# European Union Risk Assessment Report

## CHLORINE

CAS No: 7782-50-5
EINECS No: 231-959-5

## RISK ASSESSMENT

GENERAL NOTE

This document contains two different reports:

- **Part I Environment** – pages 2-86
- **Part II Human Health** () – pages 87-212

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## RISK ASSESSMENT

## (Environment)

*Final report, December 2007*

Italy

***FINAL APPROVED VERSION***

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## Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93[1] on the evaluation and control of the risks of "existing" substances. "Existing" substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as "Rapporteur", undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94[2], which is supported by a technical guidance document[3]. Normally, the "Rapporteur" and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Health and Environmental Risks (SCHER) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the "Rapporteur" to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992 and confirmed in the Johannesburg Declaration on Sustainable Development at the World Summit on Sustainable Development, held in Johannesburg, South Africa in 2002.

This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.

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[1] O.J. No L 084, 05/04/199 p.0001 – 0075

[2] O.J. No L 161, 29/06/1994 p. 0003 – 0011

[3] Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

# 0 OVERALL RESULTS OF THE RISK ASSESSMENT[4]

| | |
|---|---|
| CAS Number: | 7782-50-5 |
| EINECS Number: | 231-959-5 |
| IUPAC Name: | Chlorine |

## 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.

## Human health

### Human health (toxicity)

*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.

*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.

*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.

*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.

### Human health (risks from physico-chemical properties)

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[4] 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.

**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.

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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

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# 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 PURITY/IMPURITIES, ADDITIVES

Chlorine is distributed in various stages of purity. The purity ranges from about 90 % to almost 100 %. The main impurities as a result of production are nitrogen, carbon dioxide, oxygen, bromine and hydrogen, but nitrogen trichloride and halogenated hydrocarbons may also be present. Information on dealing with impurities is given in the BREF for the Chlor-alkali manufacturing industry (European Commission, 2001b, section 2.4.3.1).

Mercury levels in chlorine produced in mercury cell chlor-alkali plants are very low, being about 1 mg of mercury per tonne of $Cl_2$ produced or less (European Commission, 2001b, Annex B, p 129, Euro Chlor 2001, Euro Chlor 2003c). For this reason mercury emissions from the product chlorine will not be discussed further in this risk assessment.

No additives are added to chlorine as produced.

## 1.3 PHYSICO-CHEMICAL PROPERTIES

Chlorine is a greenish-yellow gas having a pungent odour at ambient temperatures and pressures and a density 2.5 times higher than air. In liquid form it is a clear amber colour. Solid chlorine forms yellow crystals.

Chlorine is soluble in water and in salt solutions, the solubility decreasing with salt strength and temperature (above 10 °C). At 25 °C the aqueous solubility is 6.9 g/l

(Budavari et al., 1989); Gerhartz et al 1986, Schmittinger 2000). Chlorine partially hydrolyses in aqueous solution to form HCl and hypochlorous acid:

$Cl_2 + H_2O = HCl + HOCl$

Below 10°C, chlorine forms hydrates which are greenish-yellow crystals. The $Cl_2$-$H_2O$-System has a quadruple point at 28.7°C.

The vapour pressure data of Ambrose et al (1979) from 205.945 to 416.90 K, and Giauque and Powel (1939) from 172.17 to 240.10 K, were used to determine the constants in the Martin-Shin-Kapoor vapour pressure equation (Martin and Longpre, 1984):

$\ln(P) = A + B/T + C^* \ln(T) + D^*T + (E^*(F-T)^*\ln(F-T))/(F^*T)$; P [kPa],

where P is in kilopascals (kPa) and T is in Kelvin (K). The values of the constants are:

$A = 62.402508$ $D = 1.0666308 \times 10^{-2}$

$B = -4343.5240$ $E = 95.248723$

$C = -7.8661534$ $F = 424.90$

The equation fits the measured data well, with an average deviation between the predicted vapour pressure and the experimental values of 0.20 %, giving a standard deviation of 0.29 % (GEST 91/168 (2002d)).

The resultant vapour pressure at 20°C can be converted to 6780 hPa, at 30 °C to 8900 hPa, and at 50 °C to 14550 hPa (Martin and Longpre 1984). Similar values are given in Gerhartz et al (1986), and in Schmittinger (2000).

The density of chlorine gas at 101.3 kPa is a function of temperature, being 3.213. $kg/m^3$ at 0 °C, 2.7 $kg/m^3$ at 50 °C, 2.33 $kg/m^3$ at 100 °C, and 2.051 $kg/m^3$ at 150 °C. (Budavari et al., 1989; Gerhartz et al 1986). The relative density of liquid chlorine at –34 °C is 1.56 $g/cm^3$ (Chim. Oggi, 1999; Budavari et al., 1989). Liquid chlorine is quite compressible, and thus the density of liquid chlorine decreases with increasing temperature, being 1.47 $g/cm^3$ at 0°C and 3698 hPa (Dow Europe SA, 1996), and 1.405 $g/cm^3$ at 20°C and 5690 hPa (Elf-Atochem, 1997).

An octanol-water distribution equilibrium cannot be defined or measured, as both chlorine and hypochlorous acid (formed in water above pH = 4) have oxidising properties, and will react with the organic phase in both the shake flask (OECD, 1995) and the HPLC (OECD, 1989) methods for log Kow determination. In addition, if an octanol water distribution equilibrium of chlorine gas were to be estimated, it would not be appropriate to estimate a bioconcentration factor because of the reactivity of chlorine.

