CHLORINE

CAS No: 7782-50-5

EINECS No: 231-959-5

SUMMARY RISK ASSESSMENT REPORT

Final Summary, September 2009

Italy

FINAL APPROVED VERSION

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PREFACE

This report provides a summary, with conclusions, of the risk assessment report of the substance chlorine 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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EUSES Calculations can be viewed as part of the report at the website of the European Chemicals Bureau: http://ecb.jrc.it

1 GENERAL SUBSTANCE INFORMATION

1.1 IDENTIFICATION OF THE SUBSTANCE

CAS Number:	7782-50-5
EINECS Number:	231-959-5
IUPAC Name:	Chlorine
Molecular formula:	Cl_2
Structural formula:	Cl_2
Molecular weight:	70.9
Synonyms:	Chlorine molecular, Chlorine molecule, Diatomic chlorine, Dichlorine.

1.2 PHYSICO-CHEMICAL PROPERTIES

Property	Value	Comment/Reference
Physical state	Gas	At room temperature and pressure
Melting point	-101 ºC	Budavari et al. (1989), Gerhartz et al (1986), as triple point in Martin and Longpre (1984).
Boiling point	-34 ºC at 1013 hPa	Budavari et al. (1989), Gerhartz et al (1986) Martin and Longpre (1984).
Relative density	1.56 g/cm^3 at -34 ºC 3.213 kg/m^3 at 0 ºC	Liquid.(Chim. Oggi (1991,) Budavari et al. (1989)) Gas. Gerhartz et al (1986)
Vapour pressure	6780 hPa at 20 ºC	Martin and Longpre 1984.
Water solubility	9.78 g/l at 10 ºC 6.9 g/l at 25 ºC	Maximum solubility at 10 ºC. Gerhartz et al (1986), Schmittinger (2000), GEST 2002b. Budavari et al. (1989)
Partition coefficient n-octanol/water (log value)		Not applicable due to oxidising properties of chlorine. See Chlorine IUCLID section 2.5.
Granulometry		Not applicable to gas or liquid
Conversion factors	1 L of liquid chlorine = 456.8 L of gas at 0 ºC and 1 atm.	Sax and Lewis (1987).
Flash point	Not Flammable in Air	Chlorine IUCLID as updated 03.11.2003
Autoflammability	Not Flammable in Air	Chlorine IUCLID as updated 03.11.2003
Flammability	Can form flammable mixtures with H2.	Kroschwitz JI, Grant MH, Howe-Grant M, 1991. GEST 91/168 (2002c)
Explosive properties	Can form explosive mixtures with H2 and some organics.	GEST 91/169 (2002c)
Oxidizing properties	Molecular chlorine is a strong oxidising agent	Kroschwitz JI, Grant MH, Howe-Grant M, 1991.
Viscosity – Liquid at 0C Viscosity – Gas at 0C	$0.385 \cdot 10^{-3}$ Pa.s $12.4 \cdot 10^{-3}$ Pa.s	Range: 1.032 x 10^{-3} Pa.s (–100 C) to 0.249 x 10^{-3} Pa.s (100C) Range: 7.9 x 10^{-3} Pa.s (–100 C) to 32.2 x 10^{-3} Pa.s (500C). GEST 91/158 (2000a).
Surface tension	18.2 mJ/m^2 at 20ºC	GEST 91/168 (2002a)
Henry's Law Constant	$9.83 \cdot 10^3$ Pa m^3 per mole	Calculated from water solubility and vapour pressure information in this table

1.3 CLASSIFICATION

1.3.1 Current classification

According to Directive EEC 67/548 Annex I and its 30th Technical Adaptation Chlorine (Index-No. 017-001-00-7) is classified as Toxic, Irritant, and Dangerous to the Environment:

Labelling: Symbol: T, N
R-Phrases: R 23: Toxic by inhalation
R 36/37/38: Irritating to the eyes, respiratory tract and skin
R 50: Very toxic to aquatic organisms

1.3.2 Proposed classification

Agreed Classification at TC C&L September 2007 (R8 in February 2007):

Labelling: Symbol: O, T, Xi, N
R-Phrases: R8: Contact with combustible material may cause fire
R 23: Toxic by inhalation
R 37/38: Irritating to the respiratory tract and skin
R 41: Risk of serious damage to eyes
R 50: Very toxic to aquatic organisms
Specific concentration limits: $C_n \geq 0.25\%$: **N, R50** (S61)

2 GENERAL INFORMATION ON EXPOSURE

Chlorine is usually produced by one of three possible processes, in each of which a chloride-salt solution is decomposed electrolytically by direct current. Generally sodium chloride is used in the process in Western Europe, but potassium chloride use accounts for about 3%-4% of the chlorine production capacity (European Commission, 2001b). The main process used in Western Europe is the mercury amalgam electrolysis process representing 46% of the plants in operation (2003 data, (Euro Chlor, 2004c)). Other processes are the diaphragm process (18%) and the membrane process (33%). The remaining 3% of production uses other processes. Based on present technology (as presently the typical diaphragm cell process uses asbestos diaphragms), membrane cell technology is preferred for new installations, and has been in operation in the EU since the early 1980s.

Chlorine is mainly used as a chemical intermediate to produce both chlorinated and non-chlorinated compounds. About 30% of chlorine is used to make chlorine-free end products. The Chlorine Industry Review for 2002-2003 (Euro Chlor, 2003a) shows that in 2002, 34% of chlorine was used in the production of poly vinyl chloride (PVC), 24% in the production of non-chlorinated polymers (isocyanates and oxygenates, which are used in the production of polyurethanes, epoxides and polycarbonates), 8% in the production of chloromethanes, 5% in epichlorohydrin production, 4% in the production of solvents, 16% for inorganic chemistry, including hydrochloric acid and sodium hypochlorite production, and 9% for other uses. Similar chlorine usage is reported for 2003 chlorine production (Euro Chlor, 2004c), where 35% of the total production was used to produce PVC, but all other use percentages remained the same as in 2002. In 1998, only 2.2% of Cl_2 production found its end-use in the elemental form (Euro Chlor, 2000).

2.1 Scenario

Chlorine has two distinct types of use. Although the majority of chlorine produced is as an intermediate in production processes, there are also non-intermediate uses of chlorine.

In 2003, 35% of chlorine production was used as an intermediate in the production of Poly Vinyl Chloride, or PVC (Euro Chlor, 2004c).

Chlorine also has non-intermediate uses, including use in water-based applications including disinfection processes. These include drinking water disinfection swimming pool disinfection, waste water disinfection, and use as a biocide in cooling water applications. There was almost no use of elemental chlorine in the areas of textile bleaching or in the pulp and paper industry.

3 ENVIRONMENT

3.1 ENVIRONMENTAL EXPOSURE

3.1.1 General discussion

Chlorine releases to the atmosphere and to water can come from both natural and anthropogenic sources. In the atmosphere, molecular chlorine releases will be converted to atomic chlorine by photolysis during daylight hours (Keene, WC, 1999). Chlorine released to aqueous systems will undergo speciation according to the pH of the environment.

3.1.2 Releases

The releases of chlorine to the environment is summarised in Table below:

Release source	**Release to air**	**Release to water**
Natural	Global estimates from 100 million to 2 billion tonnes per year.	No specific process for direct release of molecular chlorine to water identified
Production + on-site manufacture	123 metric tonnes	18.7 metric tonnes
Use as a chemical intermediate (chlorine transported off site)	Approximately 3.2 metric tonnes	Approximately 0.5 metric onnes
Cl_2 used in aqueous applications		No Chlorine gas will be released due to non-accidental use. Further information is given in the Sodium Hypochlorite Risk Assessment.

