Danish Ministry of the Environment

Survey of sodium and calcium hypochlorite

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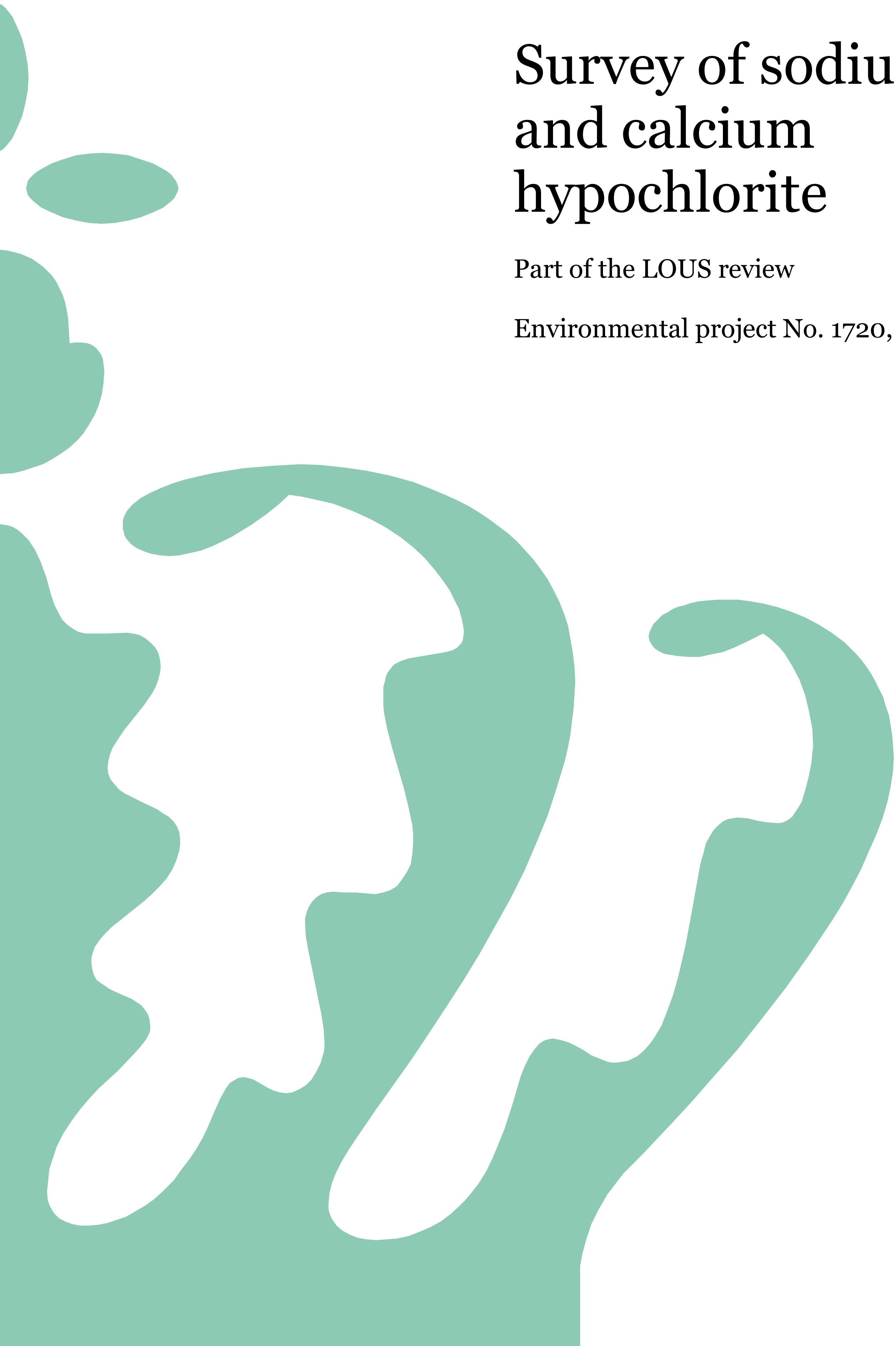

Title:

Survey of sodium and calcium hypochlorite

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Contents

Preface

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern due to the actual consumption in Denmark and for which the use should be reduced or even completely eliminated. 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 based on quantitative structure analogy relationship evaluation using computer models.

For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and/or 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, on alternatives to the substances, on existing regulation, on monitoring and exposure, and information regarding on-going activities under REACH, among others.

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

This survey concerns sodium and calcium hypochlorite, with the CAS numbers 7681-52-9 and 7778-54-3 respectively. The reason for including these substances in LOUS was the risk of formation of toxic organic by products and the risk of toxic gasses developed when the substances are mixed with acid. In addition, both hypochlorites are classified as Aquatic Acute 1, corresponding to very toxic to aquatic life (H400).

The process

The survey has been undertaken by the Norwegian Institute for Water Research (NIVA) from April to October 2014.

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

- Sidsel Dyekjær, Danish Environmental Protection Agency
- Peter Hammer Sørensen. Danish Environmental Protection Agency
- Preben Bruun, Danish Environmental Protection Agency
- Nikolai Stubkjær Nilsen, Confederation of Danish Industries
- Peter W. Knudsen, Danish Chamber of Commerce
- Saoirse Eriksen, Danish Veterinary and Food Administration
- Anders Skou, Danish Environmental Protection Agency

The report does not necessarily reflect the view of the members of the advisory group.

Data collection

This survey is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.
The information included in this survey was mainly gathered from the following sources:

- Production, import and export of substances from the SPIN database (Substances in Preparations in Nordic Countries).
- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database).
- On-going regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan).
- 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.
- Data on production, import and export of substances in mixtures from the Danish Product Register.
- 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 and OSPAR;
- (ATSDR), Information on Hazardous Chemicals and Occupational Diseases (Haz-Map).
- The Toxicology Data Network (TOXNET) and the Hazardous Substances Databank (HSDB).
- The Agency for Toxic Substances and Disease Registry (ATSDR).
- Information on Hazardous Chemicals and Occupational Diseases (Haz-Map).

Conclusion and Summary

This survey concerns sodium and calcium hypochlorite, with CAS numbers 7681-52-9 and 7778-54-3 respectively. The substances are included in the LOUS because of their harmonized classification: both hypochlorites are classified as Aquatic Acute 1. In addition, the main characteristics of these substances that give rise to concern are their oxidizing potential, the spontaneous release of toxic chlorine gas when hypochlorites solutions are contacted with acids, and the reactivity of the substance with organic matter, which can provoke the formation of toxic organohalogen by-products.

Regulatory framework
Hypochlorites are in the scope of the Regulation EU 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products. Both are being reviewed for their use as biocides in different product types. No decision has been taken so far except for human hygiene biocidal products (where calcium hypochlorite should not be used) and in-can preservatives (where the use of sodium hypochlorite is forbidden).

The OSPAR Convention does not explicitly mention sodium and calcium hypochlorites, but indicates that the use of chlorine in bleaching of pulp should be phased-out. Due to the similarities between bleaching with chlorine and with hypochlorites, it might be understood that these products should be phased-out for pulp bleaching. IMO also stablishes rules for maritime transport of the substances. They mainly involve segregation in transport and use of special packaging. The substances are also restricted in several applications if an Eco-Label is pursued.

Manufacture, uses and consumption trends
The tonnage band registered in ECHA (tonnes per year) is in the range 1,000,000 - 10,000,000 and 1,000 - 10,000 for sodium and calcium hypochlorite respectively. The production of the substances in the EU takes place mainly in the chlor-alkali industrial facilities of UK, Italy, Spain, France and Portugal. Denmark does not manufacture any of the surveyed hypochlorites.

The EU has a relevant import of both hypochlorites. The main supplier countries have been identified: China, USA and India. While the EU also acts as supplier of a significant amount of sodium hypochlorite to these countries, calcium hypochlorite is mainly imported from them.

In the European Union, sodium hypochlorite is used in household formulations, bleaching, sanitation of water (drinking, wastewater and swimming pool), textile sector and in the chemical industry. The use of calcium hypochlorite is limited to the disinfection of water in swimming pools.

In Denmark, the use of sodium hypochlorite is also, by far, the most extended of the two assessed hypochlorites. The sodium salt is found in more than 200 products under the technical scope of biocide, bleaching agent and cleaner. According to the product register, the use of the calcium salt is limited to just 18 products with the only technical function of biocide (mainly for disinfection of water in swimming pools).

Regarding the historical use of the substances, it is worth noting that from 2007 Denmark has experienced a decreasing trend in the amount of sodium hypochlorite consumed. However, the number of products containing this substance has remained relatively stable, which indicates that manufacturers have been developing formulations with lower content of this substance.

The use of calcium hypochlorite has remained almost constant during the whole assessed period (2005-2011) and it is present in a number of formulations. However, from 2007, there was a general increasing trend in number of products on the Danish market. This increase is not supported by a higher consumption of the substance, indicating that manufacturers are also including calcium hypochlorite in lower concentration in their formulations.

Waste management

Wastes containing hypochlorites in Denmark and in the EU derive mainly from the use of the substances in disinfection of swimming pools and in cleaning and bleaching products. Manufacture of sodium or calcium hypochlorites does not take place in Denmark, so no generation of waste from manufacturing processes will occur. The final sink for these substances after their (industrial /professional or consumer) use as mainly water disinfectant, bleaching agent or cleaner is the sewer system, where hypochlorites undergo chemical reactions that degrade the anion to mainly chloride. Hypochlorites derived from domestic discharges are completely removed in the sewer system even before entering the activated sludge of the urban wastewater treatment plant.

The release of hypochlorites from disposal of polluted packaging such as potential polluted bottles or other packaging types does not pose a risk to the terrestrial environment as these materials are not expected to reach any landfill. Furthermore, the substance does not have any accumulation potential in soils.

Environmental effects and exposure

Hypochlorites are classified as Aquatic Acute 1 and very toxic to aquatic life. The toxicity of the substances under the normal conditions of use is mainly due to the hypochlorous acid, that is the active biocide substance. Due to their inorganic and polar nature, bioaccumulation criteria based on lipophilic distribution does not apply to hypochlorites. This fact, in addition to the high reactivity of the hypochlorite anion and hypochlorous acid does not qualify the substances for being a PBT or vPvB substances. The substance is not a potential candidate to pollute soils, as its low stability in presence of light and organic matter leads to its degradation.

The main sources of release in the EU and in Denmark have been identified. While in the EU the substances can reach the environment by household discharges and from swimming pool, in Denmark the main environmental source derives from the domestic use of sodium hypochlorite. The emission from swimming pools is not relevant in Denmark since they are not emptied regularly.

No data has been identified regarding environmental occurrence of hypochlorites. This lack of interest relies on the high reactivity of the substances. Discharges to the environment occur just in case of accidental spill. Since hypochlorites derived from the domestic use have their sink in the sewage system and undergo further reactions that destroy the anion, the emissions from this use do not pose an environmental hazard. In industrial processes where hypochlorites are used, the potential polluted effluents are normally treated before their discharge to the sewage system or to the environment.

It is worth noting that recent studies have demonstrated the potential formation of hazardous halogenated by-products derived from the uses of hypochlorites. Available data to date indicate that these byproducts are present at low concentration and degraded in wastewater treatment plants and thus, they do not pose an environmental hazard.

Human health effects

Sodium and calcium hypochlorites are classified as corrosive and are labelled with Hazard Statement H314 (causes severe skin burns and eye damage) and additionally the calcium salt is classified as harmful if swallowed and shall be labelled with H302 (harmful if swallowed).

Studies carried out in rats demonstrate that the ingested substance rapidly reaches the bloodstream and its main excretion mechanisms are via urine and faeces. Relevant is also the endogenous nature of hypochlorous acid, which is formed from chloride anions under a response of the immune system. Its role is mainly antimicrobial. The substances cause harm if in contact with eyes and skin due to the high alkalinity of solutions containing hypochlorite.

Mutagenic effects of hypochlorites are not very clear, as the substance undergoes transformation during the test. Studies carried out in humans exposed to chlorinated water and hypochlorites to assess the potential carcinogenicity of the substances allowed to define them as not carcinogenic. Hypochlorite has also been assessed for effects in reproduction, embryotoxicity and teratogenicity in rats. Only assays carried out with extremely high concentrations (very far from the normal range of use) provoked some abnormalities in the sperm of mice.

Human exposure to hypochlorites may occur in consumer and occupational environments in both, EU and Denmark. In the occupational environment, the limits for short and long term exposure as well as the measures to avoid hazardous inhalation of chlorine gas are very well stablished.

The main exposure hazard for consumers is related to the accidental contact with the substance, ingestion or inhalation of toxic gases when hypochlorite solutions are exposed to acids or ammonia solutions. Particularly vulnerable groups in this context are children and babies, as these toxic gases are heavier than air and tend to conquer the lower layers of the room.

The data gathered from the Poison Control Center in Denmark in the period 2006-2014 indicate that the accidents took place with commercial hypochlorite solutions with a concentration about 4,5%. In average, about 183 calls pr year regarding accidents with sodium hypochlorite were reported in the assessed period. No accidents involving calcium hypochlorite were notified to the Poison Control Center.

The use of chlorinating technologies for disinfection of drinking water or swimming pools has revealed the potential of generation of hazardous halogenated organic by-products.

In Denmark, the potential hazard related to human exposure to these by-products in drinking water can be disregarded, as groundwater is mostly used and its microbiological quality is good enough to avoid chlorination. In the case of the swimming pools, where chlorination with hypochlorites (mainly of calcium) is an extended practice in Denmark, the formation of halogenated by-products should not be neglected. However, it should be highlighted that the formation of these substances does not take place if organic matter is not present in the water. A suitable management of the water quality in terms of control and proper technical elements for the removal of organic matter is then the key to overcome this potential drawback of chlorination. The available information regarding disinfection by-products on human health is not sufficient to characterize the risk.

Alternatives

Different alternatives to the use of hypochlorites have been identified for the primary uses of the substances: water disinfection (drinking, swimming pool and wastewater), bleaching and cleaning. The main objective of these potential alternatives is to achieve the same performance than hypochlorite in their uses but minimizing the hazards related to exposure to the substance and the formation of halogenated by-products.

In the case of water disinfection, some of the methods proposed are based also in oxidative reagents such as ozone, chlorine dioxide and hydrogen peroxide. Some others are based on the use of physical methods, such as irradiation of water with UV light.

In disinfection of water, the formation of halogenated by-products can be minimized or even completely avoided by a proper management of the water quality before the chlorination process. The removal of organic matter prior to addition of sodium or calcium hypochlorites is an adequate way to avoid the formation of these undesirable by-products.

From the alternatives assessed for bleaching, sodium perborate and hydrogen peroxide could be even more hazardous for the consumer than hypochlorites. Sodium percarbonate however, has been identified as a very promising reagent and a good potential candidate to replace sodium hypochlorite for bleaching purposes.

In cleaning and disinfection in both, household and industrial environment peracetic acid is the most suitable candidate to replace hypochlorites due to the lower production of organohalogen compounds and its high degradability. Despite quaternary ammonium compounds are also effective substances for disinfection in the domestic and professional environment, few reliable evidences on their toxicity is available. Its use should be minimized as they could be harmful to environment and health.

Data gaps.
Important data gaps include:

- Information regarding toxicity is old and most of the assays of the REACH database have poor reliability. Cancer and mutagenicity assays were carried out in most of the cases under non standardized procedures. The quality of the results is then doubtful and the conclusions might not be valid.

- Further information regarding formation and emission of relevant organohalogenated by-products for different uses of these substances.

- Characterisation of the content and type of organic matter in swimming pools in Denmark and correlation to the formation of organohalogenated by-products.

- Monitoring of organohalogenated by-products just exist for a very narrow type of compounds although many other compounds such as haloacetic acids, haloacids, halodiacids, iodo-THMs, haloaldehydes, halonitriles, haloketones, halonitromethane, bromate, haloamides, haloalcohols and nitrosamines might occur in swimming pools. Monitoring data on the occurrence of these substances in Danish swimming pools and correlation with water quality in terms of content of organic matter is missing.

Sammenfatning og konklusion

Denne kortlægning omfatter natrium- og calcium hypochlorit, med cas nr. 7681-52-9 og 7778-54-3. Disse stoffer er på Miljøstyrelsens Liste over Uønskede Stoffer (LOUS) på grund af den harmoniserede klassificering. Begge stoffer er klassificeret Aquatic Acute 1. Herudover er de vigtigste skadelige egenskaber ved stofferne deres oxidationspotentiale og den spontane udvikling af giftige klordampe, når stofferne kommer i kontakt med syre samt dannelsen af giftige organiske chlorforbindelser ved kontakt med organisk stof.

Regulering
Hypochloriterne er omfattet af biocidforordningen. Begge er under vurdering for deres anvendelse som biocid til forskellige formål. Der er ingen endelig afgørelse endnu, undtagen for produkter, der anvendes til hygiejne for mennesker (hvor calcium chlorit ikke er godkendt) og konserveringsmidler for produkter under opbevaring (hvor natrium hypochlorit ikke er tilladt).

OSPAR konventionen nævner ikke specifik Na- eller Ca-hypochlorit, men indikerer at anvendelsen af chlor til blegning af pulp (papirmasse) bør udfases. Dette kan opfattes som også at gælde for hypochloriterne på grund af deres lighed med chlor. IMO fastsætter regler for maritim tranport af disse stoffer, som hovedsageligt går på isolering af stofferne og særlige regler for pakningen. Stofferne er også udelukket i en lang række miljømærkekriterier.

Produktion, funktion og forbrug
Na- og Cahypochlorit er registreret under REACH. Na-hypochlorit i mængder på 1.000.000 – 10.000.000 ton/år og Ca-hychlorit 1.000 – 10.000 ton/år. Produktionen i EU foregår i klor-alkali industrien i UK, Italien, Spanien, Frankrig og Portugal. Der er ingen produktion af hypochlorit i Danmark.

Der foregår import af begge stoffer til EU. Hovedafsender landene er Kina, USA og Indien. EU eksporterer også betragtelige mængder af Na-hypochlorit til disse lande, mens Ca-hypochlorit hovedsageligt importeres herfra.

I EU bruges Na-hypochlorit i husholdningsprodukter, produkter til blegning, vandrensning (drikkevand, spildevand og svømmebade) i tekstilindustrien, og i den kemiske industri. Anvendelsen af Ca-hypochlorit er mere begrænset til desinfektion af svømmebad.

I Danmark er forbruget af Na-hypochlorit også langt større end forbruget af Ca-hypochlorit. Na-saltet findes i mere end 200 produkter som anvendes til biocid, blegemiddel eller rengøring. Ca-saltet anvendes ifølge produktregistret i 18 produkter og kun som biocid (hovedsageligt til desinfektion af svømmebade).

Det er værd at bemærke, at der har været en faldende tendens i forbruget af Na-hypochlorit sinde 2007. Men antallet af produkter er stort set dette samme, hvilket indikerer at producenterne har udviklet produkter med lavere indholdskoncentrationer af stoffet.

Anvendelsen af Ca-hypochorit har været stort set konstant gennem den undersøgte periode (2005-2011). Men fra 2007 har der været et stigende antal produkter på markedet, som ikke følges af en stigning i det samlede forbrug af stoffet. Dette indikerer, at producenterne også har nedsat mængden af stoffet i de enkelte produkter.

Affaldshåndtering

Udledningen af hypochlorit med affald/spildevand i Danmark og EU stammer hovedsageligt fra anvendelsen af stofferne som desinfektion i svømmebade, samt i produkter til rengøring og blegning. Der er ingen produktion af stofferne i DK, og således ingen affaldshåndtering forbundet hermed. Stofferne udledes hovedsageligt med spildevandet efter både privat og professionel brug. Her nedbrydes stofferne til anioniske salte, hovedsageligt chlorid. Hypoclorit fra husholdningsbrug nedbrydes fuldstændig før de når til slamfasen i renseanlægget.

Udledningen af hypochlorit fra forurenet emballage såsom flasker eller andre emballager udgør ikke en risiko for det terrestriske miljø, da disse materialer normalt ikke sendes på losseplads. Desuden akkumulerer stofferne ikke i jord.

Miljømæssige effekter og eksponering

Hypochloriter er klassificeret aquatisk acute 1 og meget giftige for organismer i vand. Under normale anvendelsesbetingelser skyldes giftigheden hypochlorsyre, som er biocidaktivstoffet. Bioakkumulering er ikke relevant for disse stoffer på grund af deres uorganiske og polære egenskaber. Dette sammenholdt med den høje reaktivitet af både hypochlorit anion og – syre betyder, at de ikke kan anses for at være PBT eller vPvB-stoffer. Stofferne vil ikke forurene jord, da den ringe stabilitet ved tilstedeværelse af lys og organisk stof medfører, at de vil nedbrydes.

De primære kilder til udledningen til miljøet i EU og DK er blevet identificeret. I EU er de primære kilder svømmebade og husholdninger. I DK er husholdningerne den primære kilde. Udledninger fra svømmebade er ikke betydelig i DK, da disse ikke tømmes regelmæssigt.

Der er ikke fundet måledata for stofferne i miljøet. Det skyldes stoffernes høje reaktivitet. Stofferne når kun miljøet, hvis der sker betydelige utilsigtede udledninger. Eftersom hypochloriter, der anvendes i husholdninger udledes til kloakken og anionen nedbrydes vil der udledninger fra husholdninger ikke udgøre en risiko for miljøet. Når stofferne anvendes industrielt, sker der normalt en behandling af spildevandet, før det når frem til spildevandssystemet eller miljøet.

Det er dog værd at bemærke, at nylige studier har vist, at stofferne potentielt kan føre til dannelse af skadelige organiske chlorforbindelser. De tilgængelige data indikerer dog at disse forbindelser vil findes i lave koncentrationer, og at de vil nedbrydes i renseanlæg og dermed ikke udgør et væsentligt miljøproblem.

Sundhedseffekter

Natrium og calcium hypochlorit er klassificeret som ætsende og skal mærkes med faresætning H314 (forårsager svære forbrændinger af huden og øjenskade). Calcium saltet er endvidere klassificeret som farligt ved indtagelse og skal også mærkes med H302 (farlig ved indtagelse).

Studier med rotter har vist at når stoffet indtages vil det hurtigt blive optaget i blodet og den primære udskillelse sker via fæces og urin. Det er også relevant at hypochlorsyre dannes endogent i kroppen fra chlorid som immunrespons. Det virker primært antimikrobielt. Stofferne er skadelige ved kontakt med hud eller øjne, da opløsninger af stoffet er stærkt basiske.

Stoffernes mutagene effekter er ikke velkendte, eftersom stoffet omdannes under analysen. Studier på mennesker udsat for kloreret vand og hypochlorit har vist at stofferne ikke skal defineres som kræftfremkaldende. Hypochlorit er også blevet undersøgt for effekter på reproduktion, embryotoksisitet og teratogenicitet i rotter. Kun studier med ekstremt høje koncentrationer (langt højere end normale anvendelsesbetingelser) viste abnormaliteter i sperm hos mus.

Human eksponering for hypochloriter forekommer i EU og I DK både i arbejdsmiljøet og hos forbrugerne. I arbejdsmiljøet er der veletablerede grænseværdier for både korttids- og langtidseksponering samt foranstaltninger til at undgå inhalation af chlordampe.

Den primære eksponering af forbrugeren sker ved utilsigtet kontakt med stoffet og indtagelse eller inhalation af giftige dampe, når hypochloritopløsninger kommer i kontakt med opløsninger med syre eller ammonium. Børn og babyer er særligt følsomme i disse situationer, eftersom de giftige dampe er tungere end luft og derfor koncentreres tæt ved gulvet.

Data fra den danske giftinformation fra perioden 2006- 2014 indikerer at ulykker sker med kommercielle blandinger af hypochlorit med en koncentration på omkring 4,5 %. I gennemsnit er der registreret 183 opringninger om året vedrørende uheld med Na-hypochlorit opløsninger. Der er ikke registreret henvendelser til giftinformationen vedrørende Ca-hypochlorit.

Anvendelsen af klorering som desinfektion af drikkevand og svømmebade har vist sig at føre til potentiel dannelse af skadelige organiske chlorforbindelser. I Danmark kan der ses bort fra de skadelige effekter i drikkevand, da vandforsyningen baseres på grundvand, hvor der ikke er behov for at tilsætte chlor. Anvendelsen af chlor i svømmebade (primært Ca-hypochlorit) medfører dog, at betydningen af den potentielle dannelse af biprodukter ikke kan negligeres. Men her er det vigtigt at bemærke, at disse stoffer ikke dannes, hvis der ikke er organisk stof i vandet. Derfor vil en nøgle til at overvinde dette problem, der opstår i forbindelse med chlorering af vandet, rent teknisk være at sørge for at fjerne organisk stof fra vandet.

Den tilgængelige information om de ovennævnte organiske biprodukter er ikke tilstrækkelig til at beskrive risikoen.

Alternativer

Forskellige alternativer til hypochloriterne er identificeret I forhold til de forskellige anvendelser af stofferne: desinfektion af vand (drikkevand, svømmebade og spildevand), blegning og rengøring. Den primære mål med disse alternativer vil være at opnå den samme funktion men samtidig at minimere skaderne forbundet med eksponeringen og de halogene biprodukter.

Når det gælder desinfektion af vand er nogle af de foreslåede metoder også baserede på oxidative stoffer, så som ozon, chlorindioxid og hydrogenperoxid. Andre er baseret på fysiske metoder, så som UV-bestråling af vand.

Når det gælder desinfektion af vand kan dannelsen af organiske klorforbindelser minimeres eller helt undgås gennem teknisk håndtering af vandkvaliteten i form af fjernelse af organiske stoffer. Hvis organisk stof fjernes, før der tilsættes Na- eller Cahypochlorit, vil disse uønskede biprodukter ikke blive dannet.

Blandt de alternativer, der blev vurderet for blegning, er natrium perborat og hydrogenperoxid muligvis mere skadelig for forbrugerne end hypochloriterne. Natriumpercarbonat er til gengæld blevet vurderet som et meget lovende alternativ og et godt potentielt alternativ til natriumhypochlorit til blegning.

Til rengøring og desinfektion i både husholdninger og industri er pereddikesyre det mest egnede alternativ til hypochloriterne pga. mindre dannelse af organiske halogener og høj bionedbrydelighed. Kvarternære ammoniumforbindelser er også effektive desinfektionsmidler i husholdninger og industri, men der er ringe viden om deres skadelige effekter. Derfor bør anvendelsen minimeres, eftersom de potentielt kan være skadelige for miljø og sundhed.

Manglende viden
Vigtig manglende viden er:

- Data om stoffernes toksisitet er gamle og mange af de data, der findes i databasen for REACH registreringer har lav validitet. Studier for kræft og mutagenitet har ikke været udført efter standardiserede metoder. Derfor er resultaterne tvivlsomme og konklusionerne muligvis ikke valide.

- Der er behov for yderligere information om dannelsen og udledningen af relevante halogene organiske biprodukter fra forskellige anvendelser af disse stoffer.

- Karakterisering af indholdet og typen af organisk stof i danske svømmebade og korrelation til dannelsen af halogene biprodukter-

- Moniteringsdata for halogene biprodukter findes kun for en begrænset type stoffer. Selvom mange andre stoffer kan findes i svømmebade. Der savnes en monitering af disse stoffer i danske svømmebade og en sammenligning med vandkvaliteten i form af indholdet af organisk stof.

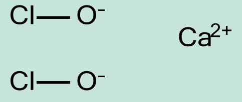
1. Introduction to sodium and calcium hypochlorite

1.1 Definition of the substances

Both sodium and calcium hypochlorite are chlorinated inorganic biocides used mainly for disinfection purposes. The hypochlorite anion is strongly active against bacteria, fungi and slime-forming algae that can cause diseases in people and animals. In Denmark, the major use of these substances is as cleaning/washing agents as well as non-agricultural pesticides and preservatives. The main identifiers of both, sodium and calcium hypochlorite are presented in table 1.

TABLE 1

NAME AND OTHER IDENTIFIERS OF SODIUM AND CALCIUM HYPOCHLORITE (ECHA DATA AND IARC MONOGRAPHS, VOLUME 52)

Parameter	Sodium hypochlorite	Calcium hypochlorite
EC number	231-668-3	231-908-7
CAS number	7681-52-9	7778-54-3
Synonims	Hyochlorous acid, sodium salt; sodium chloride oxide; sodium oxychloride	Calcium oxychloride; chlorinated lime; chlorolime; hypochlorous acid calcium salt; lime chloride
Molecular formula	$NaClO$	$Ca(ClO)_2$
Molecular weight (g/mol)	74.44	142.98
Chemical structure	$\mathrm{Cl{-}O^-}\quad\mathrm{Na^+}$	 $\mathrm{Cl{-}O^-}\quad\mathrm{Ca^{2+}}\quad\mathrm{Cl{-}O^-}$

1.2 Physical and chemical properties

Sodium hypochlorite is produced as an aqueous solution from the reaction of gaseous chlorine with alkaline water. The product is generally sold in aqueous solutions containing 5 to 15% sodium hypochlorite, with 0.25 to 0.35% free alkali (usually NaOH) and 0.5 to 1.5% NaCl. Sodium hypochlorite solutions can release hazardous gases such as chlorine and chloramines if it is mixed with acids or ammonia respectively.