Chlorine generally exhibits a valence of –1 in compounds, but it also exists in the formal positive oxidation states of +1 (NaClO), +3 ($NaClO_2$), + 4 ($ClO_2$), +5 ($NaClO_3$) and +7 ($NaClO_4$). Molecular chlorine is a strong oxidizer and a chlorinating agent, adding to double bonds in aliphatic compounds or undergoing substitution reactions with both aliphatic and aromatic species. Chlorine is very active under specific conditions but it is not explosive or flammable. Chlorine reacts easily with most elements (e.g. S, P, $I_2$, $Br_2$, $F_2$). Reactions with $N_2$, $O_2$ and C are indirect. Chlorine reacts 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 temperatures above 250°C, or in the presence of sunlight or artificial light of ca. 470 nm wavelength, hydrogen and chlorine combine explosively to form HCl (Kroschwitz JI, Grant MH, Howe-Grant M, 1991) Like oxygen, chlorine is able to form flammable mixtures with hydrocarbons and chlorinated hydrocarbons. In general, the range of flammability is somewhat less for chlorine mixtures, compared to oxygen mixtures. (GEST 91/168, 2002c). Detonation of gaseous and liquid mixtures of chlorine with selected hydrocarbons may also occur (GEST 91/168, 2002c). Also, the auto-ignition temperatures of a number of organics in chlorine are known and are found to be much lower than the corresponding value in air or oxygen. Sometimes the auto-ignition temperatures are below 150 °C, but more often values are between 150 °C and 350 °C. This means that, when a mixture of a combustible and chlorine is formed at temperatures of 100 °C and above, a serious thermal explosion hazard or flammability risk is present, when the mixture is allowed to reside for extended periods. (GEST 91/168, 2002c).

Dry chlorine reacts combustively with most metals depending on the temperature. Aluminium, arsenic, gold, mercury, selenium, tellurium, and tin react with dry $Cl_2$ in gaseous or liquid form at ordinary temperatures; steel ignites at about 170°C depending on the physical shape; titanium reacts violently with dry chlorine. Wet chlorine is very reactive because of the hydrochloric acid and hypochlorous acid. Tantalum is resistant to both dry and wet chlorine (Kroschwitz JI, Grant MH, Howe-Grant M, 1991).

The surface tension of liquid chlorine decreases with increasing temperature (GEST 91/168, 2002a). At 20°C, the calculated surface tension is 18.5 $mJ/m^2$.

**Table 1.1 Summary of physico-chemical properties**

| Property | Value | Comment/Reference |
|---|---|---|
| Physical state | Gas | At room temperature and pressure |
| Melting point | -101 °C | Budavari et al. (1989), Gerhartz et al (1986), as triple point in Martin and Longpre (1984). |
| Boiling point | -34 °C at 1013 hPa | Budavari et al. (1989), Gerhartz et al (1986) Martin and Longpre (1984). |
| Relative density | 1.56 $g/cm^3$ at -34 °C<br>3.213 $kg/m^3$ at 0 °C | Liquid.(Chim. Oggi (1991,) Budavari et al. (1989))<br>Gas. Gerhartz et al (1986) |
| Vapour pressure | 6780 hPa at 20 °C | Martin and Longpre 1984. |
| Water solubility | 9.78 g/l at 10 °C<br>6.9 g/l at 25 °C | Maximum solubility at 10 °C. Gerhartz et al (1986), Schmittinger (2000), GEST 2002b.<br>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 °C 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<br>Viscosity – Gas at 0C | 0.385 · $10^{-3}$ Pa.s<br>12.4 · $10^{-3}$ Pa.s | Range: 1.032 x $10^{-3}$ Pa.s (–100 C) to 0.249 x $10^{-3}$ Pa.s (100C)<br>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 20°C | GEST 91/168 (2002a) |
| Henry's Law Constant | 9.83 · $10^3$ Pa $m^3$ per mole | Calculated from water solubility and vapour pressure information in this table |

## 1.3.1 Transformation

Addition of chlorine gas to pure water results in the formation of a mixture of hydrochloric acid (HCl) and hypochlorous acid (HOCl) according to law of mass action:

$$k = \frac{[HOCl]x[H^+]x[Cl^-]}{[Cl_2]}$$

The equilibrium constant for this reaction depends upon temperature, as shown in **Table 1.2** below. The proportion of chlorine gas decreases with temperature (Herrmann and Wagner, 2003).

**Table 1.2 Equilibrium constant k for chlorine at equilibrium**

| Temperature, [°C] | Equilibrium constant, $k \cdot 10^4$ |
|---|---|
| 0 | 1.46 |
| 15 | 2.81 |
| 25 | 3.94 |
| 35 | 5.10 |
| 45 | 6.05 |

The following reactions occur when chlorine is added to water (species which are active biocides are in bold letters):

$\mathbf{Cl_2}$ + H2O = **HClO** + HCl (equat. 1)

**HClO** = $H^+$+ $\mathbf{OCl^-}$ (equat. 2)

HCl = $H^+$ + $Cl^-$ (equat. 3)

$Cl_2$ + 2 $OH^-$= $Cl^-$ + $\mathbf{OCl^-}$ + H2O (equat. 4)

**HClO** = $H^+$ + $Cl^-$ + **O** (equat. 5)

The disproportionation reaction of chlorine in the near-neutral pH region (equation 1) runs in a nearly quantitative manner and is completed within seconds (cf. **Table 1.2)** (Herrmann and Wagner, 2003). There are three species of chlorine in equilibrium in water: gaseous chlorine, HOCl (also a gas at room temperature and pressure), and $ClO^-$. An example of the distribution between them as a function of pH is shown in **Figure 1.1**. For example, at pH 7.5 half of the chlorine is active as HOCl and half is available as $ClO^-$. $Cl_2$ is present in significant quantities only at pH less than 3 (see **Figure 1.1**)