3.1.3 Environmental degradation

In the atmosphere, Cl_2 will degrade during daylight, with half-lives ranging from minutes to several hours, depending on latitude, season, and time of day. Chlorine is also removed from the atmosphere by wet and dry deposition processes, with a half-life of about 10 days for washout by rain.

In water, Cl_2 will disproportionate to form HOCl and OCl^- at environmentally relevant pH levels. In soil, chlorine is normally irreversibly combined with soil organics. The ultimate fate of chlorine in soil is reduction to chloride.

3.1.4 Aquatic compartment (incl. sediment)

3.1.4.1 Calculation of predicted environmental concentrations (PEC_{local})

Chlorine discharged to water will disproportionate to form hypochlorous acid (HOCl) and hypochlorite (OCl^-) at environmentally relevant pH. For many use scenarios, the tonnage of hypochlorous acid (HOCl) and hypochlorite (OCl^-) which has its source as chlorine gas has also been included in the sodium hypochlorite risk assessment. These uses are:

- Drinking Water disinfectants
- Swimming pool disinfectants
- Waste Water treatment
- Pulp and Paper industry
- Cooling water disinfection
- Textile industry

3.1.4.1.1 Calculation of PEC_{local} for production

Thus an appropriate PEC_{local} would be 10^{-22} µg/l. This equates with a negligible hypochlorite concentration resulting from chlorine production plant effluent in a standard receiving river.

3.1.4.1.2 Calculation of PEC_{local} for formulation

Chlorine gas is not used in formulated products.

3.1.4.1.3 Calculation of PEC_{local} for industrial/professional use

Calculated PEC $local_{water}$ for hypochlorite by-products[1]

Scenario	**$PEC_{localwater}$ (g/l)**		
	AOX[3]	**THM[4]**	**HAA[5]**
Swimming Pools: routine emptying		 0.02 0.67	 0.16 6.22
Sewage Treatment		7	3.5
Textile bleaching[2]	1300		
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[2]	1725		
Cooling Water		3.0	1.0

[1] This table is taken from Table 3.5 of the Sodium Hypoclorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.2.11). [2] These applications have negligible chlorine use in 2002. [3] AOX is adsorbable halogenated organic. [4]THM are trihalomethanes. [5]HAA are haloacetic acids

3.1.4.1.4 Calculation of PEC_{local} for private use

Chlorine gas is not used privately.

3.1.4.1.5 Calculation of PEC_{local} for disposal

Chlorine gas will not be released if any chlorine-containing product comes into contact with water in the environment. Any molecular chlorine will hydrolyse to form hypochlorous acid (HOCl) and hypochlorite (OCl^-) at environmentally relevant pH**.** Ultimately, chlorine in the environment will be reduced to chloride (Euro Chlor, 2000).

3.1.4.1.6 Comparison between predicted and measured levels

As hypochlorite cannot be measured at the predicted environmental concentrations, comparison between predicted and measured levels is not generally possible.

3.1.5 Terrestrial compartment

Due to its reactive and oxidative properties any molecular chlorine or hydration products (hydrochlorous acid and hypochlorite at environmental pH) which reach the terrestrial environment will be removed due to reaction with organic matter. For this reason the predicted environmental concentration of Cl_2 in the terrestrial environment is negligible.

3.1.5.1 Calculation of PEC_{local}

The concentration of chlorine and its hydration products hydrochlorous acid and hypochlorite is negligible in the terrestrial environment, due to reaction with organic matter present in the soil.

3.1.5.2 Measured levels

The concentration of chlorine and its hydration products hydrochlorous acid and hypochlorite cannot be measured in soils, due to their high oxidation potential. Due to this high reactivity, the concentration of chlorine and its hydration products in soil is expected to be negligible.

3.1.5.3 Comparison between predicted and measured levels

As chlorine can not be measured in soil due to its high reactivity with organic matter, it is not possible to compare measured and predicted concentrations. However, concentrations of chlorine and its hydration products hydrochlorous acid and hypochlorite are expected to be negligible.

3.1.6 Atmosphere

Molecular chlorine is a natural constituent of the atmosphere with average concentrations approaching the 100 pptv region. As part of the natural chlorine cycle, global chlorine fluxes from 100 million to 2 billion tonnes per year have been estimated. This natural chlorine is the largest source of chlorine in the atmosphere.

3.1.6.1 Calculation of PEC_{local}

Approximately 98% of chlorine is used to produce other chemicals, with chlorine often being generated on the same site. The initial chlorine generation and the use to produce chemicals on and off the same site will result in approximately 126 metric tonnes of chlorine emissions per year to atmosphere. Much of this chlorine will then be removed by photolysis.

3.1.6.1.1 Calculation of PEC_{local} for production

Photolysis is an important removal mechanism for atmospheric chlorine, which will reduce chlorine levels to close to zero for much of the day. As the production site emission data are annual emission data, an annual average reduction factor due to photolysis, calculated from the average of the mid-summer and mid-winter daily reduction factors has been applied to the atmospheric emissions from each site. The site emissions, reduced to account for photolysis, have then been ordered, and a 90th percentile emission, after photolysis, of 823kg/year has been determined. This 90th percentile emission has been used to determine PEC_{local} for the reasonable worst case production site, by using EUSES 2.03 (European Chemicals Bureau, 2004) to calculate the local air concentration, assuming 360 production days per year. The annual average concentration in air, 100 m from this point source emission, is 0.628µg/m^3**.** This reasonable worst-case value is taken as $PEC_{local.}$

3.1.6.1.2 Calculation of PEC_{local} for formulation

Chlorine gas is not used in formulated products.

3.1.6.1.3 Calculation of PEC_{local} for industrial/professional use

Thus it is assumed that the PEC_{local} for transported chlorine will be smaller than the PEC_{local} for the main chlorine production sites, calculated in **section 3.1.6.1.1.**

3.1.6.1.4 Calculation of PEC_{local} for private use

Chlorine gas is not used privately.

3.1.6.1.5 Calculation of PEC_{local} for disposal

Chlorine gas is not released from products which contain chlorine, after product disposal. Most chlorine is released as chloride from products after disposal (Euro Chlor 2000).

3.1.6.1.6 Measured levels

Molecular chlorine is a natural constituent of the atmosphere with average concentrations approaching the 100 pptv region. Monitoring data show a range in chlorine concentrations from below the limit of detection to 254 pptv, with lower concentrations measured in daylight conditions. If the specific volume of chlorine gas, 3.0303 kg/m^3 at 12C, is used to convert the highest measured natural chlorine level of 254 pptV to µg/m^3, then this gives 0.860 µg/m^3.

3.1.6.1.7 Comparison between predicted and measured levels

The calculated PEC_{local} for production, calculated for the 90th percentile production site emission, is 0.628µg/m^3**.** By comparison, if the specific volume of chlorine gas, 3.0303 kg/m^3 at 12C, is used to convert the average natural chlorine level of 75 +/- 50 pptV in the marine boundary layer from pptV to µg/m^3, then the average marine boundary layer concentration corresponds to 0.227 µg/m^3. The naturally occurring photolysis has already influenced the measured natural chlorine level. The highest measured natural chlorine level corresponds to 0.860 µg/m^3 (Pszenny *et al.*1993**)**, which is measured before dawn and reflects overnight build up of chlorine, before daytime removal by photolysis begins. The calculated chlorine concentration from the release from chlorine production is within the range of measured concentrations from natural chlorine.

