benzyl chloride, the substance is covered by this Danish statutory order if the concentration of benzyl chloride in chemical preparations is 0.1% or higher. Special provisions are valid for benzyl chloride when it comes to laboratory work (§17), industrial use (§17), and other applications (§29-32). §17 states that for these working processes (i.e. laboratory work and industrial use) benzyl chloride may only be used in closed processes or if no release

Legal instrument	EU/DK	Requirements which concern benzyl chloride
related to chemical agents at work		of the substance occurs. If this is not possible the substance shall not be used, and if this is not possible suitable personal protection equipment should be used. §29-32 state that for these other applications/uses an authorisation must be granted from the Danish Working Environment Authority before work with benzyl chloride is allowed.
STATUTORY ORDER no. 908 of 27.9.2005 on measures to prevent the risk of cancer when working with substances and materials - and subsequent changes (e.g. 1175 of 11.10.2007)	DK	Same as above. https://www.retsinformation.dk/Forms/R0710.aspx?id=30283 https://www.retsinformation.dk/Forms/R0710.aspx?id=31334
STATUTORY ORDER no. 1246 of 11.12.2009 on announcement from The Danish Maritime Authority concerning working environment on ships	DK	According to this Danish Statutory order (Chapter II, section C, Annex 1, section A), it is not allowed to use chemical preparations with a content of benzyl chloride of 0.1% or above on ships. https://www.retsinformation.dk/Forms/R0710.aspx?id=129083
Regulation addressing transportation of chemicals		
DIRECTIVE 2008/68/EC of 24 September 2008 on in the inland transport of dangerous goods	EU	Benzyl chloride is listed with UN no. 1738, Class 6.1 in the Annex of this Danish Statutory order. This means that benzyl chloride is covered by the rules concerning transportation of dangerous goods and should be labelled and handled accordingly. The UN no. should be used during transportation.
STATUTORY ORDER no. 788 of 27.6.2013 on road transport of dangerous goods	DK	Same as above. https://www.retsinformation.dk/Forms/R0710.aspx?id=152738

2.1.2 Upcoming legislation

A search has been performed in the EUR-Lex database concerning preparatory documents regarding benzyl chloride. No upcoming legislation regarding benzyl chloride was identified.

2.1.3 Classification and labelling

2.1.3.1 Harmonised classification in the EU

The EU harmonised classification of benzyl chloride is presented in Table 4 below. It shows that benzyl chloride is among other things classified as carcinogenic (Carc. 1B, H350 “May cause cancer"), acutely toxic (H302 "Harmful if swallowed", H331 "Toxic if inhaled"), and with a specific target organ toxicity for repeated exposure (STOT RE 2, H373 "May cause damage to organs through prolonged or repeated exposure").

TABLE 4
HARMONISED CLASSIFICATION ACCORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International chemical identification	CAS No	Classification	
			Hazard Class and Category Codes	Hazard Statement Codes
602-037-00-3	α-chlorotoluene benzyl chloride	100-44-7	Acute Tox. 4 Skin Irrit. 2 Eye Dam. 1 Acute Tox. 3 STOT SE 3 Carc. 1B STOT RE 2	H302 H315 H318 H331 H335 H350 H373

H302: Harmful if swallowed, H315: Causes skin irritation, H318: Causes serious eye damage, H331: Toxic if inhaled, H335: May cause respiratory irritation, H350: May cause cancer, H373: May cause damage to organs through prolonged or repeated exposure

2.1.3.2 Self-classification in the EU

According to the current CLP regulation companies placing chemical substances or chemical mixtures on the market in the EU are obliged to notify the classification (they apply for) to the European Chemicals Agency, ECHA. The classifications used (and notified) by the companies can be seen at the ECHA website in the Classification & Labelling (C&L) Inventory database. ECHA maintains the Inventory, but does not verify the accuracy of the information. The notified classifications for benzyl chloride can be found in Table A in Appendix 3.

The most important information derived from the notifications is the fact that the majority of the companies (288 out of 703) used the harmonised classification, while the majority of the remaining companies used notifications very similar to the harmonised classification. Only a few companies have notified other/additional effects, such as Skin Corr. 1C (H314: Causes severe skin burns and eye damage); Acute Tox. 2 (H330: Fatal if inhaled); Flam. Liq.3 (H226: Flammable liquid and vapour), and Skin Sens. 1 (H317: May cause allergic skin reaction).

2.1.4 REACH

2.1.4.1 Registration

Benzyl chloride has been registered under REACH in a tonnage band of 10 – 100 tonnes per annum (as of November 2013).

2.1.4.2 Candidate list

Benzyl chloride is not listed on the ECHA Candidate list of substances of very high concern for authorisation (as of November 2013).

2.1.4.3 Authorisation list / REACH Annex XIV

Benzyl chloride is not listed on the ECHA Authorisation list (as of November 2013).

2.1.4.4 Restrictions concerning certain dangerous substances – Annex XVII
Annex XVII of REACH contains restrictions on the manufacture, placing on the market, and the use of certain dangerous substances, mixtures, and articles. As described in Table 3 benzyl chloride is restricted by entry no. 28 concerning carcinogenic substances in Annex XVII (benzyl chloride is listed in Appendix 2 ("Entry 28 – Carcinogens: category 1B")).

Carcinogenic substances are not to be placed on the market, or used, as substances, as constituents, or in mixtures, for supply to the general public, when the individual concentration in the substances or mixture is equal to or greater than the relevant specific concentration limit. The relevant generic concentration limit (as listed in Annex 1 chapter 3.6 of the CLP Regulation No. 1272/2008) is 0.1% for category 1B carcinogens.

2.1.4.5 Community Rolling Action Plan (CoRAP)
The Community Rolling Action Plan is a list of substances to be evaluated by the Member States during the next three years. Benzyl chloride is not on the CoRAP list of substances for the period 2013-2015.

2.1.4.6 Registry of intentions
Benzyl chloride is not on any of ECHA's Registry of intentions (i.e. SVHC intentions, Harmonised Classification and Labelling intentions or Restriction proposal intentions) as of November 2013.

2.1.5 Other legislation/initiative
No other legislation/initiative has been identified for benzyl chloride.

2.2 International agreements
A search for international agreements concerning benzyl chloride was performed. The following international agreements concerning benzyl chloride (directly or indirectly) were found.

2.2.1 Basel Convention
Protection of human health and the environment against the adverse effects of hazardous waste is covered by the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal. Details on the Basel Convention can be found in Appendix 2: "Background information on regulation" to this report. Benzyl chloride is not directly mentioned in the Basel Convention, but is covered by Annex I of the Convention text: "Annex I – Categories of wastes to be controlled". In Annex I wastes which have "organohalogen compounds" as constituents, are according to the convention text regarded as being hazardous waste and are thereby covered by the Basel Convention.

2.2.2 Free Trade Agreement (the EU and Korea)
Benzyl chloride is listed in Annex 2-A "Elimination of Custom Duties" with a staging category of "0" in the Free Trade Agreement between the EU and its Members and the Republic of Korea (EU, 2011). This means that benzyl chloride shall be free of any custom duty.

2.2.3 International Conventions regarding safety and pollution at sea
The International Convention for the Safety of Life at Sea, 1974 (SOLAS), as amended, deals with various aspects of maritime safety and contains the mandatory provisions governing the carriage of dangerous goods in packaged form or in solid form in bulk. The carriage of dangerous goods is prohibited except in accordance with the relevant provisions of chapter VII which are amplified by the International Maritime Dangerous Goods (IMDG) Code.

The International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 (MARPOL), deals with various aspects of prevention of marine pollution and contains in its Annex III the mandatory provisions for the prevention of pollution by harmful substances carried by sea in packaged form. Regulation 1(2) prohibits the carriage of harmful substances in ships except in accordance with the provisions of Annex III which are also amplified by the IMDG Code.

The IMDG Code lists benzyl chloride with the UN No. 1738, transportation class 6.1 (i.e. toxic substances) and lists the special provisions, packaging instructions, proper shipping name etc. for benzyl chloride (IMDG Code, 2012).

2.3 Eco-labels

Benzyl chloride is not mentioned directly in any eco-labelling criteria (the Nordic Swan, the European Flower or the Blue Angel). However, as benzyl chloride is classified as being carcinogenic, benzyl chloride will automatically be restricted in eco-labelling criteria as no carcinogenic substances are allowed in eco-labelled products.

2.4 Other lists

Benzyl chloride is also found on the *SIN List Database developed by the International Chemicals Secretariat (ChemSec)*[5] in Sweden (data search November, 2013). The SIN List includes substances which are identified by ChemSec as fulfilling the criteria for Substances of Very High Concern as defined by the REACH Regulation. Benzyl chloride was included in the first SIN List (1.0) in September 2008 due to its classification as CMR substance (carcinogenic).

Benzyl chloride is also included in the *PRIO database*[6] *developed by KEMI (the Swedish Chemical Agency)*. The PRIO database is a web-based tool which contains 4472 substances (with properties hazardous to health and the environment) that should be prioritised in the risk reduction work. Benzyl chloride is included in the PRIO database due to its carcinogenic classification and is listed as a "phase-out substance", which means that "this is a substance with properties of particular concern. The environmental quality objective A Non-Toxic Environment, adopted by the Swedish parliament, requires that the use of particularly hazardous substances shall cease to the extent possible".

2.5 Summary and conclusions

Benzyl chloride has a harmonised classification of

- Acute Tox. 4, H302 (Harmful if swallowed)
- Skin Irrit. 2, H315 (Causes skin irritation)
- Eye Dam. 1, H318 (Causes serious eye damage)
- Acute Tox. 3, H331 (Toxic if inhaled)
- STOT SE 3, H335 (May cause respiratory irritation)
- Carc. 1B, H350 (May cause cancer)
- STOT RE 2, H373 (May cause damage to organs through prolonged or repeated exposure)

As a consequence of the carcinogenic properties of benzyl chloride, the substance is restricted as a substance or in mixtures for supply to the general public in concentrations above 0.1% and is prohibited for use in cosmetic products.

A threshold limit value of 1 ppm or 5 mg/m^3 is set for the working environment regarding benzyl chloride in the EU[7]. This threshold limit value may not at any time be exceeded. Furthermore,

[5] http://www.chemsec.org/what-we-do/sin-list
[6] http://www2.kemi.se/templates/PRIOEngframes____4144.aspx
[7] Directive 91/332/EEC

specific precautions regarding work with benzyl chloride are implemented, as benzyl chloride is carcinogenic. A limit value of 0.0008 mg/m^3 for concentrations of benzyl chloride in the air, measured at the property line of the companies, has been set for companies in Denmark.

As a hazardous substance, benzyl chloride is subject to specific regulation regarding transportation of dangerous goods[8].

Benzyl chloride has been registered under REACH in a tonnage band of 10 – 100 tonnes per annum, but it is neither on the Candidate list of substances of very high concern nor on any of ECHA's Registry of intentions - including the CoRAP list of substances for the period of 2013-2015. Benzyl chloride is, however, on the SIN List because it fulfils the criteria for Substances of Very High Concern based on its classification as carcinogenic.

The Swedish Chemicals Agency has included benzyl chloride in their PRIO database as a "phase-out substance", which means that the use of benzyl chloride "shall cease to the extent possible".

Benzyl chloride is not mentioned directly in any eco-labelling criteria, but will automatically be restricted in any eco-labelling scheme as no carcinogenic substances are allowed in eco-labelled products.

[8] Directive 2008/68/EC

3. Manufacture and uses

3.1 Manufacturing

Manufacturers of benzyl chloride in the EU are organised in The European Chemical Industry Council (Cefic). The organisation has been contacted in order to obtain updated information on the manufactured, imported and exported volumes (and uses) of benzyl chloride. However, the organisation has responded that no specific sub-group (within Cefic) deals with benzyl chloride. The reason for this is probably the fact that benzyl chloride purely is used as an intermediate chemical.

Thus, in order to obtain knowledge regarding production and use of benzyl chloride, the companies responsible for registrations regarding benzyl chloride within the REACH system have been contacted (see later).

3.1.1 Manufacturing process

Historically benzyl chloride was manufactured by the reaction of benzyl alcohol with hydrochloric acid, but today benzyl chloride is prepared industrially by the gas-phase photochemical reaction of toluene with chlorine (Ullmann's, 2006):

$$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$$

(toluene + chlorine → benzyl chloride + hydrogen chlorine)

Substitution of chlorine for hydrogen in the aliphatic side-chain occurs by means of a radical chain mechanism. The steps in the radical chain process are as follows where R equals "$C_6H_5CH_2$-" (Ullmann's, 2006):

Chain initiation:	$Cl_2 \rightarrow 2\,Cl\cdot$
Chain propagation:	$Cl\cdot + RH \rightarrow R\cdot + HCl$
	$R\cdot + Cl_2 \rightarrow \mathbf{RCl} + Cl\cdot$
Chain termination:	$Cl\cdot + Cl\cdot \rightarrow Cl_2$
	$R\cdot + Cl\cdot \rightarrow \mathbf{RCl}$
	$R\cdot + R\cdot \rightarrow RR$

Benzyl chloride is marked with bold in the chemical equations above. This chlorination is highly exothermic (Ullmann's, 2006).

In the course of radical chlorination of toluene, all three hydrogen atoms of the side-chain are successively replaced by chlorine. As a result, mixtures of the three expected compounds are obtained:

- Benzyl chloride ($C_6H_5CH_2Cl$)
- Benzal chloride ($C_6H_5CHCl_2$)
- Benzotrichloride ($C_6H_5CCl_3$)

The individual components of the mixture can be isolated in pure form by fractional distillation. According to Ullmann's (2006), numerous attempts have been made to produce benzyl chloride which is as free as possible of the secondary products benzal chloride and benzotrichloride. However, other techniques are either higher in cost or more risks are inherent in these reactions.

Benzyl chloride is sold in two quality grades identified as "benzyl chloride, pure" and "benzyl chloride, pure and stabilised". The degree of purity is in both cases more than 99%. Impurities include benzal chloride ($C_6H_5CHCl_2$), toluene ($C_6H_5CH_3$), chlorotoluene ($C_6H_4ClCH_3$), chlorobenzene (C_6H_5Cl), and hydrogen chloride (HCl) (Ullmann's, 2006). Unstabilised benzyl chloride readily undergoes a self-condensation reaction in the presence of all common metals (except nickel and lead) with the liberation of heat and hydrogen chloride. Benzyl chloride can be stabilised with e.g. sodium bicarbonate or lime when it is shipped in steel drums (TOXNET, 2013).

Benzyl chloride is capable of reacting with metals and their salts. For this reason storage of benzyl chloride in enamel, glass or lined vessels is essential. Many stabilizers have been proposed to make the storage and transportation of benzyl chloride safer. However, the emulsion that these stabilisers produce lacks thermal stability and their presence makes it impossible to carry out reactions that require anhydrous benzyl chloride (Ullmann's, 2006).

3.1.2 Manufacturing sites

The EU

According to ECHA's website[9] the following six companies have registered benzyl chloride within the REACH system – and thus produce (or import from outside EU) benzyl chloride:

- Bayer CropScience AG, Germany
- DOW BENELUX B.V., Netherlands
- Ferro SPRL, Belgium
- INEOS ChloroToluenes Belgium NV, Belgium
- Lanxess Deutschland GmbH, Germany
- Lanxess India OR Chempark, Germany

Worldwide

Information available in 1995 indicated that benzyl chloride was produced in 16 different countries over the world (IARC, 1999).

According to the OECD SIDS (1998) report on benzyl chloride, production also takes place in Japan (in 1993). This is confirmed by a more recent report on benzyl chloride from IHS Chemicals (2010) which states that benzyl chloride is produced in the United States, Western Europe and Japan.

According to TOXNET (2013) Ferro Corporation manufactures benzyl chloride in the United States (in 2003).