Table 2 shows the main physico-chemical characteristics of sodium hypochlorite for an aqueous solution with content 15% (w/w) available chlorine (unless otherwise stated). It should be noted that sodium hypochlorite can be found in products in a broad concentration range and in mixtures with some other substances. The final properties of the solution might then vary.

TABLE 2

PHYSICO-CHEMICAL PROPERTIES OF SODIUM HYPOCHLORITE. UNLESS OTHERWISE STATED, DATA REFERS TO 15% (W/W) SOLUTIONS (EU RISK ASSESSMENT REPORT, 2007, AISE, 1997).

Property	Sodium hypochlorite	Conditions
Physical state	Yellow colour and characteristic smell	
Melting point	Solidifies at around -25 °C	
Boiling point	107 °C	
Density	1.193 g/cm^3	20 °C
Vapour pressure	20 hPa	20 °C
Surface tension	82.4 mN/m	20 °C and 0.03 %
Water solubility	Totally miscible	
Log P (octanol/water)	Not measurable	

Calcium hypochlorite is generally available as a white powder, pellets, or flat plate. The substances decomposes readily in water or when heated releasing oxygen and toxic chlorine gas. Calcium hypochlorite is not flammable, but it acts as an oxidizer with combustible material and may react explosively with ammonia, amines, or organic sulphides. In Table 3, a summary with the main physic-chemical properties of this substance is presented.

TABLE 3

PHYSICO-CHEMICAL PROPERTIES OF CALCIUM HYPOCHLORITE (OECD SIDS, 2004)

Property	Sodium hypochlorite	Conditions
Physical state	White or grayish-white powder with chlorine-like odor	
Melting point	Decomposes at 175	
Boiling point	Not applicable	
Density	2.35 g/cm^3	
Vapour pressure	Not applicable	
Surface tension	Not applicable	
Water solubility	Approx. 214 g/L	20 °C
Log P (octanol/water)	Not applicable	

1.3 Characteristics and reactivity of the hypochlorite anion

Sodium and calcium hypochlorite in solution have a similar way of acting and work in a similar manner as chlorine gas. Hypochlorites in water undergo dissociation to provide hypochlorite anion according to the reactions:

$$Ca(ClO)_2 + 2\ H_2O \rightarrow 2\ HClO + Ca(OH)_2$$
$$NaClO + H_2O \rightarrow HClO + NaOH$$

The hypochlorite anion in water stablishes equilibrium between different active chlorine species, mainly: chlorine (Cl_2), hypochlorous acid (HClO) and hypochlorite ClO^-. The amount of each species is strongly dependent on physico-chemicals parameters of the solution such as temperature and ionic strength. However, the main factor influencing hydrochemical distribution of the different chorine species is the pH. As will be further discussed in the document, hypochlorous acid (HClO) is the main species with biocide properties.

The hydrochemical speciation of the hypochlorite anion as a function of pH for a chloride concentration 0.05 M is presented in Figure 1. As it is observed, the relationship between molecular chlorine, hypochlorous acid and hypochlorite is strongly pH dependent.

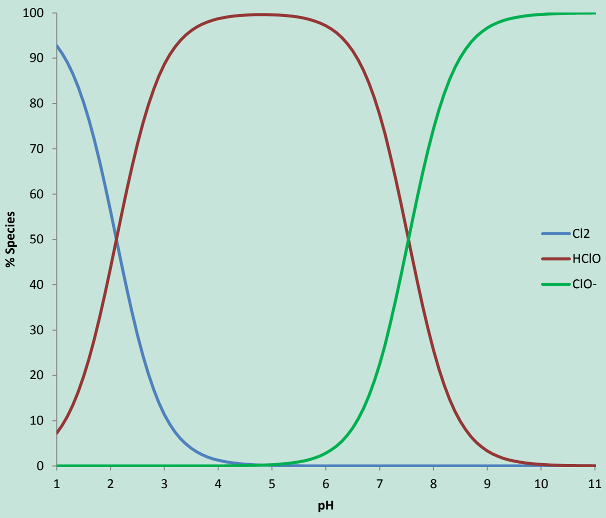


FIGURE 1

HYDROCHEMICAL SPECIATION OF HYPOCHLORITE ANION AS A FUNCTION OF PH.

Hypochlorite ion is predominant at alkaline pH values, while Cl_2 appears at pH below 4. Therefore the concentration of chlorine in an aqueous solution is generally expressed as free available chlorine (FAC) which is the sum of $Cl_2 + HClO + ClO^-$, regardless whether these species stem from dissolved gaseous chlorine or from dissolved sodium/calcium hypochlorite.

Sodium and calcium hypochlorite solutions typically placed in the market have an alkaline pH between 11 and 13. As it is illustrated in the figure, from pH 10 all the hypochlorite is found in its anionic form ClO^-. While hypochlorite solutions are hazardous because of the oxidizing behavior of the ClO^- moiety and their high alkalinity, the toxicity of the hypochlorous acid (HClO) comes from its neutral charge and small size that provides to this acid the potential to cross the cellular membrane by diffusion and modify the internal redox potentials.

In the range from 7 to about 3, mainly hypochlorite is present. Chlorine gas appears when the pH of the solution goes below approximately 4.5 according to the reaction:

$$HClO + H^+ + Cl^- \rightarrow Cl_2 + H_2O$$

The diagram clearly puts into evidence the hazard of mixing hypochlorite solutions (such as commercial bleach) with acid substances (as some cleaners). If the mixture results in a solution with pH lower than 4.5, the release of dangerous amounts of chlorine gas take place. The potential scenario of misuse of the substance will be further assessed in section 6.2.1.

It has to be remarked also the low photostability of hypochlorite anion. Direct sunlight causes rearrangement and decomposition resulting in the formation of chloride and oxygen. In natural water, the Cl_2 molecule as well as hypochlorite ions are not stable due to the presence of organic and inorganic matter, being the half-life of hypochlorite estimated to be less than 2 hours due to reduction and photolysis (OECD SIDS, 2004).

In addition to the hydrochemical speciation of the hypochlorite and its low photostability, this anion can take part in other type of reactions, mainly due to its strong oxidizing properties. The most relevant are summarized next (AISE, 1997):

- Oxidative reactions: is the major reaction mechanism under usage conditions. Hypochlorite exhibits oxidative properties against both, organic and inorganic compounds, yielding various oxidation products and chloride ions. Active oxygen species are also generated by hypochlorite as reaction intermediates.
- N-chlorination: in presence of nitrogen-containing compounds (i.e. ammonia, aminoacids, proteins) the formation of labile N-chlorinated compounds such as chloramines is an important reaction.
- Disproportionation-decomposition: during storage, hypochlorite anions can disproportionate and decompose leading to the formation of chlorate and chloride. The most active metal catalysts for these decomposition reactions are Ni, Co and Cu. Recent studies have also demonstrated that formation of other inorganic oxidative species such as perchlorate might take place (Stanford et al., 2011).
- Halogenation: the formation of organohalogen by-products can also occur by substitution reactions at carbon atoms. As will be further discussed in the document, the halogenation reaction is a key issue when assessing the hazards and risks of this substance, as it is the responsible of the formation of the organohalogen by-products when hypochlorite reacts with organic matter.

The characteristic reactivity of hypochlorite anion as a function of the reaction partner is summarized in Figure 2 below. It is worth noting that, in addition to the reactions briefly summarized previously, hypochlorite can, in presence of bromide anion, undergo oxidative reactions to produce hypobromous acid (HBrO). This species can also be active for potential halogenation of organic matter and conclude in the formation of brominated compounds. Low but significant levels of bromide, the ultimate precursor to bromate and other brominated compounds, may occur in drinking-water sources as a result of pollution and saltwater intrusion in addition to bromide from natural sources (WHO, 2000).

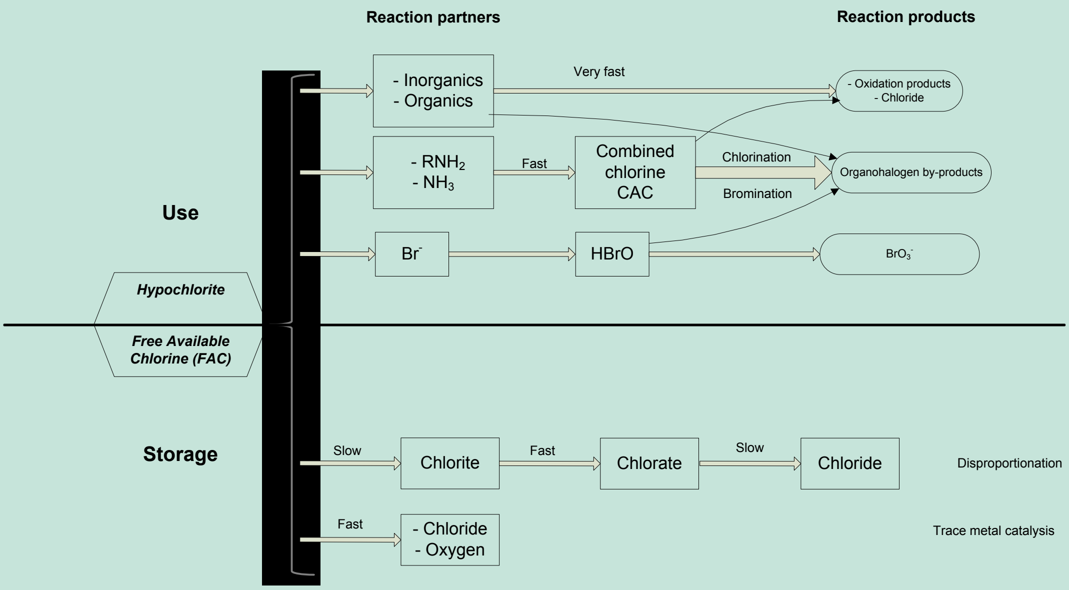


FIGURE 2

REACTIVITY OVERVIEW OF HYPOCHLORITE ANION AS A FUNCTION OF THE REACTION PARTNER. (AISE, 1997)

1.4 Function of the substances for the main application areas

Hypochlorite anion, mainly in form of sodium salt, has been used for long time mainly due to its excellent biocide characteristics as well as its excellent bleaching activity. The next table summarizes the technical characteristics that make the use of hypochlorites suitable for its main applications. The main application areas of these substances is derived from its use as bleacher and cleaner in laundries in industrial and domestic scenarios, water disinfectant in swimming pools, ponds, drinking and wastewater, chemical synthesis and pulp paper bleaching.

TABLE 4

MAIN APPLICATION FIELDS OF THE SUBSTANCES WITH TECHNICAL CHARACTERISTICS THAT EXPLAIN THEIR SUITABILITY.

	Technical characteristics	Reference
	- Excellent stain removal: high reactivity towards complex organic chromophore structures. - Removal of odours killing the bacteria responsible for malodour generation. Oxidative properties against odorous compounds such as sulphur, aldehydes and esters derivatives. - Highly-effective disinfectant action	(AISE, 1997)
Chemical synthesis	- Chlorinating and oxidizing properties towards organic compounds	(EU Risk Assessment report, 2007)
Biocide, water treatment, disinfection (including swimming pools, drinking and wastewater treatment).	- HClO molecules are neutral in charge and small in size. These properties allow them to easily diffuse through the cell walls of bacteria. This changes the oxidation-reduction potential of the cell and inactivates triosephosphate dehydrogenase, an enzyme which is essential for the digestion of glucose. Inactivation of this enzyme effectively destroys the microorganism's ability to function.	(USDA, 2006)
Bleaching-Laundry	- Low temperature reactivity of hypochlorite contributes to optimum fabric whitening and overall energy saving. - At 40°C in fabric washing in presence of hypochlorite germs are destroyed.	(AISE, 1997)
Pulp paper bleaching	- Colour removal by reaction with the remaining lignin from the pulp	(EU Risk Assessment report, 2007)

The main characteristics of these substances that give rise to concern could be summarized as:

- Oxidizing potential. Hypochlorites act as a very oxidative substance and contact with reactive materials should be avoided.
- Spontaneous release of toxic chlorine gas when hypochlorites solutions are contacted with acids that provoke a decrease of pH below 4.5.
- The reactivity of the substance through organic matter can provoke the formation of toxic organohalogen by-products.
- In presence of bromide, these reagents can provoke the formation of toxic bromate anions.

2. Regulatory framework

This chapter describes the regulatory framework that covers the use of sodium and calcium hypochlorite according to EU and Danish regulations, international agreements and Eco-label criteria.

2.1 Existing regulation

Sodium and Calcium hypochlorites are covered by the REACH regulation. Table 5 provides an overview of the main other regulations in the EU and in Denmark addressing the risks from sodium and calcium hypochlorite. The table includes the regulations addressing: products, transport, environmental emissions, waste and working environment. When a legal act concerns biocides both substances are within the scope.

TABLE 5

DANISH AND EU LEGISLATION ADRESSING SODIUM AND CALCIUM HYPOCHLORITE.

Legal instrument	DK/EU	Substance	Requirements
REGULATION ADDRESSING BIOCIDAL PRODUCTS			
Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products	EU	Biocides	Biocidal products should neither be made available on the market nor used unless authorised in accordance with this Regulation.
COMMISSION REGULATION (EC) No 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market	EU	Sodium and calcium hypochlorite	Member States may authorise the placing on the market of sodium and calcium hypochlorite for its use as biocidal products.
COMMISSION DECISION of 9 February 2012 concerning the non-inclusion of certain substances in Annex I, IA or IB to Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market	EU	Calcium hypochlorite	The substances indicated in the Annex to the Decision (where calcium hypochlorite can be found) shall not be included for the product types concerned in Annexes I, IA or IB to Directive 98/8/EC.
REGULATION ADDRESSING ENVIRONMENTAL EMISSIONS			
DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 December 2006 on the	EU	Biocidal products	The Directive establishes specific measures as provided for in Article 17(1) and (2) of Directive

protection of groundwater against pollution and deterioration			2000/60/EC in order to prevent and control groundwater pollution.
DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy	EU	Biocides	Biocides are in the Indicative List of the Main Pollutants of the Directive.
DIRECTIVE 2006/11/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 15 February 2006 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community Implemented in Denmark by Statutory Order No 1309/18/12 Bekendtgørelse om affald.	EU DK	Biocides	Member States shall take the appropriate steps to reduce pollution of water by biocides.
REGULATION ADDRESSING TRANSPORT			
Council Directive 96/49/EC of 23 July 1996, (1) as announced in Commission Directive 96/87/EC of 13 December 1996,(2) adapting to technical progress Council Directive 96/49/EC on the approximation of the laws of the Member States with regard to the transport of dangerous goods by rail	EU	Sodium and calcium hypochlorite.	Shells and their service equipment intended for the carriage of hypochlorite solutions shall be so designed as to prevent the entry of foreign matter, leakage of liquid or any building up of dangerous excess pressure inside the shell. Packaging, including IBCs (Intermediate Bulk Containers), containing hypochlorite solution of item shall be fitted with a vent.
European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR). ECCE/TRANS/225 (Vol. 1) Implemented into Danish law by Statutory Order 788 of 27 June (2013) “Bekendtgørelse om vejtransport af farligt gods”	EU DK	Sodium and calcium hypochlorite	The ADR sets the rules for transport of hazardous substances by road. Danish law requires that all transport of dangerous goods have to comply with the ADR.
Council Directive 96/49/EC of 23 July 1996 on the approximation of the laws of the Member States	EU	Hypochlorites	The Directive sets the rules for rail transport of goods. Hypochlorite solutions are

with regard to the transport of dangerous goods by rail			subject to special provisions.
International Maritime Dangerous Good Code (IMDG). Implementation into Danish law by “Søfartsstyrelsens Meddelelser B”	UN DK	Hypochlorites	IMDG sets the rules for maritime transport of hazardous substances. Hypochlorites are dangerous goods and are included in segregation groups. The Code is in force for Danish vessels and for other vessels operationg in Danish national waters.
Danish Statutory Order 763 of 11 July (2008) “Bekendtgørelse om lufttransport af farligt gods#	DK	Hazardous substances (Sodium and calcium hypochlorite)	Air Transport requires compliance with International Civil Aviation Organisation’s Technical Instructions for the Safe Transport of Dangerous Goods by Air (ICAO-TI)
REGULATION ADDRESSING WASTE			
DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 19 November 2008 on waste and repealing certain Directives In Denmark, Affalsbekendtgørelsen, Bekendtgørelse om affald. BEK nr 1309 af 18/12/2012	EU DK	Sodium and calcium hypochlorite	Among other characteristics exhibited by both, sodium and calcium hypochlorite can release toxic or very toxic gases in contact with water, air or an acid. The potential exposure to acid and release of chlorine is a property that renders both hypochlorites as hazardous.
REGULATION ADDRESSING DRINKING WATER			
Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg	DK	Chlorine, free and total	The content should be the minimum that allows keeping the microbiological quality.
REGULATION ADDRESSING WORKING ENVIRONMENT			
COUNCIL DIRECTIVE 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC) Implemented in Denmark by Statutory Order No 292; 26 April	EU DK	Hazardous chemical agents	The Commission shall evaluate the relationship between the health effects of hazardous chemical agents and the level of occupational exposure by means of an independent scientific assessment of the latest available scientific data. No occupational exposure limit has been stablished for sodium and

2001 Bekendtgørelse om arbejde med stoffer og materialer.			calcium hypochlorite.
Danish Statutory Order No. 559 of 17 June 2004. Bekendtgørelse om arbejdets udførelse.	DK	Hazardous substances	Unnecessary exposure to substances and materials must be avoided. The influence of substances and materials during work shall be reduced as much as is reasonably possible, taking into account technical progress, and established limits to be observed

2.2 Biocide regulation

The Biocidal Products Regulation (BPR, Regulation EU No 528/2012) of the European Parliament and of the Council of May 2012 concerning the making available on the market and use of biocidal products defines as biocidal products those that are necessary for the control of organisms that are harmful to human or animal health and for the control of organisms that cause damage to natural or manufactured materials. The Regulation establishes however, that biocidal products can pose risks to humans, animals and the environment due to their intrinsic properties and associated use patterns. The BPR aims to improve the use of biocidal products in the EU, ensuring human and environmental protection. The regulation was adopted on May the 22nd 2012 and entered into force in September 1st 2013.

The Regulation includes a review programme to assess the substances and products with biocidal activity in the European Union and establishes the criteria for the EU harmonised use of biocidal active substances. The biocidal products are divided in the BPR in 4 main groups and 22 product types (PTs):

<u>Main Group 1: Disinfectants</u>
Product type 1: Human hygiene biocidal products
Product type 2: Private area and public health area disinfectants and other biocidal products
Product type 3: Veterinary hygiene biocidal products
Product type 4: Food and feed area disinfectants
Product type 5: Drinking water disinfectants

<u>Main Group 2: Preservatives</u>
Product type 6: In-can preservatives
Product type 7: Film preservatives
Product type 8: Wood preservatives
Product type 9: Fibre, leather, rubber and polymerised materials preservatives
Product type 10: Masonry preservatives
Product type 11: Preservatives for liquid-cooling and processing systems
Product type 12: Slimicides
Product type 13: Metalworking-fluid preservatives

<u>Main Group 3: Pest control</u>
Product type 14: Rodenticides
Product type 15: Avicides
Product type 16: Molluscicides
Product type 17: Piscicides
Product type 18: Insecticides, acaricides and products to control other arthropods

Product type 19: Repellents and attractants
Product type 20: Preservatives for food or feedstocks

Main Group 4: Other biocidal products.
Product type 21: Antifouling products
Product type 22: Embalming and taxidermist fluids

The Regulation outlines that all biocidal products should be available in the market only after authorisation in accordance with the regulation being the active substance/s contained in the biocidal product previously approved. Then, in order to continue to market a biocidal active substance in the European Union, manufacturers and importers are required to notify the European Commission of their intent to support the use of their active substance for specific products types. There are, however, certain exceptions to this principle. For example, active substances under the review programme as well as biocidal products containing these active substances can be placed on the market while awaiting the final decision on the approval. Provisional product authorisations for new active substances that are still under assessment are also allowed on the market.

The European Chemicals Agency is the responsible of the development of specified tasks with regard to the evaluation of active substances as well as the Union authorisation of certain categories of biocidal products and related tasks. The approval of active substances takes place at Union level and the subsequent authorisation of the biocidal product at Member State level. The authorisation can be extended to other Member States by mutual recognition (ECHA, 2014) and is granted for a maximum period of 10 years.

After evaluation of the substances for the specific product types, a decision of approval or rejection is taken. The substances approved for their use within specific product types are listed in Annex 1 to the BPR (positive list in: http://ec.europa.eu/environment/chemicals/biocides/active-substances/approved-substances_en.htm). Under the BPR, the list will be continued as an Union list of approved active substances and be electronically available to the public. If the active substances are approved in the EU review process, biocidal products containing the substances may later be authorised at national level following application according to BPR procedures.

If after evaluation of the substance for the product type a non-inclusion decision is taken, the substance shall be removed from the market within 12 months of the entering into force of such decision; unless otherwise stipulated in that non-inclusion decision. A consolidated list of existing active substances for which a decision of non-inclusion into Annex I or IA of Directive 98/8/EC has been adopted, is available and also contains the dates by which products containing these active substances shall no longer be placed on the market for the relevant product-types.

According to the characteristics and use of the sodium and calcium hypochlorites, both should be considered as biocides. They are included in the Commission Regulation (EC) 1451/2007 on the second phase of the 10-year work programme of the European Parliament and of the Council concerning the placing of biocidal products in the market. Euro Chlor, merging nearly all chlorine producers in Europe as well as chlorine-related associations for derivatives has notified calcium hypochlorite as an active substance under the Biocidal Product Regulation for the product types presented next:

PT 2: Private area and public health area disinfectants and other biocidal products
PT 3: Veterinary hygiene biocidal products
PT 4: Food and feed area disinfectants
PT 5: Drinking water disinfectants
PT 11: Preservatives for liquid-cooling and processing systems

In the same way, they have notified sodium hypochlorite for the product types labelled in the Regulation as:

PT 1: Human hygiene biocidal products
PT 2: Private area and public health area disinfectants and other biocidal products
PT 3: Veterinary hygiene biocidal products
PT 4: Food and feed area disinfectants
PT 5: Drinking water disinfectants
PT 11: Preservatives for liquid-cooling and processing systems
PT 12: Slimicides

The status of sodium and calcium hypochlorite with respect to BPR is summarized as follow. The substances are being reviewed for almost all the product types previously listed. Neither sodium nor calcium hypochlorites are included in the positive list (list consulted 13/10/2014).

A decision was taken for the use of calcium hypochlorite under the scope of PT1 (human hygiene biocidal products). The substance shall not be included in this product type. The date for the product to be phased-out was 01/02/2013.
Sodium hypochlorite shall not be included in PT6 (in-can preservatives). Phase-out date for this use was 25/10/2009.

Denmark limits the use of biocidal products to those active substances included in the positive list or currently under the EU review process.

2.3 Classification and labelling

The substances and mixtures that are to be placed in the European market have to be classified, packaged and labelled according to the Regulation (EC) No 1272/2008.

2.3.1 Harmonised classification in the EU

Both, sodium and calcium hypochlorite have harmonised classification according to the CLP Regulation, (EC) No 1272/2008). Their classification is presented in the next table.

TABLE 6

EU HARMONISED CLASSIFICATION ACCORDING TO REGULATION (EC) NO 1272/2008.

Index No	International chemical identification	CAS No	Classification		
			Hazard Class and Category Code(s)	Hazard Statement Code(s)	Suppl. Hazard statement Code(s)
017-011-00-1	sodium hypochlorite, solution ... % Cl active	7681-52-9	Skin Corr. 1B Aquatic Acute 1	H314 H400	EUH031
017-012-00-7	calcium hypochlorite	7778-54-3	Ox. Sol. 2 Acute Tox. 4* Skin Corr. 1B Aquatic Acute 1	H272 H302 H314 H400	EUH031

[a] The content of active chlorine may vary.
The * with the hazard category Acute Tox. 4 indicates that the category stated shall be considered as a minimum classification.

The Hazard Statements codes related to these substances indicate:

- H272: May intensify fire; oxidiser.
- H302: Harmful if swallowed.
- H314: Causes severe skin burns and eye damage
- H400: Very toxic to aquatic life.

Sodium and calcium hypochlorite have the supplementary hazard statement code EUH031, indicating that contact with acids liberates toxic gas.

2.4 REACH

Sodium and calcium hypochlorites are both registered under REACH with a tonnage bands 1,000,000 - 10,000,000 tonnes per annum and 1,000 - 10,000 respectively. The substances are neither on the candidate list of Substances of Very High Concern (SVHC) nor in the Community Rolling Action Plan (CoRAP).

Registry of Intentions

The aim of the public Registry of Intentions (RoI) is to make interested parties aware of the substances for which a Harmonised Classification and Labelling (CLH), proposal as Substance of Very High Concern (SVHC) or restriction dossier is intended to be submitted.

Sodium hypochlorite was included in the RoI by a proposal with notification date 23/02/2012 from Netherlands. The substance, produced as a solution lower than 15% concentration, is targeted for a proposal of M-factor 100 replacing the former (M-10). As the M is a multiplying factor, the increase from 10 to 100 attempts to provide an increased weight to substances considered as very toxic for the aquatic environment when classifying mixtures containing these substances. The expected date of submission of the proposal, according to the information provided by the submitter is 15/12/2014 (http://echa.europa.eu/registry-current-classification-and-labelling-intentions).

2.5 International agreements

The Basel Convention

The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal is primarily focused on setting up a framework for controlling the transboundary movements of hazardous wastes (across international frontiers) and at present, contributes to build on this framework by emphasizing full implementation and enforcement of treaty commitments. The other area of focus of the Basel Convention is the minimization of hazardous waste generation (Basel Convention, 1992). Despite the Convention does not specifically mention hypochlorites according to Annex I and III of the document, wastes from the production, formulation and use of biocides and phytopharmaceuticals with oxidizing properties, poisonous acute or corrosive substances should be considered as wastes to be controlled. Thus, transboundary movement of untreated wastes of both hypochlorites should be controlled.

The Helsinki Convention

The Convention on the Protection of the Marine Environment of the Baltic Sea Area, known as Helsinki Convention, establishes a set of measures for the prevention and removal of the pollution in the Baltic Sea. As in the case of Basel, the Helsinki Convention does not explicitly mention hypochlorites. However, in the priority groups of harmful substances presented in the Annex I of the Convention, a group defined as “pesticides, such as fungicides, herbicides, insecticides, slimicides and chemicals used for the preservation of wood, timber, wood pulp, cellulose, paper, hides and textiles” can be found. Sodium and calcium hypochlorites are allocated to this group of harmful substances due to their biocide characteristics.

OSPAR

The OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic is a legislative instrument regulating international cooperation on environmental protection in the North-East Atlantic. OSPAR's work on hazardous substances involve the identification of substances that are of concern for the marine environment, monitoring/assessment of the sources and pathways of contaminants and their concentrations and effects in the marine environment as well as identification of actions and measures required to achieve the Strategy objectives. The OSPAR Convention, with the implementation of its Hazardous Substances Strategy has the next objectives (OSPAR, 2010):

- to achieve concentrations of contaminants at levels not giving rise to pollution effects, and contaminants in fish and other seafood for human consumption not exceeding levels established by EU legislation or other relevant standards.
- to move towards the targets of the cessation of discharges, emissions and losses of hazardous substances by the year 2020.
-

The only reference found to chlorine oxidizing species in OSPAR is the PARCOM Decision 96/2 concerns the use of molecular chlorine in the bleaching of Pulp (PARCOM Decision 96/2, 1996). The Contracting Parties to the Convention for the Prevention of Marine Pollution from Land Based Sources reported in the document the decision of phasing-out processes using Cl_2 in the bleaching of kraft and sulphite pulp process.

Also the International Maritime Organization (IMO) has included sodium and calcium hypochlorites on its Dangerous Goods List for which special provisions are required. These provisions concern mainly special packaging, segregation from other transported goods and stowing (IMO, 2012). Hypochlorite mixtures with 10% or less available chlorine are not subject to the provisions of the IMO Code.

2.6 Eco-labels

The tables presented next contain the information of Nordic and EU eco-label criteria addressing sodium and calcium hypochlorites.

TABLE 7

NORDIC-SWAN ECO-LABEL ADRESSING SODIUM AND CALCIUM HYPOCHLORITE.