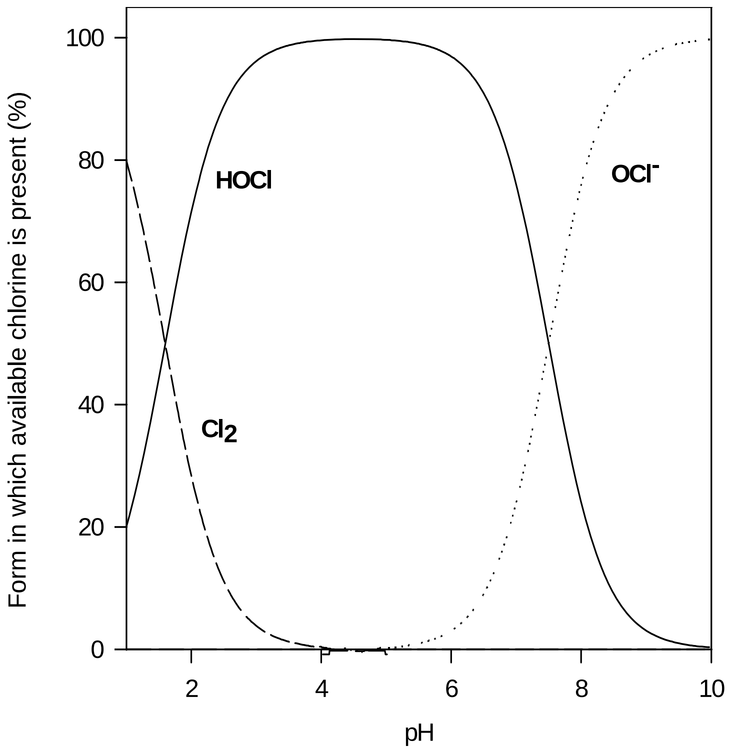

**Figure 1.1Calculated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M $Cl_2$ in water at standard temperature and pressure( GEST 91/168, 2002b)**

The speciation of chlorine in water is important for all processes in which chlorine is present in an aqueous environment. These processes include chlorine use as a biocide, for example in drinking water disinfection, swimming pool disinfection, sewage effluent disinfection, and cooling water disinfection. Chlorine speciation is also important if chlorine is used in aqueous industrial processes, as was formerly the case in the pulp and paper industry, and in the textile industry. All chlorine discharged to the aqueous environment will be present in speciated form, and this is relevant both for human toxicity and for ecotoxicity studies. In the pH range relevant for both humans and environmental biota, the relevant chlorine species will be hypochlorous acid and the hypochlorite anion.

Hypochlorous acid HClO in its non-dissociated form, predominant in the pH 5-7 region, is a more powerful oxidant than the hypochlorite anion ($OCl^-$) and chlorine. The degree of dissociation is therefore important for disinfection efficacy. It strongly depends on the pH (see **Figure 1.1**) and much less on temperature. Dissociation is poor at pH levels below 6. From pH 6 to 8.5 a nearly complete dissociation of HClO occurs. Thus for disinfection with chlorine control of pH is critical (Herrmann and Wagner, 2003). This is also important for ecototoxicity testing.

Further information concerning aqueous HOCl and its reactions, including reactions in polluted water, are given in the sodium hypochlorite risk assessment report (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 2.4 and 2.5.)

## 1.4 CLASSIFICATION

### 1.4.1 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

### 1.4.2 Proposed classification

Agreed Classification at TC C&L September 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

## 2.1 PRODUCTION

Globally, Western Europe is the second largest chlor-alkali producing region after the US. In 1994, when global chlorine production was 38 million tonnes, the United States produced 11.2 million tones of chlorine. Western Europe, including the EU, Switzerland and Norway, and Hungary, Poland, and the Czech and Slovak republics, produced 10.6 million tonnes of chlorine in 1995, while the third-ranked producing country, Japan, had 4.2 million tonnes production capacity in 1995. (Euro Chlor 2004a, European Commission, 2001b).

In 2004, Euro Chlor represented European chlorine producers in 20 countries, which had 97% of the chlorine production capacity in the 25 EU member states. Apart from 32 producers in Western Europe, Euro Chlor has also seven manufacturing members in four Eastern European countries. Full members are producers of chlorine in: Austria, Belgium, the Czech Republic, Finland, France, Germany, Greece, Hungary, Ireland, Italy, the Netherlands, Norway, Poland, Portugal, the Slovak Republic, Slovenia, Spain, Sweden, Switzerland and the United Kingdom (Euro Chlor 2004c, Euro Chlor web site 2004). In addition, chlorine producers who are not members of Euro Chlor have contributed to Euro Chlor statistical publications, such as the chlorine plant and production data available for the 84 plants in Europe (Euro Chlor 2004c).

### 2.1.1 Production processes

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. A short description of these processes is detailed below (European Commission, 2001b).

#### 2.1.1.1 Mercury amalgam electrolysis process

In the mercury electrolyser, mercury flows concurrently with brine along the base of a cell. The mercury acts as the cathode and forms an amalgam with sodium. Chlorine is formed at the anodes, which are suspended in the brine. The anodes are constructed from titanium with a suitable rare metal oxide coating and can be raised or lowered manually or automatically to achieve optimum voltage. The amalgam flows to a reactor (denuder or decomposer) where the amalgam reacts with water in the presence of carbon (graphite) to form caustic soda and hydrogen.

Weirs and water seals in the end sections ensure that hydrogen and chlorine gas streams are contained and isolated from each other and also prevent brine from mixing with the caustic soda. Chlorine gas can leave the cell directly for further treatment and drying or can leave as a two-phase flow with the anolyte. In this case, the anolyte must be dechlorinated before returning to the denuder.

