SODIUM HYPOCHLORITE

CAS No.: 7681-52-9

EINECS No.: 231-668-3

SUMMARY RISK ASSESSMENT REPORT

Final Summary, September 2009

Italy

FINAL APPROVED VERSION

Rapporteur for the risk assessmente of sodium hypochlorite is Italy.

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PREFACE

This report provides a summary, with conclusions, of the risk assessment report of the substance sodium hypochlorite that has been prepared by Italy in the context of Council Regulation (EEC) No. 793/93 on the evaluation and control of existing substances.

For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references the reader is referred to the comprehensive Final Risk Assessment Report (Final RAR) that can be obtained from the European Chemicals Bureau[1]. The Final RAR should be used for citation purposes rather than this present Summary Report.

[1] European Chemicals Bureau – Existing Chemicals – http://ecb.jrc.it

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1. GENERAL SUBSTANCE INFORMATION

1.1 Chemical identity

CAS Number:	7681-52-9
EINECS Number:	231-668-3
IUPAC Name:	Sodium hypochlorite
Structural Formula:	$Na^{+}ClO^{-}$
Molecular Formula:	ClO.Na
Molecular Mass (g/mol):	74.4

1.2 Physico-Chemical Properties

Property	Value	References
Physical state	Liquid	
Melting point	- 20°C to -30°C	Safety data sheet Hoechst AG 1994
Boiling point	96°C to 120 °C	Safety data sheet Hoechst AG 1994
Relative density	1.23 g/cm³ at 25°C	Sicherheitsdatenblatt der Bayer AG
Vapour pressure	17.4 - 20 hPa at 20°C	Safety Data Sheet Rhone Poulenc
Water solubility	Miscible [29.3 g/100 g (0 deg C) in water]	HSDB
Partition coefficient n-octanol/water (log value)	n.a.	
Granulometry	n.a.	
Conversion factors		
Flash point	n.a.	
Autoflammability		
Flammability		
Explosive properties	Anhydrous sodium hypochlorite is very explosive	HSDB
Oxidizing properties	Strong oxidizing agent usually stored and used in solution	HSDB
Viscosity		
Henry's constant	See par. 2.7	

1.3 Classification

According to Directive EEC 67/548 Annex I and its amendments sodium hypochlorite (Index-No. 017-011-00-1) is classified as follow:

Current classification according to Annex I (29th ATP):
Classification: C, N
R-sentences: 31-34-50
S-sentences: (1/2)-28-45-50-61
Specific limits:
$C \geq 10\%$: C R31-34
$5\% \leq C < 10\%$: Xi R31-36/38

According to the Dangerous Substances Directive 67/548/EEC and subsequent amendments and to the Dangerous Preparation Directive 88/379/EEC, sodium hypochlorite solutions are classified as follows:

- Solution less than 5%: Not classified
- Solution from 5% to 10% available chlorine: Irritant with the risk phrases R 31: contact with acids liberates toxic gases and R 36/38: irritating to eyes and skin
- Solution above 10% available chlorine: corrosive with the risk phrases R 31: contact with acids liberates toxic gases and R 34: causes burns.

This classification includes the risk related to the sodium hydroxide always present as a stabilizer in concentrations up to 1%.

Theoretical pure sodium hypochlorite should be classified as “very toxic to aquatic organisms” (N, R50) based on aquatic toxicity data, and as “harmful for ingestion” (Xn, R22) on the basis of the oral LD_{50} data.
This classification does not apply to solutions as their concentration is always below 25%.

2. GENERAL INFORMATION ON EXPOSURE

Sodium hypochlorite, prepared by Labarraque for the first time in 1820 using chlorine gas and sodium hydroxide and called "Eau de Labarraque", was used for disinfection (Holleman and Wiberg, 1976). The product was also used for bleaching in paper making. At present sodium hypochlorite is manufactured by the absorption of chlorine in ca. 21% caustic soda solution. The chlorine and the caustic soda are made by electrolysis of brine, and the chlorine is added as gas or liquid.
Hypochlorite is also produced naturally in vivo for cell defence processes. Hypochlorite is produced by chloroperoxidases, which are, among others, produced by mammals (in white blood cells), lichens and in many fungal species (Vollenbroek *et al.*, 1995). Active chlorine species representing chlorine at a formal + 1 oxidation state (HOCl, Cl_2, N-chloroamide, etc.) have been quantified to some extent in one study looking at the rate of conversion of oxygen into polymorphonuclear leukocytes when phagocytozing a micro-organism. It was demonstrated that 28% of the consumed oxygen is converted into active chlorinating agents (Foote *et al.*, 1983).

Sodium hypochlorite is used:

- for household and laundry cleaning, sanitation, deodorizing and disinfection
- for municipal water, sewage and swimming pool disinfection
- for medical environment disinfection
- for disinfection purposes in food industry and food manipulation
- for textile industry and pulp and paper bleaching
- for chemical synthesis
- as a multisite fungicide in agriculture and horticulture
- as an oxidant in a very wide range of activities

There are three species of chlorine in equilibrium in water: gaseous chlorine, HOCl (also a gas at room temperature and pressure), and ClO^-. For example, at pH 7.5 half of the chlorine is active as HOCl and half is available as ClO^-. The pH of commercial solutions is above 11 and the only species effectively present is ClO^-.

3. ENVIRONMENT EXPOSURE ASSESSMENT

3.1 Environmental exposure

3.1.1 Introduction

Environmental exposure may occur through the production and uses of sodium hypochlorite and additionally through the formation of hypochlorite through the use of chlorine in water. These sources of hypochlorite are all included in this risk assessment. Due to the instability and highly reactive nature of hypochlorite it will disappear very rapidly when entering the environment.

Though oxidised molecules will be the dominant by-products of hypochlorite use, chlorinated species have been viewed as the more important to assess from an environmental point of view because of the hazardous properties of certain types of chlorinated molecules. In each scenario, a calculation of an additional PEC for chlorinated reaction products measured as adsorbable organic halogens (AOX), or in the case of swimming pools, as trihalomethanes (THM), was performed. The AOX values are given as additional to the background concentration of AOX, which can vary up to a value of 10-15 μg/l. These AOX values are only descriptive calculations and cannot be used directly for risk characterisation.

3.1.2 Aquatic compartment (incl. sediment)

3.1.2.1 Calculation of AOX PEC_{local}

Two scenarios can be considered:

<u>Scenario 1 Realistic European Average</u>

In our local scenario we have hypothesized for 10,000 inhabitants (3 persons per family unit) a consumption of 1 liter of 4% (P) hypochlorite solution (mean concentration on the market is around 4) per month per each family unit.

For this scenario an AOX PEC_{local} of 0.8 μg/l has been determined.

In particular the following PEC_{local} values have been calculated for the specific by-products for the realistic scenario:

$PEC_{local\ THM}$ =0.019 μg/l (as AOX) = 0.022 μg/l as $CHCl_3$
$PEC_{local\ TCA}$ = 0.024 μg/l (as AOX) = 0.036 μg/l as TCA
$PEC_{local\ HAA}$ = 0.010 μg/l (as AOX) = 0.019 μg/l as DCA

<u>Scenario 2 Worst case</u>

This scenario is based on the Spanish consumption of 11.8 kg/person/year (expressed as 3% – 5% product), which is the highest in Europe.

For this scenario an AOX PEC_{local} of 3.9 μg/l has been determined.