Eco-Label	Document	Reference	Substance/s to avoid
Nordic-Swan	Cleaning agents for use in the food industry	Version 1.6	Reactive chloro-compounds should be avoided
	Cleaning products	Version 5.1	Reactive chloro-compounds should be avoided
	Cleaning services	Version 2.3	Reactive chloro-compounds although the substances may be used if the authority prescribes it or when disinfection of swimming pool.
	Textile services	Version 3.1	Active chlorine compounds are restricted in laundry chemicals depending on the textile category.
	Laundry detergents for professional use	Version 3.0	Reactive chloro-compounds should be avoided
	Digital Photographic Development Services	Version 3.0	Production chemicals (toner, ink and other production chemicals used in the dry lab technology or similar) must not contain sodium or calcium hypochlorite.
	Printing companies, printed matter, envelopes and other converted paper products	Version 5.5	Sodium or calcium hypochlorite must not be added to chemicals and materials.
	Remanufactured OEM toner cartridges	Version 5.1	Toner powder must not contain sodium or calcium hypochlorite

TABLE 8

EU ECO-LABEL ADRESSING SODIUM AND CALCIUM HYPOCHLORITE

Eco-Label	Document	Excluded or limited substance in mixtures
EU Flower	All-purpose cleaners and sanitary cleaners	Substances labelled as H400 (very toxic to aquatic life) must not be included.
	Industrial and Institutional Laundry Detergents	Substances labelled as H400 (very toxic to aquatic life) must not be included.
	Textile products	Bleaching agents: Chlorine agents are excluded for bleaching yarns, fabrics and end products
	Laundry detergents	Substances labelled as H400 (very toxic to aquatic life) must not be included.

Analogous regulations regarding exclusion or limitation of substances labelled as H400 exist for the following EU-Ecolabels:

- imaging equipment

- flushing toilets and urinals
- industrial and Institutional Automatic Dishwasher Detergents

However, in these cases the regulation indicates that if the substances or mixtures can change their properties through processing and thus become no longer bioavailable or undergo chemical modification in a way that removes the previously identified hazard, they are exempted. Hypochlorites are reactive species that are mostly degraded during use, producing less toxic chlorine forms such as chloride anion (section 1.3.)This characteristic is a reason for allowing the use of calcium and sodium hypochlorite in products for imaging equipment, flushing toilets and urinals as well as for industrial and institutional automatic dishwasher detergents.

2.7 Summary and conclusions

The main regulation regarding hypochlorites is the EU 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products. The substances are being reviewed for their use in almost all of their potential product types. So far, a decision has been taken for calcium hypochlorite: the substance should not be in products for human hygiene biocidal products. Sodium hypochlorite shall not be used for in-can preservative. In Denmark, the biocides that might be used are those included in the positive list or currently under the EU review process. To date, the authorised use by product type in Denmark is:

Calcium hypochlorite.
PT 2: Private area and public health area disinfectants and other biocidal products
PT 3: Veterinary hygiene biocidal products
PT 4: Food and feed area disinfectants
PT 5: Drinking water disinfectants
PT 11: Preservatives for liquid-cooling and processing systems

Sodium hypochlorite.
PT 1: Human hygiene biocidal products
PT 2: Private area and public health area disinfectants and other biocidal products
PT 3: Veterinary hygiene biocidal products
PT 4: Food and feed area disinfectants
PT 5: Drinking water disinfectants
PT 11: Preservatives for liquid-cooling and processing systems
PT 12: Slimicides

Both substances have a harmonised classification according to the CLP and none of them are in the candidate list of Substances of Very High Concern (SVHC). The hypochlorites surveyed are also affected by some international agreements. The OSPAR Convention does not include an explicit mention to them, but indicates that the use of chlorine in bleaching of pulp should be phased-out. Due to the equivalence of the surveyed substances to chlorine oxidizing bleaching, it might be understood that bleaching with hypochlorites should also be phased-out. The International Marine Organization (IMO) also provides rules regarding segregation and use of special packaging in the shipping of these substances. In Eco-Label criteria, both substances are restricted in several applications mainly related to cleaning and bleaching. Also restriction of the use of hypochlorites in the production of chemicals for digital photography, printing and reuse of toner cartridges is stated.

3. Manufacture and uses

3.1 Manufacturing

3.1.1 Manufacturing processes

Sodium hypochlorite is manufactured by the absorption of chlorine in ca. 21% caustic soda solution. The chlorine and the caustic soda are produced by electrolysis of brine and the chlorine is added as gas or liquid to the caustic soda solution. The formation of sodium hypochlorite takes place according to the reaction:

$$NaOH + Cl_2 \rightarrow NaClO + NaCl$$

Packed towers containing caustic soda are often used as emergency absorption plants for the gas venting of various chlorine handling operations and this solution is then strengthened with chlorine to provide finished material. Most of the producers are chlor-alkali manufacturers, who produce sodium hypochlorite largely as part of their chlorine production.

There are mainly three different technologies used for the chlorine gas, basis of the production of hypochlorite: the mercury cell, the diaphragm cell and the membrane cell process. Nowadays, the membrane cell technology is preferred in the new production facilities (European Union Risk Assessment Report, 2007).

Calcium hypochlorite is manufactured mainly by two production techniques: the calcium and the sodium method. The calcium method is based in the chlorination of slaked lime by direct use of chlorine gas according to the reaction:

$$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(ClO)_2 + CaCl_2 + 2H_2O$$

The sodium method is based in the reaction of sodium hypochlorite with the product of the calcium method to remove the undesirable calcium chloride (by-product of the calcium method):

$$CaCl_2 + 2NaClO \rightarrow 2NaCl + Ca(ClO)_2$$

Nowadays the sodium method is the predominant (OECD SIDS, 2004).

3.1.2 Manufacturing sites

Hypochlorites are strongly linked to the chlor-alkali industry. Major producers of sodium hypochlorite in European have been identified and are presented in Table 9.

TABLE 9

EUROPEAN MAJOR PRODUCERS FOR SODIUM HYPOCHLORITE (EU RISK ASSESSMENT REPORT, SODIUM HYPOCHLORITE, 2007).

Company	Country	Location (process used)
Akzo Nobel BV	Netherlands Sweden Finland Germany	Hengelo (Hg,) Rotterdam (M) Skoghall (M) Oulu (Hg) Bitterfeld (M), Ibbenburen (Hg)
Albemarle PPC	France	Thann (Hg)
Albion Chemicals	United Kingdom	Sandbach (Hg)
Associated Octel	United Kingdom	Ellesmere Port (M, Na/Hg)
Atofina	France	Jarrie (Hg)
BASF	Germany	Ludwigshafen (Hg, M)
Bayer AG	Germany	Leverkusen (M, HCl), Dormagen (M, HCl), Uerdingen (Hg, M)
Borregaard Industries	Norway	Sarpsborg (M)
Degussa	Germany	Lulsdorf (Hg)
Electroquimica de Hernani	Spain	Hernani (M)
Ercros	Spain	Flix (Hg), Sabiñánigo (Hg), Villaseca (Hg, M)
Finnish Chemicals	Finland	Joutseno (M)
Industrie Chimiche Caffaro	Italy	Torviscosa (Hg)
Ineos Chlor1	United Kingdom Germany	Runcorn (Hg) Wilhelmshaven (Hg)
LII Europe	Germany	Frankfurt (Hg)
Metaux Speciaux	France	Plombiere (Na/Hg)
Quimica del Cinca	Spain	Monzon (Hg)
Rhodia	France	Pont de Claix (D)
Soc. Des Produits Chimiques d'Harbonnières SA	France	Harbonnières (Hg)
Solvay SA/Solvin	Belgium Italy Portugal France Spain Switzerland	Antwerpen (M), Jemeppe sur Sambre (M) Rosignano (Hg), Bussi (Hg) Povoa (M) Tavaux (Hg, M) Torrelavega (Hg), Martorell (Hg) Zurzach (Hg)
Syndial	Italy	Assemini (M), Porto Marghera (Hg)
Tessenderlo Chemie	Belgium France	Tessenderlo (Hg) Loos (Hg)

Hg = mercury cell process; M = membrane process,

D = diaphragm process; Na = variant of the mercury process which utilises a sodium/mercury amalgam.

Regarding calcium hypochlorite, only one producer has been identified in the EU after browsing the ECHA database.

3.1.3 Manufacturing and consumption volumes

As previously stated, both substances are manufactured and imported in the EU. Sodium hypochlorite is registered with a tonnage band (t/y) 1,000,000 - 10,000,000 and calcium hypochlorite, 1,000 - 10,000 tonnes per annum. While 71 companies are registered for sodium hypochlorite only 1 company is included as registrant or supplier for calcium hypochlorite in the ECHA database. As will be further discussed, sodium hypochlorite is widely used in both, formulation of household products and industrial environments while the use of calcium hypochlorite is mostly limited to the disinfection of water in swimming pools.

In the Eurostat statistics database, sodium and calcium hypochlorites are gathered in a single group that contains also chlorites and hypobromites. Data regarding total manufacture of these substances in the period 2009-2013 in Europe and thorough production by country has been assessed and is presented in table 10.

TABLE 10

PRODUCTION OF HYPOCHLORITES, COMMERCIAL CALCIUM HYPOCHLORITE, CHLORITES AND HYPOBROMITES IN THE EU IN THE PERIOD 2009-2013 (EUROSTAT, 2014).

	YEAR				
	2009	2010	2011	2012	2013
DECLARANT	Amount (Tonnes Cl)				
EU27TOTALS	1.740.035	1.903.430	1.851.969	1.727.398	1.745.183
United Kingdom	605.462	587.267	n.a.	476.358	492.753
Italy	306.546	365.332	560.753	486.459	530.137
Spain	244.159	234.477	189.788	181.266	184.117
France	129.714	223.175	210.397	199.960	174.454
Portugal	123.564	133.934	134.625	141.065	147.140
Hungary	59.042	n.a.	n.a.	n.a.	n.a.
Germany	30.351	32.015	33.879	n.a.	n.a.
Czech Republic	21.646	25.539	n.a.	15.212	15.267
Finland	2.975	3.437,8	4.559	4.458	3.600
Bulgaria	1.180	712,3	635,7	364,2	1.228
Croatia	0,470	13,8	14,2	10.1	0,42
Slovakia	n.a.	n.a.	n.a.	28.226	n.a.
Luxemburg	0	0	0	0	0
Sweden	0	n.a.	n.a.	n.a.	n.a.
Malta	0	0	0	0	0
Estonia	0	0	0	0	0
Latvia	0	0	0	0	0
Lithuania	0	0	0	0	0
Cyprus	0	0	0	0	0
Netherlands	n.a.	n.a.	n.a.	n.a.	n.a.
Ireland	n.a.	n.a.	n.a.	n.a.	n.a.
Denmark	n.a.	n.a.	n.a.	n.a.	n.a.
Greece	n.a.	n.a.	n.a.	n.a.	n.a.
Belgium	n.a.	n.a.	n.a.	n.a.	n.a.
Iceland	n.a.	n.a.	n.a.	n.a.	n.a.
Norway	n.a.	n.a.	n.a.	n.a.	n.a.
Austria	n.a.	n.a.	n.a.	n.a.	n.a.
Poland	n.a.	n.a.	n.a.	n.a.	n.a.
Romania	n.a.	n.a.	n.a.	n.a.	n.a.
Slovenia	n.a.	n.a.	n.a.	n.a.	n.a.

n.a: Data not available

These data clearly points out that the production of these substances in Europe takes place mainly in 5 countries: UK, Italy, Spain, France and Portugal. Maximum production in that period in the EU took place in 2010, with a produced amount above 1900000 tonnes. Denmark does not appear as manufacturer of these substances.

The distribution by use of hypochlorite in Kilotonnes (KT) has been retrieved from the EU report regarding sodium hypochlorite (2007) and the information is presented in the table 11.

TABLE 11

USE OF SODIUM HYPOCHLORITE IN KT AS CL_2 EQUIVALENT IN 1994 (EU RISK ASSESSMENT REPORT, HYPOCHLORITE, 2007).

Countries	Total ind. use	House-hold	Prod. other chem.	Swim. pool	Sewage	Tex. Bleach.	Drinking water	Pulp & paper	Cooling water
Denmark, Sweden, Norway, Finland	6,83	1,22	1,27	0,44	1,46	0,32	0,31	2,4	0,11
Austria, Germany, Switzerland	43,28	3,62	33,16	2,13	4,73	1,08	0,58	1,11	0,17
Belgium, Netherlands	23,07	12,43	14,00	2,8	0,77	0,60	1,30	0,60	1,20
Ireland, United Kingdom	32,10	18,70	23,20	2,25	0,90	1,10	1,50	1,50	1,50
France	12,45	19,95	2,23	1,00	0,43	0,35	1,40	0,52	0,16
Italy, Greece	27,12	20,20	1,20	1,10	3,04	7,80	3,14	0,30	1,84
Spain, Portugal	24,25	42,45	0,90	6,50	3,85	0,50	1,30	2,10	0,60

As it may be observed in table 11, the uses of sodium hypochlorite vary in a considerable way from one European country to another. From these data, the percentage of sodium hypochlorite which is used for the different functions given above can be calculated. This information is presented in the table 12.

TABLE 12

PERCENTAGE OF USE OF SODIUM HYPOCHLORITE BY CATEGORY IN THE EU (EU RISK ASSESSMENT REPORT, HYPOCHLORITE, 2007).

Use	% use of total
Cleaning and disinfection	
- Household application	41
- Water treatment (drinking, cooling, sewage treatment)	11
- Swimming pool sanitation	26
Production of other chemicals	26
Bleaching	
- Textile industry	4
- Pulp and paper	3

In general terms it may be concluded that the main applications of the substance in the EU is in households. When this application is merged with water treatment and swimming pool sanitation, the percentage of use of the substance reaches 78%. As previously stated, the use of calcium hypochlorite is limited to the disinfection of water in swimming pools

3.2 Import and export

3.2.1 Import and export in Denmark

Sodium and calcium hypochlorite are substances with a very active trade in Denmark. Import and export of both substances in the period 1990-2013 have been extracted and are presented in the next figures. All the results are presented in Tonnes of substance.

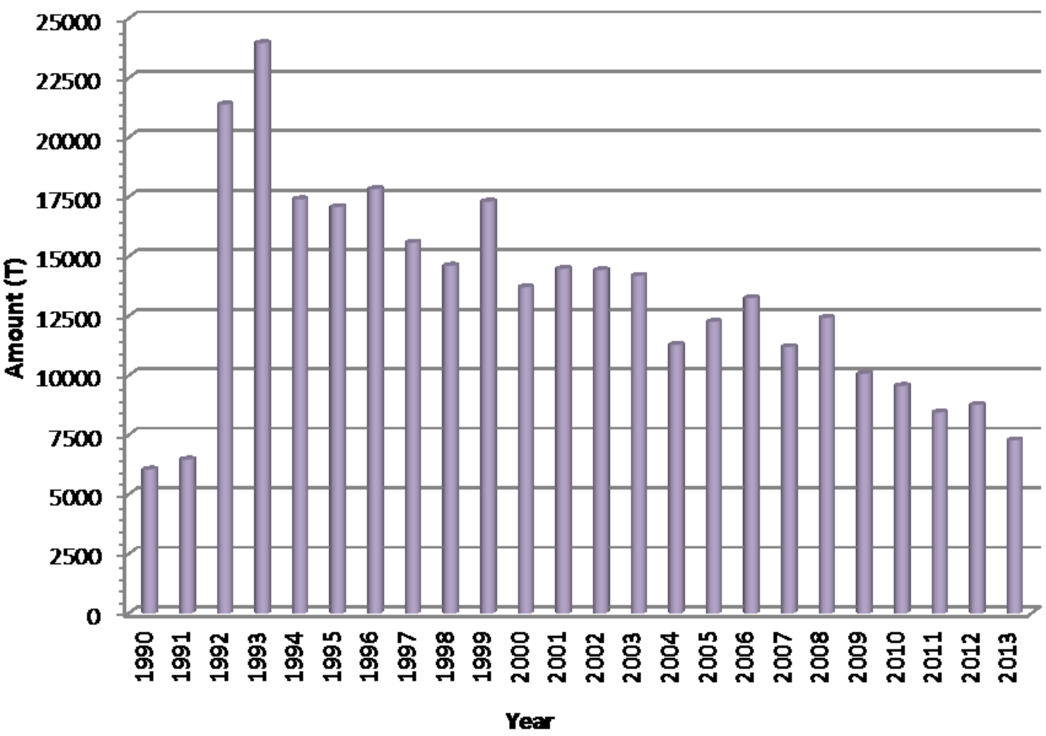


FIGURE 3
IMPORT OF HYPOCHLORITES, CHLORITES AND HYPOBROMITES (EXCLUDED CALCIUM HYPOCHLORITE) IN DENMARK COVERING THE PERIOD 1990-2013. SOURCE: STATISTICS DENMARK, CONSULTED 10-7-2014.

As it may be observed, the group of hypochlorites, chlorites and hypobromites is massively imported in Denmark. After 1991 the import of these substances highly increased from approximately 6000 tonnes until approximately 24 tonnes 1993. After this maximum, a general decreasing trend in the imported amount can be observed, reaching an almost steady consumption about 8000 tonnes from 2011.

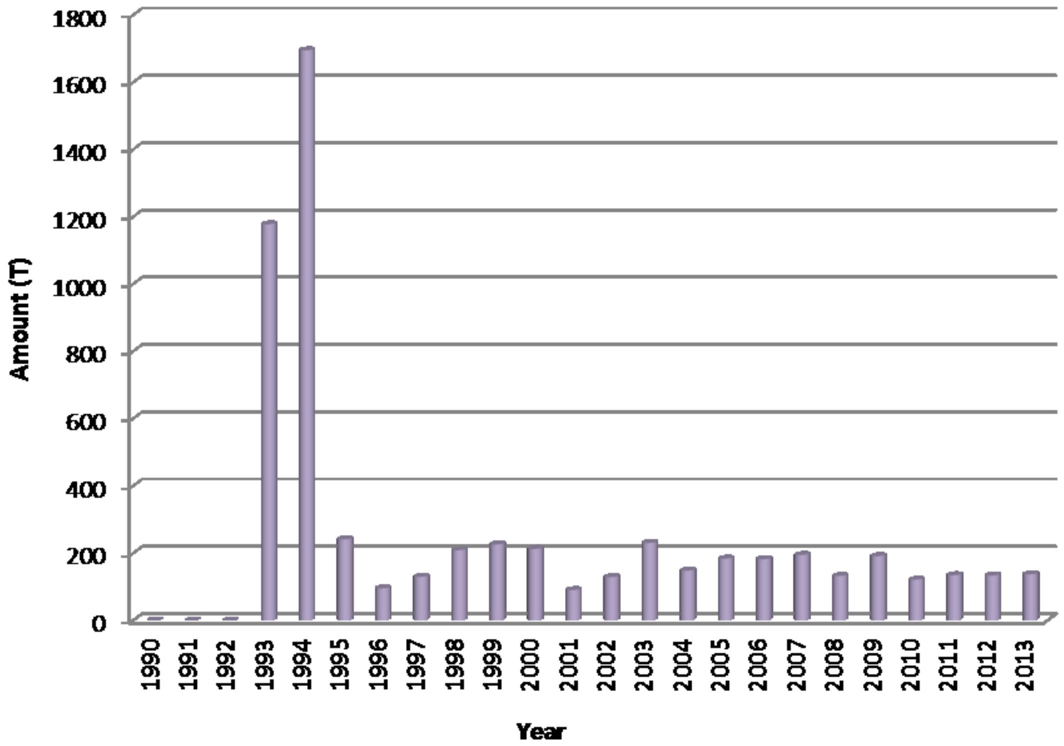


FIGURE 4.
IMPORT OF CALCIUM HYPOCHLORITE IN DENMARK COVERING THE PERIOD 1990-2013. SOURCE: STATISTICS DENMARK, CONSULTED 10-7-2014.

Statistics for calcium hypochlorite are available from 1993. The data regarding import of the substance in 1993 and 1994 indicates probably a mistake in the product register. The actual imported amount in 1993 and 1994 would vary between 80-120 tonnes (personal communication with Peter W. Knudsen). During the period 1995-2013, the imported amount of the substance varies in the range 100-200 tones/year.

Export trading was also assessed. In the next figures data regarding Danish exports of the target substances are presented.

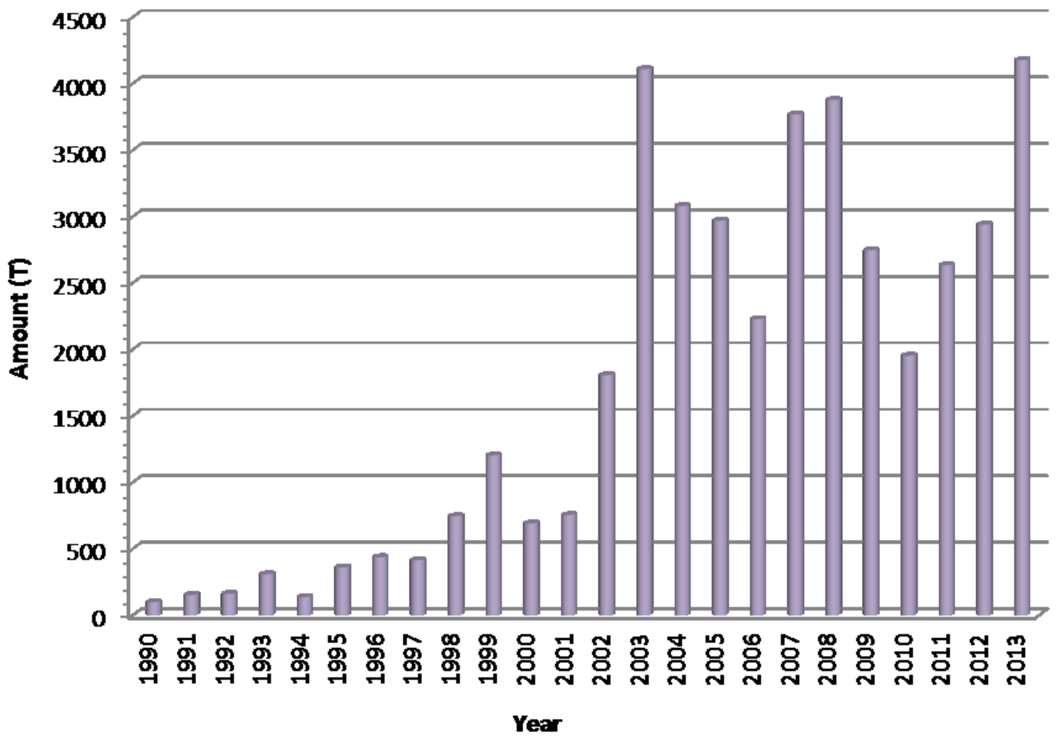


FIGURE 5.
EXPORT OF HYPOCHLORITES, CHLORITES AND HYPOBROMITES (EXCLUDED CALCIUM HYPOCHLORITE) IN DENMARK COVERING THE PERIOD 1990-2013. SOURCE: STATISTICS DENMARK, CONSULTED 10-7-2014.

As it may be seen in Figure 5, exports of hypochlorites, chlorites and hypobromites (excluded calcium hypochlorite) show a general increasing trend in the period 1990-2003, reaching a maximum exported amount about 4000 tonnes. In the period 2003-20013, exports have shown different trends and the minimum registered exportation took place in 2010 (about 1900 tonnes). The maximum exported amount in that period was in 2013, with about 4200 tonnes.

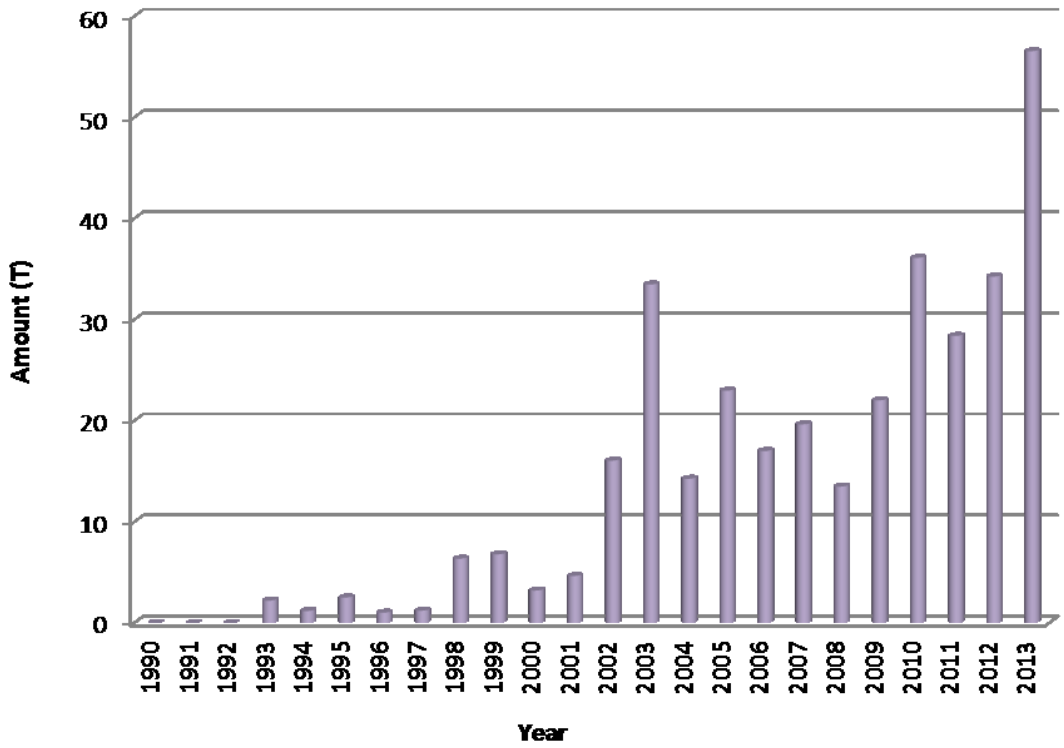


FIGURE 6.
EXPORT OF CALCIUM HYPOCHLORITE IN DENMARK COVERING THE PERIOD 1990-2013. SOURCE: STATISTICS DENMARK, CONSULTED 10-7-2014.

As in the case of import, export statistics for calcium hypochlorite are available from 1993. The data presented in figure 6 shows a general increasing trend in the period 1993-2003. After 2003 the exports have oscillated reaching a minimum in 2008 (approximately 14 tonnes). The data regarding exports in 2013 seems a potential error in the product register. The actual exported amount that year would be about 25 tonnes (personal communication with Peter W. Knudsen).

3.2.2 Import and export in the EU

Three main countries have been identified as suppliers of sodium and calcium hypochlorite to the European Union. These are: China, USA and India. Data of imported and exported amount from and to these countries has been extracted from Eurostat database and are summarized in Table 13. The period explored has been the last 5 years: from January 2009 until December 2013. It has to be remarked that, while calcium hypochlorite was included in a single group, sodium hypochlorite is included under a trade group that includes also chlorites and hypobromites.

The relative percentage of contribution of each one of the countries to the trade flow has been calculated and included in the table.

TABLE 13

HYPOCHLORITES, CHLORITES AND HYPOBROMITES (EXCLUDING CALCIUM HYPOCHLORITE) IMPORT AND EXPORT DATA FROM CHINA, INDIA AND THE UNITED STATES IN THE PERIOD 2009-2013 WITH RELATIVE CONTRIBUTION OF EACH COUNTRY. (EUROSTAT, CONSULTED 24-7-2014). AMOUNTS ARE EXPRESSED IN 100 KG.

			Country		Relative contribution (%)		
Period	**Flow**	**China**	**USA**	**India**	**China**	**USA**	**India**
Jan-Dec 2009	Import	9432	7377	2034	50,1	39,1	10,8
	Export	298	1592	1296	9,4	50,0	40,7
Jan-Dec 2010	Import	24450	3027	702	86,8	10,7	2,5
	Export	882	2073	422	26,1	61,4	12,5
Jan-Dec 2011	Import	20843	3003	1126	83,5	12,0	4,5
	Export	379	1221	350	19,4	62,6	17,9
Jan-Dec 2012	Import	20774	2442	225	88,6	10,4	1,0
	Export	185	1659	497	7,9	70,9	21,2
Jan-Dec 2013	Import	9830	2345	426	78,0	18,6	3,4
	Export	238	1983	544	8,6	71,7	19,7

The results presented in the table put into evidence the main role of China as supplier of hypochlorites, chlorites and hypobromites (excluding calcium hypochlorite) to the European Union, followed by USA. As it may be observed in the period 2010-2012 more than 83% of the amount imported to the EU was supplied by China.

From these countries USA is the first importer of hypochlorites produced in the EU.

TABLE 14

CALCIUM HYPOCHLORITE (INCLUDED COMMERCIAL) IMPORT AND EXPORT FROM CHINA, INDIA AND THE UNITED STATES IN THE PERIOD 2009-2013. (EUROSTAT, CONSULTED 24-7-2014). AMOUNTS ARE EXPRESSED IN 100 KG.

			Country		Relative contribution (%)		
Period	**Flow**	**China**	**United States**	**India**	**China**	**USA**	**India**
Jan-Dec 2009	Import	34808	48224	3007	40,5	56,0	3,5
	Export	3	6	1	30,0	60,0	10,0
Jan-Dec 2010	Import	43489	47448	1215	47,2	51,5	1,3
	Export	0	112	19	0,0	85,5	14,5
Jan-Dec 2011	Import	47863	43184	1100	51,9	46,9	1,2
	Export	16	0	6	72,7	0,0	27,3
Jan-Dec 2012	Import	45326	49265	2192	46,8	50,9	2,3
	Export	4	2	6	33,3	16,7	50,0
Jan-Dec 2013	Import	51808	47758	1953	51,0	47,0	1,9
	Export	36	10	0	78,3	21,7	0,0

In the case of calcium hypochlorite the import to the EU has its origin in China and USA, contributing both countries in a similar manner. India's supply becomes almost negligible if compared to the sum of the other two countries. In export terms China and USA are the main consumers of the calcium hypochlorite produced in the EU.