Further information on the mercury amalgam electrolysis process can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b). This includes a discussion of the parts of the process which are responsible for mercury emissions to both air and water (European Commission, 2001b, section 3.1.2.1 and following subsections, and Appendix B). Cumulative mercury emissions to air and water in 1998 are also given (European Commission, 2001, Appendix C). Due to the nature of the process, virtually no mercury is present in the chlorine gas produced.

#### 2.1.1.2 Diaphragm Electrolysis process

In the diaphragm electrolyser an asbestos diaphragm separates the anolyte and catholyte chambers. In some cases polymer modified asbestos is used as the diaphragm. Although asbestos is the most suitable material for diaphragms, new diaphragm materials are under development and are used in some facilities.

The anode is titanium with a suitable rare metal oxide coating and the cathode is steel or nickel-coated steel. The anode and cathode have a fixed position in the cell. In general the distance between the anode and the cathode is arranged for optimum voltage.

Differential hydraulic pressure causes the anolyte to flow through the diaphragm from the anolyte compartment to the catholyte compartment. Chlorine is removed from the vapour space above the anolyte normally under suction. Diaphragm cell liquor containing 9-12% caustic soda and 15-17% sodium chloride overflows from the catholyte chamber to intermediate storage and evaporation, although it can be used directly for other processes. The sodium chloride concentration of NaCl in 50% caustic soda liquor from this process is up to 1%.

Diaphragm cells can have a monopolar (cells in parallel) or bipolar (cells in series) configuration and there is a large variety of types which allows a wide range of current densities to be used. Consequently, a large number of cell designs are in operation.

Further information on the diaphragm electrolysis process can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b).

Until recently, all diaphragm plants used chrysotile asbestos as a separator within the cell. The inherent safety features of this type of separator were acknowledged by legislators and the use of asbestos in such cells remains the only derogation within the Asbestos Directive. Research and development by the industry and its suppliers has resulted in the availability of an alternative non-asbestos separator for certain geometric and electrical designs of cells. Of the nine diaphragm plants in Western Europe at the beginning of 2002, three are in the final stage of conversion to the non-asbestos substitute, one was closed permanently and announcements were made concerning the conversion of a further three to membrane technology (Euro Chlor 2003a).

#### 2.1.1.3 Membrane Electrolysis process

Membrane electrolysers can also have a monopolar or bipolar configuration. In the membrane electrolysers the anolyte and catholyte chambers are separated by an ion selective membrane.

In comparison with the diaphragm electrolyser there is no physical flow from the anolyte to the catholyte chamber. Instead, sodium ions pass through the membrane and form caustic soda and hydrogen in the catholyte. Caustic soda and hydrogen are produced in the catholyte compartment by the addition of water.

The anodes are made from titanium with a suitable rare metal oxide coating. The cathodes are constructed in steel or nickel and may or may not have a coating. There is some variation in the material used to manufacture of the membrane, which acts as a cation exchange.

The strength of the caustic soda in the membrane process is up to 33 % (with a final NaCl concentration of less than 100 ppm in 50 % caustic solution).

Further information on the membrane electrolysis process can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b).

#### 2.1.1.4 Further processing

Generally, before the chlorine can be used, it goes through a series of processes for cooling, cleaning, drying, compression and liquefaction. In some applications, it can be used as a dry gas without need for liquefaction. Very occasionally it can be used directly from the electrolysers. Further information on these processes can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b).

### 2.1.2 Production capacity

The chlor-alkali industry in Europe is very diversified with producers ranging in size from 6000 t/yr to 1.5 million t/yr chlorine capacity. Twenty percent of the producers manufacture 70% of the chlorine. The largest producer is Dow in Germany; the most geographically spread is Solvay/Solvin with production in seven European countries. Germany outstrips all other European countries in chlorine capacity. Whilst there has been some growth in capacity in Germany, the United Kingdom has seen a substantial drop. Four plants (two membrane, one diaphragm and one mixed membrane/ diaphragm) in the UK out of a total of seven have closed in the last three years. Capacity in the other countries has remained more or less static (Euro Chlor, 2003a). The locations and capacities of chlor-alkali plants in operation in Europe in 2003 can be found in Euro Chlor (2004c), which updates the data given in the BREF for the chlor-alkali manufacturing industry, figure 1.3 and table 1.1, and Appendix A. (European Commission, 2001b).

The volume of chlorine produced in the EU, and also in several nearby countries, is given in **Table 2.1**. The Western European production accounts for 83% of production capacity. Production volume in the EU has increased slightly since 1995, with the 2003 production volume being almost 107% of the 1995 value. There was a small decrease in production volume between 2000 and 2002, but in 2003 production increased to almost the 2000 production level (Euro Chlor, 2004a, Euro Chlor 2004c.)

**Table 2.1 Production volume of Chlorine in 2003**

| Producing area | Volume of $Cl_2$ produced, in thousands of metric tons[1] |
|---|---|
| Germany | 4 239 |
| Belgium and The Netherlands | 1301 |
| France | 1437 |
| Italy | 506 |
| United Kingdom | 694 |
| Spain, Portugal, and Greece | 741 |
| Norway, Sweden, and Finland | 534 |
| Switzerland and Austria | 135 |
| Eastern European Countries[2] | 595 |
| | |
| Total for EU and nearby countries | 10 180 |

1Production figures for the countries or groups of countries reported have been rounded to the nearest thousand metric tonnes. The Total production figure has been rounded up to the nearest thousand metric tonnes. [2]Eastern European Countries are Poland, Hungary, the Czech Republic, the Slovak Republic, and Slovenia.