In particular the following PEC_{local} values have been calculated for the specific by-products for the worst case scenario:

$PEC_{local\ THM}$ =0.094 μg/l (as AOX) = 0.11 μg/l as $CHCl_3$
$PEC_{local\ TCA}$ = 0.12 μg/l (as AOX) = 0.18 μg/l as TCA
$PEC_{local\ HAA}$ = 0.051 μg/l (as AOX) = 0.092 μg/l as DCA

3.1.2.2 Calculation of $PEC_{localwater}$ for chlorinated organic by-products

The derived PEC values for chlorinated organic by-products

Scenario	$PEC_{local\ water}$ (µg/l)		
	AOX	THM	HAA
Household	0.8-3.9	0.022 – 0.11	0.055 - 0.27
Swimming Pools: • routine • emptying		 0.02 0.67	 0.16 6.22
Sewage Treatment	80*	7	3.5
Textile • wool shrinkproofing	 10	 0.10	 0.21
Drinking Water: • groundwater • Surface water • Good quality • DWD compliant • Non-compliant • Upland, acid		 0.05 0.35 0.70 1.70	 0.04 (0.10 – 0.68) 0.17 (0.21 – 1.35) 0.34 (0.51 – 3.30) (1.08 – 7.80)
Pulp and paper • Bleaching (discontd) • Broke repulping	 3100 25**	 14	 1.25
Cooling Water (freshwater/marine)		3.0/0.3	1.0/0.1
Institutional and Food Industry (inc Hospitals) Hospital scenario Hospital + household	0.15 1.25 2.05 – 5.15	0.004 0.034 0.056 – 0.144	0.010 0.086 0.141 – 0.356

* Indicative figure assuming 2% Cl to AOX conversion and 10-fold dilution into receiving water

** Based on UK benchmark emission value 500 µg/l; 50% from applied hypochlorite and 10-fold dilution into receiving water

3.1.3 Atmosphere

Because hypochlorite solutions are non volatile, no significant potential for dispersion in the air exists. However, hypochlorite may release chlorine when accidentally mixed with acids.

3.1.4 Terrestrial compartment

The possible exposure routes of soils to HOCl are via contaminated sludges or via direct application of chlorinated water. As can be calculated with the model of Vandepitte and Schowanek, 1997 (Appendix 2) it becomes clear that HOCl concentrations available in domestic discharges are completely eliminated in the sewer system before entering the activated sludge system. In addition HOCl is a highly soluble molecule not likely to sorb onto activated sludges. Therefore, there is no evidence that HOCl has the potential to contaminate activated sludges. And as a consequence, contamination of soils due to dumping of with HOCl polluted sludges can be excluded.

Contamination of soils due to direct application of chlorinated water will not be of permanent origin. The high content of organic matter in a soil will allow a quick (order of seconds) reduction of HOCl.

3.1.5 Non compartment specific exposure relevant to the food chain (secondary poisoning)

No secondary poisoning exposure is thought to occur with hypochlorite as it is destroyed rapidly in contact with organic as well as inorganic species.

3.2. Effect assessment

3.2.1. Aquatic compartment (incl. sediment)

Summary of data used for the PNEC for freshwater organisms

SHORT-TERM TOXICITY				
	Valid data		Supportive information	
	Endpoint	**Study Details/Reference**	**Endpoint**	**Study Details/Reference**
Fish	-		96-168h LC50 = 60-33 µg TRC/l >30 - > 16.5 µg FAC/l (FAC > 50%)	(intermittent exposure, 40'x3 times/d) (Heath, 1977, 1978)
Crustacean (Ceriodaphnia)	24h LC50 = 5 µg FAC*/l (rated 2)	Taylor, 1993		
Algae	-		-	
LONG -TERM TOXICITY				
	Valid data		**Supportive information**	
Fish	-		134d NOEC = 5 µg TRC/l No FAC specified.	growth (field study) (Hermanutz et al., 1990)
Crustacean	-		-	
Mollusks (bivalves)	-		36d 100% mortality	50 µg TRC/l
Algae	7d NOEC = 3 µg TRC/l (rated 2) 2.1 µg FAC/l (FAC 73%)	Biomass (microcosm study) (Cairns et al., 1990)	28d EC50 = 2.1 µg TRC/l 2.1 µg FAC/l (FAC 100%)	Biomass (microcosm study) (Pratt et al., 1988)
Mesocosm study			24d NOEC = 1.5 µg TRC/l (rated 2) 1.5 µg FAC/l (FAC 100%)	(zooplankton density) (Pratt et al., 1988)

FAC (free available chlorine); TRC= total residual chlorine; *FAC as HOCl
rates: 1= valid; 2= valid with restriction; s= supportive information

Summary of ecotoxicity data selected for the determination of the pnec for brackish and sea water organisms

SHORT-TERM TOXICITY				
	Valid data		Supportive information	
	Endpoint	**Study Details/Reference**	**Endpoint**	**Study Details/Reference**
Fish	96hLC50 = 32µg TRO/l (rated 2)	Thatcher, 1978	48hEC50 = 8µg TRC/l	(eggs) Middaugh et al., 1977
Fish	96hLC50 = 90µg TRC/l (rated 1)	Bellanca and Bailey, 1977		
Crustaceans	-	-	-	-
Mollusks	48h EC50 = 26µg TRC/l (rated 2)	Roberts and Gleeson, 1978		
Algae	-	-	-	-
LONG TERM TOXICITY				
	Endpoint	**Study Details/Reference**	**Endpoint**	**Study Details/Reference**
Fish	28d NOEC = 40 µg CPO /l (rated 1)	(fry survival) Goodman et al., 1983		
Crustaceans	-	-	-	-
Mollusks	15d NOEC = 7 µg TRO/l (rated 2)	(shell deposit) Liden et al., 1980		
Algae	-		21d EC50 = 1-10 µg TRC/l	(periphytic community, intermittent exposure) Sanders et al., 1981
Phyto and Zoo-plankton	-		1y EC50 < 10 µg TRC/l	(biomass reduction) (microcosm study) Erickson and Foulk, 1980

TRO =Total residual oxidant
TRC= total residual chlorine
CPO = Chlorine-produced oxidants
rates: 1= valid; 2= valid with restriction; s= supportive information

3.2.1.1 PNEC derivation

Freshwater

A factor of 10 for the derivation of the PNEC is judged not sufficiently protective and a factor of 50 to the lowest NOEC is applied: PNEC = 3 µgTRC/l/50 = 0.06 µgTRC/l corresponding to 2.1 µgFAC/l/50 = 0.04 µgFAC/l.

Saltwater

When, after 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), as it is the case in the present assessment, the TGD recommends that a factor of 50 is applied to the lowest figure. Hence, $PNEC_{saltwater}$ = 3 µgTRC/l/50 = 0.06 µgTRC/l corresponding to 2.1 µgFAC/l/50 = 0.04 µgFAC/l.

3.2.1.2 Calculation of PEC for chlorinated organic by-products halogenated organic by-products

Trihalomethanes

The draft Risk Assessment for chloroform (Chloroform Risk Assessment, 2007) estimates a $PEC_{\text{regional water}}$ = 0.268 µg/l in surface water and a $PNEC_{\text{aquatic}}$ of 146 µg/l.
It is beyond the scope of this risk assessment to derive PNECs for the brominated trihalomethanes. However, ecotoxicological data gathered by Khalanski et al (2000) in connection with assessment of seawater chlorination suggest that the ecotoxicities of the brominated THMs are not markedly different from chloroform. In view of the above, it seems reasonable for the purposes of a broad assessment to regard the trihalomethanes as of similar aquatic toxicity and to use the chloroform PNEC for total trihalomethanes.

Haloacetic acids

The OECD SIDS risk assessment arrived at an aquatic PNEC for TCA of 0.17 µg/l based on algal toxicity and a $PEC_{regional}$ of 0.12 µg/l. It has since been accepted by the TM, and by Germany who were the Rapporteurs for the SIDS assessment, that the data is such that an assessment factor of 10 can be used rather than 50 which give rise to a PNEC for TCA of 0.85 µg/l, and this is used here.
For DCA, a PNEC of 0.72 µg/l was already set agains based on algal toxicity and using the risk assessment factor of 10 on data for TCA and MCA in the EU Risk Assessment for trichloroethylene. The comparable data for MCA would indicate a PNEC of 0.58 µg/l.
While it is similarly beyond the scope of this risk assessment to derive formal PNECs for other haloacetic acids, a broad assessment can be made, bearing in mind that in all but high bromide situations the TCA and DCA are formed in at least an order of magnitude higher concentrations than MCA or the brominated acids.

N-chloroamino compounds

N-chloramines and amides are likely to be formed in most scenarios as hypochlorite reacts with organic matter that contains amino acids and proteins. Though little eco-toxicity data for these compounds has been discovered, an indication can be obtained using QSARs.