3.3 Use

The use of sodium and calcium hypochlorite has been explored in the EU and in Denmark.

3.3.1 Registered uses by ECHA

The uses of sodium and calcium hypochlorite registered under REACH have been identified according to the register of ECHA and are presented in table 15. It should be noted that REACH includes an exemption from registration for active substances in biocidal products, but only if they are specifically included under the scope of the Biocidal Products Directive i.e non-biocidal applications must be registered.

TABLE 15

REGISTERED USES UNDER REACH ACCORDING TO ECHA (ECHA, 2014)

CAS No	Substance	Identified use
7681-52-9	Sodium hypochlorite	Manufacturing
		Formulation
		Formulation (mixing) of preparations and/or re-packaging (excluding alloys)
		Industrial use as intermediate
		Industrial use in textile industry
		Industrial use in sewage and cooling or heating water treatment
		Industrial cleaning
		Industrial use in pulp and paper
		Industrial and professional cleaning
		Industrial use: bleaching agent for textiles and bleaching agent for pulp and paper
		Intermediate in the synthesis of chemicals
		Professional cleaning use
		Professional use of detergents
		Consumer use: washing and cleaning
7778-54-3	Calcium hypochlorite	Consumer use: bleaching by dipping and pouring
		Importation and storage
		Use in industrial closed process

Sodium hypochlorite is used in industries as cleaner and bleaching agent, intermediate in chemical synthesis and disinfectant. The substance is used also for professional cleaning and included in consumer products for washing and bleaching. Calcium hypochlorite in ECHA is registered for its use at industrial sites in importation/storage and in industrial closed processes.

At present, the use of the substances for most of their potential product types are under evaluation by ECHA under the context of the Biocidal Products Regulation.

3.3.2 Registered use in Denmark

The Danish Product Register is placed in the Danish Working Environment Authority under the Ministry of Employment. The Register gathers and store information on chemical products placed in the Danish market.

Table 16 shows data from the Danish Product Register and summarizes the number of articles, companies, total and exported amount for both hypochlorites according to the registered technical function. It has to be noted that only dangerous products that are produced and imported in volumes above 100 kg/yr and intended for professional use require registration in the Danish

Product Register. Consumer products are not included in table 16 unless they are commercialised for both professional and consumer use.

TABLE 16

INFORMATION FROM THE DANISH PRODUCT REGISTER REGARDING TECHNICAL FUNCTION, NUMBER OF COMPANIES AND ARTICLES, TOTAL AND EXPORTED AMOUNT IN 2013 (DATA EXTRACTED 25-04-2014)

CAS No	Substance	Technical function	No. articles	No. companies	Total Amount (T)	Exported Amount (T)
7681-52-9	Sodium hypochlorite	Biocide	68	33	875.031	163.203
		Bleaching agent	10	8	91.487	0.202
		Cleaner	130	47	1.013.064	286.809
7778-54-3	Calcium hypochlorite	Biocide (mainly in swimming pools)	18	9	15.037.362	10.007.121

The table puts into evidence the relevant use of both substances as biocide in Denmark. The data also indicates the broad use of sodium hypochlorite as cleaner, as more than 130 articles and the highest total associated amount for this substance is registered under this technical function.

The total volume of sodium hypochlorite registered was 1372727 tonnes from which 307102 are included as exported. Professional use in the Danish market can be then calculated as the difference between the total and exported amount and indicates a national use of 1065625 tonnes. In the case of calcium hypochlorite the registered import and exported tonnage are 15037362 and 10007121 respectively. These data indicate that 5030241 tonnes where intended for use in Denmark.

3.4 Historical trends in use

The amount of sodium and calcium hypochlorite used and the number of preparations containing these substances in Sweden, Denmark, Finland and Norway in the period 1999-2011 have been assessed and data are presented in the table 17 and in figures 7 and 8.

As it may be observed, Sweden is the country with greatest sodium hypochlorite consumption, with a maximum of 6593 tonnes reported in 2011. Denmark exhibited a great increase in consumption in 2004 and 2005 followed by a general decreasing trend that in 2011 concluded in the lowest amount used of the four Scandinavian countries (only 1098.37 tonnes). Noteworthy also is the consumption profile of Finland, that in 2002 got its maximum consumption (4389.41 tonnes) followed by a sudden decay to reach its minimum in 2003 (1403.03 tonnes). Norway has exhibited a relatively stable consumption in the range about 2550-3550 tonnes.

In terms of number of preparations where sodium hypochlorite is present, a different profile compared to the consumed amount in tonnes is observed. In this case Denmark shows in general terms the highest presence of this substance in formulations. Only in the years 2004 and 2011 Sweden reported a higher presence in formulations (i.e. all purpose disinfectants, cleaners and bleachers) than Denmark. Noteworthy is also the abrupt decrease observed in Denmark in the years 2004 and 2008. The substance disappeared from 30 and 28 preparations respectively if compared to the previous year.

When calcium hypochlorite consumption is assessed, the most remarkable point is the lowest consumption in tonnes and presence in preparations when compared to sodium hypochlorite. While in sodium hypochlorite the consumption is expressed in terms of thousands of tonnes, calcium hypochlorite is consumed with scale of hundreds (in the case of Sweden and Norway) or even tens or less (in the case of Denmark and Finland). The substance has been consumed with a general increasing trend in the period 1999-2011 in Sweden, taking place the maximum consumption in 2007 with 207 tonnes. From the 4 Scandinavian countries, Denmark and Finland reported the minimum consumption in the assessed period. Remarkable is also the consumption peak of Denmark in 2008, with 65,2 tonnes. Norway consumption in this period oscillated in the range 152-91,2 tonnes.

If the number of preparations in which calcium hypochlorite appears is assessed, a general increasing trend from 2003 is observed for Sweden. It should be stated however that from 2009 the number of preparations where the substance was present has decreased. From the four Scandinavian countries, Sweden has the highest presence of the substance in preparations. In the 2000-2007 period in Denmark, the presence of the substance in formulations was approximately constant (ranging from 4 to 6). In 2008 its presence was almost doubled and in 2011 achieved its maximum with 14 preparations containing calcium hypochlorite.

TABLE 17

TOTAL USE IN TONNES OF SODIUM AND CALCIUM HYPOCHLORITE AND NUMBER OF PRODUCTS IN WHICH THE SUBSTANCES ARE INCLUDED IN THE PERIOD 1999-2013 IN SWEDEN, DENMARK, NORWAY AND FINLAND (SPIN, 2014).

	Sweden				Denmark			
	NaClO		$Ca(ClO)_2$		NaClO		$Ca(ClO)_2$	
Year	**Number**	**Amount**	**Number**	**Amount**	**Number**	**Amount**	**Number**	**Amount**
1999	143	3188	16	107	n.a.	n.a.	n.a.	n.a.
2000	152	5045	15	121	174	3443.2	4	4.1
2001	147	5051	20	135	190	3519	6	10.9
2002	159	5774	19	149	196	3541.85	6	10.9
2003	173	5266	17	159	199	3703.71	6	10.9
2004	173	6057	20	171	169	5460.47	5	9
2005	182	5894	21	174	216	5636.1	6	13
2006	189	6573	24	182	219	3961.59	5	16.67
2007	188	5171	26	207	224	4438.34	5	18.69
2008	194	5734	29	186	196	3775.95	12	65.2
2009	202	6012	32	183	202	2385.61	10	4.22
2010	217	4911	31	194	223	2378.48	12	12.34
2011	243	6593	30	194	211	1098.37	14	17.31

	Norway				Finland			
	NaClO		$Ca(ClO)_2$		NaClO		$Ca(ClO)_2$	
Year	**Number**	**Amount**	**Number**	**Amount**	**Number**	**Amount**	**Number**	**Amount**
1999	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2000	139	3402.77	6	152.22	127	n.a.	8	n.a.
2001	149	3551.07	8	149.15	134	3528.07	8	6.36
2002	143	3081.13	9	94.5	137	4389.41	8	0.91
2003	130	3521.75	9	108.72	137	1403.3	7	13.2
2004	143	2676.36	10	98.98	156	2755.9	6	3
2005	145	2670.58	12	92.32	151	3298.4	8	21.6
2006	149	2896.01	12	113.73	171	3764	8	21.5
2007	147	2705.56	11	108.45	179	3568.8	9	13.1
2008	156	2528.12	10	91.2	171	3861	10	13.3
2009	167	3116.74	17	98.4	180	4275.8	9	6.2
2010	177	2920.5	19	130.1	177	3700.9	8	10.5
2011	177	2446.58	19	108.41	184	3165	12	16.2

n.a. : Data not available

FIGURE 7

TOTAL USE IN TONNES (A) AND NUMBER OF PRODUCTS (B) CONTAINING SODIUM HYPOCHLORITE IN DENMARK, SWEDEN, NORWAY AND FINLAND IN THE PERIOD 1999-2011. (DATA RETRIEVED FROM SPIN DATABASE, CONSULTED JULY 2014).

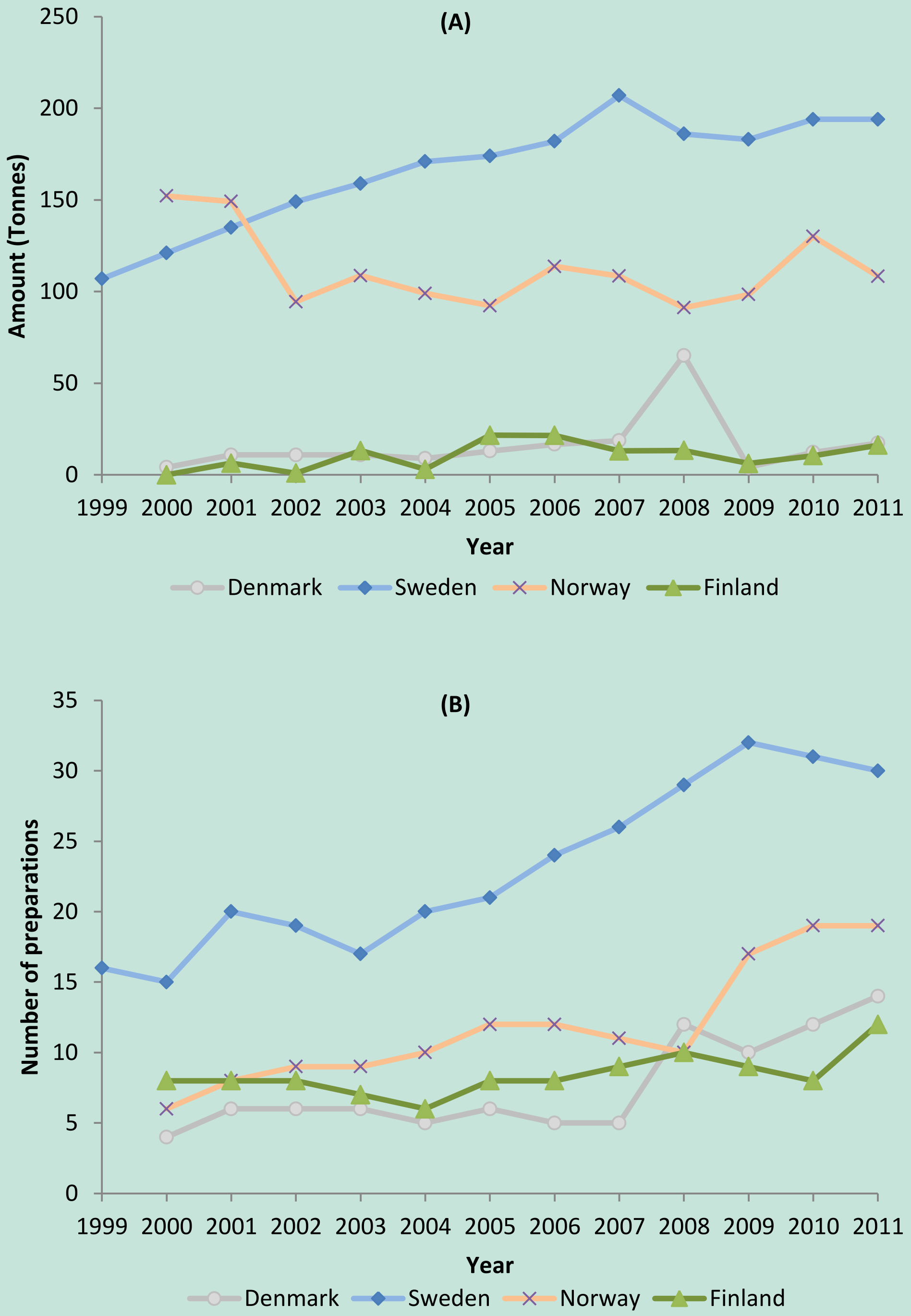


FIGURE 8

TOTAL USE IN TONNES (A) AND NUMBER OF PRODUCTS (B) CONTAINING CALCIUM HYPOCHLORITE IN DENMARK, SWEDEN, NORWAY AND FINLAND IN THE PERIOD 1999-2011. (DATA RETRIEVED FROM SPIN DATABASE, CONSULTED JULY 2014)

The total use of sodium hypochlorite in tonnes and the presence in products according to the use of the substance in Denmark in the period 2000-2011 have been assessed. The results are presented in table 18 and graphically summarized in figure 9. The same data extraction was carried out for calcium hypochlorite and the results are included in table 19. However, results for this substance are only available in the period 2005-2011. It should be mentioned that the SPIN database is only for professional use, based on reports from companies that import or produce more than 100 kg/year.

Data extracted from the SPIN database (table 18 and figure 9) point out that the main use of sodium hypochlorite in Denmark (in mass terms) is as non-agricultural pesticide and preservative followed by the use as cleaning/washing agent. The non-agricultural pesticide and preservative fraction covers the use of sodium hypochlorite as disinfection reagent in water treatment. The use of sodium hypochlorite as bleaching agent is much less compared to the other two and its consumption as laboratory chemical is almost negligible.

In terms of presence in preparations it is remarkable the highest presence in formulations for cleaning and washing followed by the use as non-agricultural pesticide and preservative. It is worth noting that despite a general decreasing trend in the amount used as cleaner and also as pesticide occurs in the period 2008-2011, the number of preparations registered under these uses remains relatively constant. A possible explanation for this disparity could be the addition of sodium hypochlorite in formulations in lower concentration.

TABLE 18

TOTAL USE IN TONNES AND NUMBER OF PRODUCTS IN CATEGORIES CONTAINING SODIUM HYPOCHLORITE IN DENMARK IN THE PERIOD 2000-2011. (DATA RETRIEVED FROM SPIN DATABASE).

	Bleaching agents		Cleaning/washing agents		Laboratory chemicals		Non-agricultural pesticides and preservatives	
	No prep.	Tonnes	No prep.	Tonnes	No prep.	Tonnes	No prep.	Tonnes
2000	14	334,2	117	2579,8	4	0,4	71	3110,6
2001	14	331	130	2756	4	0,4	78	3112
2002	14	334,2	127	2709,6	6	0,3	76	3198,8
2003	12	334	135	2803,2	6	0,3	71	3269,8
2004	7	513,9	116	4669,9	6	0,9	52	5034,7
2005	7	513,9	127	4766,4	7	0,7	54	5046,3
2006	12	276,3	146	3157,6	6	0	74	3323,5
2007	13	276	145	3163,5	4	0,5	73	3323,1
2008	10	580,2	126	2331,1	4	0,4	61	2758,1
2009	12	500,1	125	1003,4	4	0,4	64	1027,7
2010	13	501	137	976	6	0,3	69	1066
2011	10	88,1	135	564,4	6	0,3	63	432,7

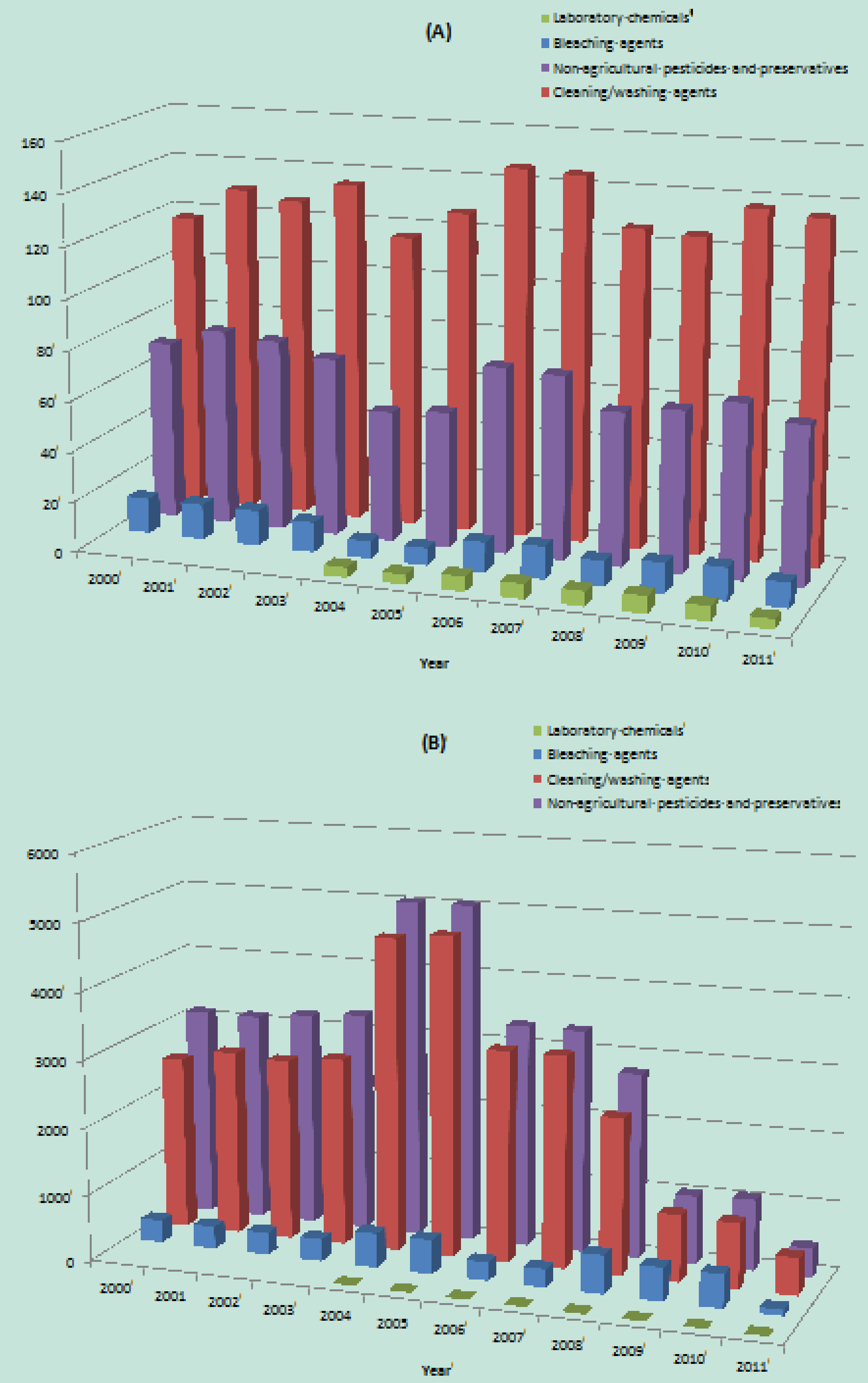


FIGURE 9

TOTAL USE IN TONNES (A) AND NUMBER OF PRODUCTS (B) CONTAINING SODIUM HYPOCHLORITE IN DENMARK IN THE PERIOD 2000-2011 GROUPED IN CATEGORIES (DATA RETRIEVED FROM SPIN DATABASE)

Calcium hypochlorite in Denmark is only registered for its use as non-agricultural pesticide and preservative and its main use (> 90%) is the disinfection of water in private swimming pools (personal communication, Peter W. Knudsen).
The use in tonnes and presence in formulations is much less than the reported for sodium hypochlorite. From 2005 the total use and number of preparations exhibit an overall increasing trend. The huge consumption reported in 2008 is probably a register error, and the actual amount should be about 13 Tonnes, as estimated from the presence of the substance in number of preparations.

TABLE 19

TOTAL USE IN TONNES AND NUMBER OF PRODUCTS IN CATEGORIES CONTAINING CALCIUM HYPOCHLORITE IN DENMARK IN THE PERIOD 2005-2011 (DATA RETRIEVED FROM SPIN DATABASE).

	Non-agricultural pesticides and preservatives	
	No prep.	Tonnes
2005	4	4.0
2006	4	9.2
2007	4	9.2
2008	12	65.2
2009	10	4.2
2010	12	13.0
2011	14	17.3

3.5 Summary and conclusions

The production of sodium and calcium hypochlorites in the European Union takes place mostly in five countries: UK, Italy, Spain, France and Portugal. The substances are mainly produced in the chlor-alkali industrial facilities, where manufacturers obtain chlorine from brine. Denmark does not manufacture any of the surveyed hypochlorites.

In terms of international commerce, the EU has a relevant import flow of both hypochlorites, being the main suppliers China, USA and India. While the EU also acts as supplier of a relevant amount of sodium hypochlorite to these countries, calcium hypochlorite is mainly imported from them.

In the European Union Sodium hypochlorite is used in a very wide range of formulations for household, institutional or industrial applications while calcium hypochlorite is mainly used for swimming pool sanitation. The main uses of sodium hypochlorite in the EU are:

- household in laundry cleaning, bleaching and disinfection
- municipal water and sewage disinfection
- sanitation of water in swimming pools
- textile industry and pulp and paper bleaching
- chemical synthesis

In Denmark, sodium hypochlorite is mainly used as cleaner and bleaching agent. Calcium hypochlorite is used primarily in the disinfection of water in private swimming pools.

In the European Union and in Denmark, the use of sodium hypochlorite is much more extended than the use of calcium hypochlorite. In Denmark, while the sodium salt is present in more than 200 products with different technical functions including biocide, bleaching agent and cleaner, the use of the calcium salt is limited to just 18 preparations with a technical function of biocide and a scope mainly limited to swimming pools.

In terms of historical use, from 2007 Denmark has experienced a decreasing trend in the amount of sodium hypochlorite used. However, the number of products containing this substance has remained relatively stable. The data indicates that the manufacturers are tending to include the substance in formulations in lower concentration as in former years.

In the case of calcium hypochlorite, its use has remained almost constant during the whole assessed period (2000-20111) and so its presence in number of formulations. However, from 2007, a general increasing trend has been observed in the Danish market. This increase is not related to a higher consumption of the substance in the same period. This may indicate that the manufacturers are including calcium hypochlorite in lower concentration in their formulations.

4. Waste management

4.1 Waste from manufacture and use of sodium and calcium hypochlorite

The production of sodium hypochlorite takes place by the reaction of chlorine with sodium hydroxide solution in controlled reactors and this production is a waste water free process. However, during occasional cleaning operations small spills of waste water (2-3 L per tonne of sodium hypochlorite solution) may take place. This waste water is treated before its discharge. Sometimes off-gas from the production of sodium hypochlorite passes through a scrubbing system. All washing solutions are discharged to waste water treatment plants and the final effluent contains mainly chloride. The final product is filled into drums or into bulk containers (EU Risk assessment report, 2007).

Calcium hypochlorite is mainly produced by the sodium method, previously described. The method is based in the conversion of the reaction product from the calcium method by addition of NaClO. Usually, the production of this substance is conducted in the same factory as sodium hypochlorite production and both processes are similar. The environmental releases from the production in the industrial sites are minimised by treatment of the effluent that includes operations such as settlement, pH adjustment and chlorine removal following the quality of the effluent with a proper analytical control (OECD SIDS, 2004).

Volatilization of hypochlorite from solutions or from tablets (in form of calcium salts) can be disregarded. No significant potential for dispersion in the air exists. Only chlorine gas or chloramines might be released when hypochlorite is in contact with acids or nitrogen compounds. Soils can be exposed to hypochlorite solutions by accidental spills. However, the strong reactivity of the hypochlorite moiety through organic matter and low stability when exposed to radiation leads to its almost immediate disappearing and transformation into harmless chloride anion.

4.2 Waste products from the use in mixtures

According to the characteristics of use of both hypochlorites, the main vehicle for its environmental release is the waste water from formulations and use of products containing these substances. As hypochlorites are mainly used in cleaning products and for water treatment, the final sink of the substance is the urban wastewater treatment plant. Despite the strong antimicrobial potential of hypochlorite anion, there is little need for concern about possible inhibition effects on the biological sewage treatment with the pattern of use of the hypochlorite. The hypochlorite anion does not provide organic load to the effluent that could affect the BOD or COD. In fact, this anion positively contributes to decrease the COD by oxidising the organic matter. The oxidative reactions in which the hypochlorite takes place provoke the disappearance of the anion even before reaching the urban wastewater treatment plant.

4.3 Release of sodium and calcium hypochlorite from waste disposal

As previously stated, the main source of hypochlorites to the environment is waste water derived from the use of formulations containing sodium or calcium hypochlorite. Once released to the environment the hypochlorite anion gets involved in redox reactions that lead to the formation of innocuous chloride anion.

The potential pollution of soils due to accidental discharge of chlorinated water will not be permanent, as the high content in organic matter and the low photostability of this anion provides reductive potential to completely remove hypochlorite after a short contact time.

Accumulation in soils and sediments is not expected due to the high reactivity of the hypochlorite anion through organic matter and to its low photostability.

The interaction of potentially polluted packaging with soils or water in Denmark can be disregarded, since just an almost negligible percentage of wastes –about 3 %- are delivered to landfill. (http://mst.dk/media/mst/Attachments/Ressourcestrategi_DK_web.pdf).

4.4 Summary and conclusions

In the EU and in Denmark, potential waste is generated from the use of the substance in disinfection of swimming pools, cleaning and bleaching products. As manufacture of sodium or calcium hypochlorites does not take place in Danish industrial facilities, the potential generation of industrial wastes can be disregarded. The use of both substances is, in general, based in previous water dispersion for both household and professional use. The final sink for the substances in any of their uses is the sewer system. Due to the high reactivity of the substance as oxidizer and its low photostability, the potential wastes of hypochlorite undergo rapid reactions that destroy the anion.

The release of hypochlorites from waste disposal does not pose any risk. In Denmark potentially polluted packaging is not expected to reach any landfill and in general the substances do not have any accumulation potential in soils.

5. Environmental effects and exposure

5.1 Environmental hazard

Hypochlorite anion is harmful to the aquatic environment but exposure rarely occurs. Household waste flushed down the drain or toilet is destroyed by redox reactions that lead to formation of chloride anion. Professional or industrial waste generally enters into waste water treatment plants, where the substance reacts and is removed before reaching the environment. Weak solutions are sometimes released directly into the environment from industrial sites such as power plants, but these levels have been assessed as being safe and not causing damage to the wider environment, due to the rapid reaction of the substance with organic matter.

5.1.1 Classification

As presented in section 2.3.1, sodium and calcium hypochlorite have harmonised classification according to the CLP Regulation, No 1272/2008). Both substances are classified as Aquatic Acute 1 and very toxic to aquatic life.

5.1.2 Toxicity in the aquatic environment

The aquatic effect of hypochlorite in the environment, where pH value is supposed to range from 6 to 8, is the same for both sodium and calcium salts. The biologically significant chemical species are hypochlorous acid or hypochlorite ion. According to the hypochlorite decay model developed by Vandepitte and Schowanek for the European Risk Assessment Report of sodium hypochlorite, it can be concluded that releases of hypochlorite to the aquatic compartment are generally low due to the rapid decay of hypochlorite anion (EU Risk Assessment Report, hypochlorite, 2007). However, punctual discharges may take place under certain local circumstances for some sewage treatment uses if an accidental spill occurs. These potential spills are limited to solutions containing the substances and might take place from pipes or hoses, bulk storage tank or valves.

Acute toxicity

Data regarding ecotoxicological acute toxicity has been retrieved from the ECHA database on registered substances. The database contains a broad volume of assays carried out with different living systems exposed to sodium hypochlorite. However and despite calcium hypochlorite is registered under REACH, no data regarding its ecotoxicology characteristics was found. As previously stated in this report, the toxicity of the substances is attributed to the hypochlorite anion itself and the role of the counterion is then neglected.

The data presented in the tables 20, 21, 22, 23 and 24 regarding ecotoxicity have been gathered from the ECHA database and filtered by their reliability factor as an indication of their quality According to the Guidance on Information Requirements and Chemical Safety Assessment (ECHA, 2011). Only data with Reliability factor (Rf) 1 and 2, indicating “reliable without restrictions” and “reliable with restrictions” respectively, are included in the next tables. EC_{50}, LC_{50}, IC_{50} and NOEC, concentrations are expressed in mg/L.