Denmark

No production of benzyl chloride take place in Denmark.

3.1.3 Manufacturing volumes

Worldwide

It has not been possible to retrieve information regarding the total volume of benzyl chloride produced worldwide today. However, historically, it could be mentioned that the total production of benzyl chloride in the western countries was approximately 93,000 tonnes in 1989 of which 26,500 tonnes was produced in the USA (IARC, 1999). According to an OECD SIDS report (1998) on benzyl chloride the production of benzyl chloride was 7,759 tonnes in Japan in 1993.

[9] http://echa.europa.eu/en/information-on-chemicals/registered-substances

The EU

Information regarding the specific amount of benzyl chloride produced within the EU is classified information. However, the reported tonnage band is 10 – 100 tonnes; thus, the amount of produced/imported benzyl chloride (from outside the EU) lies within this band. Six companies are known to produce (or import from outside the EU) benzyl chloride. All six companies have been contacted in order to retrieve information regarding their overall production volumes. However, none of the producers wished to provide this type of information. The REACH Regulation does not apply to the use of non-isolated intermediates. This means that companies producing benzyl chloride and directly uses the benzyl chloride to produce other chemicals, are not obliged to register this produced amount of benzyl chloride.

3.2 Import and export

According to Regulation No. 927/2012 concerning statistical nomenclature and the common customs tariff, benzyl chloride does not have a specific CN code (combined nomenclature), but is grouped together with other halogenated derivates of aromatic hydrocarbons under the CN code 29039990 "*Halogenated derivatives of aromatic hydrocarbons (excluding chlorobenzene, o-dichlorobenzene, p-dichlorobenzene, hexachlorobenzene [ISO], DDT [ISO] "clofenotane [INN], 1,1,1-trichloro-2,2-bis[p-chlorophenyl]ethane" and 2,3,4,5,6-Pentabromoethylbenzene)*". This CN code, however, was only effective from 2012 and forward. Previously, the code was named 29036090 – yet with the same title and coverage.

As there is no specific CN code for benzyl chloride (only an overall CN code covering halogenated derivates of aromatic hydrocarbons), no import and export statistics are presented as they will not provide a realistic picture of the import and export of benzyl chloride in Denmark or the EU.

3.2.1 Import and export of benzyl chloride in Denmark

A search in the SPIN database (Substances in Preparations in Nordic countries) demonstrates that the import of benzyl chloride in chemical preparations to Denmark has declined. According to figure 1 the imported amount of benzyl chloride has declined from 185 tonnes in 2000 to 120 tonnes in 2003. Since 2004 the amount has been listed as confidential since the number of companies importing benzyl chloride is below 4 companies. Today (2013) only 1 company in Denmark imports benzyl chloride for manufacture of chemicals and chemical products (information from the Danish Product Register (November 2013).

However, the Danish company that imports benzyl chloride has been contacted. They informed that their annual import on average is 25 tonnes of benzyl chloride; however, it may vary from year to year with up to 10 – 15 tonnes. Their entire import of benzyl chloride is used in the manufacturing of benzalkonium chloride which is sold as a preservative for use in the pharmaceutical industry (for products like nasal sprays, contact lens fluids, eye drops etc). Their production is expected to be rather constant in the future.

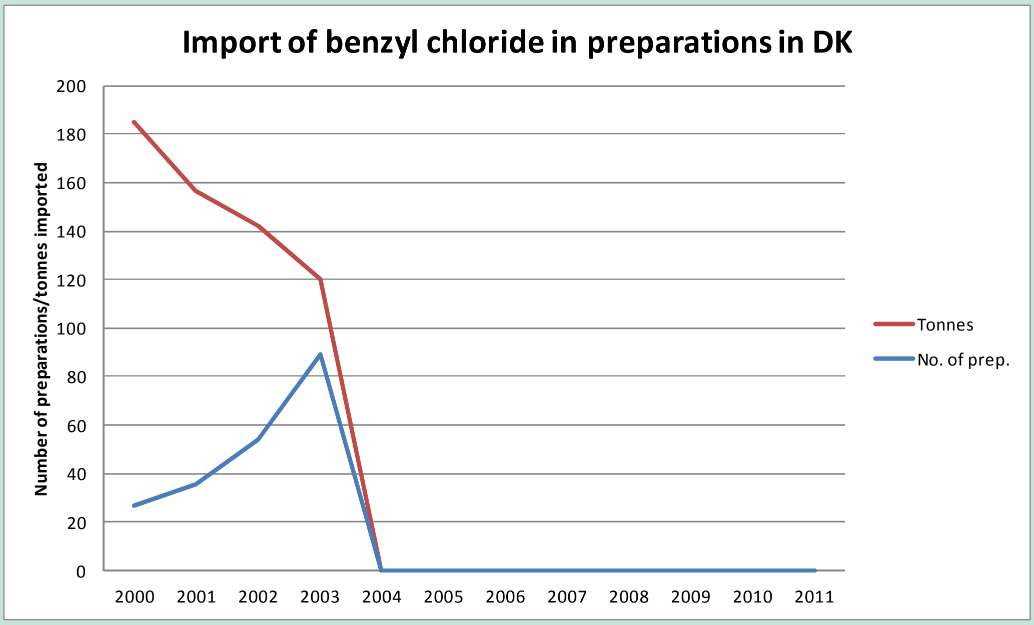


FIGURE 1
IMPORT OF BENZYL CHLORIDE IN CHEMICAL PREPARATIONS IN DENMARK 2000 TO 2011. NUMBERS FROM 2004 TO 2011 ARE LISTED AS ZERO DUE TO CONFIDENTIALITY ISSUES.

No export of benzyl chloride takes place in Denmark, as all the imported amount of benzyl chloride is used in the manufacturing of other chemicals.

3.2.2 Import and export of benzyl chloride in the EU

The exact amount of import and export of benzyl chloride in the EU cannot be listed as benzyl chloride does not have a specific CN code. Figures for benzyl chloride can only be listed covering 'other halogenated derivates of aromatic hydrocarbons' as well.

3.3 Use

3.3.1 Main uses of benzyl chloride worldwide

All information retrieved indicates that benzyl chloride is only used as an intermediate, i.e. as a substrate for the production of other chemicals. These 'other chemicals' cover a wide range, including for instance certain dyes, benzyl alcohol (and other perfumes), flavour products, and pharmaceutical products. Benzyl chloride is also used as a photographic developer and has formerly been used as an irritant gas in chemical warfare (ECD SIDS, 1998; US EPA, 2000a). Benzyl chloride is also used in the production of quaternary ammonium compounds, phthalates, and benzyl cyanide (used as a precursor for penicillin G) (IHS Chemical, 2010). Finally, one main user in Europe informed that they use benzyl chloride in the production of benzyl magnesium compounds and benzyl lithium compounds which can be used for a variety of purposes (including nerve medicine (sedatives) in the medical industry). Another informed that one of the main uses is within the detergent/cleaning agents industry.

According to IHS Chemical (2010) benzyl chloride (world wide) is mainly used for (listed in descending order):

- Chemical intermediate for production of **benzyl alcohol** (largest application)
- Chemical intermediate for production of **benzyl quaternary ammonium compounds**
- Chemical intermediate for production of **benzyl cyanide**
- Chemical intermediate for production of **phthalates, especially BBP** (IARC, 1999)

Benzyl alcohol is used in a wide range of applications such as pharmaceuticals, natural health products, cosmetics, flavour products, solvents, and textile dyes. In the United States, benzyl alcohol is no longer produced from benzyl chloride but is produced from the hydrogenation of benzaldehyde (Environment Canada, 2009a).

Benzyl quaternary ammonium products are used as active ingredients in pest control products or as a surfactant in numerous products (e.g. hard surface sanitizers, corrosion inhibitors, industrial and institutional cleaners, and household and personal care products). Quaternary ammonium compounds like e.g. benzalkonium chloride also function as bactericides/preservative in hair care products and as surfactants in machine dishwashing detergents, architectural paints, and coatings for marine yachts and industrial steel (Environment Canada, 2009a). Manufacturing of benzalkonium chloride has been identified as the only use of benzyl chloride in Denmark.

Benzyl cyanide is used as a precursor for the manufacturing of penicillin G which is also known as benzyl penicillin[10] (IHS Chemical, 2010).

The phthalate BBP (butyl benzyl phthalate) has mainly been used as plasticiser in vinyl flooring and other flexible PVC products such as food packaging (Environment Canada, 2009a). However, in EU the use of BBP has been restricted in food contact materials since 2008, (Regulation No 10, 2011). Previously (in the 1980s) more than two third of the benzyl chloride produced worldwide was used in the manufacture of the phthalate BBP (IARC, 1999; TOXNET, 2013). This trend has, however, changed in recent years. Use of benzyl chloride for production of phthalates is no longer the primary application, due to concerns raised towards the health related properties of BBP and the fact that BBP is on the Authorisation list of REACH. It is noted by IHS Chemical (2010) that the future demand for benzyl chloride for the manufacture of phthalates is unclear as the impact of the scope of regulatory changes is still difficult to evaluate. This could imply that the manufacture of BBP will be even lower in the future and therefore the demand for benzyl chloride for production of BBP will decline even further.

Other uses – minor uses – of benzyl chloride that have been identified are:
- Chemical intermediate for manufacturing of a Grignard reagent (an organic magnesium halide dissolved in a nonreactive solvent).
- Chemical intermediate for manufacturing of photographic developer and gasoline gum inhibitors (Environment Canada, 2009a).

Global consumption of benzyl chloride

In 2009, China became the largest market for benzyl chloride (35% of total consumption), followed by Western Europe (34%), North America (14%), and India (11%) (see Figure 2). Overall, Asia accounted for 48% of the global demand.

[10] http://medical-dictionary.thefreedictionary.com/benzyl+penicillin

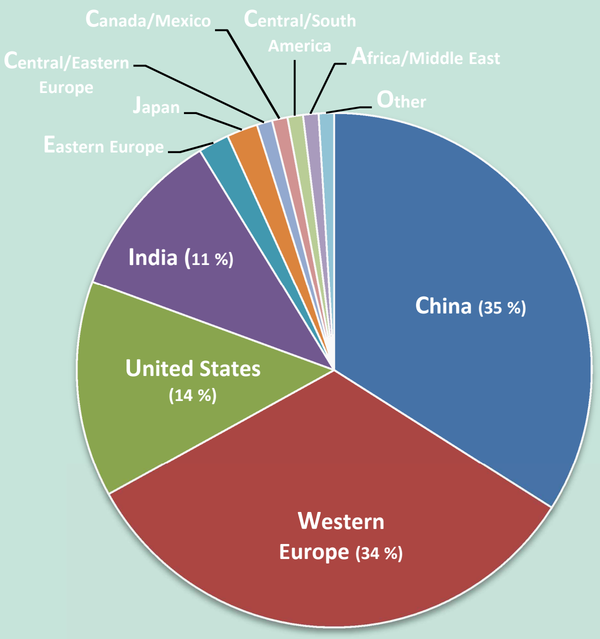


FIGURE 2
WORLD CONSUMPTION OF BENZYL CHLORIDE IN 2009 (IHS CHEMICAL, 2010).

3.3.2 Main uses of benzyl chloride in Denmark and the other Nordic countries

The main uses of benzyl chloride in Denmark and other Nordic countries can be found through information from the SPIN database. According to SPIN the following uses for benzyl chloride have historically been registered:

- Other raw materials
- Pharmaceuticals
- Manufacture of chemicals and chemicals products
- Wholesale trade, except of motor vehicles and motorcycles

Today only the two latter is registered as uses in the SPIN database (2011). However, a contact to the only Danish user of benzyl chloride reveals that benzyl chloride in Denmark only is used as a chemical intermediate to produce the preservative benzalkonium chloride.

3.3.3 Main uses of benzyl chloride in EU

In the REACH registration dossiers, it is noted that all of the manufactured benzyl chloride is used as an intermediate under strictly controlled conditions. This falls in line with other information retrieved from the literature or through contact with producers or users of benzyl chloride.

According to information from a few large producers in Europe, one of the main uses of benzyl chloride is in the detergent/cleaning agents industry and in the form of quaternary ammonium compounds.

According to information from a large 'user' of benzyl chloride in the EU, benzyl chloride is used in the manufacturing of benzyl magnesium compounds (especially benzyl magnesium chloride) and benzyl lithium compounds, of which some is used in the pharmaceutical industry.

Therefore the main uses of benzyl chloride in the EU are judged to be:

- Chemical intermediate for production of benzyl quaternary ammonium compounds
- Chemical intermediate for production of benzyl magnesium and benzyl lithium compounds for the pharmaceutical industry
- Chemical intermediate for production of other compounds as also listed for the main uses worldwide such as especially for production of benzyl alcohol

The amount of benzyl chloride used in Europe (in 2000) according to IUCLID (2000) lies between 100,000 and 500,000 tonnes.

3.3.4 Use of benzyl chloride in consumer products – as an impurity

According to the descriptions above and the OECD SIDS report on benzyl chloride (1998), benzyl chloride is only used as an intermediate, i.e. as a substrate for the production of other chemicals and therefore it is not intentionally used in consumer products. However, benzyl chloride may be present as an impurity (i.e. in very small amounts) in the manufactured chemicals and thereby also in consumer products. For this reason, the sections below shortly describe the expected impurity levels associated with the main chemicals produced based on benzyl chloride.

3.3.4.1 Impurities of benzyl chloride in benzalkonium chloride

According to a Canadian report (Environment Canada, 2009a), benzyl chloride is expected to be found as an impurity in benzalkonium chloride in cosmetic products (benzyl chloride is used to produce benzalkonium chloride which is used as a preservative in pharmaceutical and cosmetic products). As a worst case Environment Canada (2009a) assumes that 1% (w/w) benzalkonium chloride[11] is used in cosmetic products such as hair conditioner and shower gel products and that benzalkonium chloride contains a maximum level of 100 mg/kg (0.01%) benzyl chloride which results in a total worst case concentration of benzyl chloride in cosmetic products of 1 mg/kg (0.0001%).

The Danish company that imports benzyl chloride and uses it for manufacturing of benzalkonium chloride was contacted. They state that their internal limit value for impurity of benzyl chloride in the manufactured benzalkonium chloride is 0.05% (w/w) which is set by use of the specifications in the European Pharmacopoeia. However, in practice, the concentration of benzyl chloride in the finished benzalkonium chloride product is much lower. The Danish company states that in one of their benzalkonium chloride products (95% solution) they can measure a content of benzyl chloride above the detection limit of 0.001%, but below the 0.05% limit value just after production. However, when re-analysing after three months the content of benzyl chloride can no longer be detected (i.e. the concentration is below the detection limit). This is due to the fact that benzyl chloride reacts rapidly with water and forms benzyl alcohol according to the reaction equation stated below (Prieto-Blanco et al., 2009; Environment Canada, 2009a):

$$C_6H_5\text{-}CH_2Cl + H_2O \rightarrow C_6H_5\text{-}CH_2OH + HCl$$

(benzyl chloride) + (water) → (benzyl alcohol) + (hydrochloric acid)

The Danish EPA has published a number of surveys on chemical substances in consumer products. In the resulting database of chemicals in consumer products made by the Danish EPA[12], it is listed that benzyl chloride has been found in the following chemical consumer products:

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[11] As a preservative benzalkonium chloride is allowed in a maximum concentration of 0.1% in cosmetic products according to Appendix V "List of preservatives allowed in cosmetic products" (entry no. 54) in the Cosmetic Products Regulation no. 1223/2009. Otherwise benzalkonium chloride is allowed to be used in rinse-off hair (head) products in a maximum concentration of 3% (as benzalkonium chloride) according to Annex III "List of substances which cosmetic products must not contain except subject to the restrictions laid down".