3.2.2 Atmosphere

There are no data on effects of hypochlorite (ClO^-) in the atmospheric compartment but it is only present at very low levels in the atmosphere. So effect assessment is not applicable.

3.2.3 Terrestrial compartment

There are no data on effects of hypochlorite in the terrestrial compartment but it is normally not present in soil. So effect assessment is not applicable.

3.2.4 Non compartment specific effects relevant to the food chain (secondary poisoning)

No data on hypochlorite effects relevant to the food chain are available but no hypochlorite residue is thought to be present or to accumulate in the food chain. So an effect assessment is not applicable.

3.3 Risk characterisation

3.3.1 Aquatic compartment (incl. sediment)

Although a defined PNEC for sodium hypochlorite has been derived as **0.03 µg**TRC**/l** as both for freshwater and sea water, it is very difficult to quantify an exact PEC. For each scenario the risk characterisation will be discussed, based on available or predicted data.

For the aquatic compartment, PEC information has been given for both $HOCl/OCl^-$ and for reaction by-products for several of the use scenarios. These will be considered separately below.

3.3.1.1 Sodium Hypochlorite

Production or Production of other Chemicals: For about 75% of the sites for which data allowed an estimate, no residual oxidant is expected to be present in the final effluent based on the presence of chemical oxygen demand (COD). For a few sites where TRC in the effluent was below the limit of detection, it cannot be excluded that the PEC could initially be above the PNEC. However, the reactive nature of TRC ensures that it is rapidly destroyed in surface water, and it is expected that PEC_{local} concentrations will be very low at or soon after the point of release into the receiving water. Additionally, common control mechanisms at chlor-alkali production (all sites fall under IPPC BREF) and specific local regulations should ensure that no risks from hypochlorite production or intermediate use occur at or close to these sites.
Conclusion (ii)

Household, Swimming Pool, Drinking Water: Calculated PEC are between 10^{-22} and 10^{-32} µg/l of FAC based on modelling of the decay of hypochlorite in the sewer. In conclusion, these scenarios lead to a risk estimation of no concern and no risk reduction measures are applicable.
Conclusion (ii)

Sewage Treatment: Under this scenario, all available chlorine disappears rapidly leading to a calculated PEC as low as 10^{-32} µg/l of FAC based on modelling of the decay in the STP. In conclusion these scenarios lead to a risk estimation of no concern and no risk reduction measures are applicable.
Conclusion (ii)

Cooling Water: 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 TRO 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).
Conclusion (ii)

Textile Bleaching, Pulp and Paper, Institutional and Food Industry: Hypochlorite is shown to disappear rapidly from these use scenarios, either being rapidly reduced in factory effluent or in the sewer, giving calculated PEC values of 10^{-22} µg/l to 10^{-32} µg/l applies.

Conclusion (ii)

In conclusion, no risks to the environment related to NaClO as such are present for the different scenarios.

3.3.1.2 By-Products of sodium hypochlorite applications

The risk from the two major by-product types, THMs and haloacetic acids, are assessed by conventional PEC/PNEC calculations.

3.3.1.2.1 Production

No organic by-product arise during the production process

Conclusion (ii)

3.3.1.2.2 Household

Trihalomethanes

The PEC/PNEC ratio for trihalomethanes, treating them all as chloroform, by–product from household hypochlorite use in the realistic case is:

$$(PEC_{local}+PEC_{regional})/PNEC = (0.022 + 0.268)/146 = 0.0020$$

Taking the worst case scenario of 3.9 µg/l for $PEC_{local\ AOX}$, the corresponding PEC for chloroform would be 0.38µg/l, or 0.1 µg/l assuming 90% removal, both expressed as AOX. The latter equates to 0.11 µg/l as chloroform.

The PEC/PNEC ratio for chloroform by –product from household hypochlorite use is thus:

$$(PEC_{local}+PEC_{regional})/PNEC= 0.11 + 0.268 / 146 = 0.0026$$

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for TCA for the realistic is 0.184 while the worst case PEC/PNEC ratio would be 0.353

For other haloacetic acids , treating them all as DCA,

$$PEC_{local}/PNEC= 0.026 \text{ (realistic case)}$$
$$PEC_{local}/PNEC= 0.128 \text{ (worst case)}$$

Adding the risk quotients for all haloacetics acids, as they may have similar toxic modes of action, gives Risk Quotients of:

$$0.184 + 0.026 = 0.21 \text{ (realistic case)}$$
$$0.353 + 0.128 = 0.48 \text{ (worst case)}$$

Conclusion (ii)

Other identifiable molecules

Individual PECs will collectively less than 0.8µg/l (realistic case) and less than 3.9 µg/l (worst case). Each will be less than for chloroform, TCA and DCA and of the order of 1 – 100 ng/l. Although individual PNECs are not available, there is no reason to believe that the PEC / PNEC ratios would be likely to be such as to indicate a risk.

Conclusion (ii)

Non-identified reaction products

PEC/PNEC calculations for the identified, risk assessed by-products indicate no concern for trihalomethanes or haloacetic acids for worst-case scenarios.
PECs for other identified by-products are sufficiently low as to provide no cause for concern.
The remaining by-products do not increase the toxicity of treated effluents and have properties which, coupled with a total combined PEC of < 1 µg/l, suggest they are unlikely to cause adverse effects in the aquatic environment, even in the long term.

Conclusion (ii)

3.3.1.2.3 Production of Other Chemicals

Organic by-products will be entirely dependent on the reaction substrate and risks should be assessed in risk assessments dealing with those products.

3.3.1.2.4 Swimming Pools

Trihalomethanes

The PEC/PNEC ratio for trihalomethane by–products from hypochlorite use in swimming pools is thus:

Routine discharge:

$$(PEC_{local}+PEC_{regional})/PNEC = (0.02+0.268)/146 = 0.0020$$

Complete emptying (twice per year)

$$(PEC_{local}+PEC_{regional})/PNEC = (0.67+0.268) / 146 = 0.0064$$

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by–products from hypochlorite use in swimming pools is:

Routine discharge:

$(PEC_{local}+PEC_{regional})/PNEC= (0.16 + 0.12) / 0.85 = 0.33$

Compete emptying (twice per year)

$(PEC_{local}+PEC_{regional})/PNEC= (6.22+0.12) / 0.85 = 7.46$

Alternatively, assessing complete emptying vs the more appropriate PNEC intermittent of 2.58 µg/l gives:

$(PEC_{local}+PEC_{regional}) / PNEC_{intermittent}= (6.22 + 0.12) / 2.58 = 2.46$

For complete emptying, the PEC/PNEC ratio would point to a possible concern and need for further information. In this regard, the whole effluent tests conducted on chlorinated raw sewage which would be expected to contain around 40µg/l of haloacetic acids show no elevated toxicity versus unchlorinated effluents. This is consistent with standard algal toxicity tests newly conducted against standard species of algae. It should be noted that the complete emptying scenario is highly conservative.
Taking the uncertainty about the TCA, and thus DCA, PNECs, and the lack of increased toxicity in the whole effluent test together with the highly conservative scenario for pool emptying, the overall weight of evidence thus indicates no concern for the PEC_{local} of 6.22 µg/l.

Conclusion (ii)

Other halogenated organic by-products

The reaction conditions and substrates present in swimming pools are broadly comparable to those for the Household scenario and thus by-products mixtures of broadly the same nature would be expected i.e. relatively biodegradable and unlikely to bioaccumulate. The whole effluent testing conducted on chlorinated raw sewage, which is an extreme worst case for this scenario, confirms these expectations, and shows the organic by-products do not increase the toxicity of the effluent. Because swimming pool pH is maintained between 6.5 and 8.5, formation of dioxins or similar high-hazard molecules is not expected.