TABLE 20

SUMMARY OR ECOTOXICOLOGICAL DATA FOR HYPOCHLORITE: FISH. (ECHA)

			Endpoint		
Species	**Media**	**Duration**	**LC50**	**NOEC**	**Rf**
Coho salmon	Saltwater (flow-through)	96 h	0.032		2
Pink salmon			> 0.023 < 0.052		
Chinook salmon			>0.038 <0.065		
Pacific herring			0.065		
Shiner perch			0.071		
English sole			0.073		
Pacific sand lance			0.082		
Threespine stickleback			0.167		
Salmo gairdneri (*Oncorhynchus mykiss*)		24-72h	1.65-2.87		
Ocean spot (*Leiostomus xanthurus*)	Saltwater (flow-through)	96 h	0,09	0,04	
		24 h	0,14		
Salmo gairdneri (*Oncorhynchus mykiss*)	Freshwater (static)	96 h	0,2		
Bluegill (*Lepomis macrochirus*)			0,58		

TABLE 21

SUMMARY OR ECOTOXICOLOGICAL DATA FOR HYPOCHLORITE: INVERTEBRATES. (ECHA)

			Endpoint			
Species	**Media**	**Duration**	**EC50**	**LC50**	**NOEC**	**Rf**
Daphnia magna		48 h	0,04			2
Pandalus goniurus		96 h	0,063-0,119			
Neomysis sp.		96 h	0.15 - 0.175			
Physa integra (freshwater pouch snail)	Lake water	48 h		2 (as Cl_2)		
Amphipod (*Anonyx sp)*		96	0,118-0,173			
Goniobasis livescens (river snail)		48 h		10,4		
Crangon sp.		96 h	0,118-0,151			
Amphipod (*Pontogeneia sp*)		96 h	0,583-0,864			
Lymnaea emarginata angulata (freshwater pond snail)		48 h		21,8 (as Cl_2)		
Shore crab		96	1,24-1,53			
Daphnia magna	Freshwater (flow-through)	48 h	0,141		0,05	1
Ceriodaphnia dubia			0,035		0,025	

TABLE 22

SUMMARY OR ECOTOXICOLOGICAL DATA FOR HYPOCHLORITE: ALGAE. (ECHA)

				Endpoint		
Species	**Media**	**Duration**	**EC50**	**IC50**	**NOEC**	**Rf**
Protozoa (multispecies microcosm – measuring species richness)	Flow-through	7 d			0,0021	2
				0,023		

TABLE 23

SUMMARY OR ECOTOXICOLOGICAL DATA FOR HYPOCHLORITE: AQUATIC PLANTS OTHER THAN ALGAE. (ECHA)

			Endpoint	
Species	**Media**	**Duration**	**NOEC**	**Rf**
Myriophyllum spicatum	Freshwater (flow-through)	96 h	0,02	2
			0,05	
			0,05	
			0,02	
			ca 0,1- ca 0,4	

TABLE 24

SUMMARY OR ECOTOXICOLOGICAL DATA FOR HYPOCHLORITE: MICROORGANISMS. (ECHA)

			Endpoint		
Species	**Media**	**Duration**	**EC50**	**NOEC**	**Rf**
Bacteria (activated sludge)	Freshwater (static)	3 h	563	300	1
			> 3		2

*Notes and definitions.

- IC50: Half maximal inhibitory concentration. Concentration in an environmental medium expected inhibiting 50% of a specific biological or biochemical function.
- EC50: Median effective concentration. Concentration in an environmental medium expected to produce a certain effect in 50% of test organisms in a given population.
- LC50: Median lethal concentration. Concentration in an environmental medium expected to produce lethality in 50% of test organisms in a given population.
- NOEC: No observed effect level. Highest concentration of the substance which has no effect on the exposed organisms.
- LOEC: Lowest observed effect level. Lowest concentration of the substance which has effect on the exposed organisms.

The acute toxicity is a very relevant parameter for the assessment of risk for acute effects and allows establishing the environmental classification of sodium and calcium hypochlorites.

Data regarding acute toxicity clearly indicates that the most sensitive species are salmonids. However, it is not clear if pink, coho or chinook salmon, as the LC50 reported for all these species is very similar (from 0.02 to about 0.06 mg/L). From the fishes surveyed, the most hypochlorite-resistant is Salmo gairdneri (*Oncorhynchus mykiss*), with an averaged LC50 about 2.25 mg/L.

In invertebrates, the most sensitive species is *Ceriodaphnia dubi,* with an EC50 of 0.035 mg/L. The most resistant is the shore crab, with an EC50 about 1.4 mg/L.

From the different assessed groups, it is worth noting the strong resistance of bacteria (derived from activated sludge) to hypochlorites. The reported value of EC50 for this kind of bacterial community is about 563 mg/L. Remarkable is also the high sensitiveness of algae to hypochlorites: a multispecies mesocosm of protozoa has a NOEC of 0.0021 mg/L (2.1 µg/L).

Chronic toxicity

Chronic toxicity of hypochlorite

The next tables summarize the prolonged toxicity to fish (table 25)and invertebrates (table 26). In a 133 days exposure, no relationship between treatment concentration and the growth and survival of bluegill (*Lepomis macrochirus*) and rainbow trout (*Salmo gairdneri*) was observed. There was, however, a consistent pattern of reduced growth of channel catfish (*Ictalurus punctatus*) with increasing total residual chlorine concentrations. The mean final weights of catfish at the highest TRC exposure were 64% (of control). In a 147-day study with fathead minnows (*Pimephales promelas*). For long term toxicity, the lowest NOEC is 0,005 mg/L (5 µg/L), which was determined in a non-standard study with juvenile *Ictalurus punctatus*. Chronic toxicity of chlorinated water to *Brevoortia tyrannus* in a 19 day study was evaluated. Up to the maximal concentration of 0.062 mg/L no differences in survival between chlorine and reference treatments was found (OECD SIDS, 2004).

TABLE 25

SUMMARY OF PROLONGED TOXICITY OF HYPOCHLORITE TO FISH (OECD SIDS, 2004)

Species	Duration	Type of study	Endpoint	C (mg/L)
Freshwater				
Lepomis macrochirus (juvenile)	133 d	Flow through with analysis	NOEC (growth survival)	0,183
Salmo gairdneri (juvenile)	133 d	Flow through with analysis	NOEC (growth survival)	0,207
Ictalurus punctatus (juvenile)	133 d	Flow through with analysis	NOEC (growth survival)	0,005
Pimephales promelas	147 d	Flow through with analysis	NOEC (growth survival)	0,016
Saltwater				
Brevoortia tyrannus (juvenile, estuarine)	19 d	Flow through with analysis	NOEC (survival)	0,062
Leistomus (juvenile, estuarine)	20 d	Flow through with analysis	NOEC (survival)	0,062

Chronic toxicity to invertebrates has been also assessed. Data derived from a a continuous flow system for 56 days at 11°C and for 28 days reported 55% mortality at the nominal hypochlorite application of 0.5 mg Cl_2/l (i.e. 0.08 mg FRC/L) after 56 days. Investigations also in a flow-through study with *Crassostrea virginica* and *Rangia cuneata* indictated that the survival of juvenile oysters and clams was not affected after 15 days exposures at levels up to 62 µg/l. However a sublethal effect was observed (shell deposition) in oysters going from 3.5 mm in the control, which was dechlorinated (30 minutes after chlorination), to 2.3 mm when oysters were exposed to 62 µg/l. No sublethal effect was observed in clams (OECD SIDS, 2004).

TABLE 26

SUMMARY OF CHRONIC TOXICITY OF HYPOCHLORITE TO INVERTEBRATE (OECD SIDS, 2004)

Species	Duration	Type of study	Endpoint	C (mg/L)
Freshwater				
Dreissena polymorpha (zebra mussel)	28 d, 56 d	Flow through with analysis	LC50 (56d) LC50 (28d)	0.5 (nominal) = 0.08 (measured) 0.285 (free Cl, calc.)
Saltwater				
Crassostrea virginica (oyster)	15 d	Flow through with analysis	NOEC (survival)	0.062
Rangia cuneata (clam)	15 d	Flow through with analysis	NOEC (survival) NOEC (shell deposition)	0.062 0.062

3.2.1.5.3 PNEC derivation

Taking into account the mode of action of hypochlorite, that is a strong oxidizer anion, the report of the EU regarding sodium hypochlorite (2007) recommends pooling short and long term toxicity data for fresh and saltwater organisms. Doing so, a set of three valid NOEC values was obtained, one for each trophic level: fish, molluscs and algae (EU Risk Assessment Report, 2007). The results for fresh and saltwater are presented next.

Freshwater

For the derivation of the freshwater PNEC a factor of 10 applied to the lowest of three NOECs across different trophic levels is considered sufficient “only if the species tested can be considered to represent one of the more sensitive groups”. From the available NOEC dataset, the most sensitive group is algae which has a NOEC (7d NOEC =2.1 µgFAC/l) very close to the acutely toxic concentration to Daphnia (24h LC50 = 5 µgFAC/l). In addition for the primary consumer trophic level, long-term data are available only for bivalve molluscs, which play an important ecological role but are not among the most sensitive species. In fact, long-term mortality data for freshwater clams and a NOEC value for marine molluscs indicate that this group is markedly less sensitive than crustaceans (Daphnia). The same can be observed by comparing short-term toxicity data for the two groups. In a mesocosm study, zooplankton was affected at a concentration much lower than that necessary to reduce algae population. In conclusion it appears that the most sensitive group, i.e. crustacean (Daphnia) is not represented in the dataset.

Based on these considerations a factor of 10 for the derivation of the PNEC is judged not sufficiently protective and it was suggested to apply a factor of 50 to the lowest NOEC: PNEC = 3 µgTRC/l/50 = 0.06 µg TRC/l corresponding to 2.1 µgFAC/l/50 = 0.04 µgFAC/l (EU Risk Assessment Report, 2007.

Saltwater

Pooling the data from fresh and salt water the dataset consists of two long-term NOECs representing two trophic levels (e.g. algae and fish) plus a NOEC from an additional marine taxonomic group (e.g. molluscs). A factor of 50 is applied to the lowest figure and hence, PNECsaltwater = 3 µgTRC/l/50 = 0.06 µgTRC/l corresponding to 2.1 µgFAC/l/50 = 0.04 µgFAC/l (EU Risk Assessment Report, 2007).

5.1.3 Toxicity in the terrestrial environment

The available studies regarding toxicity of hypochlorite anion in the terrestrial environment demonstrate that the possible exposure routes of soils to this substance are via contaminated sludge or via direct application of chlorinated water. The direct contact of hypochlorite concentrated solutions is very unlikely. Furthermore, the model developed by Vandepitte and Schowanek and included in the EU Risk Assessment Report regarding sodium hypochlorite (2007) puts into evidence that HClO concentrations available in domestic discharges are completely removed in the sewer system before entering the activated sludge of the urban wastewater treatment plant. This fact, in addition to the low photostability and high solubility of hypochlorite allows disregarding the sorption onto activated sludge. Therefore, there is no evidence that hypochlorite has the potential to contaminate activated sludge. Consequently, contamination of soils due to dumping of with hypochlorite polluted sludge can be excluded.

Contamination of soils due to direct application of chlorinated water will not be of permanent origin since the high content of organic matter provides reductive potential enough for the complete removal of hypochlorite in very short contact time.

5.2 Environmental fate and behaviour

The route of environmental release of sodium hypochlorite from use in cleaning products is down-the-drain, with the product and/or its by-products being treated by on-site or municipal waste treatment systems.

Hypochlorite is reduced to chloride (Cl^-), with the potential for introduction of low levels of chlorate. The chlorate impurity is further reduced to chloride in the environment. The reduction of chlorate to chloride is enhanced in the presence of ferrous iron (Fe^{2+}), generally present in waste treatment plants, and when Fe^{2+} is in excess, total reduction may be achieved in minutes.

5.2.1 Photodegradation

In clean aqueous media hypochlorite anion and hypochlorous acid concentration rapidly decays due to reduction and photolysis. Taylor (1993) reported a half-life of less than 2 hours for both, hypochlorous acid and the hypochlorite ion.

5.2.2 Water stability

In water, chlorine is transformed to free available chlorine (gaseous chlorine), hypochlorous acid and hypochlorite ions, whose relative amounts depend on the pH and other physicochemical properties of the water. At environmental pH, only hypochlorous acid and hypochlorite will be present. In the water environment, photolysis, bio and chemical degradation are the main processes contributing to the fast disappearing of hypochlorite anion.

As stated in the EU Risk Assessment Report about sodium hypochlorite (2007), in natural waters containing nitrogen and organic compounds, the decay rate of hypochlorite moieties is higher and the chlorine present is likely to be a mixture of free available chlorine and chloramines. The equilibrium concentration of these products is also function of salinity. Since sea water contains a bromine concentration about 60 mg/kg, bromination rather than chlorination may predominate as salinity increases (Scott et al., 1980).

5.2.3 PBT and vPvB assessment

The ECHA database was consulted to explore the potential classification of sodium and calcium hypochlorites as PBT or vPvB. The general conclusion derived from this evaluation was that based on the high reactivity of hypochlorite anion with reducing compounds and its low photostability the anion is not considered persistent.

Regarding the bioaccumulation assessment, the relevant ECHA studies states that due to the inorganic and polar nature of the substance, bioaccumulation criteria based on lipophilic distribution do not apply. In this point also, the highly reactive nature of hypochlorites justify that the substance does not bioaccumulate.

5.2.4 Treatability in wastewater treatment plants

Sodium hypochlorite itself will not reach the environment except through misuse or accidental spills when moving or transferring hypochlorite solutions. The oxidative reactions in which the hypochlorite takes place provoke its disappearance even before entering the urban wastewater treatment plant.

The potential chlorinated by-products formed during use of hypochlorite-containing products have been shown to be biodegradable and effectively treated at activated sludge plants. The small portion of by-products not removed by wastewater treatment does not increase the toxicity of treated wastewater and the by-products are not expected to bioaccumulate or persist in the environment.

Thus, use of hypochlorite in households that are connected to waste water treatment is not likely to adversely impact the environment. In sewage, the decay of hypochlorous acid is very rapid, with nearly all the chlorine present being as chloramines (EU Risk Assessment Report, Hypochlorite, 2007).

5.3 Environmental exposure and impact

Environmental exposure may occur through the production and uses of sodium hypochlorite. Due to its low stability and highly reactive nature of hypochlorites it will disappear very rapidly when entering the environment. A regional background concentration of hypochlorite cannot then exist and therefore a regional exposure scenario is not realistic (EU Risk Assessment Report, hypochlorite, 2007). According to this, any potential impact of hypochlorite will be restricted to local conditions. The actual local impact of hypochlorite is strongly dependent on the specific conditions for each application. Therefore, the environmental exposure will be further explored according to their sources of release.

5.3.1 Sources of release

Production facilities

Both hypochlorites are produced in chlor-alkali industrial facilities. According to the risk assessment report from the European Union regarding sodium hypochlorite (2007), the emissions of hypochlorite to the environment from the production processes are minor. The available chlorine in effluent is measured as TRC (Total Residual Chlorine), but it cannot be distinguished to what extent this TRC value in the final effluent is related to hypochlorite or to other compounds with strong oxidative properties. The final production streams of the industrial facilities are usually combined with some other effluents that may include also sewage. Measurements from production sites have pointed that their discharges still contain a measurable Chemical Oxygen Demand (COD) and no available chlorine. The observation indicates that chlorine exerts its strong oxidizer properties and disappears by its reaction with probably organic substances with reductive potential. The fact that no chlorine or related oxidative species are detected indicates that they are the limiting reagent in the discharge effluent.

Household use

Sodium hypochlorite has a long history of use in the domestic environment for both, bleaching of textiles, cleaning as well as disinfection of surfaces in such places as kitchen and bathroom surfaces, in the toilet and wherever hygiene is important. In many European countries >60% of the usage is for cleaning/disinfecting hard surfaces (OSPAR, 1999).

In formulated bleach solutions there is a small conversion of hypochlorite to chlorate and chloride: 10 to 20% hypochlorite is broken down in domestic products after storage for 1 year at 20°C.

In use/sewage/environment where organic and nitrogenous materials are present, sodium hypochlorite acts as a highly reactive oxidizing agent. It reacts rapidly with organic matter and most (≈ 99%) of the available chlorine is converted to inorganic chloride (Jolley and Carpenter, 1975). If nitrogen-containing compounds are present chloramines will be formed, the specific species formed depends upon the conditions. A minor but relevant reaction that takes place when the substance is used in households is the chlorination of organic matter. It has been stablished by Schowanek et al. (1996) that in domestic uses of hypochlorite solutions, only about 1.5% of the initial available chlorine is incorporated into Organohalogen By-Products (OBPs).

Swimming pool

Water treatment is needed to obtain and maintain acceptable chemical and microbiological quality in swimming pools. In Europe, four products are mainly used to achieve these goals: sodium and calcium hypochlorites, chloroisocyanuric salts and chlorine gas. These four products finally are a source of chlorine that provides a permanent concentration of hypochlorous acid (HClO) in the water. As stated in previous sections, this substance is the main responsible of the microbiological disinfection as its neutral charge and small size allows permeating through the membrane of the cell and provokes its dead by changes in the internal redox potentials.

Water may be discharged outside the swimming pool when the filters are cleaned and in some countries it is also compulsory to completely empty the pool 2 times/year. This water is mainly discharged into the sewer system. This procedure regarding emptiying of swimming pools does not take place in Denmark (personal communication with Peter W. Knudsen).

The main regulations are related to the minimum content of FAC (free available chlorine) in the swimming pool, which is always around 0.4 mg/l, and the pH which has to be in a range of 6.5 to 8.5. The only potential contact with soil is for open swimming pools where a small quantity of water could overflow onto the sides of the pool (EU Risk Assessment Report, Hypochlorite, 2007).

Sewage treatment

According to the European Union report addressing sodium hypochlorite (2007), hypochlorite solutions are used for disinfection of sewage waters. Despite useful in some wastewater treatment schemes, it should be noted that this is not a usual practice in Denmark (personal communication, advisory group).

According to the stage in which the substance is introduced in the stream, it can be distinguished between prechlorination and postchlorination if the chlorination occurs before or after the wastewater treatment plant respectively.

Prechlorination

The chlorination of the inlet stream to waste water treatment plants has the aim of preventing sludge from bulking. When undesirable filamentous organisms or protozoans become abundant, activated sludge does not settle properly and it starts bulking. This process reduces the performance of the plant and produces turbid effluent. Addition of hypochlorite to the sewage eliminates to a certain extent the filamentous organisms which are primarily responsible for bulk formation and thus provides better sludge settling characteristics. The chlorination also reduces the number of protozoans, which are predators of the effective sewage treatment bacteria, and that if present in excess provoke a decrease in the performance of the treatment plant. This process, however, is not very extended and then is only done on a need basis. The hypochlorite added in any prechlorination stage will be quickly removed during the conventional treatment process and is not expected to be present in the discharge effluent, so should not reach the receiving surface water (EU Risk Assessment Report, Hypochlorite, 2007).

Postchlorination

Some wastewater treatment plants located near the sea include postchlorination steps as a continuous process included in their operation schemes. The aim of the postchlorination is to protect the shellfish farms and recreational zones from bacterial contamination by lowering the total coliforms below 1000 CFU/100 ml. It may also contribute to reduce the amount of organic matter in the effluent and can be used to reduce malodour (EU Risk Assessment Report, sodium hypochlorite, 2007)

Postchlorination processes used for disinfection of wastewater require a chlorine dose of 5 - 40 mg Cl_2/l and for this purpose both, hypochlorite and chlorine are used. Adapting the chlorine dose to the composition of the effluent allows minimizing the discharge of chlorine oxidizing species to the environment. Free available chlorine (FAC) will undergo a rapid reaction with reaction partners (carbon, reduced metals amines, etc.) and transform all hypochlorite to combined available chlorine (CAC). In general no hypochlorite can be measured after the treatment.

The CAC consists mainly of chloramines whose nature depends on the pH and on the ratio of hypochlorite to ammonium. These substances are only present in low concentration and no relevant risks have been identified when water is discharged after a postchlorination process (EU Risk Assessment Report, sodium hypochlorite, 2007).

Textiles

Hypochlorite for textile finishing has been very widely used during the last two centuries. Nowadays, the use of hypochlorite in textile processing in Europe is for the preshrinking of wool. Hypochlorite has been superceeded by other substances in former uses such as stonewashing jeans, whitening of cotton and decolouration of dyed textiles. After its use, the bleaching effluent is submitted to a dechlorination process by using sulphite, so the final discharge stream is free of oxidizing chlorine species (EU Risk Assessment Report, sodium hypochlorite, 2007).

Drinking water

Sodium and calcium hypochlorites are used for water supplies as source of oxidizing chlorine species for primary disinfection of the effluent and included in a low concentration (about 0,1 mg/l) in the distribution system to ensure microbiological disinfection in the whole distribution network (EU Risk Assessment Report, sodium hypochlorite, 2007). The legally permissible quantity of available chlorine in the water is set at values between 0.1-0.5 mg/l in many European countries taking of 0.5 mg/l as a worst case scenario (only applied when bad conditions such as adverse temperature and contamination are occurring).

Despite of general safety of the chlorinated water, it should be noted in views of future regulations the potential of this process to introduce unregulated amounts of by-products in the water. In addition to the formation of the well-known inorganic by-products present in hypochlorites solutions such as chloride and chlorite, recent studies have also pointed out the formation of some others such as bromate, chlorate and perchlorate when hypochlorite solutions are stored (Stanford et al., 2011). The major factors affecting the formation of these substances from hypochlorite containing solutions are the temperature, pH, ionic strength and hypochlorite concentration. As stated in the paper published by Stanford (2011), a careful control of the quality of hypochlorite employed in disinfection of drinking water is important to avoid the contamination with these substances.

Pulp and paper

Sodium hypochlorite solutions where extensively used in large amounts in the past in the pulp and paper industry. Currently, the pulp and paper industry in Europe has dramatically reduced the use of hypochlorite and chlorine from their bleaching processes and replaced chlorine oxidising species by safer and more environmentally-friendly reagents. The use of the hypochlorite and chlorine based bleaching agents in contact with the phenolic derivatives characteristics of the wood pulp gave rise to environmental concerns due to the formation of hazardous by-products such as chlorinated aromatic by-products. Nowadays Europe production of pulp and paper is based on the elemental chlorine free (ECF) process, using ClO_2 as oxidant or totally chlorine free (TCF) using hydrogen peroxide as oxidant.

Nowadays, the use of hypochlorite in this industry is mainly limited to disinfection of the paper machine to avoid microorganism proliferation. The use of hypochlorite as a system cleaner always occurs during a machine shutdown and involves the partial filling of the paper machine system with clean water to which is added a quantity of sodium hypochlorite. The water is circulated vigorously around the system for up to one hour, and is then discharged into the normal effluent treatment processes, prior to subsequent discharge. The concentration of hypochlorite in the system is low, and quantities are determined so that there is near zero residual free hypochlorite at the end of the cleaning process. No significant amounts of residual hypochlorite are expected to reach the environment after this process coupled with the following effluent treatment (EU Risk Assessment Report, 2007).

Cooling water

Hypochlorite is applied as biocide in cooling water systems as biocide to prevent biofouling. Cooling water systems are used in electrical power generation, chemical industry, refineries and base metal industry. Despite some other compounds such as chlorine dioxide and quaternary ammonium compounds might also be used for this purpose, the relatively low cost, effectiveness and easiness of handling and dose of hypochlorites have made of them the preferred group for this application (EU Risk Assessment Report, 2007).

Hypochlorite concentrations in cooling water effluents are expected to be extremely low due to its reactivity and the composition of surface water, both freshwater and saline water. For saline water total residual oxidant values, probably representing a mixture of oxidative substances have been measured of 20 µg/l nearby the discharge point, decreasing to zero after mixing with the receiving water. The amount and nature of oxidative by-products will depend mainly on dosing regime and specific local conditions, which are normally controlled by local permits in compliance with the reference document on BAT (best available techniques) to industrial cooling systems (European Commission 2001). The document states that reporting representative levels of concentrations in surface water of the biocides used for this application is a very difficult task. Quantification of emissions of substances in the discharge of cooling water has been attempted and models have been developed. However, because of site specificity, no generally applicable model can be reported taking account all aspects. Many assumptions have to be made and although they give an indication, discharges could easily be overestimated or underestimated (European Commission, 2001).

It is noticeable that besides the specific chemicals used for treatment of cooling water, by-products originating from the chemicals used can also contribute significantly to the environmental impact on the surface water. When chlorine or bromine is used as an additive, 3-5% of the product reacts to form haloform compounds such as chloroform or bromoform (European Commission 2001).

In the same document of the European Commission it is also reported that in The Netherlands the application of hypochlorite and bromine in cooling water is one of the most important sources of adsorbable organohalogens (AOX) in surface water.

5.3.2 Monitoring data

A broad bibliographic assessment has been carried in an attempt to identify monitoring programs that included hypochlorite in both, the EU and in Denmark (through the National Monitoring and Assessment Programme for the Aquatic and Terrestrial Environment, NOVANA). No data regarding environmental presence of this substance was identified. This lack of interest through the monitoring of hypochlorites in the environment might be based on its special reactivity characteristics. The fast disappearing kinetics of hypochlorite under its general use scenarios (presence of organic matter, traces of metals and light) allows hypothesizing that the substance (hypochlorite anion) does not reach the environment and thus, no further requirement on monitoring is needed.

However, as it will be further discussed in section 6.4, the use of these substances as disinfection of drinking water and swimming pools provokes the formation of undesirable halogenated organic by-products. Despite some reports can be found regarding formation and occurrence of these substances in swimming pools, they are limited to haloamines, halomethanes and haloacetonitrile (Hansen and Andersen, 2012; Borling et al., 2006). Very recent studies have demonstrated that many other compounds such as haloacetic acids, haloacids, halodiacids, iodo-THMs, haloaldehydes, halonitriles, haloketones (HKs), halonitromethanes, bromate, haloamides, haloalcohols and nitrosamines might be formed (Chowdhury et al., 2014). Monitoring of these substances in Danish swimming pools would be relevant as a tool for policy makers and regulators.

5.4 Summary and conclusions

Hypochlorites have EU harmonised classification. They are both classified as Aquatic Acute 1 and very toxic to aquatic life. The toxicity of the substances under normal conditions of use is mainly due to the hypochlorous acid, which is the active biocide substance.

Due to their inorganic and polar nature, bioaccumulation criteria based on liphophilic distribution does not apply. This, in addition to the high reactivity of the hypochlorite anion and hypochlorous acid does not qualify the substances for being classified as PBT or vPvB substances.
The potential exposure of soils to hypochlorites by contact with contaminated sewage sludge can be disregarded, as the high solubility of the hypochlorous acid and its high reactivity leads to its complete disappearing.

The sources of release in Denmark are clearly identified and derive from the household use and the addition as biocide for microbiological control in swimming pools. In this last situation, the environmental emission is not expected to be significant compared to other countries as the swimming pools are not emptied regularly in Denmark.

No data has been identified regarding environmental occurrence of hypochlorites. This lack of interest through the substance is based on its high reactivity. It is worth noting that despite the apparent harmlessness of the substance, recent studies have demonstrated the potential formation of hazardous halogenated by-products. The low concentration in which they are formed and their degradation in wastewater treatment plants indicates that they do not pose an environmental hazard. Nevertheless, the human exposure to these hazardous by-products should be further assessed in scenarios where exposure to them is probable: drinking water and activities in swimming pools.

6. Human health effects

A European Union Risk Assessment Report covering sodium hypochlorite was published in 2007 with Italy as Rapporteur. Information regarding human health effects was retrieved mainly from this source. Regarding calcium hypochlorite, extensive information on human health effects and toxicity was found in the OECD/SIDS Voluntary Testing Program for International High Production Volume Chemicals. The "Screening Information Data Set" (SIDS) program operated under the auspices of the Organization for Economic Cooperation and Development (OECD) is a voluntary cooperative international testing program that began in 1989. The SIDs program focused on developing base level test information on approximately 600 poorly characterized international High Production Volume (HPV) chemicals. The SIDS data are used to "screen" the chemicals and set priorities for further testing or risk assessment/management activities (EPA, 2011).

6.1 Human health hazard

Most of the data for toxicity of hypochlorite by the oral route have their origin in studies performed with sodium hypochlorite or chlorine gas. In biological systems, characterized by pH values in the range of 6-8, the most abundant active chemical species is HClO, in equilibrium with ClO^-. Such available chlorine is readily absorbed via the oral route and distributed into plasma, bone marrow, testis, skin, kidney and lung. Only ca. 50% is excreted mainly with the urine followed by excretion with faeces (OECD SIDS, 2004). Calcium hypochlorite is commercialized as a powder and its main hazard derives from the contact with the solid powder, their aqueous solutions or accidental mixture with acids (that provoke the release of chlorine gas). According to the information presented in section 2.3.1 regarding harmonised classification, they both cause severe skin burns and eye damage and furhermore calcium hypochlorite is harmful if swallowed.

6.1.1 Hazards assessment

Toxicokinetics, metabolism, distribution and excretion

As described in a previous section, hypochlorite in water exists as a mixture of different chlorine species, being the relative distribution of these species mainly pH-dependent. In the biological systems, characterized by pH values close to the neutrality, the most abundant species are HClO and ClO^- in equilibrium.