### 2.1.3 Transport

Only 10% of the chlorine manufactured in Western Europe is transported by road or rail. Where chlorine needs to be used at adjacent facilities, it is generally moved via inter-plant pipelines (Euro Chlor 2003a). Of the 950,000 tonnes transported in 2002, 70% was moved in bulk by rail with an average distance of 419 km, 27% by road (average distance 202 km) and 3% in drums or cylinders (average trip 306 km). Over the last 50 years there have been no fatalities caused by bulk chlorine shipments in Western Europe (Euro Chlor, 2003a).

## 2.2 USES

### 2.2.1 Introduction

Chlorine is mainly used as a chemical intermediate to produce both chlorinated and non-chlorinated compounds. Many of the highest value chlorine chain products – such as polycarbonates, polyurethanes and epoxy resins – do not contain chlorine, but depend on it for their synthesis. 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).

Chlorine use in 2003 is shown in **Table 2.2.** The top six rows of the table are based on the Chlorine Industry Review for 2002-2003 (Euro Chlor, 2003a), and include the 2003 use information described above (Euro Chlor 2004c). Most of this use will be on the same site as production, but the percentage of chlorine used on the production site depends on the individual site. However, some information on the distribution of the percentage of chlorine used at the site of production is available from a Euro Chlor internal survey. This indicates that approximately 10% of sites used more chlorine than was produced on site, and the median site used approximately 96% of the on-site chlorine production. The 10% of sites which need to import chlorine from other sites will account for much of the chlorine transported by road (**Section 2.1.3).** To estimate a further breakdown of the 9% of tonnage in the “other uses” category (Euro Chlor 2004c and Euro Chlor 2003a), the extensive survey of chlorine use carried out in 1998 (Euro Chlor, 2000) has been used. A comparison of the available 2003 and 1998 data showed that the percentages of chlorine used for most applications had not changed appreciably, except for an approximate 20% increase in the amount of chlorine used in the production of inorganic chemicals, and a 20% decrease in the amount of chlorine used in solvent production. Thus the 1998 use percentages were applied to the 2003 production tonnage for the EU and nearby countries, as shown in **Table 2.1,** to estimate the chlorine uses in 2003 for the production of chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, chloro oxygenated derivatives, and as elemental chlorine.

Of the 2.2 % of chlorine production which was supplied as elemental chlorine in 1998, 39% was used as an intermediate in the production of dyestuff and pesticides and 35% was used as an intermediate in small industry. These uses will not normally be on the site of chlorine production. It has been assumed that these uses have retained these use percentages in 2003. In 1998, a further 18% was used for the disinfection of drinking water, while 4.4% was used for swimming pool disinfection. Elemental chlorine was also used, in 1998, in the pulp and paper industry (5% of elemental chlorine production). The replacement of chlorine use in the pulp and paper industry since 1998 by other processes is discussed in **section 2.2.2.2.6.**

A survey made by Euro Chlor in 1994 showed the various uses of elemental chlorine in water-based applications such as drinking water disinfection, use in the pulp and paper industry, swimming pool disinfection, sewage treatment, cooling water disinfection and use in the textile industry. These uses represented 0.8% of the 1994 production figures. The last three uses did not appear in the 1998 survey (Euro Chlor, 2000). However, in 1994 the use of elemental chlorine in the textile industry was small, being 300 tpa. This use is now thought to be negligible, as discussed in **section 2.2.2.2.5**.

There is recent information on the use of elemental chlorine in drinking water disinfection, in cooling water disinfection, and in swimming pool and sewage treatment uses (Euro Chlor 2003b). All uses show a decline in use between 1998 and 2000, with an approximate 20% decrease in the use of chlorine as a cooling water disinfectant, and approximately 6% decrease in the other uses. The 2000 use data have been corrected by the change in total chlorine production to give approximate usage data for 2003. The internal survey (Euro Chlor, 2003b) reports combined data for swimming pool and wastewater treatment use, and it has been necessary to use the 1994 use ratios (47% sewage treatment, 53% swimming pool disinfection) in order to apportion the tonnage used between the two applications. These figures are approximate, but should be considered in the context of the overall decrease in the use of chlorine gas for these purposes, and the small percentage of overall chlorine production which these uses represent. These uses are included in **Table 2.2**. The 1998 study of chlorine flow in Europe (Euro Chlor, 2000) also included 1.5% of chlorine in the category “others”, which it is not possible to specify further.

**Table 2.2** Reported and estimated chlorine use in 2003

| Use | Type of process (closed, batch)[1] | Industry category | Use category | Quantity used<br>Thousand tonnes per annum | Percentage of total use |
|---|---|---|---|---|---|
| PVC production | Closed | 3 | 33 | 3560[2] | 35[3] |
| Non-chlorinated polymer production | Closed | 3 | 33 | 2440[2] | 24[3] |
| Production of inorganic chemicals, including sodium hypochlorite | Closed | 3 | 33 | 1630[2] | 16[3] |
| Chloromethane production | Closed | 3 | 33 | 810[2] | 8[3] |
| Epichlorohydrin production | Closed | 3 | 33 | 510[2] | 5[3] |
| Production of solvents | Closed | 3 | 33 | 410[2] | 4[3] |
| Production of chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, and chloro oxygenated derivatives | Batch | 3 | 33 | 610[2] | 6[4] |
| Elemental chlorine used offsite as an intermediate in dyestuff and pesticide production | Closed | 3 | 33 | 87[2] | 0.85[4] |
| Small industrial offsite use of elemental chlorine as an intermediate | Closed | 3 | 33 | 77[2] | 0.76[4] |
| Drinking water disinfectants | | 15 | 39 | 33[5,6] | 0.32 |
| Swimming pool disinfectants | | 5,6 | 39 | 7[5,7] | 0.07 |
| Waste water treatment | | 15 | 39 | 6[5,7] | 0.06 |
| Cooling water disinfection | | 15 | 39 | 1[5,9] | 0.01 |
| Pulp and paper industry | | 12 | 8 | Very low[8] | Very low |
| Textile industry | | 13 | 8 | Very low[10] (0.3 in 1994) | negligible |
| | | | | | |
| Total | | | | 10 187[11] | 100.2% |