Conclusion (ii)

3.3.1.2.5 Sewage Treatment

Trihalomethanes

The PEC/PNEC ratio for trihalomethane by–products from hypochlorite use in sewage treatment is thus:

$(PEC_{local}+PEC_{regional})/PNEC= (7.0+0.268)/146 = 0.050$

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by–products from hypochlorite use in sewage treatment is thus:

$$(PEC_{local}+PEC_{regional})/PNEC = (3.5 + 0.12)/0.85 = 4.25$$

This PEC/PNEC ratio would point to a possible concern and need for further information. In this regard, the whole effluent tests conducted on chlorinated raw sewage which would be expected to contain around 40µg/l of haloacetic acids shows no elevated toxicity versus unchlorinated effluents. The whole effluent test is a direct model of the use of hypochlorite in sewage disinfection, even of raw sewage, except that the whole effluent test used higher dosages of hypochlorite than normal (50 mg/l vs 10 – 20 commonly used) and a long contact time (60 mins vs 30 – 60 mins actually used).
Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence thus indicates no concern for the PEC_{local} of 3.5 µg/l.

Conclusion (ii)

Other halogenated organic by-products

The reaction conditions and substrates present in sewage chlorination are broadly comparable to those for the Household scenario and thus by-products mixtures of broadly the same nature would be expected i.e. relatively biodegradable and unlikely to bioaccumulate. The whole effluent testing directly confirms these expectations, and shows the organic by-products do not increase the toxicity of the effluent. Investigations of the sources of dioxins in sewage sludge have not identified chlorination as a significant contributor: because sewage chlorination takes place at around neutral to alkaline pH formation of dioxins or similar high-hazard molecules is not expected.

Conclusion (ii)

3.3.1.2.6 Textiles

Trihalomethanes

The maximum PEC/PNEC ratio for trihalomethane by–products from hypochlorite use in wool chlorination is :

$$(PEC_{local}+PEC_{regional})/PNEC= (0.10+0.268) / 146 = 0.0025$$

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by–products from hypochlorite use in wool chlorination is:

$$(PEC_{local}+PEC_{regional})/PNEC= (0.21 + 0.12) / 0.85 = 0.39$$

Conclusion (ii)

Other halogenated organic by-products

Chlorinated proteins and N-chloro amino acids would be expected to be biodegradable and not liable to bioaccumulation.

If dioxin formation does occur, the quantities seem limited and the effluents contain no more in TEQ terms than domestic washing machine effluent where they arise from adventitious sources via clothing.

Conclusion (ii)

3.3.1.2.7 Drinking Water

Trihalomethanes

The PEC/PNEC ratio for trihalomethane by–products from hypochlorite use in drinking water chlorination for the worst case concentrations for various raw water quality scenarios is thus:

$$(PEC_{local}+PEC_{regional})/PNEC= (PEC_{quality} + 0.268) / 146 =$$

Water source	Water quality	PEC µg/l	PEC/PNEC
Groundwater		0.05	0.0022
Surface Water:	Good quality	0.35	0.0042
	DWD compliant	0.70	0.0066
	Non-DWD compliant	1.70	0.0135

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by–products from hypochlorite use in drinking water chlorination for the worst case concentrations for various raw water quality scenarios is thus:

$$(PEC_{local} +PEC_{regional})/PNEC=(PEC_{quality}+0.12)/0.85 =$$

Water source	Water quality	PEC µg/l	PEC/PNEC
Groundwater		0.04	0.19
Surface Water:	Good quality	(0.10 – 0.68) 0.17	(0.26 – 0.94) 0.34
	DWD compliant	(0.21 – 1.35) 0.34	(0.39 – 1.73) 0.54
	Non-DWD compliant	(0.51 – 3.30)	(0.74 – 4.02)
	Upland, acid	(1.08 – 7.80)	(1.41 – 9.32)

For poorer quality surface water sources, the PEC/PNEC ratio would point to a possible concern and need for further information. Considering the cases further, the high levels of HAAs potentially arise in ordinary surface waters when several worst case assumptions are combined. For DWD compliant water, the most likely case shows a PEC/PNEC well below 1. The non-DWD compliant case should disappear as the Directive becomes fully implemented. The case of upland acid waters is less directly controlled by the DWD which focuses on THMs, but as noted in the discussion the data show that where improved treatment processes have been implemented, implicitly focused on THMs, the levels of HAAs have fallen dramatically, enough to bring HAA levels in many cases low enough not to exceed the PNEC. Since 57% of water used in the EU in 2002 came from groundwater, and upland acid waters are normally drawn upon by small populations, it seems likely that when the DWD is fully implemented only a few per cent of EU drinking water would be likely to exceed the HAA PNEC.
Another perspective is provided by the whole effluent tests conducted on chlorinated raw sewage. Effluents which would be expected to contain around 40µg/l of haloacetic acids, showed no elevated toxicity versus unchlorinated effluents. In comparison, PEC_{local} values up to 7.80 µg/l have been calculated for an extreme worst case for drinking water. The hypochlorite doses and ranges and concentrations of substrates available in raw sewage are much greater than would apply in drinking water production. The possibility that exceptionally high HAA levels in potable water might constitute an environmental risk should be noted though the risk assessment for this scenario could be refined by reassessment of the TCA and interpolated DCA PNECs.
Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence indicates no concern.

Conclusion (ii)

Other halogenated organic by-products

The reaction conditions and substrates present in sewage chlorination are broadly comparable to those for the Household scenario and thus by-products mixtures of broadly the same nature would be expected i.e. relatively biodegradable and unlikely to bioaccumulate. The whole effluent testing conducted on chlorinated raw sewage, which is an extreme worst case for this scenario, confirms these expectations, and shows the organic by-products do not increase the toxicity of the effluent. Because chlorination takes place at pH close to neutral, dioxin formation is not expected, nor is there good evidence to suggest that chlorination makes a significant contribution to the normally low dioxin levels in drinking water.

Conclusion (ii)

3.3.1.2.8 Pulp & Paper

Chlorinated by-product formation during machine cleaning is likely to be similar to that in industrial cleaning and within the boundaries of the Whole Effluent testing.

Conclusion (ii)

Trihalomethanes

The PEC/PNEC ratio for trihalomethane by–products attributable to hypochlorite use in broke repulping is :

$$(PEC_{local} + PEC_{regional})/PNEC = (14+0.268)/146 = 0.098$$

Conclusion (ii)

Haloacetic acids

The potential PEC/PNEC ratio for any haloacetic acid by–products arising from hypochlorite use in broke repulping could be:

$$(PEC_{local} + PEC_{regional})/PNEC = (1.25+0.12)/0.85 = 1.61$$

Such a PEC/PNEC ratio would point to a possible concern and need for further information. In this regard, the whole effluent tests conducted on chlorinated raw sewage which would be expected to contain around 40µg/l of haloacetic acids shows no elevated toxicity versus unchlorinated effluents.
The risk assessment for this scenario could be refined by reassessment of the TCA and interpolated DCA PNECs.
Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence thus indicates no concern for the PEC_{local} of 1.25 µg/l.

Conclusion (ii)

Other halogenated organic by-products

N-chloroamino compounds, which are expected to be the other dominant halogenated species would be expected to be biodegradable, not liable to bioaccumulation, and of low toxicity.
Since broke repulping takes place at alkaline pH, formation of dioxins is not expected. Any formation of chlorinated phenols from the low levels of lignin possibly present would be expected to be of mono- or di-chlorinated species similar to those that can occur when hypochlorite is used in sewage disinfection. While substrates in broke repulping are more restricted to cellulose and minor additives such as WSRs, the whole effluent test conducted on chlorinated raw sewage at similar hypochlorite doses for similar contact times provides some reassurance that harmful effects would not be expected.