3.1.7 Secondary poisoning

Secondary poisoning is not relevant for chlorine, as it does not bioaccumulate or bioconcentrate due to its water solubility and high reactivity (SIAR, 2003) Aqueous chlorine species do not bioaccumulate, as discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.5)

3.1.8 Calculation of $PEC_{regional}$ and $PEC_{continental}$

It is not possible to use EUSES 2.0 to calculate $PEC_{regional}$ and $PEC_{continental}$, as EUSES 2.0 requires a K_{ow} value as an input parameter in order to make these calculations, and K_{ow} cannot be measured for a reactive substance such as chlorine. However, natural chlorine release is much greater than anthropogenic contributions to atmospheric chlorine loads. Thus calculation of $PEC_{regional}$ and $PEC_{continental}$ for atmospheric data is not appropriate. It is not possible to calculate $PEC_{regional}$ and $PEC_{continental}$ for the terrestrial compartment, as any chlorine reaching soil will react immediately with organic matter present in the soil. Thus the background concentration of chlorine in the terrestrial environment will be negligible. In the aqueous environment, chlorine is transformed rapidly to hypochlorous acid and hypochlorite at environmentally relevant pH. Thus the background concentration of chlorine in the aqueous environment will also be negligible.

3.2 EFFECTS ASSESSMENT: HAZARD IDENTIFICATION AND DOSE (CONCENTRATION) - RESPONSE (EFFECT ASSESSMENT)

3.2.1 Aquatic compartment (incl. sediment)

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.5.3) has determined a PNEC aquatic for freshwater species of 0.04 µg FAC/l and for saltwater species of 0.04 µg FAC/l. The full discussion can be found in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005,, sections 3.2.1.1 and 3.2.1.2). FAC, or free available chlorine, is defined as the sum of dissolved chlorine gas, Cl_2, hypochlorous acid (HOCl), and hypochlorite (OCl^-) present in the test solution. Microorganisms

Available information on the toxicity of hypochlorite to microorganisms is given in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.4). In the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005), a PNEC is not derived for hypochlorite used in waste water treatment applications, as reactions with the organic matter present in sewage will rapidly reduce the hypochlorite concentration to values as low as 10^{-32} g/l of free available chlorine (defined as the sum of dissolved chlorine gas (Cl_2), hypochlorous acid (HOCl), and hypochlorite (OCl^-) present in the test solution). Calculations supporting this level of hypochlorite may be found in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.2.2 and Appendix 2).

3.2.1.1 Calculation of Predicted No Effect Concentration (PNEC)

3.2.1.1.1 Calculation of the PNEC for freely available chlorine

The information used to calculate the PNEC of 0.04 µg FAC/l for freshwater organisms is given in Table 3.6 of the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.1.6.). Fresh water and brackish and marine water data were combined for the calculation of the PNEC of 0.04 µg FAC/l, with algae found to be the most sensitive species and an application factor of 50 agreed for the calculation of the PNEC from the Algal NOEC.

3.2.1.1.2 Effects assessment of chlorination by-products

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.6.) discusses the PNEC information for halogenated organic by-products. Trihalomethanes are shown to be of similar aquatic toxicity, and the report recommends that the chloroform $PNEC_{aquatic}$ of 146 µg/l (from the draft Risk Assessment for chloroform, R_COM_047) be used for total trihalomethanes. The report also suggests that, as a worst case assumption, all haloacetic acids could be considered to have a PNEC of 0.85 ug/l.

3.2.1.2 Toxicity test results for sediment organisms

No specific information for sediment dwellers is available in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005). However, any chlorine in water will quickly react with org. matter in the sediment. Therefore, as no chlorine will be available in the sediment compartment, the compartment is not relevant for risk assessment.

3.2.1.3 Calculation of Predicted No Effect Concentration (PNEC) for sediment organisms

No PNEC is calculated as the sediment compartment is not relevant for risk assessment, as no chlorine will be present.

3.2.2 Terrestrial compartment

It is not relevant to carry out a terrestrial assessment for chlorine or for hypochlorous acid/hypochlorite, as these reactive species do not survive in soil (see the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.3.).

3.2.2.1 Calculation of Predicted No Effect Concentration (PNEC)

As hypochlorite will react rapidly with soil organic matter and consequently not be present in soil, a PNEC for terrestrial species is not appropriate. However, information concerning the toxicity of atmospheric chlorine to terrestrial plants can be found in **section 3.2.3.**

3.2.3 Atmosphere

No information is available concerning the toxicity of chlorine to animals in the atmosphere.

Some information is available concerning the toxicity of atmospheric chlorine to terrestrial plants. However, the tests that have been carried out are not standard tests, and more closely approximate the conditions that would occur during an accidental release or spillage of chemicals. These conditions are not generally appropriate for the environmental risk assessment of chemicals (TGD 2003, e.g. p.20).

3.2.4 Secondary poisoning

A potential for bioaccumulation or bioconcentration of active chlorine species can be disregarded, because of their water solubility and their high reactivity (SIAR, 2003).

3.3 RISK CHARACTERISATION

Chlorine releases to water are either included in the Sodium Hypochlorite risk assessment Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005)), or have been shown to result in no appreciable concentration of chlorine, hypochlorous acid, or hypochlorite in the environment. Thus 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).

Chlorine releases to the terrestrial environment result in no free chlorine, hypochlorous acid, or hypochlorite. Thus 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).

Chlorine releases to the atmosphere may, based on worst-case assumptions, result in atmospheric concentrations of chlorine which are similar to concentrations in the marine boundary layer, which is part of the natural chlorine cycle. Indicative data from chlorine effect levels of terrestrial plants under similar exposure pattern are approximately 1000 times larger than the marine boundary layer concentration. Thus 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).

3.3.1 PBT Assessment

In water, chlorine disproportionates to form hypochlorous acid and hypochlorite, which do not bioaccumulate. In the atmosphere, chlorine is not persistent, as it is rapidly removed due to photolysis. Thus chlorine does not fulfil the PBT criteria and a PBT assessment is not relevant.

4 HUMAN HEALTH

4.1 HUMAN HEALTH (TOXICITY)

4.1.1 Exposure assessment

Most of the chlorine produced is consumed on the same site because chlorine production is generally integrated in larger plants where other chlorinated substances or substances using chlorine as intermediate or raw material are produced. Chlorine is supplied in gaseous form to the consuming industries mainly by pipeline inside an industrial site or from one site to another. To a minor extent, it is distributed in liquefied form in bottles or tank cars and transported via rail tankers or by road trucks. In general, before its use, chlorine goes through a series of processes for cooling, cleaning, drying, compressing and liquefying, even if, in some applications, it can be used directly from the electrolysers.

General remark: The operations and tasks described hereafter are typical of standard chlorine production or handling facilities. There could be slight variations in the operating procedures but these will not affect the human exposure pathways and levels.

Accidental exposure to chlorine gas may occur during manufacturing or in industries using chlorine, HCl or chlorine dioxide as bleaching agents, during transport or use in swimming pools. Exposure of the general population may occur through mixing of household cleaning agents, such as hypochlorite and acids.

4.1.1.1 Occupational exposure

Where no measured data are available, EASE model is applied. When chlorine is used for water disinfection (waste water treatment and swimming pool scenarios), once added to water it reacts to form hypochlorite.