[1]The definition of closed and batch processes refers only to the steps involving chlorine. [2] These quantities used have been estimated from use percentages. [3] Data from Euro Chlor (2003). [4]Data estimated from 1998 use figures (Euro Chlor, 2000), and 2003 production figures (Euro Chlor 2004c). [5]Data estimated from 2000 information (Euro Chlor, 2003b), updated by the 2003/2000 production ratio. [6] Use in this category declined by approximately 6% between 1998 and 2000 (Euro Chlor, 2003b). [7] The 1994 chlorine use data have been used to estimate the ratio of swimming pool disinfectant to wastewater disinfectant use. [8]The replacement of chlorine use by other processes is discussed in **section 2.2.2.2.6.** [9] Use in this category declined by approximately 20% between 1998 and 2000 (Euro Chlor, 2003b). [10]The lack of any evidence for continuing use of chlorine gas in the textile industry is discussed in **section 2.2.2.2.5.** [11]This total is higher than the actual 2003 production total of 10 180 000 tonnes, due to rounding errors in the estimated use percentages.

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## 2.2.2 Scenarios

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.

### 2.2.2.1 USE of chlorine as a chemical intermediate

#### 2.2.2.1.1 Use of chlorine in PVC production

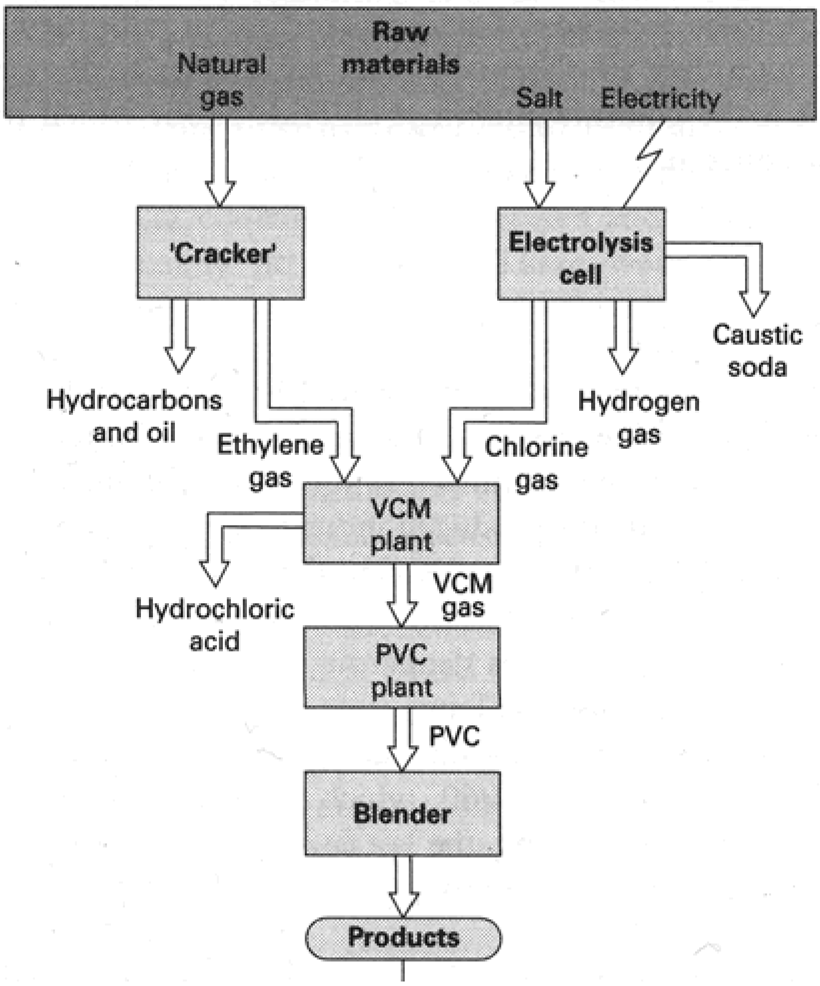
In 2003, 35% of chlorine production was used as an intermediate in the production of Poly Vinyl Chloride, or PVC (Euro Chlor, 2004c). The chemical process for making PVC involves three steps: first, production of the monomer, chloroethane (or vinyl chloride); then the linking of these monomer units in a polymerisation process; and finally the blending of the polymer with additives. In this process, shown schematically in **Figure 2.1**, ethylene and chlorine are combined to form a liquid, ethylene dichloride (i) which is then heated to give vinyl chloride (or chloroethane) (ii). Chloroethane can also be produced via the oxychlorination route, which is based on ethene, HCl and oxygen. Many plants use a combination of both processes. Chloroethane is then removed, leaving hydrogen chloride gas, which is recovered and recycled in the oxychlorination process. The chemical reaction is:

$$\mathrm{H_2C{=}CH_2 + Cl_2} \longrightarrow \underset{\text{(i)}}{\mathrm{ClH_2C\text{-}CH_2Cl}} \longrightarrow \underset{\text{(ii)}}{\mathrm{H_2C{=}CHCl}} + \mathrm{HCl}$$

Chloroethane is the main product, but both HCl and dichloroethane can also be used as end-products. HCl and dichloroethane from outside sources are sometimes fed into the system, serving as intermediates for manufacture of Chloroethane. Chlorinated hydrocarbons are formed as unintentional by-products. Chlorinated hydrocarbons are converted into HCl or are used as feedstock for other products, such as perchloroethylene (also known as PER, tetrachloroethylene or tetrachloroethene.) Some common salt may be formed as waste (Euro Chlor, 2000).