Conclusion (ii)

3.3.1.2.9 Cooling Water

Trihalomethanes

The PEC/PNEC ratio for trihalomethane by–products from hypochlorite use in cooling water treatment is thus:

Seawater case
$(PEC_{local}+PEC_{regional})/PNEC= (0.3+0.268)/146 = 0.004$

Freshwater case
$(PEC_{local}+PEC_{regional})/PNEC = (3.0+0.268)/146 = 0.022$

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by–products from hypochlorite use in cooling water treatment is thus:

Seawater case
$(PEC_{local}+PEC_{regional})/PNEC = (0.1+0.12)/0.85 = 0.26$

Conclusion (ii)

Freshwater case
$(PEC_{local}+PEC_{regional})/PNEC = (1.0+0.12)/0.85 = 1.32$

This PEC/PNEC ratio would point to a possible concern and need for further information. Though detailed data on by-products sufficient to refine the PEC have not become available, it is clear that the hypochlorite dosage regime, and thus the chronic loads of by-product discharged, will normally be much less than for the large coastal plants. Continuous dosing, where practicised at all, is likely to run for only a few weeks a year, and often will be for only part of each day.
Another perspective is provided by the whole effluent tests conducted on chlorinated raw sewage, which act as a worst case for this scenario. The effluents tested, which would be expected to contain around 40 µg/l of haloacetic acids, showed no elevated toxicity versus unchlorinated effluents.
The risk assessment for this scenario could be refined by reassessment of the TCA and interpolated DCA PNECs.
Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence thus indicates no concern for the PEC_{local} of 1.0 µg/l.

Conclusion (ii)

Other halogenated organic by-products

The reaction conditions and substrates present in cooling water chlorination are broadly comparable to those for the Household scenario and thus by-products mixtures of broadly the same nature would be expected i.e. relatively biodegradable and unlikely to bioaccumulate. The whole effluent testing conducted on chlorinated raw sewage, which is an extreme worst case for this scenario, confirms these expectations, and shows the organic by-products do not increase the toxicity of the effluent. Because current hypochlorite use is at pH close to neutral, formation of dioxins or similar high-hazard molecules is not expected.

Conclusion (ii)

3.3.1.2.10 Institutional and Food Industry Cleaning

Trihalomethanes

The PEC/PNEC ratio for trihalomethane by–products from hypochlorite use in Institutional and Food Industry Cleaning is thus:

$$(PEC_{local} + PEC_{regional})/PNEC = (0.004+0.268)/146 = 0.0019$$

For the local hospital scenarion, the ratio would be:

$$(PEC_{local} + PEC_{regional})/PNEC = (0.034+0.268)/146 = 0.0021$$

Conclusion (ii)

For a combined scenario with the hospital effluent discharging to the same sewage treatment works as household use:

0.056 – 0.144

Household: realistic case:

$$(PEC_{local} + PEC_{regional})/PNEC = (0.056+0.268)/146 = 0.0022$$

Household: worst case:

$$(PEC_{local} + PEC_{regional})/PNEC = (0.144+0.268)/146 = 0.0028$$

Conclusion (ii)

Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by–products from hypochlorite use in Institutional and Food Industry Cleaning is thus:

$$(PEC_{local} + PEC_{regional})/PNEC = (0.010 + 0.12) / 0.85 = 0.15$$

For the local hospital scenarion, the ratio would be:

$$(PEC_{local} + PEC_{regional})/PNEC = (0.086 + 0.12) / 0.85 = 0.24$$

Conclusion (ii)

For a combined scenario with the hospital effluent discharging to the same sewage treatment works as household use:

Household: realistic case:
$(PEC_{local} + PEC_{regional})/PNEC = (0.141+0.12)/0.85 = 0.31$

Household: worst case:
$(PEC_{local} + PEC_{regional})/PNEC = (0.356+0.12)/0.85 = 0.56$

Conclusion (ii)

Other halogenated organic by-products

The reaction conditions and substrates present in cooling water chlorination are broadly comparable to those for the Household scenario and thus by-products mixtures of broadly the same nature would be expected i.e. relatively biodegradable and unlikely to bioaccumulate. The whole effluent testing conducted on chlorinated raw sewage, which is an extreme worst case for this scenario, confirms these expectations, and shows the organic by-products do not increase the toxicity of the effluent. Studies on household bleaching effluents have indicated dioxins are not formed and as I&I uses of hypochlorite are carried out at neutral or alkaline pH, especially to avoid chlorine evolution, formation of dioxins or similar high-hazard molecules is not expected.

Conclusion (ii)

3.3.2 Atmosphere

This compartment is thought to be of no risk concern due to no potential exposure.

3.3.3 Terrestrial compartment

This compartment is thought to be of no risk concern due to no potential exposure.

3.3.4 Non compartment specific exposure relevant to the food chain (secondary poisoning)

This compartment is thought to be of no risk concern due to no potential exposure.

4. HUMAN HEALTH

4.1 Human Health (Toxicity) (risk assessment concerning the potential toxic effects listed in Annex IA of Regulation 1488/94)

4.1.1. Exposure assessment

Exposure to hypochlorite solutions does not comprise inhalation exposure, except in the cases in which an aerosol is formed (Sprays scenarios in I&I and Household).

Some scenarios can result in inhalation exposure to chlorination by-products, formed when sodium hypochlorite solution reacts with organic matter (i.e. swimming pool scenario).
Consumer exposure to sodium hypochlorite generally occurs via dermal contact with diluted solutions. This contact is only occasional (household, swimming pool).
Under occupational conditions, generally only accidental dermal exposure to concentrated solutions may occur. Some scenarios can result in dermal exposure to solutions with lower concentration of sodium hypochlorite and chlorination by-products **(**i.e. swimming pool scenario, I&I, etc.)**.**
Oral exposure to sodium hypochlorite and to chlorination by-products is possible for consumer via drinking water and by accidental ingestion in the swimming pool scenario.

4.1.1.1. Occupational exposure

Workers involved in sodium hypochlorite production 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.
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 goggles and gloves is mandatory in production area. So no dermal exposure is possible, except in case of accident.
Sodium hypochlorite is used as a chlorinating and oxidizing agent of organic intermediates.
Two groups of workers can be exposed to sodium hypochlorite in swimming pools: workers handling the product to disinfect the pool and swimming instructors.
The use of NaClO in textile industry is mainly related to the cotton and linen processing sector.
The exposure to sodium hypochlorite for the workers of cooling plants and waste water and drinking water treatment plants is generally accidental, in occasion of 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.

4.1.1.1.1 Institutional and Food industry (I&I)

Accurate Market Research Data recording the penetration and usage of hypochlorite products in the Industrial and Institutional Sectors is not available, so precise exposure levels cannot be calculated. However below is a descriptive overview based on company knowledge of the following scenarios:

a) Industrial Premises Cleaning/Disinfection in Food & Beverage industries
   - a.1) cleaning-in-place (CIP) application
   - a.2) open plant spray cleaning application

b) Professional general hard surface cleaning
   - b.1) mop & bucket
   - b.2) cloth & bucket
   - b.3) trigger spray with ready-to-use solution

c) Hospital Disinfection
   - c.1) general disinfection
   - c.2) instrument disinfection

d) Cleaning/Disinfection in food preparation establishments (kitchens / restaurants)
   - d.1) kitchen disinfection (mop & bucket)
   - d.2) mechnical ware washing

e) Cleaning/Disinfection in Microbiological laboratories
   - e.1) cleaning of bench tops
   - e.2) cleaning and disinfection of laboratory tools (bottles, tubes, etc.).

Conclusions of the occupational exposure assessment for sodium hypochlorite

Scenario	Activity [1]	Frequence Days/year	Duration Hours/day	Inhalation				Dermal			
				Reasonable worst case		Typical concentration		Reasonable worst case		Typical concentration	
				Unit mg/kg/day	Method[2]	Unit	Method [2]	Unit mg/kg/day	Method [2]	Unit	Method [2]
Production and Production of other chemicals											
No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3. Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided											
Formulation											
Swimming pool operators handling starting solutions (5%)	Full shift/ Short term							0.006 (0.0057 as av. Cl_2)	EASE/ Calculated		
I&I a2, b1, b2	Full shift/ Short term							0.006 (0.0057 as av. Cl_2)	EASE/ Calculated		
I&I d1, d2, e1, e2	Full shift/ Short term							0.004 (0.0038 as av. Cl_2)	EASE/ Calculated		
Uses											
Swimming pools instructors/competition swimmers	Full shift	220	6					0.0219 [3] (0.0205 as av. Cl_2)	EASE/ Calculated		
Swimming pools instructors/competition swimmers	Short term							0.00513 [3] (0.0049 as av. Cl_2)	EASE/ Calculated		
Textile bleaching	Full shift/ Short term							0.00009 (0.000085 as	EASE/ Calculated		

								av. Cl_2)			
STP, DW and CW	Full shift/ Short term							0.006 (0.0057 as av. Cl_2)	EASE/ Calculated		
I&I (b1,b2)	Full shift							0.0105 (0.01 as av. Cl_2)	EASE/ Calculated		
I&I (d1+d2)	Full shift							0.0105 (0.01as av. Cl_2)	EASE/ Calculated		
I&I (a2)	Full shift			6.8E-05 (6.48E-05 as av. Cl_2)	Calculated						
I&I (b3)	Full shift			6.0E-07 (5.7E-07 as av. Cl_2)	Calculated						

1: Full shift, short term, etc.
2: Measured, EASE, Expert judgment, Calculated, etc.
3: Dermal + oral

4.1.1.2 Consumer exposure

Exposure for general public is relevant in household, swimming pool and drinking water scenarios, and only those will be dealt with in detail.