[12] http://www.mst.dk/English/Chemicals/consumers_consumer_products/Database_of_chemicals_in_consumer_products/default.htm

- **Modelling clay:** Benzyl chloride was identified as a constituent in one of six modelling clays. Benzyl chloride was identified in modelling clay for oven baking in a concentration of about 0.078 % (780 mg/kg) (Pors & Fuhlendorf, 2002).
- **Animal care products:** Benzyl chloride was identified as a constituent in one of 12 animal care products. Benzyl chloride was identified in a shampoo for cats in a concentration of about 0.053% (530 mg/kg) (Nylén et al., 2004).
- **Car care products:** Benzyl chloride was identified as a constituent in two of 29 interior car care products. Benzyl chloride was identified in an odour remover product in a concentration of 0.037 % (370 mg/kg) and in a cleansing tissue in a concentration of 0.0077% (77 mg/kg) (Tønning et al., 2009).

It is estimated that the content of benzyl chloride in these types of products is due to the use of benzalkonium chloride. However, the content of benzyl chloride as an impurity in these products is higher than it could be expected based on the information received from the Danish producer of benzalkonium chloride and based on the calculations performed by Environmental Canada (2009a). The common denominator for these products (except for the animal care products) is that they typically do not contain water or a minimum amount of water. This could explain a higher content of benzyl chloride, as there is no water which benzyl chloride can react with. Moreover, benzalkonium chloride can be produced in different qualities. The quality for pharmaceutical products is expected to be higher (i.e. lower impurity of benzyl chloride) compared to qualities used in cosmetic products or animal care products. Finally, none of the product types above has a legal restriction on the amount of benzalkonium chloride that may be used as preservative, i.e. the concentration may be higher in e.g. cosmetic products.

3.3.4.2 Impurities of benzyl chloride in BBP

According to the SVHC support document on BBP, benzyl chloride may exist as an impurity, but in a concentration of less than 2 ppm (ECHA BBP, 2008). According to an Annex XV restriction report from the Danish EPA on proposal for restriction of DEHP, BBP, DBP, and DIBP the use of BBP in all articles on the EU market is estimated to be 8,000 tonnes in 2007. This number could, however, be lower today as the use of BBP according to IHS Chemical (2010) has declined since the 1980s. BBP is used (in 2007) in products like flooring, film/sheet coated and moulded products, adhesives, sealants and grouting agents, lacquers and paints, and other non-polymeric articles (Danish EPA, 2011). If assuming an impurity of benzyl chloride in BBP of 2 ppm and a use of 8,000 tonnes BBP in articles in the EU, the total maximum amount of benzyl chloride in BBP articles in the EU will be 16 kg per year. However, benzyl chloride will in products containing water (such as water based adhesives and paints) react with water and form benzyl alcohol. This means that the total amount of benzyl chloride in BBP containing articles will be very low or insignificant.

3.3.4.3 Impurities of benzyl chloride in benzyl alcohol

Benzyl chloride is not listed as an impurity in benzyl alcohol according to the Swedish Chemicals Agency[13]. No other information about the impurity of benzyl chloride in benzyl alcohol has been identified.

3.3.4.4 Impurities of benzyl chloride in benzyl cyanide

No information about possible impurity of benzyl chloride in benzyl cyanide has been identified.

[13] http://apps.kemi.se/flodessok/floden/kemamne_eng/benzylalkohol_eng.htm

3.3.4.5 Conclusion on the 'impurity-aspect' of benzyl chloride

Benzyl chloride is not intentionally used in consumer products, but may be present at impurity levels in some cosmetic products. It has been found in for instance modelling clay, animal and car care products. Furthermore, it is likely that the impurity of benzyl chloride exists in the cosmetic products because of an impurity of benzyl chloride in the preservative benzalkonium chloride. As stated by the Danish company using benzyl chloride, the impurity of benzyl chloride will be lowered in time as benzyl chloride reacts with water in the product and forms benzyl alcohol (a perfume ingredient and preservative) in stead.

3.4 Historical trends in use

The overall world consumption of benzyl chloride is expected to grow at an annual rate of about 4% in the period 2009-2014. Consumption in India and China is growing the fastest, with an expected average growth rate of about 7% per year from 2009 to 2014. Growth in demand is also expected to be strong in Central and Eastern Europe and Central and South America – albeit from a small basis.

In China, India, and Western Europe, consumption of benzyl chloride for manufacturing of *benzyl alcohol* has increased, due to a greater use in solvent applications, increased export to the US, and due to the use of benzyl chloride as a precursor for benzyl esters. Despite a continual rise in feedstock costs, benzyl alcohol will be the main cause for benzyl chloride consumption in these regions (IHS Chemical, 2010).

Benzyl cyanide (used as a precursor for penicillin G) will remain a market driver for demand primarily in China and to a lesser extent in India (IHS Chemical, 2010).

Benzyl quaternary ammonium compounds (benzyl quats) will contribute the most to an increased demand of benzyl chloride in North and South America (IHS Chemical, 2010).

The future demand for benzyl chloride for manufacturing *phthalates* is unclear, due to potential further regulation in this area. Stricter regulations affect the use of phthalates in Europe and other regions could follow. This may result in a worldwide reduction in the use of benzyl chloride for phthalate production. However, as phthalate production is a minor use of benzyl chloride, this will only have a minor effect on the total use of benzyl chloride (IHS Chemical, 2010).

Finally, it should be mentioned that the few companies (one 'user' and one 'producer') which have reported information (regarding the present report) expect their use of benzyl chloride to remain stable in the coming years.

3.5 Summary and conclusions

Manufacturing sites

Production of benzyl chloride takes place all over the world, among others, in Western Europe, Japan, and the United States. Six companies within the EU produce benzyl chloride (or import from outside the EU). They are located in Germany and Belgium. No producers are located in Denmark.

Production volumes

It has not been possible to retrieve information regarding the total volume of benzyl chloride produced worldwide today. However, in 1989 approximately 93,000 tons were produced in the western countries. A rough estimate on the amount produced today within the EU lies around 58,000 tons per year even though the registered tonnage band of benzyl chloride only is 10 – 100 tonnes per year. Whether this huge difference is due to the use of benzyl chloride as a non-isolated chemical intermediate or if the production and use of benzyl chloride is taking place out side of the EU is unknown.

Import and export
Only one company in Denmark imports benzyl chloride. The company informs that they import on average 25 tonnes per year; however, it may vary from year to year with up to 10-15 tonnes. No export of benzyl chloride takes places in Denmark as all imported benzyl chloride is used in the manufacturing of other chemicals.

Within the EU, it is not possible to retrieve import/export data on benzyl chloride alone since the substance in EUROSTAT is grouped with 'other halogenated derivates of aromatic hydrocarbons'.

Uses
Benzyl chloride is only used as an intermediate, i.e. as a substrate for the production of other chemicals. These other chemicals cover:

- Benzyl alcohol (largest application) (used as solvent for inks, paints, etc.)
- Benzyl quaternary ammonium compounds (used as biocide)
- Benzyl cyanide (used as a precursor for penicillin G)
- Phthalates (especially butyl benzyl phthalate (BBP))
- Certain dyes
- Flavour products
- Pharmaceutical products
- Benzyl magnesium compounds
- Benzyl lithium compounds (used as for instance in nerve medicine (sedatives))
- Chemicals used in the detergent/cleaning agent industry

Furthermore, benzyl chloride is used as a photographic developer and has formerly been used as an irritant gas in chemical warfare (ECD SIDS, 1998; US EPA, 2000a).

Benzyl chloride is not intentionally used in consumer products, but may be present at impurity levels in some consumer products, like e.g. cosmetic products, modelling clay, and car care products. Benzyl chloride will, however, react with water in the products and form benzyl alcohol. It is therefore expected that the content of benzyl chloride in cosmetic products in general is insignificant whereas the impurity of benzyl chloride may be higher in products like modelling clay which do not contain water.

The amount of benzyl chloride used in Europe (2000) lies between 100,000 and 500,000 tonnes (IUCLID, 2000). In 2009, China became the largest market for benzyl chloride (35% of total consumption), followed by Western Europe (34%), North America (14%), and India (11%). Overall, Asia accounted for 48% of the global demand.

Trends
The overall worldwide consumption of benzyl chloride is expected to grow at an annual rate of approx. 4% in the period 2009 – 2014. Highest growth rates are expected in China and India, partly due to a greater use of benzyl chloride in solvent applications and partly due to increased export to the US and a use of benzyl chloride as a precursor for benzyl esters. This trend also applies to Western Europe to a certain extent. Despite a rise in feedstock costs, benzyl alcohol will thus be the main cause for benzyl chloride consumption in these regions (IHS Chemicals, 2010).

Data gaps

- Information about impurities of benzyl chloride in other chemicals than benzalkonium chloride (e.g. benzyl alcohol, BBP). However, based on the knowledge of the impurities of benzyl chloride in benzalkonium chloride, this will hardly be a problem.

- Information regarding types of products that may contain impurities of benzyl chloride and contain water. However, based on the knowledge of the impurities of benzyl chloride in benzalkonium chloride, this will hardly be a problem.

4. Waste management

4.1 Waste from manufacture and use of benzyl chloride

Manufacture
In Denmark no manufacturing of benzyl chloride takes place. Six companies within the EU produce benzyl chloride (or import the chemical from outside of the EU).

Waste from manufacturing of benzyl chloride is generally expected to be at a minimum since the economically most feasible solution is to ship and sell all manufactured amounts. However, a high vapour pressure of benzyl chloride indicates that benzyl chloride is volatile; hence emissions of benzyl chloride can occur during manufacturing. Similarly, release of benzyl chloride via the waste water during manufacturing of benzyl chloride could occur. Benzyl chloride, however, rapidly reacts with water and forms benzyl alcohol, thus amounts of benzyl chloride released to (and contained in) air and waste-water are expected to be minor.

Waste from manufacturing of benzyl chloride is therefore only expected to be in the form of residues, e.g. in the form of minor leftovers in ‘empty’ containers.

Use
In Denmark, one company has reported use of benzyl chloride as an intermediate chemical in the production of another chemical (the preservative benzalkonium chloride). They informed that they do not have any waste of benzyl chloride except for negligible amounts in ‘empty’ chemical containers. In the EU 17 companies have notified classification of benzyl chloride within the REACH system, meaning that they use benzyl chloride. Waste from use of benzyl chloride is expected to primarily concern handling of emptied packaging and is therefore expected to be minor. Parallel to manufacturing, emission to air and release of benzyl chloride via waste water could occur during use of benzyl chloride as intermediate for production of other chemicals. Amounts of benzyl chloride contained in air/water are, however, yet again expected to be minor, due the reaction of to benzyl chloride with water.

According to the Danish statutory order on waste (Statutory order No. 1309, 2012), which is based on among other things the EU Directive 2008/98/EC on waste, waste generated from manufacture and industrial use of benzyl chloride has to be treated as hazardous waste if the waste contains substances in an amount that according to the classification rules for chemical substances and preparations would result in a classification in relation to either physical-chemical, toxicological, or environmental properties. Consequently, waste containing benzyl chloride (in an amount which would result in a classification as hazardous) should be treated as hazardous waste and be treated according to the instructions from local communities. This applies for collection of liquid and solid waste from both industries and private households. However, as benzyl chloride only is used as a chemical intermediate, benzyl chloride will be used in concentrated form which means that the waste containing benzyl chloride, from both manufacture and use, will be classified as hazardous and is therefore expected to be treated as hazardous waste according to Danish/EU regulation.

As no benzyl chloride is sold directly to consumers nor used directly in chemical products for private households, no private waste is expected to contain benzyl chloride neither in Denmark nor in the EU.

4.2 Waste products from the use of benzyl chloride in mixtures and articles

As described in chapter 3 "Manufacture and uses" benzyl chloride is used as an intermediate chemical only. This means that benzyl chloride is not expected to be present in chemical preparations (mixtures) unless it is found as an impurity. Furthermore, as described earlier, potential impurities of benzyl chloride will react with water in the product (if present) to form benzyl alcohol. The benzyl chloride content in waste originating from the use of chemical mixtures is therefore expected to be insignificant.

As described in section 3.3.4 "Use of benzyl chloride in consumer products – as an impurity", no consumer products intentionally contain benzyl chloride. However, benzyl chloride may be present (as an impurity in benzalkonium chloride) in very small amounts (typically well below 0.1 %) in some consumer products containing benzalkonium chloride (but not containing water) – e.g. cosmetic products, car care products, pharmaceutical products, and similar consumer products. Benzyl chloride will not be present in chemical consumer products containing water as benzyl chloride reacts with water and forms benzyl alcohol in the consumer product.

Similarly, benzyl chloride may be present as an impurity in other chemicals that benzyl chloride is used to produce, e.g. benzyl alcohol, quaternary ammonium compounds, and BBP. However, if such products also contain water, the benzyl chloride concentration will be close to zero due to its reaction with water.

Estimated total amount of benzyl chloride in waste from products in Denmark

A worst case estimate of benzyl chloride in waste from cosmetic products in Denmark due to impurities in benzalkonium chloride and benzyl alcohol can be calculated using worst case assumptions as described in the box below.

With the listed assumptions (the box below) this will result in a maximum amount of benzyl chloride in waste (from cosmetic products) of approximately 3.3 kg in total.

Similarly, benzyl chloride can be found as an impurity in BBP (less than 2 ppm). As calculated in section 3.3.4 "Use of benzyl chloride in consumer products – as an impurity" the yearly use of BBP in the EU will result in a maximum amount of benzyl chloride in BBP articles in the EU corresponding to 16 kg per year. However, due to the reaction of benzyl chloride with water, the total amount will be less than 16 kg per year) – thus of minor importance.

Similar calculations can be made for other consumer products. However, the calculations illustrate that the total amount of benzyl chloride in waste from mixtures and articles from private households in Denmark (and the EU) is expected to be at a very low/insignificant level.

Benzyl chloride in waste – a worst case example

This example illustrates a worst case example (calculation) of the benzyl chloride content in waste from cosmetic products in Denmark (due to the benzyl chloride impurities in benzalkonium chloride and benzyl alcohol). The following assumptions have been made:

- According to the Danish company producing benzalkonium chloride, the highest measured impurity is 0.05% benzyl chloride. It is assumed that the impurity of benzyl chloride in benzyl alcohol is at the same level, i.e. 0.05% benzyl chloride.
- The concentration of benzalkonium chloride in cosmetic products is maximum 0.1%[14] and the concentration of benzyl alcohol 1%[15].
- According to an ongoing survey on the content of preservatives in cosmetic products in Denmark initiated by the Danish EPA[16], benzalkonium chloride is used in 0.3% of the products on the Danish market and benzyl alcohol in 16.8% of the products on the Danish market (based on a survey on approximately 650 cosmetic products on the Danish market).
- The total amount of cosmetic products imported in Denmark in 2012 was 78,201 tonnes in 2012.
- It is assumed that a maximum of 10% of the total amount of cosmetic products in Denmark will be discarded as waste (with household waste). The remaining cosmetic products will be used and thus, washed out through waste water from private households.
- It is assumed that a maximum of 50% of the cosmetic products in Denmark does not contain water. In the 50% cosmetic products where water is assumed to be present, benzyl chloride will not exist as it reacts with the water and forms benzyl alcohol.

Based on these assumptions, the maximum content of benzyl chloride in waste from cosmetic products (due to impurities in benzalkonium chloride and benzyl alcohol) is **approximately 3.3 kg** in total.

4.3 Release of benzyl chloride from waste disposal

As described above the content of benzyl chloride in private household waste and in chemical waste is regarded to be minor.

If waste should contain small amounts of benzyl chloride, the waste can be incinerated, treated as hazardous waste, reused/recycled or deposited at landfills. It is not expected that benzyl chloride containing waste will be either reused/recycled or deposited at landfills. The expected fate of the small amount of benzyl chloride found in either chemical waste or regular household waste is described below.