In further stages of the production process, pressure is applied to vinyl chloride (dispersed in water as a suspension or an emulsion) in high pressure chambers at temperatures of 50-70°C. The role of water is to remove and control the heat given off in the polymerisation process. PVC forms as tiny particles which grow and when they reach a desired size the reaction is stopped and any unreacted vinyl chloride is distilled off and re-used. The PVC is separated off and dried to form a white powder (Bristol University website, 2001).

**Figure 2.1 Schematic of the PVC production process (Bristol University Website, 2001)**



In the PVC production process, chlorine is usually generated on site, and delivered to the required location by pipelines which have been constructed specifically for the purpose of chlorine gas transport. Thus chlorine releases to air are minimal. Any chlorine releases, to air or to water, due to PVC production will have been included in the chlorine releases which are reported as emissions due to chlorine production on the manufacturing site.

### 2.2.2.1.2 Other intermediate uses of chlorine

In most of the larger applications below, chlorine gas will generally be produced on site, as described for PVC production (**section 2.2.2.1.1).** Note that 90% of all chlorine used is produced on site, or transferred to neighbouring installations by pipeline (Euro Chlor, 2003a). Also any chlorine releases, to air or to water, due to production of other chemicals at sites at which chlorine production occurs will have been included in the chlorine releases which are reported as emissions due to chlorine production on the manufacturing site.

### Chloromethanes

In 2003, 8% of chlorine production was used in the production of chloromethanes. These products are principally intermediates in other chemical processes and include methylchloride, methylene chloride, chloroform and carbon tetrachloride. Methylene chloride is mainly used as a solvent. In 1998, this chain consumed 8.4% of the total chlorine available with a recycling index of 30%. Thus 30% of the total chlorine used in these products came from recycled sources (Euro Chlor, 2000).

There are two routes for the production of chloromethanes. One route is based on methane and chlorine, while the other route utilises methanol, hydrogen chloride (HCl) and chlorine, with surplus HCl being recycled (Euro Chlor, 2000).

The main products are monochloromethane (methyl chloride), dichloromethane (methylene chloride), trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride). The principal by-product is hydrochloric acid, an aqueous solution of HCl. Waste products are generated as chlorinated hydrocarbons (CHCs) and salt.

### Other C2 derivatives, solvents and intermediates

This chain contains a number of products, some of which are chlorinated (e.g. the solvents trichloroethylene and perchloroethylene) and others which are not (e.g. ethene amines, polyvinylidenefluoride and some hydrofluorocarbons). Between the early 1980s and 1998 there was a 45% reduction in production of these chemicals, largely due to emission control improvements by dry cleaning units and the phase-out of emissive uses of 1,1,1 trichloroethane under the Montreal Protocol. In 1998, this chain consumed 5% of chlorine production. It did not appear as a separate entry in the 2002 or 2003 use information (Euro Chlor, 2000; Euro Chlor 2003a, Euro Chlor 2004c).

C2 derivatives cover a range of chlorinated compounds made using various production processes. Raw materials (input) can be chlorine, hydrogen chloride, light-end-chlorinated hydrocarbons and dichloroethane. HCl, chlorinated hydrocarbons and tetrachloroethene can be both raw materials and end-products (Euro Chlor, 2000).

The products in this category are: the solvents trichloroethene (TRI), tetrachloroethene (PER) and 1,1,1-trichloroethane and the monomer 1,1-dichloroethene (VDC). There is also a small production of vinyl chloride monomer and tetrachloromethane arising as by-products from some of these processes, which are part of the C2 chain. Additional by-products from all processes are HCl and chlorinated hydrocarbons, with salt as a waste product.

### Allyl chloride-epichlorohydrin (AC-ECH)

Allyl chloride is used for manufacturing pharmaceuticals, pesticides and is the precursor for epichlorohydrin used for epoxy resins. Although only utilising 5% of chlorine production, there has been a 35% increase since 1983(Euro Chlor, 2000).

Epichlorohydrin (ECH), or 1-chloro-2,3-epoxypropane, the main chlorine-containing end-product of this chain, is produced in three steps. The first step (a) is the formation of chloropropene-1 (allyl chloride, AC) by chlorination of propene-1. In the second step (b) conversion of AC with hypochlorite into 1,2- and 1,3-dichlorohydroxy-propene (dichlorohydrin, DCH) takes place. In the final step (c) DCH is converted into ECH with either sodium hydroxide or calcium hydroxide (Euro Chlor, 2000).

Epichlorohydrin is a liquid at room temperature and pressure. Other end-products in these processes are allyl chloride, 1,3-dichloropropene (DCP) and 1,2,3-trichloropropane (TCP). HCl is a by-product, with CHCs and chloride as waste products.

Polyurethanes, epoxides and polycarbonates

In 2002 and 2003, 24 % of chlorine produced was used in the production of non-chlorinated products, including isocyanates and oxygenates, which are used in the production of polyurethanes, epoxides and polycarbonates. Polyurethanes themselves do not contain chlorine and the di-isocyanate production process yields large amounts of HCl which is variously used in ethylene dichloride (dichloroethane) production, the merchant hydrochloric acid market or neutralised to common salt. The precursors for polyurethanes are propene oxide and diisocyanates. Polycarbonates are versatile engineering plastics. There is no chlorine in the end product and chlorine is discharged from this chain in the form of innocuous inorganic chloride. Methylene chloride is also used as a reaction medium (Euro Chlor, 2000).