Studies in Animals

In vivo studies carried out by Abdel-Rahman and Suh (1983) in Sprague-Dawley rats orally administered with different quantities of HClO solution with the radioactive atom ^{36}Cl were able to successfully track the fate and behaviour of the substance in animal tissues. The study demonstrated that ^{36}Cl was readily absorbed and found into the bloodstream: a peak of radioactivity in rat plasma occurred 2 hours after $H^{36}ClO$ administration in fasted rats and 4 hr after administration in non-fasted rats. The ^{36}Cl radioactivity was distributed throughout the major tissues at 96 hr after the ingestion of the marked hypochlorite administration. The higher levels were found in plasma, whole blood, bone marrow, testis, skin, kidney and lung. The lower levels were found in the liver, carcass and fat tissue. $H^{36}ClO$derived radioactivity was not detected in expired air throughout the 96 hr-study. 36.43% ± 5.67 (mean ± standard error.) of the administered dose was excreted through the urinary route, while 14.8% ± 3.7 was recovered in the faeces, giving a poor total recovery of 51.23% ± 1.97.

It has been reported that HClO in inflammation processes is not enzymatically metabolised and its biotransformation occurs by direct reactions with organic compounds or with other chemicals present in the cellular environment, including hydrogen peroxide. The toxicokinetic study showed that chloride ion accounted for >80% ^{36}Cl radioactivity present in rat plasma. When Sprague-Dawley rats were administered HClO at 0, 1, 10 or 100 mg/L daily in drinking water for one year, no significant chloroform concentrations were observed in rat blood at 4, 6, 9 and 12 months (Abdel-Rahman et al., 1984; EU Risk assessment report, 2007).

Endogenous occurrence

Hypochlorous anions are present in the human body, as they are formed by white cells of the blood (neutrophils and monocytes) and act as a powerful antimicrobial agent during inflammation processes.

When the recognition of “non-self” proteins in an invading microorganism triggers the immune response, the enzyme myeloperoxidase located in mammalian neutrophils catalysed hypochlorous acid formation trough the oxidation of chloride ion in combination with hydrogen peroxide (IARC, 1991). The endogenously formed hypochlorous acid plays a key role in the process of phagocytosis through which bacteria are killed. Due to its potent cytotoxic action, hypochlorite is also responsible for neutrophil-mediated tissue damage associated with the inflammatory response. Its high efficiency as antimicrobial agent is associated with the lack of a catalytically active detoxifying mechanism for HClO in both bacteria and mammalian cells.

Although it has been suggested that HClO-induced cytotoxicity can be associated to the degradation of a number of functionally important molecules (Weiss, 1989; Bernofsky, 1991) the primary mechanism of action is still not fully elucidated (EU Risk assessment report, 2007). In inflammation-prone tissues a role for hypochlorous acid is probable cause of oxidative cell damage (Burcham, 1999).

Besides being an oxidant itself, HClO can react with H_2O_2 and superoxide anion to generate other highly reactive oxidizing molecules (singlet oxygen and hydroxyl radical), which very likely contribute to the onset of toxicity. In addition, hypochlorite can react with a number of cellular components, such as amino-acids, thiolic compounds, nucleotides and lipoproteins, forming organochloride species (Weiss, 1989; Bernofsky, 1991; Fleming, 1991; EU Risk assessment report, 2007), some of which endowed with their own toxicity. As well as many N-chloramines, derived from reaction with both nucleotides and amino acids, chlorohydrins of unsatured fatty acids (Winterbourn, 1992) and chlorinated sterols (Hazen et al., 1996 a ,b) have been identified as by-products of *in vitro* reactions of the myeloperoxidase/peroxidase/chloride system. Based on a mean HClO production rate of 3.15 x 10-8 µM/cell-h for the myeloperoxidase catalysed reaction and assuming that about 0.1% of total neutrophils are triggered at any one time, Haas (1994) estimated a production ratio of 16 µM/day HClO from the human immune system. Considering a possible 1-5% yield, the total amount of hypochlorite corresponds to a total generation of organochlorine compounds in the human body in the range of 5.7 to 28 µg/day (equal to 0.16 - 0.8 µM/day) (EU Risk assessment report, 2007).

Acute toxicity

The toxic effects of sodium and calcium hypochlorites are primarily due to the corrosive properties of the hypochlorite anion itself and to the alkalinity of the solutions that contain it. Hypochlorite causes tissue damage by liquefaction necrosis. Fats and proteins are saponified, resulting in deep tissue destruction. Further injury is caused by thrombosis of blood vessels and the extension of the injury increases with hypochlorite concentration and with the pH. Symptoms may be apparent immediately or delayed for a few hours. As described in previous sections, these hypochlorites can release toxic gases when their solutions become acidic or contacted with ammonia. Thus, use to hypochlorite solutions involves risk of exposure to hazardous gases in a misuse scenario.

Irritation and sensitisation

As stated in table 6, both hypochlorites are classified as irritant to the skin according to the regulation EC 1272/2008. Severe damage in the eyes and soft tissues can take place when exposure to these substances or their solutions occurs.

According to the OECD SIDS Initial Assessment Report on calcium hypochlorite, where sensory irritation of chlorine in mice and rats was evaluated, no sensory irritation response appeared at 0.7 ppm (2.1 mg/m^3) (Barrow et al., 1977). The concentration that resulted in a 50 % decrease in respiration rate (RD50) after 60 min exposure was 3.5 ppm (10.5 mg/m^3). For 10-min exposure, the RD50 for mice was 9.3 ppm (27.9 mg/m^3) (Gagnaire et al., 1994). The histological changes caused by the irritation were investigated. In rats and mice, moderate to severe lesions in the respiratory tract after exposure to 9 ppm (27 mg/m^3) chlorine for 6 h/d for 1, 3 and 5 days were reported: mainly in the nasal passage, epithelial necrosis, cellular exfoliation, erosion, ulceration and squamous metaplasia. The changes were noted to associate with widespread loss of respiratory and olfactory cilia. Generally, much of the toxicity seen in repeated inhalation and dermal exposure is irritant in nature. This may have prevented to elevate the dose level enough to show systemic effects (OECD SIDS, 2004).

A recent study carried out in Europe pointed out that people who often use hypochlorite bleach to clean their homes are less likely to have atopic sensitization. The observation was attributed to the reduction of the concentration of allergens. However, the authors pointed out that very frequent use of bleach was associated with more respiratory symptoms (Zock et al., 2009).

Repeated dose toxicity

The table presented next shows representative repeated dose studies. Long-term inhalation studies carried out with chlorine gas in rats and mice demonstrated the appearance of local effects in the respiratory and oropharyngeal tract (Wolf et al., 1995). Testing programs developed in the same animals exposed to sodium hypochlorite demonstrated no systemic effect of chlorine was observed. No specific target organ could be identified, except that a decrease of body weight and body weight gain presumably due to low water intake were observed after oral administration at the highest dose (Furukawa et al., 1980; NTP, 1992).

TABLE 27

EFFECTS OF REPEATED EXPOSURE OF HYPOCHLORITE/CHLORINE IN MAMMALS (OECD SIDS, 2004).

Dose level	Exposure time	Effects of repeated exposure	Reference
0, 0.4, 1.0, 2.5 ppm 1 ppm = 3 mg/m^3	2 years inhalation study in rats 6 h/d, 5 d/week males, 6 h/d, 3 d/week females. In mice 6 h/d, 5 d/week males and females.	Lesions of the nasal passage in males and females; most severe in the anterior nasal cavity. All the group exposed to chlorine showed the change of some significance, NOELs were not deduced in both species.	(Wolf et al. 1995)
0, 70, 140, 275 mg/L chlorine in drinking water. for male rat 0,4.8,7.5,13.9 mg/kg bw day for female rat 0,3.8, 6.9, 13.2mg/kg bw day for female mouse	life-time drinking water study in mice and rats	No clinical findings, alterations in hematologic parameters and biologically significant differences in relative organ weights at 14/15-week and 66-week interim evaluations. No microscopic abnormalities in a comprehensive range of tissues and organs.	(NTP, 1992)

0,8,14,24 mg/kg bw day for male mouse 0,7,14,24mg/kg bw day			
0, 0.05, 0.1 % (males) 0.1, 0.2 % (females) NaClO 0, 13.5 27.7 mg/kg bw day (male) 0,34, 63 mg/kg bw day(female)	2 year drinking water study in rats	Dose-related decrease in body weight gain.	(Hasegawa et al., 1986)
0, 0.025, 0.05, 0.1, 0.2 to 0.4 % NaClO 0, 7, 14, 28, 55 to 118 mg/kg bw day	13 weeks drinking water, study in rats	Decrease in body weight gain was observed in both sexes. No histological changes attributable to the treatment.	(Furukawa et al., 1980)
Sprague-Dawley rats at 0, 25, 100, 175 and 250 mg chlorine/L correspond to 0, 3.5, 12.6, 19.5 and 24.9 mg chlorine/kg bw/day (male) and to 0, 2.1, 7.5, 12.8 and 16.7 mg chlorine/kg bw/day (females)	90-day study, chlorine in drinking water.	The highest dose of chlorine tested (250 mg/L in drinking water, 17–25 mg/kg bw/day) was concluded to be a NOAEL, because no toxic effects were observed in any dose group.	(Daniel et al, 1990; Daniel et al., 1991)
B6C3F1 mice at 0, 12.5, 25, 50, 100 and 200 mg chlorine/L correspond to 0, 2.7, 5.1,	90-day study, chlorine in drinking water.	In mouse non-specific effects (decreased body weight gain, reduced organ weight and lower levels of serum enzymes) were observed, which could be a consequence of the decreased water consumption,	(Daniel et al, 1990; Daniel et al., 1991)
0, 0.4, 1.0, 2.5 ppm 1 ppm = 3 mg/m3	2 years inhalation study in rats 6 h/d, 5 d/week males, 6 h/d, 3 d/week females. In mice 6 h/d, 5 d/week males and females.	Lesions of the nasal passage in males and females; most severe in the anterior nasal cavity. All the group exposed to chlorine showed the change of some significance, NOELs were not deduced in both species.	(Wolf et al. 1995)

Mutagenicity

Chlorine and hypochlorite solutions have been extensively tested for mutagenicity in assays both, *in vivo* and *in vitro*. However, the methodology employed and the number of results presented does not allow getting a clear conclusion. In general terms, the majority of the *in vitro* assays have shown positive responses suggesting that sodium hypochlorite may be mutagenic *in vitro*. Some *in vivo* assays (sperm head abnormalities and micronucleus formation in mice) with sodium hypochlorite have indicated slight positive effects. However, the significance of these positive responses can be questioned as the increases were small and just outside the historical control range. Sodium hypochlorite was clearly negative in another, well-conducted mouse micronucleus assay. Based on the available mutagenicity data, sodium hypochlorite is not considered to be mutagenic *in vivo* (EU Risk Assessment Report, Chlorine, 2007). The most relevant *in vitro* and *in vivo* studies reported in literature are summarized presented next.

***In vitro* studies**

The majority of the *in vitro* assays have shown positive or ambiguous responses. Chromosomal aberrations were analysed in Chinese hamster cells treated for 24 or 48 hours with three different doses of calcium hypochlorite, in the absence of metabolic activation. A positive increase in chromosomal aberrations was observed only in a culture treated with 0.5 µg/ml (6.7 µmol/L = approx. 3.5 µmol/L active chlorine) for 48 hours. All the other reported experimental results were negative (Kawachi et al., 1980; Ishidate et al., 1981; Ishidate et al., 1984). Chinese hamster cells were treated for three hours with 0.5 µg/mL (6.7 µmol/L = approx. 3.5 µmol/L active chlorine) of the agent in the presence of a metabolic activation system with S9 mix from the livers of PCB-treated Wistar rats. A slight increase of chromosomal aberration was observed (Matsuoka et al., 1979).

In human cells, a non-standard embryo fibroblast line (HE2144) was used for the analysis of chromosomal aberrations and sister chromatid exchange (SCE). In these cells no increase of chromosomal aberrations was reported at both 0.0744 µg/mL (10^{-6} mol/L) and 0.1488 µg/mL (2×10^{-6} mol/L). No other information was provided. In the same cell line the agent was tested for the induction of SCE after 40–48 hours treatment. A doubling and a 50% increase of the background level of SCE was produced at the highest (0.1488 µg/mL) and the lowest tested doses (0.0744 µg/mL), respectively (Sasaki et al., 1980).

The data of these studies suggest that chlorine/hypochlorite solutions are mutagenic in these tests. However, the relevance of the available data set is limited due to the chemical property of the test substance that rapidly deteriorates the test systems.

***In vivo* studies**

In a series of assays, sodium hypochlorite has been tested for its ability to induce chromosomal aberrations and micronuclei in bone marrow of CD-1 mice (Meier et al., 1985). In these assays, chlorine at pH 8.5, where hypochlorite predominates, was administered orally at dose levels equivalent to 1.6, 4 and 8 mg/kg/day for 5 days (1 mL of a solution of 200, 100 or 40 mg/L per animal). In a mouse micronucleus assay, a small but statistically significant increase in the percentage of micronucleated polychromatic erythrocytes was observed in the combined male and female data, but not separately. The results were in the range of other control groups in the same study. The statistical significance of the increase is considered to be due to the low value recorded in the concurrent vehicle control rather than to any clastogenic effects of sodium hypochlorite. In the same study in CD1 mice, no statistically or biologically significant increase in the frequency of either structural or numerical chromosomal aberrations was observed.

Some other assays with mouse micronucleous demonstrated no statistically or biologically significant increase in micronucleated polychromatic erythrocytes in the bone marrow following a single intraperitoneal injection at dose levels from 312.5 to 2500 mg/kg of sodium hypochlorite. An additional study involving the use of 4 repeated doses of 300 mg/kg, 24 hours apart, with a single sampling time at 24 hours following the final dose, was also clearly negative (Hayashi et al., 1988). A negative result in the induction of chromosomal aberrations in rat bone marrow has been reported by Kawachi et al. (1980).

At the level of germ cells the induction of sperm head abnormalities has been evaluated in B6C3F1 mice treated for 5 days with 1.6 or 4 or 8 mg/kg (Meier et al., 1985). Statistically significant increases in the frequency of sperm head abnormalities, at 3 weeks post-treatment, were observed at the two higher doses. No abnormalities were detected for sampling times of 1 and 5 weeks. The effect was reproduced in an independent repeated experiment and, in addition, an increase was observed at 1.6 mg/kg/day. The increases were, however, small (approximately 2 fold), and plateau between 4 and 8 mg/kg/day. The range of values observed in the vehicle historical control was wide, and the values observed in the animals treated with hypochlorite were only slightly outside this range.

In another assay, rats given 900 mg/kg orally showed no evidence of oxidative DNA damage, detected as 8-hydroxyguanosine, in the kidney (Kasai et al., 1987).
The overall data suggest that chlorine/hypochlorite solutions are not mutagenic *in vivo*.

Carcinogenicity

Among the explored literature, the most relevant results are the gathered in the OECD SIDS report regarding calcium hypochlorite (2004) and in the EU Report on sodium hypochlorite.

The most relevant studies regarding carcinogenicity of chlorine are based in 2-years inhalation study in Fisher 344 rats and B6C3F1 mice (Wolf et al., 1995), in a long-term studies via chlorinated drinking water (by addition of NaClO) in Fisher 344 rats and/or B6C3F1 mice (Hasegawa et al., 1986; Kurokawa et al., 1986; NTP, 1992), furthermore, within a multigeneration study in BDII (cPah albino) rats administered highly chlorinated drinking water (Druckrey et al., 1968). One promotor/initiator study was reported (Kurokawa et al., 1984).

The carcinogenic potential of sodium hypochlorite was examined in F344 rats. Groups of 50 males or 50 females were given sodium hypochlorite in their drinking-water, at concentrations of 0.1 and 0.05% for males and 0.2 and 0.1% for females, for 104 wk. Similar numbers of male and female rats received distilled water without supplement throughout the experiment. All surviving rats were killed at week 112 (after 8 weeks on untreated tap-water). Rats of both sexes given the chemical showed a reduction in body-weight gain, but haematological and biochemical examination of the blood showed no changes due to treatment, and no significant lesions attributable to the treatment were detected in any tissue in the histopathological investigation. Although a variety of tumours developed in all groups, no dose-related change in either the incidence or latent period of tumours was observed for any organ or tissue in either sex. Under the experimental conditions described, therefore, sodium hypochlorite was not carcinogenic in F344 rats.

Inhalation

In inhalation studies in rats and mice, the incidence of neoplasia was not increased by exposure, indicating that inhaled chlorine in rodents is an upper respiratory tract toxicant (Wolf et al., 1995, OECD SIDS, 2004).

Oral

In a two years study in F344 rats and B6C3F1 mice receiving 70, 140 or 275 mg/L in drinking water, there was no evidence of neoplastic effects in the animals, but a marginal, not clearly dose-related increase in the incidence of mononuclear cell leukaemia in female rats (control, 8/50; low-dose, 7/50; mid-dose 19/50; high-dose 16/50). The proportion of female rats that died of leukaemia before the end of the study and the mean time for observation of animals dying with leukaemia were similar among all dose groups and controls. Although the marginal increase in leukaemia incidence in the mid- and high-dose female rats suggested a possible association with the administration of chlorinated water, the incidence of leukaemia was not clearly dose related. There was no indication of reduced latency of leukaemia and the incidence of leukaemia in concurrent controls was less than the mean for historical controls; furthermore there was no supporting evidence of an effect in male rats and both sexes of mice (OECD SIDS, 2004).

In a study of Hasegawa, et al. (1986), 50 males and females F344 rats were supplied drinking water containing sodium hypochlorite at concentrations of 0, 0.05 or 0.1 % for males and 0, 0.1 or 0.2 % for females. After treatment for 104 weeks, all surviving animals were given untreated tap-water for a further 8 weeks, and then examined. The overall incidence of tumours in each group was 98-100 % in males and 70-80 % in females. There were no significant differences between the control and sodium hypochlorite-treated groups with respect to the total tumour incidences of the animals. It was concluded that the tumours observed in this study were unrelated to treatment of sodium hypochlorite at levels up to 0.1% in males and 0.2 % in females. Sodium hypochlorite had no carcinogenic effect in F344 rats.

In a study of Kurokawa, et al. (1986), 50 males and females F344 rats and B6C3F1 mice were supplied drinking water containing sodium hypochlorite at concentrations of 0, 300 or 600 ppm for rats and 0, 250 or 500 ppm for mice. After treatment for 85 weeks, no statistically significant differences were observed in the incidences of tumour formation in rats. In mice, the combined incidences of hyperplastic nodules and hepatocellular carcinomas of the liver in low-dose group, and adenomas and adenocarcinomas of the lung in a high-dose group, were marginally increased compared to controls. However, these incidences in treated males were within the range of values of historical control data.

Highly chlorinated water containing free chlorine at a level of 100 mg/L was given daily as drinking water over the whole lifespan (maximum of 2 years) to 236 BDII (cPah albino) rats in seven consecutive generations. There was no difference in survival or in tumour incidence in any generation group when compared to the untreated controls (Druckrey et al., 1968).

In conclusion, there was no evidence of carcinogenicity in mice and in male rats, but equivocal evidence in female rats. The overall genotoxicity data evaluated in this document suggest that aqueous solutions of chlorine/hypochlorite are not mutagenic *in vivo*. This is consistent with the absence of any definite carcinogenic effects in the oral carcinogenicity bioassays in rats or mice.

Studies in Humans

From the available literature, there is no evidence of a possible carcinogenic effect in human populations exposed to low levels of chlorine at the workplace for up to 20 years or even longer (WHO, 1982; Mvros et al., 1991). Several epidemiology studies attempted to evaluate the carcinogenicity of chlorinated drinking water (McGeehin et al., 1993; Cantor et al., 1998; Hildesheim et al., 1997). In the majority of these studies, weak associations between consumption of chlorinated surface water and increased relative risks for getting cancer of the gastro-intestinal tract (including stomach, colon, rectum, and bladder) have been calculated.

The IARC review in 1991 stressed the shortcomings of these studies and the difficulties in the interpretation of the data for an evaluation of the carcinogenicity of chlorinated drinking water. In the performed studies, there are several methodological inadequacies, many confounding variables, and no causal link between an apparent increased cancer risk with the expectation of some correlation between the higher risk for cancer of urinary bladder and the long-term consumption of chlorinated drinking water in some studies. Therefore, the IARC overall evaluation was that chlorinated drinking water and hypochlorite salts are not classifiable as to their carcinogenicity to humans and that there is inadequate evidence for the carcinogenicity of chlorinated drinking water and hypochlorite salts in humans (IARC, 1991).

Reproductive effects, embryotoxicity and teratogenicity

According to the report of the WHO regarding Chlorine in drinking water (2003), mice administered drinking-water with a residual content of chlorine of 10 mg of residual chlorine per litre (1.9 mg/kg of body weight per day) for 6 months demonstrated not to have adverse reproductive effects (Les, 1968). In a seven-generation study in which rats were given drinking-water chlorinated at 100 mg/litre (10 mg/kg of body weight per day), no treatment-related effects on fertility were found (Druckrey, 1968).

Oral administration of hypochlorite ion or hypochlorous acid at 100, 200, or 400 mg of chlorine per litre (1.6, 4.0, or 8.0 mg/kg of body weight per day) resulted, in the case of hypochlorite, in dose-related increases in the amount of sperm-head abnormalities in male B6C3F1 mice. A NOAEL of 8.0 mg/kg of body weight per day was identified for hypochlorous acid and a LOAEL of 1.6 mg/kg of body weight per day for hypochlorite ion (Meier et al., 1985).

Endocrine disruption
No evidences have been found regarding the potential endocrine disruption activity of the target substances of this survey.

6.2 Human exposure

Sodium and calcium hypochlorite solutions have also been utilized extensively in the disinfection of drinking-water. Exposure to hypochlorite might occur through accidental events during the use of either calcium hypochlorite for disinfection of swimming-pools or from the use of hypochlorite-containing cleaning products (OECD SIDS). Intake of a small quantity of bleach generally results in irritation of the oesophagus, a burning sensation in the mouth and throat, and spontaneous vomiting. In these cases, it is not clear whether it is the sodium hypochlorite or the extremely caustic nature of the bleach that causes the tissue injury (WHO, 2003).

6.2.1 Direct exposure

Consumer exposure
The main exposure of the substances to the consumer is relevant in mainly three scenarios: household products, swimming pools and intake from drinking water. These three are described in the next subsections.

Household
There are three typical usage conditions of products containing sodium hypochlorite:

- Hard surface cleaning/disinfection
- Hand washing/laundry pre-treatment
- Surface cleaning with spray products

In each of these conditions exposure is likely to be less than 30 minutes. The characteristic odour of "bleach" arises from the volatility of the hypochlorous acid which is present in solutions at very low concentrations given the pHs applying during both neat and diluted usage (pH ≥ 9.0).
Household hypochlorite preparations are sold in Europe at concentrations which vary between 0.5-12.5% available chlorine levels, with a prevalence of concentrations ranging from 3-5%.
In some countries, depending on the end usage (e.g. laundry, hard surface cleaning), a dosage recommendation is made. If the product is used for disinfection purposes then a dosage recommendation is made which is designed to guarantee the level of microbial life remaining after cleaning is below that which is believed to be dangerous to health. The dosage recommendation will depend on the level of bleach in the product and the end usage (EU Risk Assessment report, 2007).

Dermal exposure
Hypochlorite can be considered as a substance in a non-volatile medium (household bleach), which is diluted for normal use.
Under normal use conditions, the key route of exposure to hypochlorite is via dermal contact when hands may be dipped into a diluted hypochlorite solution in a laundry bleaching or household cleaning task. Typical diluted concentrations range from 0.1-0.5 g/l (or 0.01-0.05%) (AISE, 1997).

Exposure to concentrated solutions (25-50 g/l, or 2.5 – 5.0 %) is less frequent and is due to undiluted use in toilet bowl cleaning for example (AISE, 1997). The concentrated solutions will rarely be in direct contact with skin for any appreciable time period, as a cleaning implement will be used and the skin will be wiped or rinsed after contact with the concentrated bleach product.
The potential dermal exposure can be calculated considering the two typical usages of NaClO which could lead to exposure to the substance: hand washing/laundry pre-treatment and hard surface cleaning. To this end, the habits and practice data collected by industry (AISE companies of HERA, http://www.heraproject.com/Index.cfm) and included in the updated version of the TGD (Appendix submitted to ECB in 2002) have been used. The total dermal exposure was estimated assuming 2 laundry bleaching tasks/ week plus 1 hard surface cleaning task / day (both are maximum use data). The total amount of hypochlorite to which the skin may be exposed externally as well as the potential uptake via skin has been determined the two common exposure scenarios:

- Laundry bleaching/pre-treatment: 0.002 mg/kg BW/d.
- Hard surface cleaning: 0.035 mg/kg BW /d.

BW: Average female bodyweight (default, 60 kg).
The total dermal exposure in the household using the conservative dermal uptake assumption of 10% is therefore 0.002 + 0.035 = 0.037 mg Hypochlorite/kg BW/day corresponding to 0.035 mg/kg BW day as av. Cl_2 (EU Risk Assessment report, Hypochlorite, 2007)

Inhalation exposure
The pH of solutions of sodium hypochlorite can range from as low as 9 (diluted) to 13 (concentrated) and as such the dominant species are the hypochlorite anion and hypochlorous acid with the former predominating and the latter giving the typical odour (AISE, 1997). No chlorine gas is predicted at these pHs. The only occasion when chlorine can be formed is through conditions of misuse by mixing with strong acids.

Some household products designed for hard surface cleaning are formulated as sprays. Such products typically contain 500 ml of a < 5 % sodium hypochlorite solution (Typical conc. 1 - 3 %). Based on industry data, an average product use of 20 g/day in a total of 30 min (0.5 h) spray cleaning time/day is used for this assessment (0.5 h is the total time assumed for this scenario/day, consisting of several tasks lasting few minutes each). The spray is generated using a purpose-designed trigger mechanism, which forms part of the product packaging.

Trigger spray bottles for household cleaners are useful for disinfection of surfaces. These products are designed to deliver essentially all their contents to the surface to be cleaned. Unlike spray containers that are under pressure, trigger sprayers do not have sophisticated delivery systems to deliver a fine, mist-like spray. They are designed to mostly deliver product in large particles (average > 75 µm) or as foam to the surfaces to be cleaned. Small amounts of product will become temporarily suspended in air, but only particles smaller than 30 µm will remain in the air for any appreciable time. The standard trigger spray apparatus is designed to minimize the numbers of particles ejected that may become airborne.
Industry has some knowledge about the amount of airborne particles discharged from trigger spray bottles of different manufacturers (data from repeated internal control measurements as well as product & packaging development). Based on that data, the consumer exposure to this airborne fraction of hypochlorite-containing spray products is calculated below.
Aerosol measurements were done on hypochlorite-based trigger spray cleaners typical of the EU market. Based on the high end hypochlorite concentration for household spray products of 3 %, the inhalable hypochlorite concentration from this measured mean mass concentration is:

$$C \text{ air inhalable} = 56 \times 0.03 = 1.68\ [\mu g/m^3]$$

Hypochlorite solutions can liberate toxic gases such as chlorine. Chlorine’s odor or irritant properties generally provide adequate warning of hazardous concentrations. However, prolonged, low-level exposures, such as those that occur in the workplace, can lead to olfactory fatigue and tolerance of chlorine's irritant effects. Chlorine is heavier than air and can cause asphyxiation in poorly ventilated, enclosed, or low-lying areas.

Children exposed to the same levels of gases as adults receive a larger dose because they have greater lung surface area: body weight ratios and higher minute volumes: weight ratios. Children are more vulnerable to corrosive agents than adults because of the smaller diameter of their airways. In addition, they are exposed to higher levels than adults in the same location because of their short height and the higher levels of chlorine found nearer to the ground (EU Risk Assessment report, Hypochlorite, 2007).

Misuse

Contact with eyes and skin

During normal use conditions, consumers are exposed to the diluted product only via the skin, primarily of the hands. Contact of skin or eyes with undiluted product occurs essentially in case of accidents.

Given the corrosiveness of >10% active chlorine solutions, these may cause chemical burns to the eyes and skin if they are not rinsed immediately with plenty of water. In practice, however, no permanent damage has been reported from accidental exposures to hypochlorite. Solutions of 5% hypochlorite can cause irritation to the eye upon direct contact and to the skin upon prolonged contact. The effects are reversible. Total recovery was obtained within 48 hours for 98% of the cases. In the remaining 2%, which all were with concentrated hypochlorite solutions, total recovery was obtained within 10-30 days. Only a minority of cases reported to Poison Control Centers (PCCs) relate to eye and skin irritation. Ocular exposures may occur while pouring hypochlorite solution for dilution and use (AISE, 1997).