Inhalation exposure

In chlorine production, four exposure scenarios have been considered (cell-rooms operators, maintenance operators, filling operators and lab workers). Using as a reasonable worst case the 90th percentile of the distribution of the exposure levels observed at each location, but limited to the level detected by the alarm of 0.5 ppm (1.5 mg/m^3), the short term inhalation exposure to chlorine in the four scenarios considered varies from 0.084 to 0.180 ppm, while the long term exposure is 0.235 ppm (0.705 mg/m^3).

When chlorine is used as chemical intermediate, four exposure scenarios have been considered (production operators, maintenance operators, filling operators and laboratory workers). Using as a reasonable worst case the 90th percentile of the distribution of the exposure levels observed at each location, but limited to the level detected by the alarm of 0.5 ppm (1.5 mg/m^3), the short term inhalation exposure level to chlorine in the four scenarios considered is 0.167 ppm (0.501 mg/m^3), while the long term exposure is 0.235 ppm (0.705 mg/m^3).

When chlorine is used in water disinfection applications two scenarios have been considered (storage and connection-disconnection operators), which also cover the distribution system. In storage area, the worst case, short term inhalation exposure level as calculated by EASE model is 0.1 ppm (0.3 mg/m^3), while, based on the 90th percentile of the distribution of the exposure levels observed at each location, the short term inhalation exposure to chlorine for connection-disconnection operators is 0.167 ppm (0.501 mg/m^3). There is no need to consider a long term exposure due to the occasional character of the operations (low frequency and short time operation)

Dermal exposure

There is no dermal exposure to chlorine. When chlorine is used in water applications, it is converted to hypochlorite. Dermal exposure to hypochlorite in swimming pool and wastewater treatment scenarios has been discussed in sodium hypochlorite Risk Assessment Report.

Conclusions of the occupational exposure assessment

		Inhalation				Dermal			
		Reasonable worst case		Typical concentration		Reasonable worst case		Typical concentration	
Scenario	**Activity [1]**	**Unit: ppm [mg/m^3]**	**Method[2]**	**Unit: ppm [mg/m^3]**	**Method [2]**	**Unit**	**Method [2]**	**Unit**	**Method [2]**
Production									
Subscenario 1	Long term	0.235 [0.705]	Measured	0.102 [0.756]	Measured	NONE		NONE	
Cell-room operators	Short term	0.180 [0.540]	Measured	0.072 [0.216]	Measured	NONE		NONE	
Subscenario 2	Long term	0.235 [0.705]	Measured	0.102 [0.306]	Measured	NONE		NONE	
Maintenance operators	Short term	0.160 [0.480]	Measured	0.082 [0.246]	Measured	NONE		NONE	
Subscenario 3	Long term	0.235 [0.705]	Measured	0.102 [0.756]	Measured	NONE		NONE	
Filling operators	Short term	0.166 [0.498]	Measured	0.077 [0.231]	Measured	NONE		NONE	
Subscenario 4	Long term	0.235 [0.705]	Measured	0.102 [0.756]	Measured	NONE		NONE	
Laboratory	Short term	0.084 [0.252]	Measured	0.046 [0.138]	Measured	NONE		NONE	
Formulation									
Subscenario 1	Long term	NA		NA		NA		NA	
No Formulation	Short term	NA		NA		NA		NA	
USES : CHLORINE AS CHEMICAL INTERMEDIATE									
Subscenario 1	Long term	0.235 [0.705]	Measured	0.102 [0.756]	Measured	NONE		NONE	
Production operator	Short term	0.180 [0.540]	Measured	0.072 [0.216]	Measured	NONE		NONE	
Subscenario 2	Long term	0.235 [0.705]	Measured	0.102 [0.306]	Measured	NONE		NONE	
Maintenance operator	Short term	0.167 [0.501]	Measured	0.075 [0.225]	Measured	NONE		NONE	
Subscenario 3	Long term	0.235 [0.705]	Measured	0.102 [0.306]	Measured	NONE		NONE	
Filling operators	Short term	0.167 [0.501]	Measured	0.075 [0.225]	Measured	NONE		NONE	
Subscenario 4	Long term	0.235 [0.705]	Measured	0.102 [0.306]	Measured	NONE		NONE	
Laboratory operators	Short term	0.167 [0.501]	Measured	0.075 [0.225]	Measured	NONE		NONE	
USES: CHLORINE IN WATER DISINFECTION									
Subscenario 1	Long term	NONE		NONE		NONE		NONE	
Storage	Short term	0.1 [0.3]	EASE	0 [0]	EASE	NONE		NONE	
Subscenario 2	Long term	NONE		NONE		NONE		NONE	
Connection-disconnection	Short term	0.166 [0.498]	Measured	0.077 [0.231]	Measured	NONE		NONE	

4.1.1.2 Consumer exposure

As the use of chlorine is limited to professional and industrial applications, there is no direct consumer use of chlorine and consequently no direct public exposure is expected.

Gaseous chlorine can be released from a sodium hypochlorite solution when it is mixed with strong acids. This may happen only in accidental case, during swimming pool water disinfection and during household use of hypochlorite for cleaning. Hypochlorite solutions are labelled to inform the consumer of the risk. Exposure to chlorine from chlorinated water (drinking water or swimming pool water) cannot take place, because chlorine can be released only at very low pH (see chapter 2.2.2).

4.1.1.3 Humans exposed via the environment

Due to the properties of chlorine the substance will only remain in the water compartment for a very short period of time. Depending on the specific conditions of the receiving surface water chlorine will rapidly volatilise to air, transform into other oxidants or react with organic matter. Therefore emissions to water are not relevant at the regional or continental scale, and human exposure via the environment from water emissions will not occur.

Emissions to air on a European level will be predominantly from natural origin. However, whether natural or anthropogenic, all chlorine released to air will undergo rapid removal or transformation. Depending on environmental conditions it will degrade due to photolysis, undergo wet or dry deposition or transform into other substances. Therefore, anthropogenic emissions to air are not relevant at the regional or continental scale, and human exposure via the environment from air emissions will not occur.

Data on emissions from chlorine production plants have been collected and evaluated. Following a worst case approach, a local PEC of 0.628$\mu g/m^3$ has been calculated. This value is taken forward to the Risk Characterisation.

The scenarios considering human exposure to solutions containing hypochlorous acid and hypochlorite ions, both directly and via the environment, have been treated extensively in the Risk Assessment Report for sodium hypochlorite. The main conclusion of this report is the following: “Due to the physical-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”.

4.1.1.4 Combined exposure

No such exposure is thought to occur.

4.1.2 Effects assessment: Hazard identification and dose (concentration)-response (effect) assessment

4.1.2.1 Toxicokinetics, metabolism and distribution

Chlorine is a strong oxidising agent which forms both hypochlorous and hydrochloric acid in contact with most mucous membranes. The former compound decomposes into hydrochloric acid and oxygen free radicals (O_2^-). Damage results from the disruption of cellular proteins caused by its strong oxidising nature.

In biological systems, characterised by pH values in the range 6-8, the most abundant active chemical species is HOCl, in equilibrium with ClO^-. The latter is predominant at alkaline pH values, while Cl_2 is mainly present at pH below 4. Therefore, ADME studies performed with hypochlorite and its salts are used in this document. Limited data are available only for the oral route.

Hypochlorite readily reacts with organic material such as amino acids, proteins, nucleic acids, lipids and carbohydrates. The resulting organic compounds may possess their own inherent toxicity as well as causing lower damage to cells (BIBRA, 1990).