4.1.1.2.1 Household

There are three typical usage conditions of bleach products:

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. 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%.

4.1.1.2.2 Swimming Pool

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 (e.g. 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.
An estimation of exposure of swimming pool workers to water chlorination by-products is difficult, because of the high variability of available data, which depends on operational practices. Therefore this exposure is not further assessed in this Risk Assessment Report.

4.1.1.2.3 Drinking water

The general population is exposed to free available chlorine derived from the use of sodium hypochlorite in drinking water treatment.
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**.**

4.1.1.3 Indirect exposure via the environment

Hypochlorite will not reach the environment via the sewage treatment system, as the quick transformation of the applied hypochlorite (as FAC) in the sewage system assures the absence of any human exposure to hypochlorite. Also in recreational zones located close to discharge points of chlorinated waste water, the potential for exposure to hypochlorite originating from waste water treatment is negligible as the emission of unreacted hypochlorite is non-existent.

By-products have been measured under sewage treatment conditions. The main species identified was chloride. Additionally chlorate, monochloramine and to a less extent trihalomethanes and chloroacetic acids have been measured.

Due to the physico-chemical properties of sodium hypochlorite no indirect exposure is thought to occur via the human food chain. Thus no indirect exposure to sodium hypochlorite is thought to occur via the environment.

4.1.2 Effect assessments: Hazard identification and Dose (concentration) - response (effect) assessment

4.1.2.1 Toxicokinetics, metabolism and distribution

In the biological systems, characterised by pH values in the range 6-8, the most abundant active chemical species are HOCl and ClO^-, in equilibrium. The latter is predominant at alkaline pH values, while Cl_2 is mainly present at pH below 4. Sodium hypochlorite readily interacts with organic molecules and cellular components, leading to the formation of chlorinated organic compounds possessing their own inherent toxicity (BIBRA, 1990).
Very few data have been produced on ADME for HOCl and are limited to the oral route. No information is available on dermal exposure or inhalation.
Hypochlorous ions are physiologically present in the human body, being formed by white blood cells (neutrophils and monocytes) as a powerful antimicrobial agent during inflammation processes. The endogenously formed hypochlorous acid plays a key role in the process of phagocytosis through which bacteria are killed. Animal data suggest that after exposure via oral route, HOCl is absorbed and excreted mainly through urine as chloride (36.43% + 5.67 of the administered dose after 96h); a lesser extent of $HO^{36}Cl$-derived radioactivity not necessarily associated with absorption was detectable in the faeces 96h after exposure (14.8% + 3.7). Once in the body, it reacts directly with organic molecules to form some organochlorinated compounds, characterised by their own toxicity. No data are available for other routes of exposure, including dermal and inhalation.
Human data are very scant and indirect. Absorption is suggested by some transient and not severe systemic symptoms following ingestion, although the possibility they are secondary to a local effect could not be ruled out with certainty.

4.1.2.2 Acute toxicity

The acute toxicity of marketed hypochlorite solutions by the oral route is low. The LD_{50} values for solutions containing active chlorine concentrations up to 12.5 % are greater than 5.8 g/kg. The data for dermal acute toxicity as well as inhalation toxicity indicate a low level of toxicity even for these routes of administration.

Accidental human data are reported for ingestion and parenteral route: it can be concluded that the effects of accidental ingestion of domestic sodium hypochlorite bleaches are not expected to lead to severe or permanent damage of the gastro-intestinal tract as recovery is rapid and without any permanent health consequences. The LD_{50} and LD_0 values were calculated as follows:

LD_{50}= 12.5% (% of available Cl_2 in sol.) x 8.83 (g/kg BW LD_{50} of the sol. to female rat) = 1.1 g/kg BW (LD_{50} as available Cl_2) = 1100 mg/kg BW NaClO as av. Cl_2

LD_0= 12.5% (% of available Cl_2 in sol.) x 5.01 (g/kg LD_{50} of the sol. to female rat) =
0.626 g/kg BW (LD_{50} as available Cl_2) = 626 mg/kg BW NaClO as av. Cl_2

The only study on inhalation acute toxicity available did not show an effect on rat. This confirms that inhalation is not a route of exposure for sodium hypochlorite, except in case of aerosol formation.

4.1.2.3 Irritation/corrosivity

4.1.2.3.3 Summary data on irritation/corrosivity of the skin, eye and respiratory tract

Concerning skin irritation, some irritant responses have been recorded at around 5% hypochlorite under exaggerated conditions. Nixon et al. (1975) observed only slightly irritating effects at 5% - 5.25% available chlorine solutions in a four-hour patch test where abraded skin results were also included in the evaluation. However given the fact that in the Osterberg study, no significant irritation is observed at 4.74 % concentration where the contact time was 24 hours, the findings in the Nixon study should not raise any concern. In addition, data on human skin do not contradict this conclusion as they clearly indicate an irritating effect at 5% and above. Altough in older studies some effects were seen at lower concentrations, these would not be considered irritant according to current classification criteria.

Concerning eye irritation, some irritant responses have been recorded below 5% available chlorine on rabbits. However, the study results cannot be compared on a common basis, because different protocol variations were used and the original data on which the scores were determined are not retrievable from the study reports.
With respect to corrosivity, animal data show that a 12.7% hypochlorite solution produced severely irritant or corrosive effects to the eye. However, the same concentration applied to rabbit skin does not show corrosive effects there, as only moderate irritation was observed. Sodium hypochlorite aerosols may be irritant to the respiratory tract.
Despite some difficulties in interpreting the older animal data, the overall evaluation of both animal and human data supports the current EU classification as irritant above 5% and as corrosive above 10%.

4.1.2.4 Skin Sensitization

Three separate animal tests carried out according to standard sensitisation test protocols indicate that there is no potential for skin sensitisation from hypochlorite in animals.
Also standard sensitization patch tests in healty human volunteers do not indicate a potential for hypochlorite to induce contact sensitization.

Reports from dermatological case studies indicate that there have been a few isolated cases of allergic contact sensitization. However, these isolated cases are poorly reported and not fully conclusive. Events like the case studies reported are very scarce in view of the extensive use of hypochlorite in the marketplace. Based on the systematic animal and human study data as well as on the scarcity of alleged sensitization cases reported from the market it is concluded that sodium hypochlorite does not pose a skin sensitization hazard.

4.1.2.5 Repeated Dose Toxicity

The NTP (1992) study is used as the key study for deriving a NOEL for risk characterisation for the oral route.
From this study a NOEL of 13.75 mg/kg bw/d (or 275 mg/l available chlorine) administered in drinking water can be identified for repeated oral exposure in the rat following exposure to sodium hypochlorite. This was the highest level tested and it is the lowest NOEL that can be calculated among all studies. Additionally, the selection of this NOEL seems to be more reliable than the one from the same study on mouse which is 23.3 mg/kg bw/day (or 140 mg/l available chlorine). Indeed the rat looks somewhat more sensitive than the mouse as a study identified 24 mg/kg bw/d (450 mg/l available chlorine) as a LOEL in rat.
Slight local irritant effects have been observed following dermal exposure to a 1000 mg/l sodium hypochorite solution. No systemic effects were seen following dermal exposure to 10000 mg/l sodium hypochlorite. A NOEL of 1% from the study of Kurokawa (1984) is chosen to evaluate the local dermal effects from repeated exposure to sodium hypochlorite solutions.
For the evaluation of the effects of repeated inhalation exposure to hypochlorite aerols, it is proposed to use data from chlorine. The NOAL for repeated exposure to chlorine gas is 0.5 ppm, as confirmed by studies in rhesus monkeys and human volunteers.