4.3.1 The fate of benzyl chloride in incineration facilities

Benzyl chloride is expected to be converted into hydrochloric acid and water when burned in incineration facilities according to the following reaction equation:

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[14] As a preservative benzalkonium chloride is allowed in a maximum concentration of 0.1% in cosmetic products according to Appendix V "List of preservatives allowed in cosmetic products" (entry no. 54) in the Cosmetic Products Regulation no. 1223/2009. Otherwise benzalkonium chloride is allowed to be used in rinse-off hair (head) products in a maximum concentration of 3% (as benzalkonium chloride) according to Annex III "List of substances which cosmetic products must not contain except subject to the restrictions laid down". Rinse-off hair products will contain water and will therefore not contain impurity of benzyl chloride (reacts with water).

[15] As a preservative benzyl alcohol is allowed in a maximum concentration of 1% in cosmetic products according to Appendix V "List of preservatives allowed in cosmetic products" (entry no. 34) in the Cosmetic Products Regulation no. 1223/2009.

[16] Survey on the use of preservatives in cosmetic products. Ongoing project which is part of the Danish EPA programme: Survey of chemicals in consumer products.

$$2\ C_6H_5\text{-}CH_2Cl + 17\ O_2 \rightarrow 14\ CO_2 + 6\ H_2O + 2\ HCl$$
(benzyl chloride) + (oxygen) → (carbon dioxide) + (water) + (hydrochloric acid)

The hydrochloric acid will be neutralised in connection with the flue gas cleaning process at the incineration facility. The residue product containing chlorine from the flue gas cleaning process will be deposited in special landfills.

4.3.2 The fate of benzyl chloride when handled as 'hazardous waste'

Benzyl chloride is not intentionally used in chemical mixtures or articles, but may be present as impurities if no water is present in the mixture/articles. Therefore the other chemicals in the chemical mixture determine whether the chemical waste must be regarded as hazardous waste or not. However, 'empty' containers which have contained pure benzyl chloride have to be treated as hazardous waste.

In Denmark (and the EU) benzyl chloride is considered hazardous waste and must be handled as such. The different municipalities are responsible for making sure that hazardous waste from different companies is handled correctly. In Denmark, the company Nord (which is a company authorised to handle hazardous waste) categorises benzyl chloride as waste category B: Waste with halogens and sulphur[17]. Nord disposes of the chemical waste by burning it at a temperature of approximately 1200 °C[18]. As described above burning of benzyl chloride will result in the formation of carbon dioxide, water, and hydrochloric acid. The hydrochloric acid is neutralised in the flue gas cleaning process in line with the process at regular incineration facilities.

4.4 Summary and conclusions

Waste from manufacturing and use

Waste from manufacturing of benzyl chloride is expected to be minor due to the fact that the economically most feasible solution is to ship and sell all manufactured amounts. Waste from manufacturing of benzyl chloride is therefore only expected to be in the form of residues, e.g. in the form of minor leftovers in 'empty' containers. Waste from manufacturing is expected to be treated as chemical waste according to EU regulation.

Waste from use of benzyl chloride is expected to be in the form of handling 'empty' packaging and is therefore considered to be minor. Emptied packaging has to be treated as hazardous waste and will in Denmark be incinerated at a special incineration site for handling of chemical waste (Nord).

Waste from products containing impurities of benzyl chloride

The content of benzyl chloride in private household waste and in chemical waste is regarded to be insignificant due to the fact that benzyl chloride is not intentionally added to chemical mixtures or consumer products. However, benzyl chloride may be present (as an impurity) in very small amounts (typically well below 0.1%) in some consumer products – cosmetic products, car care products, pharmaceutical products, and similar consumer products. Many of these consumer products contain water which rapidly reacts with benzyl chloride and forms benzyl alcohol. Benzyl chloride is therefore only expected to be present as an impurity in products that do not contain water, such as car care products and modelling clay.

Treatment of waste containing benzyl chloride

If waste should contain small amounts of benzyl chloride, the waste is expected to be incinerated (for regular household waste) or treated as hazardous waste (in Denmark incineration at a special incineration site for handling of chemical waste).

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[17] http://www.nordgroup.eu/da-DK/Service/Sådan-håndterer-I-affald/Sorteringsvejledning/Detaljevisning.aspx?Action=1&NewsId=10&M=NewsV2&PID=2908

[18] http://www.nordgroup.eu/da-DK/Affaldsbehandling/Behandlingsteknologier/Forbrænding-og-røggasrensning.aspx

Data gaps

- Information about impurities of benzyl chloride in other chemicals than benzalkonium chloride (e.g. benzyl alcohol, BBP). However, based on the knowledge of the impurities of benzyl chloride in benzalkonium chloride, this will hardly be a problem.
- Information regarding types of products that may contain impurities of benzyl chloride and contain water. However, based on the knowledge of the impurities of benzyl chloride in benzalkonium chloride, this will hardly be a problem.

5. Environmental effects and fate

Release of benzyl chloride into the environment may occur from industrial processing of chemical intermediates, product preparation, accidental spills as well as emissions from waste incineration (Environment Canada, 2009a). Fugitive emissions or venting during handling, transport, or storage of benzyl chloride could be a source of emissions to the atmosphere (Environment Canada, 2009a), while industrial effluents can course emission of benzyl chloride to water.

The data in the following sections is mostly based on information from the OECD SIDS (1998) report on benzyl chloride from Environment Canada (2009a) and from RIVM (2010). However, information in the Registered Substances database of ECHA (2013) as well as IUCLID datasheets has been used as well.

5.1 Environmental hazard

5.1.1 Toxicity to aquatic organisms

The high volatility and hydrolysis rate of benzyl chloride put special demands on the aquatic toxicity studies as the major part of the benzyl chloride may be hydrolysed or evaporated within the time frame of the test conditions (96 hours for fish), (RIVM, 2010).

Several data exists regarding acute toxicity to fish whereas data on acute toxicity to algae is limited. RIVM (2010) has assessed the reliability of the existing toxicological studies on benzyl chloride using the Klimisch score (Klimisch et al., 1997) and found most of them unreliable based on the above reasons (hydrolysis and evaporation). The toxicological studies which were found reliable (however with restrictions) are reproduced in Table 5 below. In the ECHA Registered Substances Database (2013) most of the ecotoxicological information listed for benzyl chloride is listed in the RIVM (2010) report as well. The studies which have not been reported in the RIVM (2010) report are listed in Table 5 below as well.

Environment Canada (2009a) lists several modelled data for the aquatic toxicity of benzyl chloride. The data is reproduced in Table 6. Environment Canada points out that the modelled results may overestimate the toxicity (especially to fish) as they do not account for the rapid hydrolysis of benzyl chloride to the less toxic benzyl alcohol.

Test organism	Type of test	Endpoint	Value	Reference
Acute toxicity				
Daphnia magna (water flea)	Acute (48 h)	EC_{50}	3.2 mg/L	OECD SIDS (1998) in RIVM (2010)
Daphnia magna (water flea)	Acute (48 h)	EC_{50}	6.1 mg/L	Study from 1982 (Exp Key Short-term toxicity to aquatic invertebrates.001) in ECHA Registered Substance Database (2013)
Poecilia reticulata (guppy)	Acute (14 days)	LC_{50}	0.39 mg/L	OECD SIDS (1998) in RIVM (2010)
Vibrio fischeri (bacteria)	5 minutes	EC_{50}	1.92 mg/L	Kaiser and Palabrica (1991) in RIVM (2010)
Chronic toxicity				
Daphnia magna (water flea)	21 days	NOEC	0.1 mg/L	OECD SIDS (1998) in RIVM (2010)

TABLE 5
EMPIRICAL DATA FOR AQUATIC TOXICITY FOR BENZYL CHLORIDE

Test organism	Type of test	Endpoint	Value (mg/L)	Reference
Fish	Acute (96 h)	LC_{50}	0.26	EPIsuite (2007) in Environment Canada (2009a)
Fish	Acute (14 days)	LC_{50}	0.17	EPIsuite (2007) in Environment Canada (2009a)
Fish	Acute (14 days)	LC_{50}	34.86	ECOTOX (2006) in Environment Canada (2009a)
Pimephales promelas (fathead minnow)	Acute (96 h)	LC_{50}	2.70	AIEPS (2003-2007) in Environment Canada (2009a)
Daphnid	Acute (48h)	LC_{50}	16.84	EPIsuite (2007) in Environment Canada (2009a)
Daphnia magna (water flea)	Acute (48 h)	EC_{50}	6	TOPKAT (2004) in Environment Canada (2009a)
Green alga	Chronic		63.74	EPIsuite (2007) in Environment Canada (2009a)

TABLE 6
MODELLED DATA FOR AQUATIC TOXICITY FOR BENZYL CHLORIDE

RIVM (2010) reports a long-term No Observable Effect Concentration **(NOEC) of 0.1 mg/L** for *Daphnia magna* (test endpoint reproduction, 21 days). The same NOEC value is described in OECD SIDS (1998) where they use this NOEC value to calculate a Predicted No Effect Concentration – **PNEC value of 0.001 mg/L** by using an assessment factor of 100. Environment Canada (2009a) on the other hand uses the LC_{50} value of 0.39 mg/L for *Poecilia reticulate* (test endpoint mortality, 14 days) and an assessment factor of 100 to calculate a PNEC value of 0.0039 mg/L.

5.1.2 Toxicity to microorganisms

The only information found on the toxicity of benzyl chloride to microorganisms is retrieved from the ECHA Registered Substances Database (2013). One study shows a toxicity threshold EC_5 of the bacteria *Pseudomonas putida* of 4.8 mg/L (test conditions 16 hours, growth inhibition effect). Another study shows a toxicity threshold EC_5 of the protozoa *Entosiphon sulcatum of* 25 mg/L (test conditions 72 hours, growth inhibition effect). Both studies were published in 1980 by Bringmann and Kühn.

5.1.3 Toxicity to sediment living organisms

No information on the toxicity to sediment living organism was identified.

5.1.4 Toxicity to terrestrial organisms

OECD SIDS (1998) reports a single test study from 1980 (Samoiloff et al.) regarding the toxicity to terrestrial organisms. They found a LC_{60} of approximately 126 mg/L (96 hour testing on *Panagrellus redivivus* (Nematoda)).

5.1.5 Toxicity to the atmosphere

No information on the biotic or abiotic effects in the atmosphere was identified.

5.1.6 Classification

Benzyl chloride does not have a harmonised classification with respect to environmental effects.

Nevertheless, some notifiers have suggested environmental classifications. Out of a total of 706 notifiers 93 suggested the following environmental classification:

- H411 “Toxic to aquatic life with long lasting effects”

No hazard class is listed together with the suggested hazard statement of H411; however, the matching hazard class would be Aquatic Chronic 2.

According to the CLP classification (table 4.1.0 in EU Regulation No. 286/2011 (of CLP 1272/2008)), substances with chronic NOEC > 0.01 but ≤ 0.1 mg/l should be classified with “Aquatic Chronic 2; H411 (Toxic to aquatic life with long lasting effects)” if the substance is rapidly degradable. The aquatic chronic NOEC of 0.1 mg/l in the 21 day crustacea test on *Daphnia magna* described in RIVM (2010) leads to the evaluation that benzyl chloride fulfils the criteria for classification as “Aquatic Chronic 2; H411 (Toxic to aquatic life with long lasting effects)” which has also been suggested by 93 notifiers.

5.1.7 Classification of the reaction product benzyl alcohol

Benzyl chloride reacts rapidly with water and forms benzyl alcohol. For this reason the harmonised classification of benzyl alcohol is presented as well. *Benzyl alcohol does not have any environmental classification* but is classified with the health classification Acute Tox. 4, H302 “Harmful if swallowed”.

5.2 Environmental fate

The environmental fate of benzyl chloride after release to air, water, and soil has been estimated in a number of reports (OECD SIDS, 1998; Environment Canada, 2009a; RIVM, 2010). The estimations show a uniform picture from which it appears that benzyl chloride to a large extent will remain in the compartment to which it is released (see Table 7).

Emission profile	Distribution (% of total emitted)			
	Air	Water	Soil	Sediment
Equal parts to air/water/soil	7.0 %	19%	73%	0.35%
100% to water	7.9 %	90%	0.16%	1.6%
100% to air	94 %	3.9%	2.0%	0.0701%
100% to soil	0.91 %	0.54%	99%	0.00962%

TABLE 7
ESTIMATED DISTRIBUTION OF BENZYL CHLORIDE AFTER RELEASE TO AIR, WATER AND SOIL (SOURCE: RIVM, 2010)

The fate of benzyl chloride in each environmental compartment is summarised briefly below in section 5.2.1 to 5.2.5.

5.2.1 Air

A high vapour pressure of 0.16 kPa at 25 °C indicates that benzyl chloride is volatile. If released to air, benzyl chloride will exist solely as vapour in the ambient atmosphere. Reaction with hydroxyl radicals will be the dominant removal mechanism (Environment Canada, 2009a).

Environment Canada (2009a) reports that the characteristic travel distance for benzyl chloride is estimated to be approximately 1,100 km. This indicates that benzyl chloride is expected to be transported through the atmosphere to areas moderately far from its emission source. However, as benzyl chloride is only moderately persistent in air, and given that it has a low potential to bioaccumulate and furthermore moderate acute toxicity to aquatic organisms, long-range transport is not considered a concern for benzyl chloride (Environment Canada, 2009b). According to SEPA (2014), benzyl chloride reacts rapidly with other substances and is therefore generally removed within a few days which is also indicated by the half-life in air (3.69 days for photodegradation) (Environmental Canada, 2009a).

5.2.2 Water

If released into water, benzyl chloride is expected to moderately adsorb to suspended solids and sediment based upon the calculated moderate octanol/water coefficient log K_{ow} of 2.69. Ready-biodegradation test for benzyl chloride shows 71% biodegradation over 28 days which indicates that the ultimate degradation half-life in water is 'days or weeks' and that the substance is unlikely to persist in the water compartment. Several QSAR models for biodegradation in water come to the same overall conclusion that benzyl chloride is readily biodegradable (Environment Canada, 2009a). Also a key study (from the Japanese Ministry of International Trade and Industry in 1992) reported on biodegradability in the ECHA Registered Substances Database (2013) for benzyl chloride and stated that benzyl chloride is readily biodegradable.

Hydrolysis is the dominant removal mechanism of benzyl chloride, with a hydrolysis half-life of 9.48 hours at pH 7 and 25°C (Environment Canada, 2009a). The hydrolysis half-life of benzyl chloride in water is dependant on the temperature: the half-life is approximately 6.5 days at 5 °C whereas the half-life is approximately 6 hours at 30 °C (OECD SIDS, 1998).

During the hydrolysis benzyl chloride is rapidly hydrolysed to benzyl alcohol and is readily biodegradable (70.9% after 2 weeks) (OECD SIDS, 1998).

Volatilisation from water surfaces is possible, based upon the estimated Henry's Law constant for benzyl chloride (Environment Canada, 2009a). This is also indicated by the estimated distribution of benzyl chloride (see Table 7) when emitted 100% to water (this will result in approximately 8% distribution to air).

5.2.3 Sediment

If released into water, benzyl chloride is expected to moderately adsorb to suspended solids and sediment based upon the calculated moderate octanol/water coefficient log K_{ow} of 2.69. Hydrolysis will be the dominant removal mechanism with a hydrolysis half-life of 9.48 hours at pH 7 and 25°C. Modelled data indicates that benzyl chloride is not expected to be persistent in sediment (Environment Canada, 2009a).

5.2.4 Soil

If released to soil, the majority of the benzyl chloride will remain in this compartment, as illustrated by the emission profile in Table 7. Based on the calculated octanol/water coefficient log K_{ow} of 2.69 benzyl chloride will have a moderate adsorptivity. Mobility in soil may be mitigated based on the hydrolysis of benzyl chloride in water. However, benzyl chloride may also volatilise from dry soil surfaces due to its high vapour pressure. Modelled data indicates that benzyl chloride is not expected to be persistent in soil (Environment Canada, 2009a). Little leaching to groundwater is therefore expected (SEPA, 2014).