Due to the reactive nature of chlorine, the question can be raised whether it is chlorine or a by-product that is responsible for any effect. Studies examining the formation of chlorinated by-products in the gastro-intestinal tract involved administration of higher concentrations of chlorine versus those that would be encountered in chlorinated drinking water. Consequently, the by-products formed may not be representative of the by-products that would be seen in the consumption of modest to moderate levels of chlorinated drinking water. The high organic carbon concentration relative to chlorine that would be encountered in the gastrointestinal tract when water is consumed at low concentrations should dissipate the disinfectant before sufficient oxidative power would be present to break down substrates to small molecules. The bulk of the by-products formed remain as higher molecular weight products, which may have little toxicological importance. (IPCS 1999, Environmental Health Criteria for disinfectants by-products, EHC 216.)

Chlorine reacts at the site of contact where its primary activity is destruction of organic molecules present. It will therefore not be absorbed into the bloodstream.

Oral administration of a hypochlorous acid solution in rats resulted in a quick uptake and distribution of the chlorine-ion in the blood, with a peak concentration between 2 and 4 hours and a half-life between 2 and 4 days. Interaction of chlorine and stomach can result in the possible formation of chlorinated organic compounds as chloroform, DCAN, DCA, TCA and chlorinated amino acids.

There are no data on kinetic behaviour of chlorine gas upon dermal exposure. It can be assumed that no systemic exposure to chlorine will occur after dermal absorption. Therefore, dermal absorption is not taken into account.

4.1.2.2 Acute toxicity

Clinical and morphological observations together with lung function tests confirm that exposure to chlorine results in effects on lung function and histological integrity of the respiratory system.

A reliable study with human volunteers showed that an exposure to chlorine up to 0.5 ppm (1.5 mg/m^3) during a few days did not result in an inflammatory effect in the nose nor shows changes in the respiratory function (NOAEL).

Based on a selected set of animal experiments an LC_{50} value of 300-400 ppm (900-1200 mg/m^3) was reported for an exposure of 30 minutes. Concentrations higher than 1000 ppm (3000 mg/m^3) may be lethal at shorter exposure periods (about 10 minutes).

When added to water, chlorine reacts to form hypochlorous acid and/or hypochlorite (see chapter 2.2.2). The acute dermal and oral toxicity of these solutions is described in the EU RAR of Sodium hypochlorite (chapter 4.1.2.2).

Applicability of Haber's law and classification proposal

The LC50 at 4 hours needed for acute toxicity classification should be extrapolated from the available experimental data.

Table 4.13 indicates the LC50 for mouse and rat at 10, 30 and 60 minutes. Haber's rule (concentration x time = constant) seems applicable between 10 and 30 minutes, but already bends at 60 minutes as these levels are more than half those of the 30 minute exposures. Extrapolation from 60 minutes to 4 hrs should therefore not necessarily require a factor 4. Moreover, data from different species are difficult to compare. Mice seem to be more sensitive to acute toxicity then other species (LC50 a factor 4 lower then for rats), probably because of their greater respiration rate. Therefore, animal data could not reflect the human situation.

A document developed by US EPA to derive AEGL (Acute Exposure Guideline Levels, 2004) uses the more general relationship C^n x t = k. EPA AEGL uses a factor 2 in concentration between 1 and 4 hours for the serious effects (AEGL 3), and a constant concentration irrespective of time for discomfort/irritation (AEGL 1).

The available data does not seem to be sufficient as to make a final decision regarding the applicability or not of Haber's law. In the equation C^n x t = k, 'n' is depending on time extrapolation and species and shows large variability among different evaluations.

For classification purposes, we should consider that

- according to Annex VI of the directive 67/548/EEC: T+ classification should be given when LC50 ≤ 0.5 mg/l/4hours in rats
- humans are expected to be less sensitive than rats (see conclusions for repeated dose toxicity, chapter 4.1.2.6.3)
- the best available LD50 in rats is 1.3-2 mg/L (see table 4.13)
- when applying the US EPA factor 2 in the equation C^n x t = k for serious effects, the values extrapolated at 4 hours is 0.65 mg/l (below the limit value for T+ classification)

it is proposed to take the US AEGL approach, resulting to an extrapolated 4 hr – LC50 of 0.65 mg/L and confirming the current classification of chlorine as toxic by inhalation (T, R23).

4.1.2.3 Irritation

Currently solutions of sodium hypochlorite with 5-10 % active chlorine are classified as irritating (R36, Irritating to the eyes; R38, Irritating to skin) in the European Union, while solutions of sodium hypochlorite with 10 % active chlorine or more are classified as corrosive in the EU.

Standard guideline studies to determine the irritation/corrosivity potential of chlorine can not be done because chlorine is a gas at ambient temperature. Furthermore primary references which describe the effect of chlorine on the human skin have not been found.

Based on a recently approved international hazard assessment (SIDS Initial Assessment Profile, SIAP), chlorine is corrosive to the skin (OECD, 2003). Furthermore secondary references and also internal documentation of chlorine producers shows that gaseous chlorine (and liquid chlorine) is irritating/corrosive to the skin. Contact with liquid chlorine will cause skin burn and frostbite. However, it is not possible to derive a threshold concentration for skin irritation or corrosion for gaseous chlorine because the data are not available and because the effects on the skin will also depend on the duration of exposure. It should be realised that there is no need to determine these threshold concentrations because the target organ of chlorine is the respiratory tract.

Acute inhalation studies with animals show that gaseous chlorine is irritating to the eyes. Based on human data, irritating effects on the eyes were reported at a chlorine concentration range of 0.2 to 4 ppm (0.6 to 12 mg/m^3). According to secondary literature exposure to chlorine can result in injury of the cornea and enduring impaired vision and blindness(corrosive effect).

Many animal and human studies have been reported about the effect of chlorine on the respiratory tract. A well documented study with human volunteers, done according to Good Clinical Practice, showed no inflammatory response or irritant effects on the nasal epithelium at 0.5 ppm (1.5 mg/m^3) and for this reason 0.5 ppm (1.5 mg/m^3) is considered a NOAEC for respiratory irritation.

4.1.2.4 Sensitisation

Solutions of chlorine in water contain hypochlorous acid and/or hypochlorite. Within the EU Risk Assessment of Sodium hypochlorite (chapter 4.1.2.4) it was concluded that:

“Based on the systematic animal and human study data as well as on the scarcity of alleged sensitisation cases reported from the market it is concluded that sodium hypochlorite does not pose a skin sensitisation hazard.”

Incidental human case reports on hyper-reactivity/hypersensitivity on exposure to chlorine gas appear to be pseudoallergic, not immune-mediated responses and relate to individual disposition. No case reports were found showing a sensitisation potential in humans (OECD, 2003).

Because sodium hypochlorite does not pose a skin sensitisation hazard and because no human case reports have been found for chlorine showing a sensitisation potential, chlorine is considered to have no skin or respiratory sensitisation hazard.

4.1.2.5 Repeated dose toxicity

A 6-week study in rats and 2-year repeated-dose studies in rats and mice are available for the inhalation route. In the 6-week study, major effects observed were inflammation throughout the respiratory tract with hyperplasia and hypertrophy of epithelial cells of the respiratory bronchioles, alveolar ducts and alveoli of rats exposed to 9 ppm (27 mg/m^3). Changes in male rats at 1 or 3 ppm (3 or 9 mg/m^3) consisted of focal inflammation of the nasal turbinates and a slight to moderate inflammatory reaction around the respiratory bronchioles and alveolar ducts.