Ingestion

Ingestion of the substances is very rarely to take place accidentally. The unpleasant taste, caustic characteristics and emetic effect prevents the intake of large volumes (sodium hypochlorite solutions) or mass (calcium hypochlorite tablets). Deliberated ingestion might take place in case of suicide attempts.
Children might be also a potential special risk group, however child resistant packaging (child resistant closures, CRCs) is compulsory for preparations classified as "Corrosive". Hypochlorite solutions above 10% Active Chlorine fall into this category (AISE, 1997).

Inhalation

The hypochlorite anion does not volatilise from aqueous solutions. Therefore, the exposure of users to hypochlorite does not involve inhalation, except in when products that dose in aerosol form are used. The inhalation hazard of the hypochlorite anion (or the small fraction of hypochlorous acid present in the household products) can be neglected. However, under misuse conditions, hypochlorite can react with other household cleaning products, particularly with acidic products and ammonia. The gases liberated (chlorine or chloramines) are very irritant and warn the user immediately, significantly reducing the risk of prolonged contact. Particularly sensitive to this issue are babies and children. It is important to remark that chlorine gas and chloramines are heavier than air and thus, when these gases are formed misusing hypochlorite solutions they tend to drop to the ground. This provokes not only the replacement of the air from the lower layers of the room but also the development of a toxic atmosphere. Special caution has to be taken then when handling these substances in presence of babies and children in the household. To avoid its misuse, both hypochlorites are commercialised with specific instructions about incompatibilities in mixing with other products.

Data from Poison Control Centers

In recent years many European and American Poison Control Centres (PCCs) have reviewed their hypochlorite data concerning involuntary accidents and voluntary poisoning. In some countries, hypochlorite is the source of a large number of exposures, which can be explained by its very wide use. However, involuntary exposures to hypochlorite solution are not considered a major issue for Poison Control Centers. An overview of the exposure routes to the substance is presented in the table below.

TABLE 28

EXPOSURE ROUTES TO HYPOCHLORITE REPORTED BY POISON CONTROL CENTERS IN THE PERIOD 1989-1992 (AISE, 1997)

	Lyon (Fr)	Milan (It)	Rome (It)	Brussels (Bg)	Athens (Gr)	Ankara (Tk)	Madrid (Sp)
Ingestion	74,1	72,7	63,6	37,3	53,3	74,9	32,2
Inhalation	16,8	18	33,9	49,4	46	21,9	25,7
Skin	3,8	1,8	1,1	3,7	0,2	2,5	1,7
Eyes	4,4	1,8	1,4	5,8	0,6	0,8	9,1

The data reported from the different Control Centers indicate that the main route of poisoning with sodium hypochlorite solutions is the ingestion in almost all the countries. Inhalation is the second route and contact with skin or eyes is a minor route.

The Poison Control Center in Denmark was asked about the historic register of domestic accidents involving sodium and calcium hypochlorites. Only accidents with a commercial household product containing 4,5% of sodium hypochlorite were reported and no incidents with calcium hypochlorite were stated (personal communication with Niels Ebbehøj, Poison Control Center, Denmark). The number of calls to the Danish Poison Center in the period 2006-2014 is summarized in the next table. In average, about 183 calls regarding accidents with sodium hypochlorite were reported in the assessed period.

TABLE 29

REPORTED CALLS TO THE POISON CONTROL CENTER OF DENMARK REGARDING SODIUM HYPOCHLORITE IN THE PERIOD 2006-2014.

Year	Calls
2006	98
2007	168
2008	161
2009	218
2010	187
2011	204
2012	238
2013	165
2014	204

The initial risk assessment in the total of 15 cases was "life threatening", probably indicating a self-harming exposure (personal communication with Niels Ebbehøj, Poison Control Center, Denmark)

Swimming pools

Both, sodium and calcium hypochlorite are disinfectants used frequently in heavily used pools. During their presence in the swimming pool, swimmers remain in contact with water containing 400 to 1400 µg/l of available chlorine, 600µg/l maximum of combined chlorine (chloramines) and chlorinated (chloroacetic acids, chloral, etc.) or non-chlorinated (aldehydes) by-products. In some EU countries such as Denmark the content of available chlorine should be constantly kept in the range of 1-3 mg/l in swimming pools. The upper limit of 3 mg/l is used for exposure assessment as a conservative approach.

The average contact time of the general public with the atmosphere of the closed swimming pool is generally around one hour. Long-time swimmers or sportsmen stay for a much longer time, breathing the atmosphere just at the surface of the pool, which contains a higher content of volatile by-products (EU Risk Assessment Report, Hypochlorite, 2007).

Inhalation

Swimmers and pool users inhale from the atmosphere just above the water's surface, and the volume of air inhaled is a function of the intensity of effort and time. Individuals using an indoor pool also breathe air in the wider area of the building housing the pool. However, the concentration of pool-derived chemical in the pool environment will be considerably diluted in open air pools. Inhalation exposure will be largely associated with volatile substances that are lost from the water surface, but will also include some inhalation of aerosols, within a hot tub (for example) or where there is significant splashing. The normal assumption is that an adult will inhale approximately 10 m^3 of air during an 8-h working day. However, this will also depend on the physical effort involved. There will, therefore, be significant individual variation depending upon the type of activity and level of effort (WHO, 2006).

Dermal contact

The skin will be extensively exposed to chemicals in pool water. Some may have a direct impact on the skin, eyes and mucous membranes, but chemicals present in pool water may also cross the skin of the pool, hot tub or spa user and be absorbed into the body. Two pathways have been suggested for transport across the *stratum corneum* (outermost layer of skin): one for lipophilic chemicals and the other for hydrophilic chemicals. The extent of uptake through the skin will depend on a range of factors, including the period of contact with the water, the temperature of the water and the concentration of the chemical (WHO, 2006).

In Denmark, an assessment of the exposure of different users to the substance was carried out by the Ministry of Environment (2006). The results of exposure to free chlorine were dependent on the age and level of exposure to the swimming pool water. The most relevant results under the scope of this survey are presented in the table 30 for the three main user groups: children (1 and 10 years old) and adults.

TABLE 30

AVERAGE DAILY DOSE OF FREE CHLORINE FOR A DIFFERENT POPULATION GROUPED PER AGE WHO BATHS IN SWIMMING POOLS ONCE A WEEK.

Action	1 year child	10 years child	Adult
Inhalation	--	--	--
Ingestion	0,0075 mg/Kg bw	0,05 mg/Kg bw	0,0021 mg/Kg bw
Absorption	0,0077 mg/Kg bw	0,0128 mg/Kg bw	0,0099 mg/Kg bw
Dosis/week	0,0152 mg/Kg bw/w	0,0628 mg/Kg bw/w	0,0120 mg/Kg bw/w
Dosis/day	0,0022 mg/Kg bw/d	0,009 mg/Kg bw/d	0,0017 mg/Kg bw/d

Drinking water

In the table 31, the population served by water distribution network and the drinking water production by country is presented. With this data, it is possible to define the exposure of the general population to free available chlorine (the sum of molecular chlorine, hypochlorous acid and hypochlorite ion expressed in mass equivalent of chlorine) derived from the use of sodium hypochlorite in drinking water treatment. The European population served by water distribution network is around 325 – 335 million of inhabitants (90% of total population) and generally this water is treated with different disinfectants.

TABLE 31

EUROPEAN USE OF TREATED DRINKING WATER (EU RISK ASSESSMENT REPORT, HYPOCHLORITE, 2004)

Member state	population served by water distribution network (%)	population served by water distribution network ($x10^6$)	drinking water average production (million m^3/yr)
Austria	56	4,125	450
Belgium	98	9,868	735
Germany	98	77,420	5.800
Denmark	92	4,784	480
Spain	91	35,035	1479
Finland	80	4,000	412
France	76	43,852	7000
Great Britain	98	56,840	6890
Greece	n.a.	n.a	n.a.
Ireland	98	3,500	511
Italy	90	55,860	7940
Luxembourg	100	0,400	15
The Netherlands	100	15,400	1231
Portugal	86	8,480	525
Sweden	86	7,396	

Assuming almost 50% of European population served by water treated by NaClO, the number of inhabitants "exposed" to NaClO is around 185 million. The admissible concentration of available chlorine in drinking water varies from country to country from 0.1 to 0.5 mg/l (EU Risk Assessment Report, 2007). Assuming that a daily per capita consumption of 2 litres by a person weighing 60 kg (the more conservative TGD default - for a female) and that the concentration of admissible available chlorine admissible in the water is 0.1 mg/l in many European countries, the uptake per person of available chlorine derived from water treated with NaClO is 0.003 mg/kg/day.

For a 10 year children weighing 30 kg the uptake of av. Chlorine per day is calculated as 0.0033. The acute exposure can be estimated considering the consumption of a glass of water (0.2 l) and the value is: 0.1 mg/l x 0.2 l /70kg = 0.0003 mg/kg BW for an adult and 0.0007 for a 10 year children weighing 30 kg.

Additional daily exposure could include ingestion of residual quantity of water used to wash fruits and vegetables or to cook food, as well as some indirect routes, such inhalation of volatile substances and dermal contact during bathing or showering. Considering the typical levels of 0.00001-0.00005%, the potential dermal exposure during washing is considered to be negligible (EU Risk Assessment Report, Hypochlorite, 2007).

In addition to the intake of hypochlorite by drinking water, it is worth noting that hypochlorite solutions might contain also other oxyhalide species such as perchlorate and bromate. These oxyhalides might be formed during and after manufacturing. Such oxyhalide species have the potential to contaminate drinking water if adequate control measures are not taken to minimize their formation during manufacture, shipment and storage of hypochlorite solutions (Stanford et al., 2011).

6.2.2 Occupational exposure

Under occupational conditions, generally only accidental exposure to concentrated solutions (in the case of sodium hypochlorite) or to solid products (in the case of calcium hypochlorite) may occur. Some scenarios can result in dermal exposure to solutions with lower concentration of sodium hypochlorite and chlorination by-products (EU Risk assessment Report, 2004).

Usually, the production of these substances is conducted in chlor-alkali facilities and, despite no specific regulations concern these substances in the occupational environment, there are some recommendations for chlorine exposure. Exposure to gaseous chlorine can occur through accidental events in various industries (e.g. during filling operations of chlorine gas, in the pulp and paper industry using chlorine, HCl or chlorine dioxide as bleaching agents), during transport and storage, or during professional water purification and disinfection measures for swimming-pools (OECD SIDS, 2004).

As in the case of the consumer exposure, the occupational exposure has different scenarios that should be assessed. These are: production facilities, swimming pools, textile industries, sewage treatment, drinking water and cooling water treatment.

Production facilities

As previously stated, sodium hypochlorite production is in most cases integrated in a Chlor-Alkali industry, where chlorine and other chlorinated substances are produced. Also calcium hypochlorite is usually produced in the same facilities. Workers involved in hypochlorite production facilities can be exposed to chlorine in the atmosphere, which could be emitted during chlorine production or during its use for the synthesis of hypochlorite and other chlorinated chemicals. Chlorine emissions can take place when the closed system is breached, for maintenance purposes or during coupling and decoupling of pipelines, both during hypochlorite and chlorine production (EU Risk assessment report, 2004). The table below shows occupational exposure limits for chlorine in European countries. In almost all countries, the limit for long-term exposure (8 hours time weighted average, or TWA) is 0.5 ppmV or 1.5 mg/m^3 . The only exception is The Netherlands, where limits are higher. In some cases, a short-term exposure limit (STEL) of 1 ppmV is applied (EU Risk assessment report, 2007).

TABLE 32

OCCUPATIONAL EXPOSURE LIMITS FOR CHLORINE IN EUROPEAN COUNTRIES. (EU RISK ASSESSMENT REPORT, CHLORINE, 2007).

	Limit	
Country	**Long term exposure**	**Short term exposure**
Austria	MAK: 0.5 ppmV; 1.5 mg/m^3	Ceiling: 0.5 ppmV; 1.5 mg/m^3
Belgium	8-hour TWA: 0.5 ppmV; 1.5 mg/m^3	15-minute STEL: 1 ppmV, 2.9 mg/m^3
Denmark	TWA: 0.5 ppmV, 1.5 mg/m^3	
France		VLE (valeur limite d'exposition): 1 ppmV, 3 mg/m^3
Finland	8-hour limit: 0.5 ppmV, 1.5 mg/m3	15-minute limit: 1 ppmV, 2.9 mg/m3
Germany	TRGS 900 limit value: 0.5 ppmV, 1.5 mg/m^3	MAK value should never be exceeded.
Greece	8-hour TWA: 1 ppmV, 3 mg/m^3	15 minute (STEL: 1 ppmV, 3 mg/m^3
Ireland	8-hour OEL (TWA): 0.5 ppmV, 1.5 mg/m^3	15-minute OEL (STEL): 1 ppmV, 3 mg/m^3
The Netherlands	MAC ceiling: 1 ppmV, 3 mg/m^3	
Norway	Threshold limit value: 0.5 ppmV, 1.5 mg/m^3	ceiling value: 1 ppmV, 3 mg/m^3
Spain	8-hour (VLA-ED): 0.5 ppmV, 3 mg/m^3	15-minute STEL (VLA-EC): 1 ppmV, 3 mg/m^3
Sweden	Level Limit Value (NGV) 0,5 ppm V, 1,5 mg/m^3	Ceiling Limit Value (TGV): 1 ppmV, 3 mg/ m^3
Switzerland	TWA 0.5 ppmV, 1.5 mg/m^3	STEL 0.5 ppmV, 1.5 mg/m^3. Freq. X Duration in minutes/shift: 15 min
United Kingdom	TWA 0.5 ppmV, 1.5 mg/m^3	STEL 1 ppmV, 2.9 mg/m^3

Note: Italy and Portugal have adopted the limit values published by ACGIH (American Conference of Governmental Industrial Hygienists), corresponding, for chlorine, to TLV-TWA of 0.5 ppmV or 1.5 mg/m^3 (for long term exposure) and TLV-STEL of 1 ppmV or 3 mg/m^3 (for short term exposure).

Regarding dermal exposure, normally, no dermal contact with sodium hypochlorite should occur, as the process is closed. In case of opening of the system for maintenance purposes, safety procedures are applied in order to prevent dermal exposure to hypochlorite. The use of protective equipment such as safety glasses and gloves is mandatory in production area.

The hypochlorite solution in the concentrations of the manufacture scenario is corrosive. Therefore, it can be assumed that PPE are always used in case of breaching of the closed system and no dermal exposure is possible, except in case of accident. (EU Risk Assessment Report, hypochlorite, 2004).

Swimming pools

Occupational exposure to sodium hypochlorite for workers handling the product in swimming pools does not normally occur, as the product is added via closed circuits. Filling of storage tanks from bulk tank trucks and introduction of hypochlorite into swimming pools is done through PVC or PE pipes, provided with control systems. Generally workers are obliged to take into account a minimum of safety measures. Hypochlorite has to be introduced in a main water header and not directly in the swimming pool. All pipes have to be rigidly secured, while keeping the length as short as possible. In order to prevent reaction with acids and the production of gaseous chlorine, hypochlorite and hydrochloric acid are placed in separate bunds and hypo and acid pipes have to be clearly labelled.

When handling the product, workers shall wear safety glasses and PVC rubber gloves. If necessary, an approved gas mask has to be used. Sodium hypochlorite producers recommend to use the same PPE used during production when handling concentrated solutions. Adequate ventilation has to be assured. Maintenance and repairs of pumps, dosing and automatic control systems have to be carried out only by specialised companies (EU Risk Assessment Report, 2004).

Textile industry
Sodium hypochlorite solutions are used mainly in cotton and linen processing sector. The use of this substance accounts only 1% of the total bleaching agents used, being hydrogen peroxide (H_2O_2) used for about 85%. Linen is treated with sodium hypochlorite before dyeing to complete the removal of lignin residues. The use for cotton is limited to some finished products such as to bleach jeans.

An important use of sodium hypochlorite is the washing of machinery previously used with dark colours, before starting a new dyeing cycle with light colours. In all cases a 13% NaClO solution is the starting one. For bleaching purposes the solution is diluted to provide a concentration in the range 0.05 – 0.07%. To wash machinery the starting solution is used. Sodium hypochlorite is filled into the machinery and then processing is carried out in closed system, including the final step with sodium bisulphite ($NaHSO_3$) to remove hypochlorite residues. The only stage where workers could be exposed to NaClO is during its transfer from the reservoir tank to the machinery. Indeed, in some cases the substance could be filled into buckets and then manually filled into the machinery. In such cases workers are committed to use adequate PPE, as the solution used is corrosive. It should be also taken into account that the use in textile is not continuous and the frequency of machinery loading is normally once per week. In a typical textile plant where sodium hypochlorite is used only as washing agent for machinery, the consumption is 1300 kg/year (EU Risk Assessment Report, 2004).

Sewage treatment, drinking water and cooling water treatment
The exposure to sodium hypochlorite for the workers of cooling plants, waste water and drinking water treatment plants is generally accidental, in occasion in operations such as filling or displacement of the storage tanks. The closed disinfection system can be opened especially in occasion of filling of the disinfection product or extraordinary maintenance. The lines of delivery of the product are normally protected for corrosive liquids. The time of exposure during the phases of spilling is limited to the operations of coupling and decoupling and a conservative value can be of 5 minutes (EU Risk Assessment Report, 2007).

6.3 Bio-monitoring data

Data regarding the bioaccumulative potential of these substances indicate that the bioaccumulation of hypochlorite can be disregarded due to the high water solubility and reactivity of this anion. As previously stated, hypochlorite anion can be found in living organisms as it is formed *in vivo from* chloride anion as a naturally cell defence process (OECD SIDS, 2004).

6.4 Exposure to chlorinated organic by-products

Despite of the apparent harmlessness of hypochlorites it is remarkable that the use of these products is generally associated with the formation of trihalomethanes, chloroacetic acids and other compounds due to the reaction between chlorine species and organic matter, especially when surface waters are treated. There might be a potential risk of exposure to these organohalogen by-products through e.g. drinking water or by activities in swimming pools.

The principal types of chlorinated by-products formed during chlorination of drinking water are the haloforms or trihalomethanes (THMs), principally chloroform, and haloacetic acids (HAA). Though the levels vary according to raw water quality, pH, temperature, dose, contact time, treatment methods and sequence, and chlorination agent, THMs and HAAs will typically be an order of magnitude more abundant than each of the other main types, which include haloacetonitriles, haloaldehydes, haloketones and normally very small quantities of chlorinated phenols. These by-products are formed by reaction with humic, and fulvic acid derivatives and other natural organic matter in the raw water (EU Risk Assessment Report, 2007).

Typical ranges of most common disinfection by-products in drinking water are shown in table 33. The table presents also WHO guidelines values (WHO, 2006), defined taking into consideration available toxicity data. The Directive 98/83/EC on the quality of water intended for human consumption regulates only the concentration of trihalomethanes.

The available information concerning the concentrations of the different by-products shows that in most cases the reported quantities are below the guideline values indicated by WHO for drinking water. Therefore, any relevant consumer exposure to disinfection by-products through drinking water can be excluded.

Although the link between water disinfection treatment and by-products occurrence is evident, the high variability of concentration data shows a dependency on the way the disinfection treatment is carried out. The quantity of these substances is related, among others, to the quality of the treated waters and the good maintenance and cleanliness of the water distribution networks. It is important to remark that organohalogen by-products would not occur in drinking water in absence of organic matter. The optimisation of the treatment process (reduction of organic matter before the treatment, control of operative conditions, etc.) is thus the solution to reduce by-products concentration in chlorinated drinking water. For example, a cut-off value in terms of organic type and concentration in the original water should be defined, above which the use of NaClO must be discouraged due to the high production of by-products.

TABLE 33

OCCURRENCE OF MOST COMMON DISINFECTION BY-PRODUCTS IN DRINKING WATER IN UK AND US. GUIDELINE VALUES REPORTED BY THE WHO AND THE DIRECTIVE 98/83/EC ON THE QUALITY OF WATER INTENDED FOR HUMAN CONSUMPTION (ADAPTED FROM EU RISK ASSESSMENT REPORT, HYPOCHLORITE, 2007).

By-product	Concentration (µg/l)	WHO guidelines (µg/l)	Directive 98/83/EC
Chloroform	Around 50	300	Sum of trihalomethanes (THM) 100 The Member States should strive for a lower value, where possible, without compromising disinfection
Bromodichloromethane	Up to 25 (UK), up to 50 (US); higher concentration in case of ozonation followed by chlorination of water rich in bromide	60	
Chlorodibromomethane	Below 20, up to100 in case of ozone treatment of water rich in bromide	100	
Bromoform	Up to 4.4 (US), around 10 in case of ozone treatment of water rich in bromide 6.26-26.72	100	

Monochloroacetic acid	Around 5	20	Not regulated
Dichloroacetic acid	0.9-62, the highest concentrations in water rich in humic and fulvic acids 0.83-1.07	50	Not regulated
Trichloroacetic acid	0.3-86 0.1-86	200	Not regulated
Dichloroacetonitrile	Around 2, some samples up to 24	20	Not regulated
Bromochloroacetonitrile	Up to 10	Not established	Not regulated
Dibromoacetonitrile	Up to 2.5	70	Not regulated
Chloral hydrate	Up to 2.6 (UK) or 19 (US); unstable, it decomposes to give trichloromethane		Not regulated
Halogenated phenols	2-chlorophenol+2,4-dichlorophenol+2,4,6-trichlorophenol: less than 1; median concentration: 0.01-0.1	Not established	Not regulated
Nitrotrichloromethane (chloropicrin)	Up to 5.6; higher concentrations with pre-ozonation	200 for 2,4,6 trichlorophenol	Not regulated

In Denmark when controlling the quality of the pool water, the by-products are divided into three groups: free chlorine, bound chlorine and trihalomethanes. The free chlorine fraction is the gaseous chlorine and hypochlorite; bound chlorine comprises inorganic and organic chloramines; and trihalomethane is a collective term for the following four substances, chloroform, bromodichloromethane, dibromochloromethane and bromoform.

A recent research review from Chowdhury et al. (2006) stablished that the main organohalogenated by-products occurring in swimming pools are trihalomethanes and haloacetic acids. A report from the Miljøministeriet in Denmark (Borling et al., 2006) assessed the intake of the halomethanes chloroform and bromodichloromethane in Danish swimming pools and assessed the risk according to the Tolerable Daily Intake (TDI) reported by the Environmental Protection Agency. In Table 34 the calculated average daily doses of chloroform and bromodichloromethane at different concentrations of THMs in swimming pools are presented.

TABLE 34

ESTIMATED AVERAGE DAILY DOSES (MG/KG BW/DAY) OF CHLOROFORM AND BROMODICHLOROMETHANE AT DIFFERENT LEVELS OF THM IN SWIMMING POOLS (BORLING ET AL., 2006).

Substance	Child		Adult	
Chloroform	**1 year**	**10 year**	**Motion**	**Competition**
18 µg/l (20 µg/l THM)	0,26	0,5	0,36	9,2
22,5 µg/l (25 µg/l THM)	0,33	0,62	0,45	11,5
45 µg/l (50 µg/l THM)	0,66	1,24	0,89	23,0
90 µg/l (100 µg/l THM)	1,32	2,48	1,78	46,0*
Bromodichloromethane				
2 µg/l (20 µg/l THM)	0,018	0,036	0,025	0,70
2,5 µg/l (25 µg/l THM)	0,023	0,045	0,031	0,88
5 µg/l (50 µg/l THM)	0,046	0,090	0,062	1,76
10 µg/l (100 µg/l THM)	0,092	0,180	0,124	3,52*

* For competitive swimmers, the highest exposure is not very likely, because it corresponds to the maximum allowable concentration in pool water in tanks <25 m.

The WHO Guidelines for Drinking water Quality can be used to assess the risks derived from disinfection by-products generated in swimming pools and similar environments. Although there are data indicating that the concentrations of chlorination by-products in swimming pools and similar environments may in some cases exceed the WHO guideline values for drinking-water (WHO, 2004), available evidence indicates that for reasonably well managed pools, concentrations less than the drinking-water guideline values can be consistently achieved. Since the drinking-water guidelines are intended to reflect tolerable risks over a lifetime, this provides an additional level of reassurance. Drinking water guidelines assume an intake of 2 litres per day but ingestion of water from swimming pool is considerably less –estimated about 100 mL- (WHO, 2006). The World Health Organization recommends that, for sporadic adult swimmers and pool attendants/lifeguards in chlorine disinfected pools operated under typical conditions, with low chloroform levels in air and water, the presence of disinfectant by-products is not an issue and guideline values are not required in indoor or outdoor pools. For worst case exposure scenarios, and for children and competitive swimmers, control of exposure by good ventilation, use of alternative disinfectants, pre-ozonation, effective flushing and control of precursor addition through preswimming showering and toilet use are recommended in the WHO report (WHO, 2000).

THM are lipophilic volatile substances of low water solubility, resulting in a relatively high concentration of the substance just above the water surface and can be absorbed by dermal via. Uptake via skin absorption and inhalation is proportionally greater than from drinking water and is significant, but the low oral intake allows a margin that can, to an extent, account for this. Under such circumstances, the risks from exposure to chlorination by-products in reasonably well managed swimming pools would be considered to be small and must be set against the benefits of aerobic exercise and the risks of infectious disease in the absence of disinfection (WHO, 2006).

In any case, it is recommended that the concentration of THMs in pool water should be as low as possible. The indicative value provided by the Danish Environmental Protection Agency for the content of THMs in pool water is 25 µg/l for indoor pools of at least 25 m and 50 µg/l for other basins, and the maximum allowed values are respectively 50 and 100 µg /l (Miljøstyrelsen, 1988).

The Environmental Protection Agency in Ireland published a document regarding water treatment for disinfection (2011) where they outline different approaches to restrict the formation of trihalomethanes (Chloroform, Bromodichloromethane, Chlorodibromomethane and Bromoform). The general rules, briefly summarized next, are also applicable for the other organohalogen by-products.

i) Avoid chlorinating raw surface water and untreated groundwater susceptible to surface contamination, and treat the water in advance of chlorination to remove precursors (as indicated by colour, TOC, UV absorbance) as far as possible;
ii) Limit free chlorine concentrations and contact times to the minimum required for the process (and distribution systems);
iii) Dechlorinate as soon as possible after breakpoint chlorination;
iv) Use chloramination to provide a residual in disinfection;
v) Keep pH low as THM formation increases with pH increase;
vi) Consider the use of an alternative oxidant or UV for primary disinfection.

Whilst it is possible to remove THMs using air stripping, GAC or nanofiltration, this approach is costly compared with minimising formation, and is little used. The efficiency of TOC removal, the main precursor of disinfection by-product formation, is very much dependent on pH and alkalinity with optimal removal at a pH 6.5 or below.

6.5 Summary and conclusions

Sodium and calcium hypochlorites are subject to EU harmonised classification and labelling. Both of them are labelled with a Hazard Statement Code H314 (causes severe skin burns and eye damage) and additionally the calcium salt is labelled with H302 (harmful if swallowed). Studies carried out in animals with radioactive chlorine species demonstrated that hypochlorite is readily absorbed and transferred to the bloodstream. The substance is excreted through the urine and faeces.

It must also be highlighted that hypochlorite does also occur endogenously. Hypochlorous anion is formed in the human body during inflammation processes and plays an important antimicrobial role.

The acute toxic effects of sodium and calcium hypochlorites are due mainly to their corrosive nature. The high alkalinity of solutions containing hypochlorite provokes saponification of fat tissues and results in deep tissue destruction.

Regarding mutagenicity, hypochlorite solutions have been extensively assessed in both: *in vivo* and *in vitro* assays. The relevance of the data however is limited, as the substance rapidly changes its nature during the tests.

Studies carried out in humans exposed to chlorinated water and hypochlorites to assess the potential carcinogenicity of the substances allowed to define them as not carcinogenic. Hypochlorite was also assessed for effects in reproduction, embryotoxicity and teratogenicity in rats. Only assays carried out with extremely high concentrations (very far from the normal use) provoked some abnormalities in the sperm of mice.

Human exposure to hypochlorites may take place mainly from consumer products and in the working environment. Only sodium hypochlorite one is included in domestic formulations for bleaching and cleaning. A critical exposure can occur mainly by accident or misuse. The special reactivity of hypochlorites could provoke serious accidents when mixing with some other products such as acids and ammonia. When a mixture of hypochlorite solutions with acids leads to a pH lower than about 4.5, the release of toxic chlorine gas takes place. The formation of this gas is directly linked to the acidity of the solution, so a large excess of acid provokes a massive release of chlorine gas. Children and babies are particularly vulnerable, as the gas is heavier than air and tends to fall, replacing the oxygen and provoking a poisonous local atmosphere in the area next to the floor.

In the case of mixture with ammonia, the formation of chloramines also occurs. This kind of accidents take place mainly in domestic situations, since products containing relatively high concentration of ammonia or amine derivatives are placed in the market as cleaners.

These substances are volatile and are released from the solution, provoking a potential inhalation hazard. In the occupational environment, the limits for short and long term exposure as well as the measures to avoid hazardous inhalation of chlorine gas are very well established.