5.2.5 Biota

Experimental log K_{OW} values between 2.3 and 2.8 for benzyl chloride suggest that this chemical has a relatively low potential to bioaccumulate in the environment (Environment Canada, 2009a).

No experimental bioaccumulation data is available; however, calculated/modelled bioconcentration factors (BCF) lie between 11 and 63 which supports the low bioconcentration potential of the substance (RIVM, 2010; Environment Canada, 2009a). OECD SIDS (1998) calculates an expected bioconcentration factor of 50.

5.2.6 PBT

In a PBT assessment, benzyl chloride cannot be considered to meet the screening criteria for persistent (P) or very persistent (vP) as the half-life in water is considered to be 'days or week' (Environment Canada, 2009a) i.e. lower than the half-life of 40 or 60 days respectively, which is the requirement for being categorised as persistent[19]. The available information on bioaccumulation shows that benzyl chloride does not meet the bioaccumulation criterion (B) or very bioaccumulative criterion (vB) of BCF>2000 or BCF>5000 respectively. However, benzyl chloride does meet the classification criterion for toxicity (T) as benzyl chloride has a harmonised classification of Carc. 1B and STOT RE 2. Yet, the quick hydrolysis of benzyl chloride into the non-toxic benzyl alcohol must also be considered. Overall, benzyl chloride cannot be considered being a PBT substance.

[19] Table R.11-1 in ECHA Guidance R.11, 2012

5.2.7 Conclusion
Benzyl chloride is regarded as readily biodegradable and not bioaccumulating, thus non-persistent in the environment. If benzyl chloride is released into air, water, or soil, it will reside predominantly in the compartment to which it is released but will fairly quickly ('days or weeks') be degraded through hydrolysis to benzyl alcohol, which is also readily biodegradable and non-toxic in the environment. Overall, benzyl chloride cannot be considered being a PBT substance.

5.3 Environmental exposure

5.3.1 Main sources of release
As benzyl chloride is used in closed systems and furthermore not included in consumer products beyond impurity levels, its release to the environment may occur only from production sites, during transportation or storage, or through waste handling (incineration). Environment Canada (2009a + 2009c) predicts that benzyl chloride would be released in relatively small quantities, mainly to air, but also to some extent to water. Release to soil seems only to be relevant in the case of accidents during transportation.

According to the US EPA benzyl chloride emissions have also been observed from municipal solid waste landfills (US EPA, 2008).

5.3.1.1 Other sources to release of benzyl chloride to the environment
Literature indicates that benzyl chloride may be released to the environment during:
- Burning of fossil fuels (coal)
- Wildfires[20]

Below the burning of fossil fuels is described in more details. It has not been possible to locate further information regarding the release of benzyl chloride from wildfires other than the data set which is presented in section 5.3.2 "Monitoring data".

Burning of fossil fuels (coal)
As benzyl chloride has been measured to be released from burning of fossil fuels (coal) and wildfires it suggests that it is likely that benzyl chloride can be formed and released from all types of combustion plants or firing systems, in particular plants that use biomass as fuel (straw, chipwood, wooden pellets, fire wood etc.). However, information is missing in this area. Combustion plants using either gas or oil presumably have a very low release of benzyl chloride, as liquid or gaseous fuels normally have a very effective combustion and thereby a low emission of combustion products[21].

Literature from the US EPA[22] indicates that benzyl chloride may be released into the atmosphere during the burning of fossil fuels (coal). In their AP-42 programme "Compilation of Air Pollutant Emission Factors", US EPA has listed benzyl chloride as a substance that is emitted during coal combustion (bituminous and subbituminous coal and lignite[23]). Based on an extensive literature study on measured emissions from different coal-fired boilers, benzyl chloride emissions were registered in the air from 2 out of 3 of the coal-fired boilers. A factor of 20,000 was found between the two measurements over the detection limit. The highest concentration (see section 5.3.2 for specific numbers) was found from the coal-fired boiler *without* flue-gas desulfurization and wet limestone scrubber (US EPA, 1993). Because of the low solubility of benzyl chloride in water, the reducing effect from a desulfurization in a wet limestone scrubber would be relatively low, but if the plant has dosing of activated carbon, e.g. for mercury removal, it is expected to also remove benzyl

[20] http://www.epa.gov/ttn/chief/conference/ei20/session9/rmickler_pres.pdf
[21] Based on experiences from FORCE Technology
[22] http://www.epa.gov/ttnchie1/ap42/ch01/final/c01s07.pdf
[23] Lignite is a coal in the early stages of coalification.

chloride very efficiently. However, no Danish coal-fired plant uses activated carbon in their flue gas cleaning.

However, Canadian studies have shown that no significant quantities of benzyl chloride were released from industrial facilities of coal-fired power plants, iron and steel facilities, landfills, and solid and hazardous waste incinerator sites. Recent Canadian measurement data of ambient (outdoor) and indoor air was also low (Environment Canada, 2009c).

A search has been made in GABI6 (a database program for carrying out life cycle assessments). There is no reporting of benzyl chloride emissions from coal-fired energy sources which could suggest that release of benzyl chloride from coal-fired energy sources is not considered to be a general problem.

The information above suggests that benzyl chloride may be released during burning of coal, but not necessarily from all coal-fired boilers and presumably also from burning of biomass. The information from the US EPA (1993) suggests that use of flue gas cleaning will ensure no or a minimum release of benzyl chloride. All coal-fired boilers in Denmark use flue gas cleaning; however, it is not common for coal-fired plants in Denmark to use activated carbon in the flue gas cleaning which would be the best solution to avoid benzyl chloride release. This suggests that small releases of benzyl chloride could be expected in Denmark from coal-fired plants or biomass-fired plants or even from private woodburning stoves. Information is, however, lacking in this area.

5.3.2 Monitoring data

Available monitoring data regarding benzyl chloride is very limited. This may be due to the fact that benzyl chloride is readily biodegradable, undergo rapid hydrolysis to benzyl alcohol, and the fact that benzyl chloride is not expected to bioaccumulate in organisms. Monitoring data has only been identified from Canada and the USA.

Canada

In the Environment Canada (2009a) report it is stated that no monitoring data was identified for concentrations of benzyl chloride in water or soil in Canada. However, under the National Pollutant Release Inventory, industrial facilities in Canada reported an annual release of 5 kg and 1 kg of benzyl chloride to air in total in the years 2000 and 2006 respectively. These release amounts are based on a yearly usage of benzyl chloride of 100 to 1000 tonnes in Canada in 2006 – mainly for the production of quaternary ammonium compounds - similar to the type of use in Denmark (Environment Canada, 2009a+2009c). As the yearly import and use of benzyl chloride in Denmark are much smaller (approximately 25 tonnes) the released amount of benzyl chloride to the air is expected to be well below 1 kg annually in Denmark.

Benzyl chloride has been measured in ambient air in Canada (Environment Canada, 2009a). The levels measured are listed below:

- Selected Canadian cities 2001-2003: Concentration range of 0.002 – 1.17 µg/m^3 (mean value of 0.022 µg/m^3).
- Windsor, Ontario, Canada 2006: Highest concentration was 0.029 µg/m^3 (mean value of 0.001 µg/m^3).
- Fort Saskatchewan, Canada 2004-2006: Concentration range 0.010 – 0.018 µg/m^3.

The USA

Under the US hazardous air pollutants measurement program conducted in the 1980s, it was reported that ambient air levels of benzyl chloride in US cities ranged up to 8.28 µg/m^3 (Environment Canada, 2009a).

In the above-mentioned US EPA programme, benzyl chloride emissions were measured from 2 of 3 coal-fired burners. A factor of 20,000 was found between the two measurements. The highest concentration measured was 1.4 x 10^{-3} lb/ton coal – here no flue gas cleaning was used. The lowest concentration measured was 7.1 x 10^{-8} lb/ton coal – here flue gas cleaning in the form of flue-gas desulfurization and wet limestone scrubber was used (US EPA, 1993). These two emission values from the US in 1993 correspond to emission concentrations of 0.08 mg/m^3 and 3.9 ng/m^3 in the flue gas respectively, when using a flue gas amount of 8,200 m^3/tonne coal at 10% oxygen. These are very low concentrations and with the dispersal from the chimneys, especially the high power plant chimneys, the concentration in the environment will be extremely small. Furthermore, benzyl chloride reacts with water in the environment and will therefore be degraded/reacted in the matter of days.

Projecting the two emission values from the US in 1993 on the Danish coal combustion in 2012, the result is an emission of benzyl chloride in Denmark of approximately 130 g to 2.6 kg in 2012, i.e. small amounts.

Benzyl chloride emission from burning coal

This example estimates the level of benzyl chloride emissions from coal burning facilities in Denmark in 2012. The following assumptions have been made:

- According to the Danish energy statistics approximately 100 million GJ coal was used in 2012 in Denmark (Energistyrelsen, 2013).
- The calorific value of coal is 24.23 GJ/tonne (Energistyrelsen, 2013).
- The two measured US emissions from 1993 are used in the calculations, i.e. 7.10 x 10^{-8} lb/ton coal and 1.4 x 10^{-3} lb/ton coal respectively are used as the emission factor for benzyl chloride.
- 1 lb equals 0,453 kg.

The result is an emission of benzyl chloride from burning of coal in Denmark of **approximately 130 to 2,600 g** in total for 2012.

Emission of benzyl chloride was also identified in an air monitoring project in Louisiana, USA. In this project a total of 97 (24 hours) air samples were collected from three different locations from March to October 2006 because of odour complaints from a refinery. The mean concentration of benzyl chloride was 0.00 ppb (volume) for all three locations. The maximum concentration of benzyl chloride measured was 0.01 ppb (volume), i.e. very low concentrations (DEQ Louisiana, 2006).

During a wildfire in the USA (Pains Bay, North Carolina), a benzyl chloride emission of 1.97 ppb (volume) was measured (Mickler, 2012).

According to the US EPA (2008) benzyl chloride emissions have been seen from municipal solid waste landfills. In 24 test reports the minimum concentration of benzyl chloride in landfill gas was 1.72 ppb whereas the maximum concentration was 29.6 ppb. The mean concentration of benzyl chloride in landfill gas was calculated to 18.1 ppb. It is not described in the report whether benzyl chloride was identified in all 24 tests (US EPA, 2008).

The US EPA has in 2000 published their national air pollutant emission trends for the period 1900-1998. In this report it is stated that the annual emissions of benzyl chloride for the period of 1990 to 1993 are estimated to be 33.6 tonnes per year. Of these 28.2 tonnes per year are emitted in urban areas and 5.4 tonnes in rural areas. 32 tonnes or 95% are emitted by point sources (e.g. power plants) (US EPA, 2000b). This estimated emission of benzyl chloride seems high in comparison to the Danish estimated emissions even when considering the differences in Danish and American population. However, the American estimation is based on trends for the period 1990-1998, whereas the Danish estimation is calculated based on the actual coal consumption in 2012.

5.4 Environmental impact

Benzyl chloride is mainly used as a chemical intermediate and high volumes are therefore used in certain facilities in Denmark and in the EU.

Environment Canada (2009a+2009c) predicts that benzyl chloride would be released in relatively small quantities from production facilities, mainly to air, but also to some extent to water. The few monitoring data for benzyl chloride in air illustrates that benzyl chloride is found in small concentrations ($\mu g/m^3$ to ng/m^3) in air. Monitoring data concerning benzyl chloride in water is missing.

Minor releases to the environment may also occur when transported or when treated as waste. The impurities of benzyl chloride in consumer products are generally on a very low level resulting in insignificant levels of benzyl chloride entering the environment through waste water or after incineration of waste. The remaining un-reacted benzyl chloride released to the environment can be considered to be insignificant.

Benzyl chloride is readily biodegradable and not bioaccumulating, thus non-persistent in the environment. When benzyl chloride is released to water or air, it will reside predominantly in the compartment to which it is released, but will fairly quickly ('days or weeks') be degraded through hydrolysis to benzyl alcohol, which is also readily biodegradable and non-toxic in the environment. To conclude: It is not considered likely that benzyl chloride pollution has any effects on the global environment (SEPA, 2014).

OECD SIDS (1998) has calculated a **PEC/PNEC** ratio in order to assess the effects on the environment. OECD SIDS calculates a local predicted environmental concentration (PEC_{local}) based on a yearly release of benzyl chloride from a Japanese manufacturer as well as information on volume of the effluent into the local river and a dilution factor. This results in a PEC_{local} of 0.0018 mg/L and a PEC_{local}/PNEC ratio of 1.8, i.e. above the critical value of 1. OECD SIDS, however, points out that it is unrealistic to use this ratio for risk assessment of benzyl chloride because it is unstable in the aquatic environments (is hydrolysed to benzyl alcohol). Therefore OECD SIDS performs the same calculation of the PEC/PNEC ratio with the toxicity data of benzyl alcohol instead and comes to the result of a PEC/PNEC ratio of 0.015, i.e. well below 1, and therefore concludes that the effects of benzyl chloride and the subsequent related effect of benzyl alcohol on aquatic ecosystems are at low concern. However, the hydrolysis rate of benzyl chloride depends on water temperature and the PEC/PNEC ratio varies from season to season and/or country to country (OECD SIDS, 1998).

Environment Canada (2008a) also calculates a PEC/PNEC ratio for benzyl chloride for a worst case example of a possible industrial release of benzyl chloride to the Canadian aquatic environment. Several assumptions are made in this calculation, e.g. that the possible release is 5% of the quantity used. No exact value of the PEC/PNEC ratio is given, but it is concluded that in this worst case calculation the PEC/PNEC ratio is below the PNEC of 0.0039 mg/L as used by Environment Canada (see description in section 5.1.1). Environment Canada (2009a) therefore concludes that 'benzyl chloride is not entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity'.

5.5 Summary and conclusions

Benzyl chloride does not have a harmonised classification with respect to environmental effects, but a classification of Aquatic Chronic 2, H411 "Toxic to aquatic life with long lasting effects" has been suggested by several notifiers. This is also the environmental classification that benzyl chloride should have according to CLP classification.

Benzyl chloride is regarded as readily biodegradable and not bioaccumulating, thus non-persistent in the environment. If benzyl chloride is released into air, water, or soil, it will reside predominantly in the compartment to which it is released, but will fairly quickly ('days or weeks') be degraded through hydrolysis to benzyl alcohol which is also readily biodegradable and non-toxic in the environment. Overall, benzyl chloride cannot be considered as being a PBT substance.

As benzyl chloride is used in closed systems and is not present in consumer products beyond impurity levels, its release to the environment may occur only from production sites, when transported or stored, or when waste is treated in waste incineration facilities. Environment Canada predicts that benzyl chloride would be released in relatively small quantities, mainly to air, but also to some extent to water. Release to soil seems only to be relevant in the case of accidents during transportation.

Other sources to release of benzyl chloride to the environment may be burning of fossil fuels (coal), wildfires, and emissions from municipal solid waste landfills. However, these sources of releases seem to be of minor importance.

Available monitoring data concerning the levels of benzyl chloride in the environment is very limited. This may be due to the fact that benzyl chloride is readily biodegradable, undergoes rapid hydrolysis to benzyl alcohol and the fact that benzyl chloride is not expected to bioaccumulate in organisms. Monitoring data has only been identified from Canada and the USA. The few monitoring data for benzyl chloride in air illustrates that benzyl chloride is found in small concentrations ($\mu g/m^3$ to ng/m^3) in air.

To conclude: Based on the current usage-pattern of benzyl chloride, the substance can not be expected to enter the environment in a quantity or concentration that has an immediate or long-term harmful effect on the environment.