4.1.2.6 Mutagenicity

The positive results produced in bacteria assays and the induction of chromosome aberrations (including gaps) and SCE in mammalian cells suggest, even if mammalian cell gene mutation studies are lacking, that sodium hypochlorite may exert an in vitro mutagenic activity.
Sodium hypochlorite was without effect in a well-conducted mouse micronucleus assay suggesting that sodium hypochlorite is not mutagenic in vivo.
The available data are not conclusive with respect to genotoxicity. Although, since sodium hypochlorite has shown lack of carcinogenicity effects, no additional testing is required.

4.1.2.7 Carcinogenicity

There are no relevant studies of sodium hypochlorite *per se* looking at its reproductive toxicity potential in animals. However, relevant studies have been conducted using chlorine as the test substance, administered in solution by gavage or in drinking water.
In a teratogenicity study, in which exposure was confined to the gestation period, no significant differences in the incidence of skeletal or soft tissue abnormalities were observed in treated groups when compared to controls. A small, but statistically significant increase in sperm head abnormalities was seen in mice, although the effect was not dose-dependant. However, no effects were seen in a well conducted one-generation reproductive toxicity study in rats up to a concentration of 5 mg/kg bw of aqueous chlorine (expressed as HOCl - maximum dose tested) (Carlton, 1986). Even if the value is expressed as HOCl, it is equivalent to available chlorine since the measure method used detects all the chlorine

species in water. Therefore, the value of 5 mg/kg bw available chlorine is used in the risk characterisation as NOEL for reproductive toxicity. Long-term toxicity studies provide also additional assurance that the substance is not a reproductive toxicant as they did not identify the testes or ovaries as target organs.
The Carlton study appears relatively more updated and reliable with a number of animals more suitable for statistical analysis.
There are no studies performed at dose levels able to induce systemic toxicity.
A pragmatic approach is to accept the NOEL derived from the Carlton study because it is the best study available even if no severe effects are shown in all dosed groups.
Although limited data are available in animals, the available studies are sufficient in their design and quality to draw the conclusion that there is no evidence to suggest that sodium hypochlorite would present adverse effects on development or fertility. Similarly, no such evidence is forthcoming from epidemiological studies on populations consuming chlorinated drinking water.

4.1.3 Risk characterisation

The following relevant toxicological endpoints have been taken into account for the risk characterisation for the human health:

Substance name	Inhalation (N(L)OAEL)	Dermal (N(L)OAEL)	Oral (N(L)OAEL) mg/kg/day (as av. Cl_2)
Acute toxicity			626 (LD_0)
Irritation / corrositivity			
Sensitization			
Repeated dose toxicity (local)	0.5 ppm (NOEL for chlorine gas)	0.1% as sodium hypochlorite	
Repeated dose toxicity (systemic)			13.75
Mutagenicity			
Carcinogenicity			
Fertility impairment			
Developmental toxicity			5.0

For acute toxicity/RDT/Reprotox the minimal MOS of 50 for workers has been derived taking into account the following Assessment Factors:

1. a factor of 4 allometric scaling factor for rats.
2. a factor of 2.5 for remaining interspecies differencies
3. a factor of 5 for human intraspecies variation

while the acute toxicity/RDT/Reprotox minimal MOS of 100 for consumers has derived taking into account the following Assessment Factors:

1. a factor of 4 allometric scaling factor for rats.
2. a factor of 2.5 for remaining interspecies differencies
3. a factor of 10 for human intraspecies variation

The calculation of MOSs and the conclusions are presented in tables below.

Occupational risk assessment for acute toxicity

	Inhalation				**Dermal**				**Combined (Dermal+oral)**			
Minimal MOS = 50	**Exposure (mg/kg/day) as Cl_2 eq.**	**LD0 (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day) as Cl_2 eq.**	**LD0 (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day) as Cl_2 eq.**	**LD0 (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**
Production and Production of other chemicals												
No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3.												
Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided												
Formulation												
Swimming pools operators handling 5% solutions					0.0057	626	1.1E+05	ii				
I&I (a2, b1 and b2)					0.0057	626	1.1E+05	ii				
I&I (d1, d2, e1 and e2)					0.0038	626	1.6E+05	ii				
Uses												
Swimming pools instructors/comp. swim.									0.0049	626	1.3E+05	ii
Textile Bleaching					0.000085	626	7.4E+06	ii				
STP, DW and CW					0.0057	626	1.1E+05	ii				

Occupational risk assessment for repeated dose toxicity

	Inhalation				Dermal				Combined			
Minimal MOS = 50	**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day as Cl_2 eq.)**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day as Cl_2 eq.)**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**
Production and Production of other chemicals No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3. Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided												
Formulation												
Swimming pool operators handling starting solutions (5%)					0.0057	13.75	2.4E+03	ii				
I&I a2, b1, b2					0.0057	13.75	2.4E+03	ii				
I&I d1, d2, e1, e2					0.004	13.75	3.4E+03	ii				
Uses												
Swimming pools instructors/comp. swim.									0.0205	13.75	670	ii
Textile Bleaching					0.000085	13.75	1.6E+05	ii				
STP, DW and CW					0.0057	13.75	2.4E+03	ii				
I&I (b1,b2)					0.010	13.75	1310	ii				
I&I (d1+d2)					0.010	13.75	1310	ii				
I&I (a2)	6.48E-05	13.75	2.12E+05	ii								
I&I (b3)	5.7E-07	13.75	2.41E+07	ii								

Occupational risk assessment for reproductive toxicity

	Inhalation				Dermal				Combined			
Minimal MOS = 50	**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**
Production and Production of other chemicals												
No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3.												
Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided												
Formulation												
Swimming pool operators handling starting solutions (5%)					0.0057	5	877	ii				
I&I a2, b1, b2					0.0057	5	877	ii				
I&I d1, d2, e1, e2					0.004	5	1250	ii				
Uses												
Swimming pools instructors/comp. swim.									0.0205	5	244	ii
Textile Bleaching					0.000085	5	5.9E+04	ii				
STP, DW and CW					0.0057	5	877	ii				
I&I (b1,b2)					0.0105	5	476	ii				
I&I (d1+d2)					0.0105	5	476	ii				
I&I (a2)	6.48E-05	5	7.72E+04	ii								
I&I (b3)	5.7E-07	5	8.77E+06	ii								

Consumer risk assessment for Acute toxicity

		Inhalation[1]/Oral[2]				Dermal				Combined (Dermal+oral)			
Minimal MOS = 100		**Exposure (mg/kg/day) as Cl_2 eq.**	**LD0 (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day as Cl_2 eq.)**	**LD0 (mg/kg/day as Cl_2 eq.)**	**MOS**	**Conclusion**	**Exposure (mg/kg/day)**	**LD0 (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**
Uses													
Household		0.000003[1]	626[1]	2.1E+08	ii	0.035	626	1.8E+04	ii				
Swimming pool swimmers	Adults									0.00519	626	1.3E+05	ii
	Childrens 1 y									0.031	626	2.02E+04	ii
	Childrens 10 y									0.011	626	5.69E+04	ii
Drinking water	Adults	0.0003[2]	626[2]	2.1E+06	ii								
	Childrens 10 y	0.0007	626	8.9E+06	ii								

[1] Inhalation
[2] Oral

Consumer risk assessment for Repeated dose toxicity

		Inhalation[1]/Oral[2]				**Dermal**				**Combined (Dermal+oral)**			
Minimal MOS = 100		**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**	**Exposure (mg/kg/day) as Cl_2 eq.**	**NOAEL (mg/kg/day) as Cl_2 eq.**	**MOS**	**Conclusion**
Uses													
Household		0.000003[1]	13.75[1]	4.6E+06	ii	0.035	13.75	393	ii				
Swimming pool swimmers	Adults									0.0021	13.75	6.5E+03	ii
	Childrens 1 y									0.00235	13.75	5.7E+03	ii
	Childrens 10 y									0.0016	13.75	9.0E+03	ii
Drinking water	Adults	0.003[2]	13.75[2]	4.6E+03	ii								
	Childrens 10 y	0.0033	13.75	4.2E+03	ii								