In the 2-year studies in rats and mice, chlorine-induced lesions including respiratory and olfactory epithelial degeneration, septal fenestration, mucosal inflammation, respiratory epithelial hyperplasia, squamous metaplasia and goblet cell hypertrophy and hyperplasia, and secretory metaplasia of the transitional epithelium of the latera meatus, were observed in the anterior nasal cavity. Many of these nasal lesions exhibited an increase in incidence and/or severity that was related to chlorine exposure concentration and were statistically significantly increased at all chlorine concentrations studied. Inhaled chlorine in rodents is an upper respiratory tract toxicant. For chronic inhalation exposure, an LOAEL of 0.4 ppm (1.2 mg/m^3) for respiratory irritation has been identified in rats and mice.

A one year study in monkeys revealed effects of chlorine in the upper respiratory tract at 2.3 ppm while changes observed at 0.5 and 0.1 ppm were of questionable clinical and toxicological significance (Klonne *et al,* 1987). Monkeys appear to be less sensitive to chlorine than rats. A NOAEL of 0.5 ppm (1.5 mg/m^3) was established in this study. Ibanes et al. (1996) gives increased value to the monkey study compared to rats and mice. Respiratory tract airflow characteristics play a major role in lesion distribution and interspecies differences in severity. Lesions in monkeys involve more the respiratory tract, while in rats/mice (obligatory nose breathers) they are confined to the nasal region. In this study, it is concluded that the monkeys are better models for humans than rodents.
A 3-days exposure human voluntaries study by Schins et al. (2000) shows no effect at 0.5 ppm (1.5 mg/m^3), confirming the NOAEL of the monkey studies.

No systemic effects were observed in repeated dose exposure studies in rats, mice and monkeys. Human repeated exposure to chlorine is not expected to lead to effects other than irritation observed in the study by Schins et al. (2000). We can then take forward to the Risk Characterisation the NOAEL of 0.5 ppm (1.5 mg/m^3) from the human volunteers study, supported by repeated dose study in monkeys. Additionally, chlorine was discussed by SCOEL and an OEL of 0.5 ppm (1.5 mg/m^3) was agreed based on these studies, with removal of the 8-hour TWA. The justification was that the effects appear to be related to concentration in the air and not to duration of exposure (SCOEL, 1998).

In the Risk Assessment report on sodium hypochlorite, it was concluded that an NOAEL of 275 ppm as available chlorine administered in drinking water (13.75 mg/kg bw/day) can be identified for chronic oral exposure. For dermal exposure, available information is indicating a slight irritant effect with a 1000 mg/l solution, but no systemic effect was related to 10000 mg/l.

4.1.2.6 Mutagenicity

As *in vitro* mutagenicity tests are performed in an aqueous medium, data of hypochlorite are relevant for the assessment of the *in vitro* genotoxicity of chlorine and can be used in this risk assessment. See for a description of the studies, the RAR on Sodium Hypochlorite.

Sodium hypochlorite has been studied in a fairly extensive range of mutagenicity assays, both *in vitro* and *in vivo*. There are deficiencies in the conduct and/or reporting of most of the studies. 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, chlorine/sodium hypochlorite is not considered to be mutagenic *in vivo*.

4.1.2.7 Carcinogenicity

Carcinogenicity studies in rats and mice are available for the inhalation route. The incidence of neoplasia in these studies was not increased by exposure, indicating that inhaled chlorine in rodents is an upper respiratory tract toxicant but not a carcinogen.

Long term animal carcinogenicity studies on chlorinated drinking water are presented in sodium hypochlorite RAR. The conclusion is that the available animal studies are not sufficient to indicate a clear relationship between the oral administration of sodium hypochlorite in drinking water and cancer.

No human data are available on carcinogenicity and the only data are related to chlorinated drinking water for which the epidemiological data are not sufficient to suggest a causal relationship between the use of chlorinated drinking water and increased cancer risk.

The International Agency for Research on Cancer (IARC, 1991) has concluded that there is inadequate evidence for the carcinogenicity of sodium hypochlorite in animals and that sodium hypochlorite is not classifiable as to its carcinogenicity in humans (Group 3). This conclusion is still valid, taken into account the more recent available data.

4.1.2.8 Toxicity for reproduction

A number of studies in animals are available which can be used to assess the potential reprotoxic effects of chlorine administered in solution by gavage. 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 available chlorine (expressed as HOCl - maximum dose tested) (Carlton, 1986) and this value is considered as NOEL for reproductive toxicity for sodium hypochlorite.

Limited epidemiological data, essentially on chlorinated drinking water is available. Two case-control studies did not identify any concern relative to pregnancy outcomes (including miscarriage). A cross-sectional study reported a possible increased risk of shorter body length and shorter cranial circumference in newborns from mothers drinking chlorinated tap water.

Because of evident deficiencies in methodology and obvious bias, the results cannot be considered as reliable. A possible association between risk of spontaneous abortion and chlorinated tap water drinking has been reported in a review of a series of retrospective studies (but inconclusive because of obvious bias). In a recent prospective study, an increased risk of abortion was associated only with high consumption of cold tap water in the same area where the association has been recorded previously but not in two others areas. This association appears to be not consistent with the causality hypothesis involving chlorinated drinking water by-products and especially THMs.

Based on available epidemiological data, there is no clear evidence of toxic effects on foetus development in human. More details on the epidemiological studies, are reported in the sodium hypochlorite RAR.

Sodium hypochlorite RAR concludes that 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.

No developmental or fertility studies in rodents are available for the inhalation route. Nevertheless, given the corrosivity of chlorine gas, it is impossible to reach blood levels of HClO or chloride which would even approach the concentrations that can be reached with sodium hypochlorite. Therefore, we can conclude that for inhalation exposure reproductive toxicity is no relevant hazard.

4.1.3 General aspects

The human population may be exposed to chlorine at the workplace (during manufacturing and use of chlorine as chemical intermediate), use in water disinfection, and indirectly via the environment. For occupational exposure, the relevant route of exposure is inhalation. Human exposure to chlorine gas may lead to local effects on the upper respiratory tract due to the corrosive effects of chlorine. Clinical and morphological observations together with lung function tests confirm that exposure to chlorine results in effects on lung function and histological integrity of the respiratory system. There is conclusive evidence that 0.5 ppm (1.5 mg/m^3) is a NOAEL in humans both for acute and repeated inhalation exposure to chlorine. Appropriate personal protective equipment should be used as needed when exposure to chlorine is possible. Due consideration should also be given to potential corrosive effects of chlorine on skin and eyes.

The endpoints considered in the risk characterisation and their N(L)OEAL have been listed in Table below

Substance name: chlorine	Inhalation (N(L)OAEL)	Dermal (N(L)OAEL)	Oral (N(L)OAEL)
Acute toxicity	0.5 ppm [1.5 mg/m^3 (humans)]	NR	NR
Irritation / corrositivity	Corrosive to eyes and skin and irritant to respiratory tract	NR	NR
Sensitization	Not a sensitiser	NR	NR
Repeated dose toxicity (local)	0.5 ppm [1.5 mg/m^3 (humans)]	NR	NR
Repeated dose toxicity (systemic)	No systemic effects	NR	NR
Mutagenicity	Not mutagenic	NR	NR
Carcinogenicity	Not carcinogenic	NR	NR
Fertility impairment	No data available	NR	NR
Developmental toxicity	Not data available	NR	NR

4.1.3.1 Workers

In chlorine manufacturing, four exposure scenarios have been considered cell-rooms operators, maintenance operators, filling operators and laboratory. Short term exposure (STEL) data are to be used for the Risk Characterisation for all endpoints. Human repeated exposure to chlorine is not expected to lead to effects other than irritation observed in the study by Schins et al. (2000). Additionally, SCOEL committee concluded that chlorine effects appear to be related to concentration in the air and not to duration of exposure (SCOEL, 1998).