Data gaps

- Most of the uncertainty concerning the risk characterisation of benzyl chloride relates to exposure. Although there is reliable data for current use patterns, there is an uncertainty about the quantity released to water.
- There is no monitoring data for concentrations of benzyl chloride in water.
- The hydrolysis rate of benzyl chloride in water could be investigated further.
- Information about the formation of benzyl chloride during burning of coal or biofuels is missing. Only a few data exists.
- In conclusion, data on benzyl chloride emission to the environment is missing. However, based on the environmental effects and fate of benzyl chloride (fairly quickly degraded) the emission has to be significant in order to cause environmental concern.

6. Human health effects

The Environment Canada (2009a) report provides a good overview of the available toxicological data on benzyl chloride. This information has been supplemented with the data listed in ECHAs Registered Substances Database (2013)[24] as well as the OECD SIDS (1998) report. The above reports are the three primary references used for describing the human health hazards of benzyl chloride. In general the same data is used in these three major sources of information for human health hazard. Only in a few cases newer studies are presented in the ECHAs Registered Substances Database (2013). In these cases the new data is presented as well. A search has been performed in order to find newer data, but the new data available since the latest Environment Canada (2009a) report has been limited and no important new data has been found.

6.1 Human health hazard

6.1.1 Classification

The harmonised classification of benzyl chloride according to CLP is (as also presented in Table 4):

- Acute Tox. 4, H302 "Harmful if swallowed" (former R22)
- Skin Irrit.2, H315 "Causes skin irritation" (former R38)
- Eye Dam. 1, H318 "Causes serious eye damage" (former R41)
- Acute Tox. 3, H331 "Toxic if inhaled" (former R23)
- STOT SE 3, H335 "May cause respiratory irritation" (former R37)
- Carc. 1B, H350 "May cause cancer" (former R45)
- STOT RE 2, H373 "May cause damage to organs through prolonged or repeated exposure" (former R48 with R20, R21 or R22)

6.1.2 Toxicokinetics, absorption, distribution, metabolism and excretion

Exposure to benzyl chloride may occur through inhalation, ingestion, or dermal contact. Benzyl chloride is absorbed through the lungs and the gastrointestinal tract (TOXNET, 2013). Test with rats and dogs shows that benzyl chloride is absorbed through the gastrointestinal tract after oral administration (OECD SIDS, 1998). Information concerning the absorption of benzyl chloride through skin is lacking.

Distribution studies with C^{14}-labelled benzyl chloride after 48 hours of oral administration to rats revealed that the concentration of the radioisotopes was highest in the stomach, gastric content, gastric wash, ileum, and the duodenum. Approximately 76 % of the initial dose was excreted by the kidney during the 72 hours. About 7 % was detected in expired air as C^{14}-labelled CO_2 while less than 1.3 % was present as C^{14}-labelled benzyl chloride or C^{14}-labelled benzyl chloride metabolites in the expired air during the 72 hours. Metabolism studies revealed that mercapturic acid, benzyl alcohol ($C_6H_5CH_2OH$), and benzaldehyde (C_6H_5CHO) were the metabolites present in urine (OECD SIDS, 1998).

ECHAs Registered Substances Database (2013) reports of another toxicokinetic study with rats and C^{14}-labelled benzyl chloride which shows that the highest levels of radioactivity were found in the

[24] Annex VIII of REACH "Standard information requirements for substances manufactured or imported in quantities of 10 tonnes or more" lists requirements for the toxicological information that must be reported for benzyl chloride being imported in the tonnage band of 10 – 100 tons per annum. The data listed in ECHAs Registered Substance Database seem to live up to the requested information.

heart, stomach, lungs, fat, muscle, and blood 3 hours after dosing. Concerning distribution of benzyl chloride, the highest levels of radioactivity were consistently found in the gastrointestinal tract and at 24hours the concentration of the radioisotope in the squamous stomach was about 4 times higher than that in the glandular stomach. Furthermore, the benzyl chloride isotope rapidly excreted from the body in males as well as females rats via urine (at 6 hours approximately 40–55 % was excreted from the body; at 24 hours approximately 65–75 %). It is concluded from this study that the renal route is the major route of excretion of benzyl chloride and/or its metabolites which is preferentially accumulated and retained in the squamous stomach. Hence the squamous stomach can be considered a target organ for the toxic effects of benzyl chloride.

6.1.3 Acute toxicity

The lowest lethal doses/lethal concentrations reported are summarised in Environment Canada (2009a) and are listed below:

- Oral: LD_{50} (rats) = 440 mg/kg bw
- Inhalation: LC_{50} (mice, 2 h) = 390 mg/m^3 = 355 ppm (v)
- Dermal: LD_{50} (rabbits, 24 h) = > 145 mg/kg bw/day

ECHAs Registered Substances Database (2013) reports the same LD_{50}/LC_{50} concentrations for oral and inhalation studies, as listed above, whereas a dermal LD_{50} value of > 794 but < 1000 mg/kg bw is reported (however, no information on which type of animals or exposure time).

Benzyl chloride has a moderate oral acute toxicity but a higher dermal toxicity and toxicity by inhalation. The above data on oral toxicity is in accordance with an Acute Tox. 4 classification as the existing harmonised classification for benzyl chloride. However, the above data on toxicity by inhalation and dermal toxicity will result in an Acute Tox. 2 classification (according to EU Regulation no. 286, 2011), which is not identical with the harmonised classification of benzyl chloride (Acute Tox. 3 for inhalation and no dermal acute toxicity classification).

Human exposure studies show that concentrations of 6-8 mg/m^3 for 5 minutes cause a slight conjunctivitis (inflammation of the mucous membrane of the eyeballs). Airborne concentrations of 50-100 mg/m^3 cause weeping and twitching of eyelids and in concentrations of 160 mg/m^3 it is unbearably irritating to eyes and mucous membranes of the nose (TOXNET, 2013). Benzyl chloride concentrations are thereby irritating in concentrations below the LC_{50} concentration (for mice).

6.1.4 Skin and eye irritation

Exposure of the rabbit ear skin to 0.5 ml benzyl chloride for 24 hours resulted in severe reddening, swelling, and subsequent necrotic changes. Rabbits and cats exposed to 462 mg/m^3 (95 ppm) for 8 hours/day for 6 days showed eye and respiratory tract irritation. Furthermore, irritation of mucous membranes and conjunctivitis has been seen at exposures of 100-1000 mg/m^3 (21-205 ppm) for 2 hours (OECD SIDS, 1998).

In repeated toxicity studies with mice (inhalation study) and rats (oral study) irritation was reported at the following levels (OECD SIDS, 1998):

- Inhalation study (mice, 6 hours/day in 14 days): Irritation of both the respiratory and olfactory tract was produced at 224 mg/m^3 (46 ppm).
- Oral study (rats, 3 times/week for 26 weeks): Gastric irritation was reported at the 125 and 250 mg/kg dose levels.

ECHAs Registered Substances Database (2013) reports of an eye irritation study where rabbits were exposed to 0.1 mL undiluted benzyl chloride for 24 hours. Immediately after the exposure, the rabbits exhibited discomfort. The reaction to the test substance increased and the maximum reaction was reached after 24 hours. At this point the rabbits displayed areas of barely perceptible corneal dullness, severe erythema (abnormal redness of the skin), slight to moderate oedema (accumulation of fluid), and copious discharge. From 48 to 168 hours there was a gradual improvement. Thus results indicate that benzyl chloride should be considered as a mild irritant to the eyes.

Human exposure studies (TOXNET, 2013) show that permanent eye damage may result from contact with benzyl chloride in the form of liquid or vapour. Concentrations of 6-8 mg/m^3 cause a slight conjunctivitis after 5 minutes of exposure. Airborne concentrations of 50-100 mg/m^3 cause weeping and twitching of eyelids, and in concentrations of 160 mg/m^3 it is unbearably irritating to the eyes and mucous membranes of the nose. In comparison the threshold limit value (TLV) for the working environment in Denmark is set at 5 mg/m^3 for benzyl chloride (Arbejdstilsynet, 2007).

Based on this data benzyl chloride is regarded as irritating for skin, eyes, and respiratory system. Benzyl chloride has the harmonised classification Skin Irrit.2, H315 "Causes skin irritation" (former R38) and Eye Dam. 1, H318 "Causes serious eye damage" (former R41).

6.1.5 Skin sensitisation

The OECD SIDS (1998) report refers to old data (1936) of benzyl chloride being sensitising to guinea pig. Other older reports (1955) state that the response was strong. ECHAs Registered Substances Database (2013) reports of a new study (2010) performed according to OECD guidelines LLNA (Local Lymph Node Assay). Here the conclusion is that based on the results from this study benzyl chloride should be classified as skin sensitiser (Category 1) and labelled as H317: "May cause an allergic skin reaction" according to the Regulation (EC) No 1272/2008. However, the current harmonised classification of benzyl chloride does not include a classification as skin sensitiser.

6.1.6 Repeated dose toxicity

A range of studies with inhalative, oral, and dermal application and with short repeated periods (a few days) up to subchronic exposure (50 weeks) on different species (guinea pigs, mice, and rats) have showed effects on the lungs, liver, forestomach, and skin. Skin tumours were observed after exposure to benzyl chloride on the skin for 50 weeks. The studies which serve as the background for the classification with STOT RE 2, H373 "May cause damage to organs through prolonged or repeated exposure" (former R48 with R20, R21 or R22) are collected and presented in Appendix 4.

6.1.7 Chronic toxicity and carcinogenicity

Long-term oral exposure to benzyl chloride has shown effects in the form of carcinomas (tumours in the epithelial tissue) in the forestomach and the lungs. Long-term dermal exposure to benzyl chloride has produced carcinomas on the skin. This illustrates that benzyl chloride is carcinogenic. No inhalation studies are described (Environment Canada, 2009a). Benzyl chloride also has the harmonised classification of Carc. 1B, H350 "May cause cancer". Two of the tests with mice leading to this carcinogenic classification are described shortly below.

In an oral chronic toxicity study, groups of 52 male and 52 female mice were administered benzyl chloride by gavage at 0, 21.4 or 42.9 mg/kg bw/day, 3 times/week for 104 weeks. At the high dose the male mice had a statistically significant increase in the incidences of hemangioma (benign tumour consisting of blood vessels), forestomach carcinoma, and forestomach carcinoma/papilloma (benign tumour of the skin). In the high dose the female mice had a statistically significant increase in the incidence of forestomach carcinoma/papilloma and lung alveolar-bronchiolar carcinoma/ adenoma (a benign tumour originating in a secretory gland). Furthermore, a statistically significant increase in the incidence of carcinoma/adenoma in the liver cells was observed in the low dose male mice (Environment Canada, 2009a).

In a dermal chronic toxicity study, one group of 20 female mice was administered 2.5 mg diluted benzyl chloride in benzene to a final volume of 25 µL on the skin, twice weekly, for 50 weeks. Three mice developed squamous cell carcinomas on the skin. No skin tumours were observed in the controls (benzene only) (Environment Canada, 2009a).

Two human studies are described by Environment Canada (2009a) and in ECHAs Registered Substance Database (2013). A cancer mortality study from 1983 of workers at a British organic chemical factory investigated 163 exposed and 790 unexposed factory workers employed for at least 6 months between 1961 and 1970. For all causes and for causes other than cancer, standardised mortality ratios tended to increase with time since first employment. The authors conclude that exposed workers employed before 1951 had an increased risk of cancer of the respiratory and digestive systems. No real measurement on exposure to benzyl chloride is done and no specific results are available. Altogether, these parameters raise uncertainties on the conclusion of the impact of benzyl chloride on workers. However, it gives little evidence and raises concerns on benzyl chloride impacts on workers (ECHA Registered Substance Database, 2013).

Another cancer mortality study from 1984 of workers exposed to benzyl chloride, benzotrichloride, and benzoyl chloride was conducted at a chlorination plant in the United States. 697 male workers had been employed from less than 1 year to more than 35 years, and almost all were potentially exposed to all three chemicals. The authors estimated that there is evidence of an increased mortality from respiratory cancer amongst the exposed group of a chemical plant producing the intermediate benzoyl chloride. Several limitations in the studies raise uncertainties (i.e. lack of occupational exposure levels, confounding factors such as smoking cigarettes); however, it is concluded that it gives little evidence and raises concerns on benzyl chloride impacts on workers (ECHA Registered Substance Database, 2013).

6.1.8 Reproductive and developmental toxicity

Only two studies are mentioned in the literature concerning reproductive and developmental toxicity and one of the studies is considered as not assignable due to insufficient documentation (ECHA Registered Substance Database, 2013).

An older test study (not assignable due to insufficient documentation) from 1980 sets an oral LOAEL value of 0.0006 mg/kg bw/day based on increased embryonal lethality in rats exposed to benzyl chloride in sunflower oil by gavage at doses of 0, 0.00006, 0.0006 or 208 mg/kg bw/day on days 1-19 of gestation (Environment Canada, 2009a).

In a developmental toxicity study from 1986 a LOAEL of 100 mg/kg bw/day is set based on significantly reduced fetal length in female rats exposed to benzyl chloride in corn oil at 0, 50 or 100 mg/kg bw/day by gavage on days 6-15 of pregnancy. There were no effects on the number of implantations, resorptions, live fetuses, mean fetal body weight or external appearance or on skeletal or visceral examination. There was no evidence of maternal toxicity (Environment Canada, 2009a). A NOEL of 50 mg/kg bw/day was set for fetal toxicity and a NOEL of 100 mg/kg bw/day was set for teratogenicity as no teratogenic changes were observed (OECD SIDS, 1998).

6.1.9 Genotoxicity

The genotoxic properties of benzyl chloride are ambiguous. ECHAs Registered Substance Database (2013) reports 5 reliable studies, concerning genotoxicity of which 3 were positive and 2 negative.

OECD SIDS (1998) and Environment Canada (2009a) both report on both positive and negative genotoxic results; however, the findings seem to show evidence of genotoxicity *in vitro* and more mixed results *in vivo*. OECD SIDS (1998) concludes that the balance of evidence supports that benzyl chloride might be weakly genotoxic.

6.1.10 Neurotoxicity

In an inhalation study from 1983 a LOAEC of 62 mg/m^3 was set based on behavioural changes in male mice exposed to benzyl chloride by whole-body inhalation doses of 0, 62, 88, 94 or 114 mg/m^3 for 4 hours. Benzyl chloride caused a concentration-dependant extension of duration of the immobility phase by 32, 52, 71 and 84% compared with the controls, respectively (Environment Canada, 2009a).

According to another inhalation study from 1974 on mice the conclusion seems to be that benzyl chloride may have a neurotoxic potential. However, the responses observed were not consistent with the *in vitro* experiment and it is concluded that further testing would be requested to conclude about the neurotoxic potential of benzyl chloride. However, this study is not fully described and is considered as not assignable due to insufficient documentation (ECHA Registered Substance Database, 2013).

6.1.11 Immunotoxicity

In an inhalation study from 1986 female mice were exposed to saturated vapours of benzyl chloride in individual cages for 3 hours or daily during 3 hours for 5 days. Mice exposed were challenged by pathogens to assess the viability of their immune system. The authors did not find a statistical difference between the treated mice and the controls in the infectious aerosol challenge. However, in the bactericidal activity in the lungs, the authors found a significant difference between the treated and the control mice when exposed to a single exposure session. However, these results were not similar with the repeated dose inhalation. These results prove that benzyl chloride may be considered as a potent immuno-modulator and further testing would be required to clarify the situation (ECHA Registered Substance Database, 2013).

6.1.12 Endocrine disruption

No data regarding the endocrine disrupting potential of benzyl chloride has been found. Benzyl chloride is not on the EU list of potential endocrine disruptors.

6.1.13 Combination effects

No data regarding combinations effects of benzyl chloride has been found.