[1] Inhalation
[2] Oral

Consumer risk assessment for Reproductive toxicity

		Inhalation[1]/Oral[2]				Dermal				Combined (Dermal+oral)			
Minimal MOS = 100		Exposure (mg/kg/day as Cl_2 eq.)	NOAEL (mg/kg/day) as Cl_2 eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl_2 eq.	NOAEL (mg/kg/day) as Cl_2 eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl_2 eq.	NOAEL (mg/kg/day as Cl_2 eq.)	MOS	Conclusion
Uses													
Household		0.000003[1]	5[1]	1.7E+06	ii	0.035	5	143	ii				
Swimming pool swimmers	Adults									0.0021	5	2380	ii
	Childrens 1 y									0.00235	5	2232	ii
	Childrens 10 y									0.0016	5	3289	ii
Drinking water	Adults	0.003[2]	5[2]	1.7E+03	ii								
	Childrens 10 y	0.0033[2]	5[2]	1.5E+03	ii								

[1] Inhalation
[2] Oral

4.1.3.1 Man exposed via the environment

No indirect exposure is thought to occur in man due to the rapid decay of hypochlorite under use conditions. As a consequence, this exposure route is of no concern.

4.1.3.2 Combined exposure

No combination of exposure is thought of concern with sodium hypochlorite.

4.1.3.3 Risk Characterization for local effects

4.1.3.3.1 Inhalation

For local irritation effects, no study is available to determine a NOAEL for hypochlorite. As a surrogate, a respiratory inhalation study conducted for chlorine gas is used (Klonne et al, 1987). NOAEL in that study is 0.5 ppm chlorine, or 1.5 mg/m^3 chlorine.

<u>Consumers:</u>
MOS = 1.5/0.00168 mg/m^3 = 892

<u>I&I scenario b.3):</u>
MOS = 1.5/0.00168 mg/m^3 = 892

4.1.3.3.2 Dermal

The critical endpoint for repeated dermal exposure to sodium hypochlorite is irritation. The NOEL for this effect depends on the concentration of the solution.
For the evaluation of the risk of local dermal effects, the NOAEL of 0.1% (as sodium hypochlorite) has been taken into account.

Workers
Table below shows the results of the Risk Characterisation for workers repeated dermal exposure to sodium hypochlorite. For concentrations above the irritation limit (5%) it can be assumed that PPE are always used.

Workers risk assessment for repeated dermal exposure

Scenarios	Repeated Dermal exposure			
Minimal MOS = 1 NOAEL = 0.1%	Exposure to neat solution (% as available chlorine)	Exposure to in-use solution (% as available chlorine)	MOS	Conclusion
Swimming pool operators handling disinfection solution	5%: the use of PPE is assumed	No exposure		
Swimming pool: lifeguards, swimming instructors and competitive swimmers	No exposure	0.0005%	1000	ii
Textile operators	13%: the use of PPE is assumed	0.05 – 0.07%	10 - 7	ii
Sewage, drinking water, cooling water	13%: the use of PPE is assumed	No exposure		
I&I scenarios				
a1: Cleaning in Place	4-8%: the use of PPE is assumed	0.04 - 0.08%	12.5 – 6.25	ii
a2: open plant spray cleaning	4-8 the use of PPE is assumed	No exposure (1)		ii
b1: mop&bucket	4-5%: the use of PPE is assumed	0.05%	10	ii
b2: cloth&bucket	4-5%: the use of PPE is assumed	0.05%	10	ii
b3: trigger spray	No exposure	0.05%	10	ii
d1: kitchen disinfection and hospital disinfection	2-3%: in this case, exposure is accidental and not repeated	0.05%	10	ii
d2: mechanical ware washing	1-2%: in this case, exposure is accidental and not repeated	0.003%	166	ii
e1-e2: laboratories (bench top cleaning and tools cleaning)	3-4%: in this case, exposure is accidental and not repeated	0.05%	10	ii

(1) The cleaning operation is a wet exercise and operators are dressed up with watertight clothing, boots and facial masks.

Consumers

The table below shows the the results of the Risk Characterisation for consumer repeated dermal exposure to sodium hypochlorite.

Consumer risk assessment for repeated dermal exposure

Scenarios	Repeated Dermal exposure			
Minimal MOS = 1 NOAEL = 0.1%	Exposure to neat solution (% as available chlorine)	Exposure to in-use solution (% as available chlorine)	MOS	Conclusion
Laundry bleaching	1% -5% in this case, exposure is accidental and not repeated	0.05%	2	ii
Household cleaning	0.5 – 5% in this case, exposure is accidental and not repeated	0.01 – 0.25%	10- 0.4	ii (1)
Swimming pool: swimmers	No exposure	0.0005%	200	ii

(1) Repeated dose exposure to concentrations above 0.1% is uncommon

Conclusion

We conclude that no risk is expected from repeated dermal exposure of consumers and workers to sodium hypochlorite solutions.

Conclusion (ii)

4.2. Human health (physico-chemicals properties)(risk assessment concerning the properties listed in Annex IIA of Regulation 1488/94)

4.2.1. Exposure assessment

4.2.1.1. Occupational exposure

Exposure to concentrated solutions (> 10% available chlorine) may occur.

4.2.1.2 Consumer exposure

Mainly exposure to diluted solutions (< 5% available chlorine) is occurring.

4.2.1.3 Indirect exposure via the environment

No such exposure is thought to occur.

4.2.2 Hazard identification and Dose (concentration) – response (effect) assessment

4.2.2.1 Explosivity

Anhydrous sodium hypochlorite is very explosive (National Fire Protection Association, 1986). However, in common uses, sodium hypochlorite is always utilized in diluted or very diluted aqueous solutions.

4.2.2.2 Flammability

Not flammable. No information on a flash point is available (US Coast Guard, 1984-85).

4.2.2.3. Oxidizing potential

Sodium hypochlorite is one of the more commonly used oxidizing agents and a very efficient disinfectant against viruses, bacteria and fungi (Venkobachar *et al.*, 1977).

4.2.3. Risk Characterisation

4.2.3.1 Workers

Handling of concentrated products should be done with care due to the oxidizing properties. Contacts with organic materials as well as metals should be avoided. Such precautions are generally well known by workers from the chemical industry as well as those from the other use industries.
Conclusion (ii)

4.2.3.2 Consumers

Due to exposure to diluted solutions, the oxidizing potential of hypochlorite should not be of concern.
Conclusion (ii)

4.2.3.3. Man exposed indirectly via the environment

No risk is identified due to no potential exposure.
Conclusion (ii)

5 RESULTS

5.1 INTRODUCTION

5.2 ENVIRONMENT

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

5.3 HUMAN HEALTH

5.3.1 Human health (toxicity)

5.3.1.1 Workers

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) applies to all scenarios.

5.3.1.2 Consumers

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) applies to all scenarios.

5.3.1.3 Humans exposed via the environment

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) applies to all scenarios.

5.3.1.4 Combined exposure

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) applies to all scenarios.

5.3.2 Human health (risks from physico-chemical properties)

Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.

Conclusion (ii) applies to all scenarios.

Glossary of terms

ABBREVIATIONS

AOX	Adsorbable Organic Halogens
BAT	Best Available Technique
CIP	Cleaning in place
COD	Chemical Oxygen Demand
CPO	Chlorine Produced Oxidants
FAC	Free Available Chlorine
I&I	Institutional and Food industry
MAK	Maximal Arbeitsplatz Koncentration
MOS	Margin Of Safety
OEL	Occupational Exposure Limit
TGD	Technical Guidance Document
THM	Trihalomethanes
TLV	Threshold limit value
TRC	Total Residual Chlorine
TRO	Total Residual Oxidant