The use of chlorinating technologies for disinfection of drinking water or swimming pools has revealed the potential of generation of hazardous halogenated organic by-products. In Denmark, the exposure to these products by the drinking water can be neglected, as groundwater is mostly used as water source and its microbiological quality is good enough to avoid chlorination. Different is the case of the swimming pools, where chlorination with hypochlorites is an extended practice in Denmark (Miljøstyrelsen, 1988). The exposure to the main halogenated by-products in swimming pools –trihalomethanes and haloacetic acids- has been assessed and just the group of professional swimmers is exposed to the highest concentration of by-products. However, according to the World Health Organization, the risk from exposure to chlorination by-products in properly managed swimming pools is small and must be set against the benefits of exercise and risks of infections.

It should be highlighted, nevertheless, that the formation of these substances will not take place if organic matter is not present in the water. A suitable management of the water quality in terms of control and proper technical elements for the removal of organic matter is thus the key to overcome the potential drawbacks of chlorination in terms of formation of halogenated organic by-products.

7. Information on alternatives

The current section describes the potential alternatives on the main specific applications of sodium and calcium hypochlorites: water disinfection (drinking, wastewater and swimming pools), cleaning and bleaching agents.

7.1 Water disinfection

Despite chlorination of water has been widely used for decades, the demonstrated formation of toxic chlorination by-products has stimulated the research and development of different technologies in an attempt to overcome the drawbacks of chlorination. A survey of the different available technologies has been carried out and their description and discussion is presented next. Methods of reducing the formation of organohalogen by-products are well developed. They include improving raw water quality before chlorination, use of chloramination, and use of alternative disinfectants such as ozone, chlorine dioxide or UV. In most countries, the nature of the water distribution system demands a ‘chlorine residual’ is maintained to the consumer’s tap (EU Risk Assessment Report, sodium hypochlorite, 2007).

The potential chemicals candidates to substitute hypochlorites in water treatment have been assessed according to their hazard characteristics reported in the ECHA database. The summary is presented in the next table.

TABLE 35

CLASSIFICATION OF ACTIVE SUBSTANCES BEING POTENTIAL ALTERNATIVES TO HYPOCHLORITES IN WATER TREATMENT.

Substance	EC number	CAS number	Hazard Class and Category Code(s)	Hazard Statement Code(s)
Ozone	233-069-2	10028-15-6	Ox. Gas 1 Skin Irrit. 2 Eye Irrit. 2 Acute Tox. 1 STOT SE 3 Muta. 2 STOT RE 2	H270 H315 H319 H330 H335 H341 H373 H400
Chlorine dioxide	233-162-8	10049-04-4	Acute Tox. 3 Skin Corr. 1B Eye Dam. 1 Aquatic Acute 1 Ox. Gas 1 Liq. Gas Acute Tox. 2	H270 H280 H301 H314 H318 H330 H400

Sodium dichloroisocyanurate	220-767-7	2893-78-9	Acute Tox. 4 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H302 H319 H335 H400 H410
Hydrogen peroxide	231-765-0	7722-84-1	Ox. Liq. 1 Acute Tox. 4 Skin Corr. 1A Acute Tox. 4 STOT SE 3	H271 H302 H314 H318 H332 H335
Monochloramine	234-217-9	10599-90-3	Skin Irrit. 2 Eye Irrit. 2 Skin Corr. 1A STOT SE 3 Aquatic Chronic 3	H315 H319 H314 H335 H412

7.1.1 Ozone

Ozone is a powerful disinfectant compared with chlorine and chlorine dioxide. It is the only chemical that can provide effective inactivation of either Giardia or Cryptosporidium at dose levels not much greater than those used routinely for water treatment. It is, however, an expensive disinfection technology in terms of capital and operating costs and has primarily been used as a pre-disinfection treatment process for the destruction of organic micropollutants (particularly pesticides). It can achieve also a good performance in the removal of compounds responsible of taste and odour when used in conjunction with Granular Activated Carbon (GAC) filtration (EPA Ireland, 2011).

Two systems have been developed for the production of ozone for water treatment in swimming pools: the corona discharge and the photochemical method. The most common in Europe is the corona discharge that generates ozone by exposing pressurized, dried air to high voltage electricity. The ozone gas is then directed into the bottom of the pool and seen as very small bubbles rising to the surface. The ozone can be introduced into a separate chamber or directly to the pool. The ultraviolet or photochemical method of ozone production passes the pressurized, dried air next to a UV bulb within a chamber, where the UV rays bombard the oxygen molecules and produce ozone. The UV method is more common for spas or private small pools and is less expensive to operate (Missouri Department of Health and Senior Services Section for Environmental Public Health Swimming Pool and Spa Water Chemistry).

Although ozone provides good disinfection, chlorine is usually used as a primary disinfectant after an ozonation process on waters abstracted from surface sources.

Potential hazardous exposure to ozone is extremely unusual and can be disregarded, since this substance is normally prepared in situ and introduced in the water stream. The gas moreover has a pungent odour readily detectable at volumetric concentrations in the range 0.02-0.05 ppm, which is below concerning concentrations.

7.1.2 Ultraviolet radiation

Effective primary disinfection can be provided by a suitable intensity and duration of UV radiation to give a UV “dose” usually expressed in mJ/cm^2. The target dose will depend on the application, but a dose of 40 mJ/cm^2 is commonly used for UV disinfection systems, validated for the broad spectrum inactivation of possible waterborne pathogens such as bacteria, viruses and protozoan parasites such as Cryptosporidium. The main advantages of this kind of technology are that it is a compact process and can be suited to sites with space constraint. In addition to being effective for inactivation of Cryptosporidium and other pathogens, when UV irradiation is used in conjunction with chlorination, it can reduce the subsequent chlorination dose (EPA Ireland, 2011).

The main drawback of UV radiation is its unsuitability for treatment of water with high levels of suspended solids, turbidity, colour or soluble organic matter since they can block or absorb the UV radiation reducing the disinfection performance.

Hazardous exposure to UV radiation in water treatment can be disregarded, since lamps for water treatment are placed in sealed systems.

7.1.3 Use of monochloramine

Monochloramine is formed when ammonia and chlorine are dosed, and react, under well controlled conditions. The process is known generically as "chloramination". Good process control is essential to prevent the formation of strong tastes and by-products.

The disinfection capability of monochloramine is poor compared with chlorine and it is generally used to provide a disinfectant residual concentration to ensure the microbiological quality during distribution, rather than being used for primary disinfection. It is much less effective against viruses and protozoa than hypochlorous acid. However, the substance has some advantages:

- it does not form trihalomethanes (THMs), or other chlorination by-products when in the presence of organic matter
- the taste threshold is typically much greater than for chlorine alone. As a result the introduction of chloramination can significantly reduce customer complaints relating to chlorine tastes (EPA Ireland, 2011).

Potential human exposure to hazardous concentrations of monochloramine from water treatment facilities is unusual and can be disregarded, since the reagent is prepared in situ in closed vessels and included into the water stream. The Integrated Risk Information System of the US EPA (IRIS) states that studies about monochloramine as human carcinogen are inadequate.

7.1.4 Chlorine dioxide

Chlorine dioxide is a more powerful disinfectant than chlorine, and the pure chemical forms less THMs by reaction with humic substances. Chlorine dioxide is generated on demand, usually by reaction between sodium chlorite and hydrochloric acid; it can also be made by reaction between sodium chlorite and chlorine, although careful control is required to ensure by-product formation is small (EPA Ireland,2011). The compound acts as a broad spectrum sanitizer and is effective against bacteria, fungi and viruses. It undergoes redox reactions with proteins and fatty acids within the cell membrane that result in loss of permeability control and disruption of protein synthesis (US EPA, 1999). Compared with hypochlorites, chlorine dioxide requires much lower concentrations to achieve microbial mortality.

Chlorine dioxide reacts more selectively with compounds present in microbial cells as opposed to reacting with organic compounds in general. This ability allows chlorine dioxide to function in more organically loaded solutions, though as organic load increases, efficacy does decrease. Chlorine dioxide functions well over a pH range of about 6 to 10, thus allowing increased mortality of some microbes at higher values. This substance shows also the advantage of generating less organic halogenated by-products than hypochlorite.

The exposure to chlorine dioxide gas from water treatment facilities is not relevant, as the substance is usually electrolytically generated in closed systems and injected in the water stream.

Data retrieved from the toxicological review of the substance of the US EPA (2000) based on human ingestion studies have found no adverse effects in adults and neonates living in areas with chlorine dioxide-disinfected water. However, these studies are fraught with methodological problems, such as lack of characterization of exposure to other agents in the drinking water and control of potential confounding factors.

7.1.5 Hydrogen peroxide and peroxone

The use of hydrogen peroxide in the treatment of potable water has been very limited. This is in part due to its instability in storage and the difficulty in preparing concentrated solutions. Despite being a strong oxidising agent, it is a poor disinfectant that can achieve little or questionable inactivation of bacteria and viruses (EPA Ireland, 2011). Hydrogen peroxide can be stored, but is subject to deterioration with time and is a hazardous material requiring secondary containment for storage facilities.

Although of little value itself, hydrogen peroxide has been used in conjunction with other disinfectants to achieve improved oxidation of organic matter. Its use with ozone and ultraviolet light produces increased concentrations of hydroxyl radicals. These are short-lived, very strongly oxidising chemical species, which react with the organic matter.

One of the most common of these processes involves adding hydrogen peroxide to ozonated water, a process commonly referred to as peroxone consequent to the addition of hydrogen peroxide. Hydroxyl radicals are produced during the spontaneous accelerated decomposition of ozone. By accelerating the ozone decomposition rate, the hydroxyl radical concentration is elevated, which increases the oxidation rate.

This procedure increases the contribution of indirect oxidation over direct ozone oxidation. As an oxidizing agent, peroxone can be used to remove natural organic carbon, organic micropollutants such as pesticides and increase the biodegradability of organic compounds.

However while peroxone is an effective disinfectant, slightly more effective than ozone against bacteria, viruses, and protozoa, it is difficult to use it for disinfection purposes because it is highly reactive and does not maintain a measurable residual level. The difficulty in verifying peroxone systems in use makes it inappropriate for use as a drinking water disinfectant (EPA Ireland, 2011).

The health hazards of hydrogen peroxide are based on its oxidizing nature. Exposure to hydrogen peroxide cause local irritation and, in extreme and uncommon cases, corrosion of the skin, eye, gingivae or the teeth. Most of the effects reported (e.g. eye irritation, irritation of the gingivae and the throat, sensitivity and inflammation of tooth pulp, and morphological changes in tooth surface) are transient or are considered mild. However, even rather dilute solution of H_2O_2 (3%) may cause danger, if swallowed in large enough volume accidentally (Risk assessment report, hydrogen peroxide, 2003).

In properly managed water treatment facilities, human exposure to the substance should occur just accidentally, since it is usually automatically pumped from appropriate containers or drums to the water stream.

7.1.6 Chloroisocianuric acid salts

For routine treatment of public water supplies, there is little or no use of other disinfectants. Some chemicals, such as chloro-isocyanurate compounds are widely used as a stable source of chlorine for the disinfection of swimming pools and in the food industry, sodium dichloroisocyanurate is used for temporary emergency disinfection applications as a source of free available chlorine in the form of hypochlorous acid (HClO) with the attendant residual formation of cyanuric acid from its addition to water (EPA Ireland, 2011).

This family of chemicals is in wide use for swimming pool chlorination. It is composed of sodium dichloro-s-triazinetrione (dichlor) and trichloro-s-tria zinetrione (trichlor) – chlorine compounds that contain cyanuric acid as stabilizer. The dichlor is more soluble and provides 56% or 62%

available chlorine, depending on formulation. Dichlor provides 90% available chlorine and is used when a slow release of chlorine over a period of time is desired. The dichlor compound has little effect on pH, while trichlor is extremely acid (pH 2.8 -3.0). Dichlor can be added directly to the pool; trichlor is generally fed through an erosion-type feeder, but never through the skimmer basket.

The major effect of cyanuric acid on hypochlorous acid is to keep it from being decomposed by ultraviolet light from the sun. Because it is readily decomposed by UV radiation, the dosage of a chlorinating agent that is sufficient for an indoor pool is dissipated rapidly in an outdoor pool. Cyanuric acid bonds with the available chlorine in a manner that does not use up the chlorine. At high stabilizer levels (over 100 ppm), chlorine's efficiency may be reduced (Missouri Department of Health and Senior Services Section for Environmental Public Health Swimming Pool and Spa Water Chemistry).

Information retrieved from the ECHA database indicates that the substance is neither carcinogenic nor mutagenic in studies performed in rats. The main hazard of the substance derives from its misuse, as the accidental exposure of dichloroisocyanurates to acidic solutions provoke the release of toxic chlorine gas.

7.1.7 By-products derived from the use of disinfectants

Disinfection processes can result in the formation of both organic and inorganic disinfection by-products (DBPs). The most well-known of these are the organohalogenated by-products such as trihalomethanes (THM) and haloacetic acids (HAAs), related to chlorination, although the latter group of by-products is of increasing concern in water supply. The concentrations of these organochlorine by-products are a function of the nature and concentration of oxidizable organic material in the water, the pH, temperature, the free chlorine concentration and its contact time with the organic material.

In addition to the organic halogenated compounds, there are also inorganic by-products. Among the most relevant chlorate and bromate can be found.

The by-product issues of concern with the main disinfection processes available for water disinfection are briefly summarised in Table 36.

TABLE 36

BY-PRODUCT IMPLICATIONS OF DIFFERENT DISINFECTANTS IN WATER DISINFECTION

Technology	By-product issues
Chlorination	Trihalomethanes and trihaloacetic acids are formed by reaction with natural organic matter in water. Where chlorine is obtained from hypochlorite, chlorate and bromate formation can be an issue depending on bromide content of salt used in manufacture and subsequent conditions of storage of hypochlorite. Can be controlled by appropriate product specification and management of storage.
Chloramination	No significant by-product issues. Nitrite formation in distribution has been an indirect issue.
Ozone	Bromate formation in waters with high concentration of bromide
Chlorine dioxide	Dosage rates in the future are likely to be limited by consideration of inorganic by-products (chlorate and chlorite).
UV	No significant by-product issues.

Surface water sources are more susceptible to organochlorine by-product formation than ground waters because they receive organic matter in runoff from lake and river catchments. This organic matter comprises mostly humic substances from decaying vegetation, much of which can be in dissolved form as well as in colloid form. The concentration of this organic matter in surface water catchments can vary quickly after severe rainfall events or more slowly on a seasonal basis. The greater the portion which makes its way through the treatment process the greater the potential for the production of disinfection by-products.

While properly operated coagulation-filtration processes will remove most of the colloids, oxidation processes and/or filtration through granular activated carbon may be required to reduce elevated levels of dissolved organic matter prior to disinfection. The key to limiting organochlorine by-product formation is effective treatment for the reduction of TOC which in its various forms is the precursor of these by-products.

Surface waters in contrast to groundwater vary in temperature seasonally with an increase in the rate of organochlorine by-product formation when temperatures increase. Over the usual range of final treated water pH, the impact of pH on organochlorine by-product formation differs in respect of trihalomethanes and haloacetic acids. Where excessive residual TOC exists in the treated water following treatment and the dose rate is sufficiently high to form by-products, trihalomethanes formation increases with increased pH while HAAs increases in tandem with decreasing pH.

Following application of chlorine as part of the treatment process, organochlorine by-products can continue to form within downstream treated water storage and distribution systems depending on the length of retention times in storage tanks and pipelines and the strength of the disinfectant dose required to maintain chlorine residual in the peripheral areas of a distribution system.

The different potential technologies for water disinfection are presented in table 37. The summary encompasses drinking, swimming pool and wastewater.

TABLE 37

PERFORMANCE OF THE MOST WIDELY USED WATER DISINFECTION TECHNOLOGIES ON KEY CHARACTERISTICS (SNOWDEN-SWAN ET AL., 1998)

	Cl_2	NaClO	$Ca(ClO)_2$	ClO_2	Chloramines	Ozone	UV
Disinfection capability							
Bacteria	Good	Good	Good	Good	Poor	Very good	Very good
Viruses	Poor	Poor	Poor	Good	Poor	Very good	Fair
Cysts	Poor	Poor	Poor	Fair	Poor	Good	No effect
Generation of Hazardous Disinfection byproducts	THM & HAA	THM & HAA	THM & HAA	Less THM than Cl_2 Chlorite and chlorate	Less THM than Cl_2	Bromine Low levels of THM formed	None
Persistent Residual	Good	Good	Good	Fair	Very good	None	None
Safety Concerns	High	Low-medium	Low	Medium-High	Medium	Medium	Low
Complexity of Operations/ Maintenance)	Minimal	Minimal	Moderate	Moderate	Minimal	Moderate	Minimal
Size Applicability	All sizes	All sizes	Small-medium	Small-Medium	All sizes	Medium-large	Small-medium
Relative Cost	Low	Low	Low	Moderate	Low	High	Moderate

Long term applicability							
Potable water	Low	Medium	Medium	Medium	Effective only for residual purposes	Medium	Medium
Waste-water	Medium	Medium	Medium	Low	None	High	High

THM: Trihalomethanes

HAA: Haloacetic acids

7.2 Cleaning and disinfection

Hypochlorite has been identified as effective disinfectant for surfaces and materials in the household and professional environment. Its use in bathrooms helps prevent the transfer of fungus, bacteria and other pathogens and then, the potential spread of diseases. In industrial kitchens and also in domestic with heavy use of perishable food (such as meat or fish), it can be used to avoid the cross-contamination of food with microorganisms that may cause poisoning and spoilage. Hypochlorite is one of the fastest, most effective and economical antimicrobial agents and active even at low temperatures (Cahn, 1993). Nevertheless, its use should be limited to situations in which the potential of propagation of hazardous microorganisms is an issue.

Among the alternative methods for cleaning, combinations of detergent and water are the most widely used. Mixtures of water and detergents are only partially effective in reducing the concentration of microorganisms but, in many cases it is enough as a routine cleaning procedure in the domestic environment. The massive use of biocides such as hypochlorites in the domestic environment should be avoided and the use of these substances kept to situations in which the potential of growing of bacteria and spread of diseases might be suspected.

The Danish EPA generally advice consumers to avoid the use of disinfectants in normal households, since it is considered as a unnecessary use of harmful chemicals and a regular cleaning process with detergents is sufficient to keep cleanliness. (personal communication, Sidsel Dyekjær).

The potential chemicals candidates to substitute hypochlorites in cleaning and disinfection have been evaluated according to their hazard characteristics reported in the ECHA database. The summary is presented in table 38

TABLE 38

CLASSIFICATION OF ACTIVE SUBSTANCES BEING POTENTIAL ALTERNATIVES TO HYPOCHLORITES IN CLEANING AND DISINFECTION

Substance	EC number	CAS number	Hazard Class and Category Code(s)	Hazard Statement Code(s)
Peracetic acid	201-186-8	79-21-0	Flam Liq. 3 Org. Perox. D Acute Tox. 4 Skin Corr. 1A Acute Tox. 4	H226 H242 H302 H312 H314 H332 H400
Quaternary ammonium compounds, benzyl-C8-18-alkyldimethylchlorides	264-151-6	63449-41-2	Acute Tox. 4 Skin Corr. 1B Aquatic Acute 1	H302 H312 H314 H400

7.2.1 Peracetic Acid

Peracetic acid is used for industrial disinfection as an effective sanitizer active against microorganisms and spores. Its acting mechanism is based in the disruption of chemical bonds within the cell membrane and these substances are frequently paired with stabilized hydrogen peroxide. The substance provides an acceptable microbial mortality even below ambient temperature. The peroxyacetic acid is effective also in the removal of biofilms and is more active than hypochlorites (Schmidt, R.H. 2003).

The sanitizers based in peracetic acid as the molecule break down into harmless acetic acid, oxygen and water. They have the advantage also of being less corrosive than hypochlorite to metals, so it is very suitable to the disinfection of metallic surfaces.

The main human hazard of the substance is the direct exposure, since it is corrosive. Information retrieved from the ECHA database indicates that peracetic acid is not genotoxic in rats and mice. No conclusion can be outlined about the carcinogenicity of the substance, as the results presented in the ECHA database are not reliable.

7.2.2 Quaternary Ammonium Compounds

Quaternary ammonium compounds, also defined as QACs, are complex chemicals based in positively charged nitrogen organic compounds. These cations bind the acidic phospholipids in the microbial cell wall and block the uptake of nutrients into the microbial cell and the discharge of waste (McBain, et al., 2004).

These substances are effective against a wide range of microbes, although the spore phase is unaffected. They are commonly applied in solution in household and professional environments to disinfect surfaces. They are normally sprayed and allowed to dry. Once dry, a residue of these compounds remains and provides germicidal activity until degradation occurs. These substances also act as detergents when present in high concentration, since the compound has both, hydrophobic and hydrophilic chemical groups.

These substances are odourless, non-staining, non-corrosive and relatively non-toxic to users. They exert their function well over a broad range of temperatures and pHs, although their optimal performance is at warmer temperatures and in alkaline conditions. However, few reliable evidences on the potential toxicity of these substances are available. Based on the precautionary principle, the use of these substances should also be kept to a minimum as they are could be also harmful to environment and health.

7.3 Bleaching

Alternative to the use of sodium hypochlorite for bleaching are available. The most relevant are based also in oxidative reactions promoted by oxygen active species.

A comparative assessment of the different substances in terms of hazards is presented in the next table. Sodium perborate and hydrogen peroxide have a harmonized classification according to the CLP. Among the most remarkable hazards, it is noteworthy the H360Df classification of sodium perborate, indicating that the substance is suspected to damage the fertility and the unborn child as well as the H318 that indicates that may cause serious eye damage. In the case of hydrogen peroxide the most special concern when stored or used is due to its strong oxidizing properties as, according to its CLP classification may cause fire or explosion (H271).

TABLE 39

CLASSIFICATION OF ACTIVE SUBSTANCES BEING POTENTIAL ALTERNATIVES TO HYPOCHLORITES IN BLEACHING.

Substance	EC number	CAS number	Hazard Class and Category Code(s)	Hazard Statement Code(s)
Sodium perborate	234-390-0	11138-47-9	Ox. Sol.3 Acute Tox. 4 Eye Dam. 1 STOT SE 3 Repr. 1B	H272 H302 H318 H335 H360Df
Hydrogen peroxide	231-765-0	7722-84-1	Ox. Liq. 1 Acute Tox. 4 Skin Corr. 1A Acute Tox. 4 STOT SE 3	H271 H302 H314 H332
Sodium percarbonate	239-707-6	15630-89-4	Acute Tox. 4 Eye Dam. 1	H302 H318

The information regarding sodium percarbonate has been retrieved from the notifiers of ECHA. As it may be observed, from the different alternatives to the use of hypochlorites, sodium percarbonate is the less hazardous in terms of safety and exposure.

7.3.1 Hydrogen peroxide

Replacing the traditional use of sodium hypochlorite as bleaching agent is a very challenging task. Some of the bleachers are based in hydrogen peroxide oxidation. Since molecules exposed to hydrogen peroxide might encounter free radicals, their destruction rather than the desired oxidation may result. A successful bleaching with hydrogen peroxide requires higher temperatures than sodium hypochlorites and longer reaction times. This finally involves an extra cost in terms of energy and equipment.

7.3.2 Sodium percarbonate

Sodium percarbonate is mainly used as a bleaching chemical in laundry detergents, laundry additives and machine dishwashing products. The pure product is also available for consumers as a laundry additive. This reagent is widely used as a bleaching chemical in laundry detergents (tablets, compact or regular powders), laundry additives and machine dishwashing products. Bleach booster products with a sodium percarbonate concentration between 65 and 85 % are placed on the market. Minor amounts of sodium percarbonate may be used in products for drain cleaning, multipurpose cleaning or for denture cleansing (Human & Environmental Risk Assessment on ingredients of European household cleaning products, 2002).

7.3.3 Sodium perborate

Sodium perborate is used by industry to formulate a variety of cleaning products including powders or tablets sold as laundry detergents, dishwashing products, or a variety of other cleaning products. The substance is soluble in water and releases hydrogen peroxide. Unlike percarbonate, perborate is not just an addition compound of peroxide, but contains true peroxygen bonds. In dilute solution, an equilibrium exists that still contains peroxoborate anions. These peroxoborate species are able to deliver the hydroperoxide anion at a lower pH than when H_2O_2 is used. Sodium perborate monohydrate and tetrahydrate contain theoretically about 34% and 22% hydrogen peroxide, respectively.

The generation of active oxygen in aqueous solutions is the basis for the use of sodium perborate as bleaching component in detergent products and bleaching agents. The purity of the technical products is characterized by their active oxygen content. The crystalline reagent is available as a hydrate with the general formula $NaBO_3 \cdot n\ H_2O$ (n: 1 or 4). Sodium perborate mono- and tetrahydrate are used as oxidising and bleaching agents mainly in detergents (approximately 96%; household detergents as well as detergents for institutional uses) and also in cleaning (e.g. automatic dishwashers, stain removers in form of bleach booster tablets).

The data presented in the ECHA database identify the substance as bacterial genotoxic in *in vitro* but data regarding its genotoxicity *in vivo* are missing. The substance was also identified as mutagenic in studies carried out *in vitro*. No data are available on mutagenicity *in vivo* are available.

7.4 Summary and conclusions

Alternatives to the use of hypochlorites have been identified. In the last years, many efforts have been made to avoid the use of chlorine based reagents in an attempt to increase the safety against the accidental release of toxic chlorine gas and chloramines in households and to avoid the formation of potential hazardous by-products in environments such as swimming pools. Very appropriate documents to assess the different alternatives are the Guidance Manual of the US EPA on alternatives to disinfectants and oxidants (1999), the assessment on alternatives to chlorine as disinfectant in swimming pools provided by the Danish EPA (2007) and the different reports of the World Health Organisation.

The non-chlorine-based disinfection technologies for drinking, swimming pool and wastewater treatment (ozone and ultraviolet light) have relatively high capital costs. Moreover, ozone is a very toxic gas that could seriously threat safety of users and operators in case of a potential leak. These techniques have also high implementation capital costs and in the case of ozone based-technologies, additional systems to monitor the potential leakages must be implemented in the occupational environment. Their main advantage is the good performance in disinfection of water and the low potential to generate halogenated organic by-products. It should be stated that the use of sodium and calcium hypochlorites is an excellent tool for the disinfection of water. Its main drawback, the formation of halogenated organic by-products can be avoided by an adequate management of the influent water. An accurate control and management of the content of organic matter in the water previous to its chlorination would avoid the formation of these undesirable by-products.

In cleaning and disinfection, different alternatives in the professional and domestic environment have been assessed. Among them, the use of peracetic acid is the most suitable candidate to replace hypochlorites due to the lower production of organohalogen compounds and its high degradability.

From the alternatives exposed for bleaching, sodium perborate and hydrogen peroxide could be even more hazardous than sodium hypochlorite. Sodium percarbonate however, has been identified as a very promising reagent and a good potential candidate to replace sodium hypochlorite for bleaching purposes in both, domestic and industrial uses.

8. Abbreviations and acronyms

ATSDR	Agency for Toxic Substances and Disease Registry
BOD	Biological Oxygen Demand
BPR	Biocidal Products Regulation
CAC	Combined Available Chlorine
COD	Chemical Oxygen Demand
CLP	Classification, Labelling and Packaging Regulation
CoRAP	Community Rolling Action Plan
ECHA	European Chemicals Agency
EPA	Environmental Protection Agency
EU	European Union
FAC	Free Available Chlorine
GAC	Granular Activated Carbon
HAA	Haloacetic acids
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IMO	International Maritime Organization
IRIS	Integrated Risk Information System
LOUS	List Of Undesirable Substances
MAC	Maximum Allowable Concentration
MAK	Maximal Arbeitsplatz Koncentration
OECD	Organization for Economic Cooperation and Development
OEL	Occupational Exposure Limit
PCC	Poison Control Center
PPE	Personal Protection Equipment
PT	Product Type
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SCE	Sister Chromatid Exchange
SIDS	Screening Information Data Sets
SPIN	Substances in preparations in the Nordic Countries
STEL	Short-Term Exposure Limit
TRC	Total Residual Chlorine
TWA	Time Weighted Average
THM	Trihalomethanes
UNEP	United Nations Environment Program
USDA	United States Department of Agriculture
UV	Ultraviolet Radiation
TDI	Tolerable Daily Intake
WHO	World Health Organization

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Appendix 1: Background information to Chapter 3 on legal framework

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 regulate 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 Regulation1 and the CLP Regulation2 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 tonnes/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 risk 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 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 publish 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.

On-going 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:

1. It has to be identified as a SVHC leading to inclusion in the candidate list3
2. 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)
3. 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

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. 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.

Survey of sodium and calcium hypochlorite

This survey is part of the Danish EPA's review of the substances on the List of Undesirable Substances (LOUS). The survey concerns sodium and calcium hypochlorite. The report present information on the uses and existing regulation. It also includes information on environmental and health effects and on alternatives to these substances.

Denne kortlægning er et led i Miljøstyrelsens kortlægninger af stofferne på Listen Over Uønskede Stoffer (LOUS). Kortlægningen omhandler Na- og Ca hypochlorit. Rapporten indeholder en beskrivelse af brugen og eksisterende regulering, samt beskrivelser af miljø- og sundhedseffekter og alternativer til disse stoffer

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