6.2 Human exposure

6.2.1 Direct exposure

6.2.1.1 Consumers

As benzyl chloride is used as an intermediate chemical only, no benzyl chloride is found in consumer products except at impurity levels. The following impurities have been identified:

- Impurity of benzyl chloride in the preservative benzalkonium chloride.
  - In cosmetic products in general and in some animal care products (highest impurity 530 ppm).
  - In certain car care products (highest impurity 370 ppm).
  - In certain modelling clay (highest impurity 780 ppm).
- Impurity of benzyl chloride in the phthalate BBP (impurities approximately 2 ppm).
  - In e.g. vinyl flooring (where the resulting impurity will be well below 2 ppm).

Exposure of consumers to benzyl chloride will therefore be in the form of impurity levels when using the consumer products. Exposure may happen by direct skin contact or by inhalation. However, the exposure is judged to be minor and insignificant.

6.2.1.2 Occupational exposure

Occupational exposure of workers to benzyl chloride may occur:

- In workplaces where benzyl chloride is manufactured

- In workplaces where benzyl chloride is used as an intermediate chemical to produce other chemicals

Occupational exposure at production sites can be expected in drum and tank filling operations. The major route of exposure is inhalation. The information on occupational exposure is limited – only data from Japanese factories manufacturing benzyl chloride and an Australian factory manufacturing quaternary ammonium chlorides is reported. The data is described below.

Manufacture of benzyl chloride
Concentrations in the atmosphere measured with the duration and frequency of each operation were at a Japanese factory manufacturing benzyl chloride (OECD SIDS, 1998) as follows:
- Drum filling: average concentration 1 mg/m³ (duration 150 minutes, 127 times per year)
- Tank filling: average concentration 4.4 mg/m³ (duration 90 minutes, 235 times per year)

Manufacture of quaternary ammonium chlorides
Occupation exposure levels measured in an Australian factory manufacturing quaternary ammonium chlorides using benzyl chloride were 0.46 – 0.55, 2.3 and 0.74 mg/m³ for drum decanting, benzyl chloride charging, and unspecified operation, respectively. The resulting estimated human exposures for these operations were less than the cases in the Japanese production factory (OECD SIDS, 1998).

The Danish company manufacturing benzalkonium chloride has reported that they have measured a maximum concentration in air at approximately 10% under the occupation threshold limit value of 5 mg/m³, i.e. approximately 4.5 mg/m³, which is in line with the maximum measured Japanese concentration. The cases in Japan were also below the (Danish) occupational threshold limit value.

Impurity in BBP
ECHAs Registered Substances Database (2013) reports of a study that has measured the concentration of benzyl chloride that workers are exposed to in a PVC flooring plant. The benzyl chloride concentration near the processing machines was measured to be 0.03 mg/m³. However, there is no mention of the quantification method neither on the sampling method. Results are not sufficiently described and the specific context of the occupational exposure is not clear. Therefore, this study is considered as not assignable due to insufficient documentation.

6.2.2 Indirect exposure
Humans are exposed to benzyl chloride via the environment predominantly through the air.

6.2.2.1 Air
As described in section 5.3.2 ”Monitoring data” only a few monitoring data has been identified for benzyl chloride in the air (data from Canada and USA). The few monitoring data for benzyl chloride in air illustrates that benzyl chloride is found in small concentrations (µg/m³ to ng/m³) in air. The maximum concentration measured (in the 1980s in the US) was 8.28 µg/m³ and 1.17 µg/m³ (in Canada in 2001-2003). Newer data from Canada (2006) is lower – 0.029 µg/m³.

6.2.2.2 Soil
No monitoring data for benzyl chloride in soil has been identified. The levels in soil can be considered as negligible as the substance hydrolyses rapidly (Environment Canada, 2009b).

6.2.2.3 Drinking water
No monitoring data for benzyl chloride in drinking water has been identified. The levels in drinking water can be considered as negligible as the substance hydrolyses rapidly (Environment Canada, 2009b).

6.2.2.4 Food

No monitoring data for benzyl chloride in food or beverages has been identified. Environment Canada (2009b) mentions that benzyl chloride may be used in the production of a specific type of coating for fruit bins. However, as not all bins are coated with this product and since benzyl chloride rapidly hydrolyses, it is concluded that the possible exposure from food can be considered to be negligible.

Benzalkonium chloride is allowed for use in food with a maximum residue level of 0.01 mg/kg detected in food according to EU Regulation No. 396/2005. Hence, it is also possible that benzyl chloride residues could be in food – however, as most food contains water, the concentration will be negligible because of benzyl chloride being rapidly hydrolysed. The German risk assessment organisation BfR has assessed the risk of benzalkonium chloride in food and reaches the conclusion that a chronic risk for consumers is unlikely. Furthermore, BfR concludes that an acute risk for consumers in form of irritation would be unlikely (BfR No. 032, 2012).

To conclude, there is no reason to expect any significant exposure from benzyl chloride in food and beverages.

6.2.2.5 Indoor climate

A few measurements exist concerning the levels of benzyl chloride in indoor air. A maximum concentration of 0.073 µg/m^3 (mean concentration of 0.003 µg/m^3) was measured in Windsor, Ontario, Canada in 2006. Older data from the 1980s on the other hand shows levels as high as 32 µg/m^3 as the mean concentration (Environment Canada, 2009a).

6.3 Bio-monitoring data

As benzyl chloride is rapidly excreted in urine and does not accumulate in the body bio-monitoring data in humans would only express the exposure a short time before the measurement.

No bio-monitoring data has been found.

6.4 Human health impact

A search for data did not reveal any new data from the publishing of the Environment Canada (2009a) report until January 2014. Consequently, the conclusions made in the Environment Canada report are still relevant.

6.4.1 Consumers

6.4.1.1 Impurities in consumer products

Environment Canada (2009a) has made a worst-case risk assessment based on the residues of benzyl chloride in benzalkonium chloride in cosmetic products. They assume a maximum concentration of 1% (w/w) benzalkonium chloride in cosmetic products and a maximum residual level of 100 mg/kg (0.01%) benzyl chloride in benzalkonium chloride resulting in 0.0001% (1 ppm) concentration of benzyl chloride in cosmetic products. Based on an applied amount of 14 g of a hair conditioner as an example, an exposure duration of 4 minutes, an exposed skin area of 1440 cm^2, a use frequency of 104 times/year, a room volume of 10 m^3, and a ventilation rate of 2 L/hour, they calculated the following estimated consumer exposures to benzyl chloride:

- Inhalation: 1.3 µg/m^3
- Dermal: Acute applied dose: 0.2 µg/kg bw
- Dermal: Chronic applied dose: 0.06 µg/kg bw

Comparison of these values with the lowest inhalation LOEC and oral LOEL (as a conservative approach in the light of lack of dermal effect level) results in margins of exposure of approximately

48,000 and 13,000 respectively. Environment Canada (2009a) therefore concludes that these margins are sufficient to be protective against the induction of non-cancer effects in the general population.

As mentioned in section 6.2.1.1 on human exposure for consumers, levels of benzyl chloride found in consumer products have been found at higher levels than the assumed 1 ppm concentration used in the calculations above. In animal care products a concentration of 530 ppm was identified, in car care products a concentration of 370 ppm was identified, and in modelling clay a concentration of 780 ppm was identified. Modelling clay and car care products; however, have a lower use frequency than hair conditioner as well as a smaller dermal exposure area. Therefore it is not expected that benzyl chloride will have any health impacts in these consumer products either.

It is not known whether the measured concentration of 530 ppm in an animal care product could be representative of other cosmetic products. If this concentration is used in the above calculation performed by Environment Canada (2009a), the resulting margins of exposure would instead be 91 and 25 for inhalation and dermal exposure respectively, i.e. in both cases below the acceptable margin of safety of 100. It should, however, be emphasised that it is worst-case calculations and that benzyl chloride will react with the water in the product over time. It is therefore not expected that the possible residues of benzyl chloride in cosmetic products will produce any health effects. Cosmetic products that do not contain water could have a higher impurity level of benzyl chloride, but on the other hand cosmetic products that do not contain water are not in the need of a content of a preservative (benzalkonium chloride), which means that benzyl chloride may not be present in these products either.

6.4.2 Workers

As described above in section 6.2.1.2 “Occupational exposure” the highest measured concentrations at workplaces are 4.4 mg/m^3 (duration 90 minutes, 235 times per year) measured in Japanese factories and 4.5 mg/m^3 measured in Denmark.

In the OECD SIDS (1998) report, the worst case exposure is calculated for a worker assigned to drum filling and tank filling as daily operations for a year without a mask. The daily intake is calculated to be 0.096 mg/kg/day (based on 70 kg bw and a respiratory volume of 1.25 m^3/hour, and the value of 4.4 mg/m^3). The dermal exposure was estimated to be zero to 0.15 mg/kg/day for tank filling operations (based on an estimated dermal exposure of 0.1 mg/cm^2/day, a surface area of 840 cm^2, and a yearly average working hours per day). Of course use of protective gloves would minimise exposure.

Using a NOEL of 6.4 mg/kg bw/day this results in a safety margin of approximately 67, i.e. below 100. This is, however, for a worst case scenario where the measurements have been performed only when the drum and tank filling operations were performed and in which the workers do not wear masks. In normal working conditions the exposure is therefore expected to be much lower. Therefore the exposure of benzyl chloride is not expected to constitute a health risk.

6.4.3 Indirect exposure

6.4.3.1 Inhalation of benzyl chloride by air

Environment Canada (2009a) has made a worst-case risk assessment on benzyl chloride based on the concentrations of benzyl chloride in indoor air. They use the highest measured concentration in indoor air in Canada of 0.073 µg/m^3 and compare this value to the LOEC for inhalation exposure of 62 mg/m^3 (see Table 8). They even add an estimate of the total daily intake of benzyl chloride via the environmental media (based on the maximum outdoor air concentration of 1.17 µg/m^3) of 0.04 µg/kg bw/day and still end up with a margin of exposure of approximately 850,000. Environment Canada therefore concludes that this margin of exposure is sufficient to be protective against induction of non-cancer effects in the general population.

A higher indoor concentration of 32 µg/m^3 was measured in the 1980s, i.e. a concentration that is 440 times higher. Using this concentration instead (even though the concentration was considered to be an outlier, i.e. way higher than the rest of the measurements) would still result in a sufficiently high margin of exposure (app. 1,930) and would not alter the conclusion made by Environment Canada (2009a).

6.4.3.2 Intake of benzyl chloride by food

The Environment Canada (2009a) makes no calculations on the indirect exposure of benzyl chloride by food as no available monitoring data exists in this area. Environment Canada assumes that the concentrations in food and beverages are expected to be negligible based on the uses and physical and chemical properties of benzyl chloride.

OECD SIDS (1998), however, has made some worst-case calculations of the indirect exposure from drinking water and food via fish because it would be possible to be exposed through drinking water processed from the surface water near a benzyl chloride production facility and through fish which may accumulate benzyl chloride near an emission of benzyl chloride from a production facility. This is of course a worst-case calculation as benzyl chloride in the matter of days or weeks will be hydrolysed to benzyl alcohol. The calculations are based on an emission from a Japanese production facility that results in a PEC of 1.8 x 10^{-3} mg/L (see section 5.4 "Environmental impact"). Based on this PEC they calculate the following:

- Daily intake through drinking water: 6.00 x 10^{-5} mg/kg bw/day (based on 2 liter per day and 60 kg bw)
- Daily intake through fish: 1.35 x 10^{-4} mg/kg bw/day (based on BCF = 50, 90 g fish/day, 60 kg bw)

Using a NOEL of 6.4 mg/kg bw/day this results in a safety margin of approximately 33,000. This illustrates that benzyl chloride has a very low potential for human risk via indirect exposure as this exposure only will be relevant for humans residing near production sites. Furthermore, OECD SIDS points out that it is unrealistic (i.e. absolutely worst case) to use these concentrations of benzyl chloride for the risk assessment because it is unstable in the aquatic environments (being hydrolysed to benzyl alcohol).

6.5 Summary and conclusions

Toxicokinetics, absorption, distribution, metabolism and excretion

Most of the benzyl chloride inhaled or ingested can be found in the heart, stomach, lungs, fat, muscle, and the bloodstream. There is no information about dermal absorption of benzyl chloride. Benzyl chloride is rapidly distributed in the body and rapidly excreted from the body via urine (with a $T_{½}$ of approximately 6 hours). The squamous stomach can be considered a target organ for the toxic effects of benzyl chloride. Benzyl chloride does not accumulate in the body (OECD SIDS, 1998; ECHAs Registered Substances Database, 2013).

Human health hazard

Benzyl chloride has a moderate oral acute toxicity (Acute Tox. 4, H302 "Harmful if swallowed"), but a higher dermal toxicity and toxicity by inhalation (Acute Tox. 3, H331 "Toxic if inhaled"). Benzyl chloride is regarded as irritating for skin, eyes, and respiratory system. Benzyl chloride has the harmonised classification Skin Irrit.2, H315 "Causes skin irritation", Eye Dam. 1, H318 "Causes serious eye damage" and STOT SE 3, H335 "May cause respiratory irritation". However, data presented in the section above (regarding toxicity by inhalation and dermal exposure) indicate that an Acute Tox. 2 classification (according to EU Regulation no. 286, 2011) would be relevant as well. Furthermore, the information described in the previous sections indicate, that benzyl chloride should be classified as skin sensitiser (Category 1) and labelled as H317: "May cause an allergic skin reaction" according to the Regulation (EC) No 1272/2008. However, the current harmonised classification of benzyl chloride does not include a classification as skin sensitiser.

Benzyl chloride is considered to be carcinogenic and is classified as Carc. 1B, H350 "May cause cancer". Furthermore, benzyl chloride is suspected of being weakly genotoxic (evidence of genotoxic potential *in vitro*, but evidence *in vivo* is more limited). Long-term studies show that benzyl chloride may cause damage to organs through prolonged or repeated exposure (STOT RE2, H373).

I in experimental animals exposure to benzyl chloride has also induced non-cancer effects in a range of target tissues, including the liver, forestomach, and lungs. Effects on the liver have been seen at both oral studies and inhalation studies whereas effects in the stomach are observed at oral studies. Effects on the lungs have been seen in inhalation studies.

Reproductive studies are limited and a single neurological study with insufficient documentation indicates that benzyl chloride has a neurotoxic effect.

Exposure sources
The human exposure sources are considered to be:

- Consumers: Inhalation and dermal exposure through low levels of impurities in consumer products like cosmetic products, modelling clay, PVC flooring.
- Occupational exposure:
  - In workplaces where benzyl chloride is manufactured
  - In workplaces where benzyl chloride is used as an intermediate chemical to produce other chemicals
- Indirect exposure via the environment: Mainly via air as benzyl chloride is rapidly hydrolysed in the aquatic environment.

Human health impact
Risk assessments (worst case scenarios) related to the use of products containing impurities of benzyl chloride, inhalation of indoor air with measured content of benzyl chloride, and intake of benzyl chloride by food, generally all result in large safety margins (from 13,000 to 850.000). However, a worst case scenario – in which workers did not wear masks and where the measurements were only done during filling operations (where the benzyl chloride concentrations are high) resulted in a margin of exposure below 100 (67). However, it is not expected under normal working conditions, where the exposure is lower, that the exposure of benzyl chloride will constitute a health risk.

Concentrations of benzyl chloride in drinking water, food, or soil are likely to be negligible and the human health impact therefore low or insignificant. The exposure due to the use of consumer products containing residual quantities of benzyl chloride is not expected to produce health impacts.

Risk assessments carried out by Environment Canada (2009a) and OECD SIDS (1998) illustrate that the most important human health impact from benzyl chloride is occupational exposure. However, none of the identified studies reporting measured values of benzyl chloride in the working environment exceeds the Danish occupational threshold limit; thus the risk related to occupational exposure is assessed to be low.