Using the 90th percentile of the distribution of the maximum exposure levels observed at each location, the short-term inhalation exposure to chlorine in the four scenarios considered varies from 0.084 to 0.180 ppm (0.252 to 0.540 mg/m^3).

When chlorine is used as a chemical intermediate, three exposure scenarios have been considered (production operators, maintenance operators and filling operators). Using the 90th percentile of the distribution of the maximum exposure levels observed at each location, the short term inhalation exposure level to chlorine is 0.180 ppm (0.540 mg/m^3) for production operator and 0.167 ppm (0.501 mg/m^3) for the other tasks.

When chlorine is used in water disinfection applications two scenarios have been considered (storage and connection-disconnection operators) which also cover the distribution system. In storage area, the worst case, short term inhalation exposure level as calculated by EASE model is 0.1 ppm (0.3 mg/m^3), while based on the 90th percentile of the distribution of the maximum exposure levels observed at each location, the short term inhalation exposure to chlorine for connection-disconnection operators is 0.166 ppm (0.498 mg/m^3).

Measured levels of chlorine in chlor-alkali manufacturing plants and in plants using chlorine as chemical intermediate are in most cases lower than the occupational exposure limit for chlorine (0.5 ppm, 1.5 mg/m^3 as the proposed STEL). Therefore, the typical average concentrations are mentioned as well and these are generally far below 0.5 ppm (1.5 mg/m^3). In specific cases in which measured concentrations can be higher than the limit (i.e. during maintenance), adequate PPE are worn and strict safety procedures are applied. If peaks are measured, their duration is normally very short (around one minute). In most cases, they do not represent real exposure because workers wear PPE when they expect to be exposed to chlorine (i.e., during maintenance). However, the presence of peaks influences the 90-percentile and makes this value not representative of real exposure.

Chlor-alkali manufacturing plants have alarm systems in place with a pre-alarm level at 0.25 ppm (0.75 mg/m^3)and an alarm level at 0.5 ppm (1.5 mg/m^3), requesting the use of a mask. The operators are not expected to be exposed to concentrations higher than 0.5 ppm (1.5 mg/m^3), even when the personal monitor is indicating higher values.

There is no dermal exposure to chlorine.

4.1.3.1.1 Acute toxicity

The NOAEL (0.5 ppm, 1.5 mg/m^3) used for risk characterisation is based on human studies. According to the TGD, the minimal MOS for workers therefore only needs to take into account an intra-species factor of 5. See Table below for summary of results of the risk characterisation.

	Inhalation – typical average concentration				Inhalation – 90th percentile of the distribution of the maximum exposure levels			
Minimal MOS = 5	Exposure ppm [mg/m^3]	NOAEL ppm [mg/m^3]	MOS	Conclusion	Exposure ppm [mg/m^3]	NOAEL	MOS	Conclusion
Production								
Cell-room operators	0.072 [0.216]	0.5 [1.5]	6.94	ii	0.180 [0.540]	0.5 [1.5]	2.8	iii
Maintenance operators	0.082 [0.246]	0.5 [1.5]	6.1	ii	0.160 [0.480]	0.5 [1.5]	3.1	iii
Filling operators	0.077 [0.231]	0.5 [1.5]	6.49	ii	0.166 [0.498]	0.5 [1.5]	3.0	iii
Laboratory	0.046 [0.138]	0.5 [1.5]	10.9	ii	0.084 [0.252]	0.5 [1.5]	5.9	ii
Uses: Chlorine as chemical intermediate								
Production operators	0.072 [0.216]	0.5 [1.5]	6.94	ii	0.180 [0.540]	0.5 [1.5]	2.8	iii
Maintenance operators	0.075 [0.225]	0.5 [1.5]	6.7	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii

Filling operators	0.075 [0.225]	0.5 [1.5]	6.7	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Laboratory	0.075 [0.225]	0.5 [1.5]	6.7	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Uses: Chlorine in water disinfection								
Storage	0 [0]	0.5 [1.5]	∞	ii	0.1 [0.3]	0.5 [1.5]	5	ii
Connection-disconnection	0.077 [0.231]	0.5 [1.5]	6.49	ii	0.166 [0.498]	0.5 [1.5]	3.0	iii

The overall conclusion for all occupational scenarios based on typical average concentrations, which are a more realistic approach considering the high level of adequate protecting measures already in place in plants manufacturing or using chlorine, is:

Conclusion (ii)

4.1.3.1.2 Irritation and corrosivity

The NOAEL (0.5 ppm, 1.5 mg/m^3) used for risk characterisation is based on human studies. According to the TGD, the minimal MOS for workers therefore only needs to take into account an intra-species factor of 5. See Table below for summary of results of the risk characterisation.

	Inhalation – typical average concentration				Inhalation – 90th percentile of the distribution of the maximum exposure levels			
Minimal MOS = 5	**Exposure ppm [mg/m^3]**	**NOAEL ppm [mg/m^3]**	**MOS**	**Conclusion**	**Exposure**	**NOAEL**	**MOS**	**Conclusion**
Production								
Cell-room operators	0.072 [0.216]	0.5 [1.5]	6.94	ii	0.180 [0.540]	0.5 [1.5]	2.8	iii
Maintenance operators	0.082 [0.246]	0.5 [1.5]	6.1	ii	0.160 [0.480]	0.5 [1.5]	3.1	iii
Filling operators	0.077 [0.231]	0.5 [1.5]	6.49	ii	0.166 [0.498]	0.5 [1.5]	3.0	iii
Laboratory	0.046 [0.138]	0.5 [1.5]	10.9	ii	0.084 [0.252]	0.5 [1.5]	5.9	ii
Uses: Chlorine as chemical intermediate								
Production operators	0.072 [0.216]	0.5 [1.5]	6.94	ii	0.180 [0.540]	0.5 [1.5]	2.8	iii
Maintenance operators	0.075 [0.225]	0.5 [1.5]	6.7	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Filling operators	0.075 [0.225]	0.5 [1.5]	6.7	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Laboratory	0.075 [0.225]	0.5 [1.5]	6.7	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Uses: Chlorine in water disinfection								
Storage	0 [0]	0.5 [1.5]	∞	ii	0.1 [0.3]	0.5 [1.5]	5	ii
Connection-disconnection	0.077 [0.231]	0.5 [1.5]	6.49	ii	0.166 [0.498]	0.5 [1.5]	3.0	iii

The overall conclusion for all occupational scenarios based on typical average concentrations, which are a more realistic approach considering the high level of adequate protecting measures already in place in plants manufacturing or using chlorine, is:

Conclusion (ii) for all scenarios

4.1.3.1.3 Sensitisation

Based on the available animal and human data, it is concluded that chlorine does not pose a skin sensitization hazard.

Conclusion (ii) for all scenarios

4.1.3.1.4 Repeated dose toxicity

The NOAEL (0.5 ppm, 1.5 mg/m^3) used for risk characterisation is based on human studies. According to the TGD, the minimal MOS for workers therefore only needs to take into account an intra-species factor of 5. See Table below for summary of results of the risk characterisation.