Data gaps
Benzyl chloride is a fairly well examined substance. However, in some areas data are missing or are weak:

- Information on dermal absorption is missing for benzyl chloride; however benzyl chloride is rapidly excreted from the body.

- Perhaps the inhalation and dermal acute toxicity should be investigated further in order to determine if benzyl chloride ought to have a 'higher' acute toxicity classification for these aspects.
- A recent study (2010) concludes that benzyl chloride should be classified as skin sensitiser (Category 1) and labelled as H317: "May cause an allergic skin reaction". However, the current harmonised classification of benzyl chloride does not include a classification as skin sensitiser.
- Reproductive studies are missing (only one study available).

7. Information on alternatives

As benzyl chloride is exclusively used as a chemical intermediate in the manufacturing of other chemicals it is necessary to look at the possibility of producing these other chemicals in an alternative way – in order to find alternatives to benzyl chloride. This has been done for the major chemicals which are produced with benzyl chloride (i.e. benzyl alcohol, quaternary ammonium compounds (e.g. benzalkonium chloride which is the only use of benzyl chloride in Denmark), benzyl cyanide, and BBP).

For other uses no information on alternatives is available (it has neither been identified by RMO (2010) nor Environment Canada (2009a)).

7.1 Identification of possible alternatives

7.1.1 Alternatives for use as chemical intermediate for production of benzyl alcohol

Benzyl alcohol is used in a wide range of applications such as pharmaceuticals, natural health products, cosmetics, flavour products, solvents, and textile dyes. In the United States, benzyl alcohol is no longer produced from benzyl chloride but is produced from the hydrogenation of benzaldehyde (Environment Canada, 2009a). Concerning health impacts, this alternative seems to be a better alternative than using benzyl chloride as benzaldehyde has the harmonised classification of only Acute Tox. 4, H302 "Harmful if swallowed" in comparison with the harmonised classification of benzyl chloride as among others carcinogenic, toxic if inhaled, skin irritating, eye damaging, and damaging to organs through prolonged or repeated exposure.

Benzyl alcohol can also be prepared via a Grignard reaction by reacting phenylmagnesium bromide (C_6H_5MgBr) with formaldehyde[25]. However, it has been discovered (see section 3.3.1) that in the step previous to this Grignard reaction, benzyl chloride is used as an intermediate. Therefore, even though this is an alternative method to produce benzyl alcohol, benzyl chloride still occurs as a part of the production process. Furthermore, formaldehyde is among other things classified as toxic and carcinogenic (Carc. 2) and is therefore not considered to be a better or safer alternative.

Another alternative production method which has been identified is the oxyacetoxylation of toluene with acetic acid and oxygen that produces benzyl acetate which can then be hydrolyzed to benzyl alcohol by transesterification (alcoholysis) using homogeneous and heterogeneous catalysts. This process needs heating and the most effective reaction was obtained using microwave heating which resulted in a higher reaction rate (Wolfson, A., 2012). As this process needs heating as a catalyst, the process is more energy consuming compared to using benzyl chloride. In addition, toluene is classified as e.g. toxic and reprotoxic (Repr. 2) and is therefore not considered to be a better or safer alternative.

A more untraditional method is the possibility of producing benzaldehyde and benzyl alcohol by means of the mushroom Polyporus tuberaster (Kawabe, T. and Morita, H., 1994). Also production of benzyl alcohol has been discovered to be possible by yeast and Botrytis cinerea isolated from grape musts and wines (Delfini et al., 1991). Even though these methods exist, they cannot be seen

[25] http://tirupatichemicals.com/benzylalcohol_fr.html

as direct alternatives to the production of benzyl alcohol by the use of benzyl chloride, as these processes are more the results of a theoretical research.

7.1.2 Alternatives for use as chemical intermediate for production of benzyl quaternary ammonium compounds

Quartenary ammonium compounds are used as antiseptics, bactericides, fungicides, sanitizers, and softeners, but are also used in deodorants and as conditioning agents in hair cosmetics. In a report regarding disinfectants manufacturing works (Chemical works, 1995), it is stated that quaternisation is often carried out with methyl chloride or benzyl chloride. However, in older processes alkyl bromides were used, for example in production of Cetrimide. No additional information is provided about how alkyl bromide can be used to replace of benzyl chloride in the process.

In addition the Danish company which imports benzyl chloride was contacted. They were asked about possible alternatives for benzyl chloride, and in their oppinion it is not possible to use an alternative to benzyl chloride for the production of benzalkonium chloride.

7.1.3 Alternatives for use as chemical intermediate for production of benzyl cyanide

Benzyl cyanide is an intermediate for a variety of compounds and is used in the production of phenobarbital, methylphenidate, and other amphetamines and also compounds like methadone and ketobermidone. Additionally benzyl cyanide is used in organic synthesis for dyes, perfumes, pesticides, and pharmaceuticals, especially penicillin precursors. After investigating the production of benzyl cyanide, no alternative methods than using benzyl chloride as an intermediate have been found. The only reaction mechanisms found describes that benzyl chloride is being used[26].

7.1.4 Alternatives for use as chemical intermediate for production of phthalates (especially BBP)

BBP is used in a range of soft PVC products such as flooring, packaging, and artificial leather. After investigating the production of phthalates with emphasis on BBP, there has not been identified any alternative methods for the production other than using benzyl chloride as an intermediate.

7.2 Summary and conclusions

As benzyl chloride is exclusively used as a chemical intermediate in the manufacturing of other chemicals it is necessary to look at the possibility of producing these other chemicals in an alternative way in order to find alternatives to benzyl chloride. This has been carried out for the major chemicals that are produced with benzyl chloride.

The only production, where use of an alternative production process takes place, is for the production of benzyl alcohol, where the US already uses a hydrogenation process of benzaldehyde instead. This alternative seems to be a better alternative, concerning health impacts, as benzaldehyde has a less severe harmonised classification (Acute Tox. 4, H302 “Harmful if swallowed”) than benzyl chloride.

For other uses no information on alternatives is available (it has neither been identified by RMO (2010) or Environment Canada (2009a)), and the searches performed in this project have only resulted in alternative processes that are not suitable for commercial production or are more energy consuming and thereby more expensive.

Thus, it can be concluded, that even though alternatives to the use of benzyl chloride as an intermediate exist, in general none of the identified methods seems to be valid in terms of replacing

[26] E.g. http://ebooks.gutenberg.us/WorldeBookLibrary.com/rgsyn.htm#1_0_6

the current use of benzyl chloride. The identified alternatives are, in general, either theoretical methods identified for research purposes, which are not suitable for commercial production, or the processes/methods are more energy consuming or were actually used in the past, but have been replaced by the use of benzyl chloride. This indicates that the use of benzyl chloride for various reasons is more beneficial. Furthermore, the alternatives are not safer alternatives than benzyl chloride, as the alternatives are classified as toxic and carcinogenic or reprotoxic.

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Appendix 1: Abbreviations and acronyms

BBP	Butyl benzyl phthalate
BCF	Bioconcentration factor
CLP	Classification, Labelling and Packaging Regulation
CoRAP	Community Rolling Action Plan
DEFRA	Department for Environment, Food and Rural Affairs (UK)
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EPA	Environmental Protection Agency
EU	European Union
HELCOM	The Baltic Marine Environment Protection Commission (Helsinki Commission)
Kow	Octanol/water partitioning coefficient
LC	Lethal effect concentration
LLNA	Local Lymph Node Assay
LOEC	Lowest observable effect concentration
LOAEL	Lowest observable adverse effect level
LOUS	List of Undesirable Substances (of the Danish EPA)
NOEC	No observable effect concentration
NOEL	No observable effect level
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PBT	Persistent, bioaccumulative and toxic
PEC	Predicted environmental concentration
PNEC	Predicted no effect concentration
QSAR	Quantitative Structure and Activity Relationship
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SIDS	Screening Information Data Sets
SPIN	Substances in Preparations in the Nordic countries
SVHC	Substance of Very High Concern

Appendix 2: Background information on regulation

The following annex provides some background information on subjects addressed in Chapter 2. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 2.

EU and Danish legislation
Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.

- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).
- The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, (e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.

- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulates to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation

REACH and CLP

The REACH Regulation[27] and the CLP Regulation[28] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration

All manufacturers and importers of chemical substance > 1 tonne/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tonnes or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 tonne per year, and substances dangerous to aquatic organisms or the environment above 100 tonnes per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tonnes per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tonnes per year.

Evaluation

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction

If the authorities assess that that there is a risks to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised

[27] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

[28] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publishes the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

Ongoing activities - pipeline

In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)

The EU member states have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV

Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

3. It has to be identified as a SVHC leading to inclusion in the candidate list[29]
4. It has to be prioritised and recommended for inclusion in ANNEX XIV (these can be found as Annex XIV recommendation lists on the ECHA web-site)
5. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions

When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intensions in relation to Annex XV dossiers divided into:

- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

[29] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

for the three types of Annex XV dossiers.

International agreements

OSPAR Convention

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- issues of importance
- agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out
- guidelines or guidance setting out the way that any programme or measure should be implemented
- actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention
The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;
- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties;
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels
Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the ecolabelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower
The EU ecolabelling Regulation lays out the general rules and conditions for the EU ecolabel; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan
The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Ecolabelling Board consists of members from each national Ecolabelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Ecolabelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New criteria are applicable in Denmark when they are published on the Ecolabelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).

Blue Angel (Blauer Engel)
The Blue Angel is a national German eco-label. More information can be found on: http://www.blauer-engel.de/en.

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Appendix 3: Self classification

TABLE A
NOTIFIED CLASSIFICATIONS FOR BENZYL CHLORIDE – CAS 100-44-7 (FROM ECHA C&L DATABASE, NOV. 12, 2013). CLASSIFICATIONS IDENTICAL TO THE HARMONISED CLASSIFICATION ARE MARKED IN BOLD.

Classification		No. of notifiers
Hazard Class and Category Codes	Hazard Statement Codes	
Acute Tox. 4 Skin Corr. 1C **Eye Dam. 1** Acute Tox. 2 **STOT SE 3** **Carc. 1B** **STOT RE 2**	**H302** H314 **H318** H330 **H335** **H350** **H373**	308 notifiers
Acute Tox. 4 **Skin Irrit. 2** **Eye Dam. 1** **Acute Tox. 3** **STOT SE 3** **Carc. 1B** **STOT RE 2**	**H302** **H315** **H318** **H331** **H335** **H350** **H373**	180 +50+34+8+6+4 +3+2+1 = 288 notifiers*
Reported as 'blank' Flam. Liq. 3 **Acute Tox. 4** **Skin Irrit. 2** **Eye Dam. 1** **Acute Tox. 3** **STOT SE 3** **Carc. 1B** **STOT RE 2**	H411 H226 **H302** **H315** **H318** **H331** **H335** **H350** **H373**	93 notifiers

Classification		No. of notifiers
Hazard Class and Category Codes	Hazard Statement Codes	
Acute Tox. 4 **Skin Irrit. 2** Skin Sens. 1 **Eye Dam. 1** **Acute Tox. 3** **STOT SE 3** **Carc. 1B** **STOT RE 2**	**H302** **H315** H317 **H318** **H331** **H335** **H350** **H373**	8 notifiers
 Acute Tox. 4 **Skin Irrit. 2** **Eye Dam. 1** **Acute Tox. 3** **Carc. 1B** **STOT RE 2**	**H335** **H302** **H315** **H318** **H331** **H350** **H373**	3 notifiers
Acute Tox. 4 **Skin Irrit. 2** **Eye Dam. 1** **Acute Tox. 3** **STOT SE 3** **Carc. 1B**	**H302** **H315** **H318** **H331** **H335** **H350**	1 notifier
Acute Tox. 4 **Skin Irrit. 2** **Eye Dam. 1** **Acute Tox. 3** **STOT SE 3** **STOT RE 2**	**H302** **H315** **H318** **H331** **H335** **H373**	1 notifier
Acute Tox. 4 **Skin Irrit. 2** Skin Sens. 1 **Eye Dam. 1** **Acute Tox. 3**	**H302** **H315** H317 **H318** **H331**	1 notifier

Classification		No. of notifiers
Hazard Class and Category Codes	Hazard Statement Codes	
STOT SE 3 Carc. 1B STOT RE 2	H335 H350 H373	

H226: Flammable liquid and vapour
H302: Harmful if swallowed
H314: Causes severe skin burns and eye damage
H315: Causes skin irritation
H317: May cause an allergic skin reaction
H318: Causes serious eye damage
H330: Fatal if inhaled
H331: Toxic if inhaled
H335: May cause respiratory irritation
H350: May cause cancer
H373: May cause damage to organs through prolonged or repeated exposure
H411: Toxic to aquatic life with long lasting effects
* Several identical classifications are for some reason listed separately in the C&L Database, but have in this table been joined (listed in the same row).

Appendix 4: Relevant repeated toxicity studies on benzyl chloride

Test	Description	NOEL or LOEL value	Reference
Inhalation			
Guinea pigs, subacute, inhalation	Exposed by whole body to benzyl chloride at 0, 60, 180 or 530 mg/m3, 6 hours/day for 4 weeks. Effect was distended alveoli in the lungs.	LOAEC = 180 mg/m3	Monsanto (1983) in Environment Canada (2009a)
Mice, subacute, inhalation	Exposed to benzyl chloride at 0, 107 or 224 mg/m3, 6 hours/day for 4, 9 and 14 days. Effects were respiratory and olfactory epithelial lesions.	LOAEC = 224 mg/m3 NOAL = 107 mg/m3	Zissu (1995) in Environment Canada (2009a)
Guinea pigs, subchronic, inhalation	Exposed by whole body to benzyl chloride at 0, 5, 62 or 148 mg/m3, 6 hours/day, 5 days/week for 27 weeks. Effect was increased relative liver weight.	LOEC = 62 mg/m3	Monsanto (1984) in Environment Canada (2009a)
Oral			
Mice, subchronic, oral	Exposed to benzyl chloride by gavage at 0, 2.7, 5.4, 10.7, 21.4, or 42.9 mg/kg bw/day, 3 times/week for 26 weeks. Effect was moderate, occasionally severe, hyperplasia in liver.	LOEL = 2.7 mg/kg bw/day	Lijinsky (1986) in Environment Canada (2009a)
Rats, subchronic, oral	Exposed to benzyl chloride by gavage at 0, 6.4, 12.9, 26.6, 53.6 or 107.1 mg/kg bw/day, 3 times/week for 26 weeks. Effect was hyperkeratosis in the forestomach.	LOAEL = 12.9 mg/kg bw/day NOEL = 6.4 mg/kg bw/day	Lijinsky (1986) in Environment Canada (2009a)
Dermal			
Mice, subchronic, dermal	Exposed to benzyl chloride painted on the skin in a dose of 10 µL/animal/painting, first 3 times/week for 4 weeks and then followed by 2 times/week for 37 weeks. No deaths occurred and no tumour was found in controls or test animals.	No NOEL identified because of the experiment not being adequately designed	Fukuda et al. (1981) in ECHAs Restricted Substances Database (2013)
Mice,	Exposed to benzyl chloride painted on the	No NOEL	Fukuda et al.

Test	Description	NOEL or LOEL value	Reference
subchronic, dermal	skin in a dose of 2.3 µL/animal/painting, first 2 times/week for 50 weeks. Mortality at termination was 20% in the controls compared and 50% in the treated group. Tumours were observed at the treated skin (for 25% of the mice). 3 mice of the test group developed squamous–cell carcinomas of the skin (of which 2 in metastasis), 1 had a leiomyosarcoma of the uterus; 2 treated and 2 control mice had lung adenomas. The difference in skin cancer incidence was not statistically significant between the two groups.	identified because of the experiment not being adequately designed	(1981) in ECHAs Restricted Substances Database (2013)

TABLE 8
SUMMARY OF THE RELEVANT REPEATED TOXICITY STUDIES ON BENZYL CHLORIDE

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