	Inhalation – typical average concentration				Inhalation – 90th percentile of the distribution of the maximum exposure levels			
Minimal MOS = 5	Exposure ppm [mg/m^3]	NOAEL ppm [mg/m^3]	MOS	Conclusion	Exposure ppm [mg/m^3]	NOAEL	MOS	Conclusion
Production								
Cell-room operators	0.072 [0.216]	0.5 [1.5]	6.94	Ii	0.180 [0.540]	0.5 [1.5]	2.8	iii
Maintenance operators	0.082 [0.246]	0.5 [1.5]	6.1	ii	0.160 [0.498]	0.5 [1.5]	3.1	iii
Filling operators	0.077 [0.231]	0.5[1.5]	6.49	ii	0.166 [0.498]	0.5 [1.5]	3.0	iii
Laboratory	0.046 [0.138]	0.5[1.5]	10.9	ii	0.084 [0.252]	0.5 [1.5]	5.9	ii
Uses: Chlorine as chemical intermediate								
Production operators	0.072 [0.216]	0.5 [1.5]	6.94	ii	0.180 [0.540]	0.5 [1.5]	2.8	iii
Maintenance operators	0.075 [0.225]	0.5 [1.5]	4.9	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Filling operators	0.075 [0.225]	0.5 [1.5]	4.9	ii	0.167 [0.501]	0.5 [1.5]	3.0	iii
Laboratory	0.075 [0.225]	0.5 [1.5]	4.9	ii	0.167 [0.705]	0.5 [1.5]	3.0	iii
Uses: Chlorine in water disinfection								
Storage	0 [0]	0.5 [1.5]	∞	ii	0 [0]	0.5 [1.5]	∞	ii
Connection-disconnection	0 [0]	0.5 [1.5]	∞	ii	0 [0]	0.5 [1.5]	∞	ii

The overall conclusion for all occupational scenarios based on typical average concentrations, which are a more realistic approach considering the high level of adequate protecting measures already in place in plants manufacturing or using chlorine, is:

Conclusion (ii)

4.1.3.1.5 Mutagenicity

The available data for solution of chlorine in water are not entirely conclusive with respect to mutagenicity/genotoxicity. Since chlorine/sodium hypochlorite is not carcinogenic, no additional testing for mutagenicity is required. It is concluded that chlorine is of no concern to workers with regard to mutagenicity.

Conclusion (ii) for all scenarios

4.1.3.1.6 Carcinogenicity

Chlorine gas is not carcinogenic in rodents. Carcinogenicity studies with sodium hypochlorite administered in drinking water to rats and mice did not show any carcinogenic effect. The human epidemiological data are not sufficient to suggest a causal relationship between the use of chlorinated drinking water and an increased cancer risk. It is concluded that chlorine is of no concern to workers with regard to carcinogenicity.

Conclusion (ii) for all scenarios

4.1.3.1.7 Toxicity for reproduction

For chlorine gas, no data are available on reproductive effects. Only limited data is available for sodium hypochlorite; however, there is no evidence to suggest that sodium hypochlorite would cause any adverse reproductive effects in humans, especially at current exposure levels. It is concluded that chlorine is of no concern to workers with regard to reproduction toxicity.

Conclusion (ii) for all scenarios

4.1.3.1.8 Summary of risk characterisation for workers

For all occupational scenarios and for all end-points there are no concerns (**conclusion ii**).

4.1.3.2 Consumers

As the use of chlorine is limited to professional and industrial applications, there is no direct consumer use of chlorine and consequently no direct public exposure is expected. Consumers can be exposed to chlorine gas in case of accidental mixing of bleach and acids. Humans exposed via the environment

Emissions to water are estimated to be about 19.2 t/y from anthropogenic releases, natural releases to water occur but no estimation of quantities is available. Air emissions are estimated to range from 126 million t/y to over 2 billion t/y, with contributions of 100 milion-2 billion t/y from natural sources, 132 t/y from production sites, including on-site use and 3.2 t/y maximum from off-site use.

Due to the properties of chlorine the substance will only remain in the water compartment for a very short period of time. Depending on the specific conditions of the receiving surface water chlorine will rapidly volatilise to air, transform into other oxidants or react with organic matter. Therefore emissions to water are not relevant at the regional or continental scale, and human exposure via the environment from water emissions will not occur.

Emissions to air on a European level will be predominantly from natural origin. However, whether natural or anthropogenic, all chlorine released to air will undergo rapid removal or transformation. Depending on environmental conditions it will degrade due to photolysis, undergo wet or dry deposition or transform into other substances. Therefore, anthropogenic emissions to air are not relevant at the regional or continental scale, and human exposure via the environment from air emissions will not occur.

Using the data on emissions from chlorine production, a local PEC of 0.628 $\mu g/m^3$ has been calculated. Since the NOEL for all endpoints is 1.5 mg/m^3, we can conclude that no risk is expected for humans exposed via the environment.

The scenarios considering human exposure to solutions containing hypochlorous acid and hypochlorite ions, both directly and via the environment, have been treated extensively in the Risk Assessment Report for sodium hypochlorite. The main conclusion of this report is the following: "Due to the physical-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".

4.1.3.3 Combined exposure

No such exposure is thought to occur.

4.2 HUMAN HEALTH (PHYSICO-CHEMICAL PROPERTIES)

4.2.1 Exposure assessment

4.2.1.1 Workers

Production and downstream uses take place in automated, closed systems and stringent exposure and hazard controls are in place, both during normal production and maintenance. Containers used for transportation and storage meet special safety requirements. Loading and unloading facilities are well equipped to avoid any leakage or spill during operating procedures. Exposure of workers to levels of chlorine causing physico-chemical hazards during normal handling and use is well-controlled and negligible.

4.2.1.2 Consumers

As the use of chlorine is limited to professional and industrial applications, there is no direct consumer use of chlorine and consequently no direct public exposure is expected.

4.2.1.3 Humans exposed via the environment

Exposure of humans via the environment is discussed in **section 4.1.1.3**.

As there is no human exposure to chlorine via the environment, no effects occurring from its physico-chemical hazard are expected.

4.2.2 Effects assessment: Hazard identification

4.2.2.1 Explosivity

Chlorine has no explosive properties.

Chlorine can react with NH_3 to form the explosive NCl_3.

Chlorine gas does not react with H_2 at normal temperatures in absence of light. However, at higher temperatures, or in the presence of sunlight or artificial light of ca. 470 nm wavelength, hydrogen and chlorine combine explosively to form HCl.

4.2.2.2 Flammability

Chlorine has no flammable properties. Due to its oxidizing property, it can increase the risk of combustion/oxidation of some substances, including steel, at higher temperatures (>170°C). See **section 1.3**.

4.2.2.3 Oxidizing potential

Molecular chlorine is a strong oxidizer and a chlorinating agent.

4.2.3 Risk characterisation

4.2.3.1 Workers

As the occupational exposure to chlorine is well-controlled and negligible during normal handling and use, no risk occurring from its physico-chemical hazard is expected.

4.2.3.2 Consumers

As the use of chlorine is limited to professional and industrial applications, there is no direct consumer exposure to chlorine and consequently no risk is expected.

4.2.3.3 Humans exposed via the environment

Exposure of humans via the environment is discussed in **section 4.1.1.3**.

As there is no human exposure via the environment to chlorine, no risk is expected.

5 RESULTS [2]

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.

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.

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.

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.

[2] Conclusion (i) There is a need for further information and/or testing.
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 (iii) There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

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.