*Propene oxide production*

Production of propylene oxide (propene oxide, PO) by the chlorohydrin route takes place in two main steps: (a) hydrochlorination of propene into 1-chloro-2-hydroxypropene (propylene chlorohydrin) and (b) conversion of 1-chloro-2-hydroxypropene into 1,2-epoxypropene (propene oxide, PO). Non-chlorine based production can use peroxidate of isobutene or ethylbenzene in co-production with 1,1-dimethylethanol or styrene. In the mid-1990s, half of total European capacity was based on the chlorine route (Euro Chlor, 2000).

The end-product of this production process is almost exclusively propene oxide. By-products are dichloropropene and chlorinated hydrocarbons, and chloride is the main waste product (Euro Chlor, 2000).

The chlorinated hydrocarbons are incinerated to HCl or are used as feedstock for the chemical industry. Chloride is a waste stream and enters the natural environment. Chlorine in chlorinated hydrocarbons appears as chloride in HCl, chlorine in chlorinated compounds or, when neutralised, inorganic chloride (Euro Chlor, 2000).

*Phosgene derivatives*

Phosgene is used as a precursor in the production of di-isocyanates, which are precursors of polyurethanes. This is its largest use, in terms of chlorine volume. It is also used to produce polycarbonates, which are second in volume of chlorine use. The third type of phosgenation product, in volume of chlorine use, is the isocyanates, which are intermediates for manufacture of crop protection agents and pharmaceuticals. This group of products is an important supplier of recycled hydrogen chloride in the chlorine industry, either as feedstock for oxychlorination or hydrogen chloride electrolysis (Euro Chlor, 2000). These groups will be described below.

### *Phosgene derivatives: Diisocyanate production:*

Production of most isocyanates is based on phosgenation of primary amines. Toluene diisocyanate (TDI) production is based on the raw materials toluene diamine (a mixture of 2,4- and 2,6- isomers) and phosgene, and either monochlorobenzene or orthodichlorobenzene is used as solvent/reaction medium. The resulting diisocyanate isomers are separated by distillation or crystallisation. During diisocyanate formation, chlorine is converted into HCl (Euro Chlor, 2000).

Diphenylmethane diisocyanate (MDI) production is based on the raw materials diphenylmethane diamine and phosgene, whilst monochlorobenzene is the reaction medium. The phosgenation step yields an aromatic diisocyanate mixture, similar in composition to the polyamine. Typically, a mixture of MDI and its dimer and trimer is produced. Polymeric MDI is formed after phosgenation of a polymethylphenyl amine. Also, in the case of MDI, HCl is formed as a by-product. Other diisocyanates formed by phosgenation processes are the aliphatic diisocyanates (ADI), which consist of hexamethylene diisocyanate (HDI), hydrogenated MDI, isophoron diisocyanate (IPDI) and trimethylhexamethylene diisocyanate (TMDI). In all cases, HCl is released during phosgenation, which takes place in a solvent (Euro Chlor, 2000).

The only chlorine-containing by-product of these production processes is HCl. The end-products are diisocyanates. Where no HCl is recovered, chlorine appears as waste chloride from neutralisation of the HCl (Euro Chlor, 2000).

### *Phosgene derivatives: Polycarbonate production*

In a two-phase process, phosgene reacts with bisphenol-A (BPA) to yield the acid chloride of diphenyl propane dicarbonate. Polymerisation and polycondensation gives polycarbonate. The two phases are methylene chloride (MC) and an aqueous solution of sodium hydroxide. During the process, enrichment of polycarbonate takes place in the MC phase. Hydroxide in the other phase neutralises the HCl released by the reaction at the water-MC interface. A small amount of chain terminator is added (phenol or p-tertiary butylphenol) and triethyl amine is used as a catalyst. Water/organic solution separation and washing of the MC solution gives polycarbonate (Euro Chlor, 2000).

The process yields polycarbonate, an amorphous thermoplastic material with interesting characteristics for many technical applications. Polycarbonates do not contain chlorine, and chlorine flow ends at the stage of polymerisation and polycondensation: chlorine, phosgene, and chloride in solution. During production, methylene chloride (sometimes monochlorobenzene) is used and losses lead after a certain period to chloride by physical degradation (in nature or by incineration). In Germany, a polycarbonate recycling process is in use for recovering used CDs to make products such as computer housing (Euro Chlor, 2000).

### Chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, and chloro oxygenated derivatives

In 2003, approximately 6% of chlorine production was used to produce chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, and chloro oxygenated derivatives.

### *Chlorinated paraffins*

Chlorinated paraffins are a group of chemicals manufactured by chlorination of liquid n-paraffins or paraffin wax and contain 30-70% chlorine. During production, HCl is formed as a by-product. For a given feedstock, increasing chlorine content results in products with higher viscosity and density. Chlorinated paraffins are grouped into a number of distinct families, depending on the chain-length of the feedstock. These are short-chain, $C_{10}$ to $C_{13}$ paraffins, medium-chain, $C_{14}$ to $C_{17}$ paraffins, long-chain, $C_{18}$ to $C_{20}$ paraffins, and wax, with a $C_{25}$ average chain length (Euro Chlor, 2000).

### *Chlorinated acyclic derivatives*

Production of higher alkanes and alkenes - excluding chlorinated paraffins - takes place by chlorination of the corresponding alkanes and alkenes, where chlorine is the only chlorine-containing raw material. The products are chlorinated rubbers, chlorinated polyolefins (Cl-PVC, Cl-PE), chlorobutenes (chloroprenes) and linear alkylbenzenesulfonate (LAS), made by sulfonation of linear alkylbenzene. HCl is a by-product and chlorinated hydrocarbons are waste products (Euro Chlor, 2000).

### *Chloro aryl derivatives*

Chlorination of arenes (such as benzenes and toluenes) gives substitution of hydrogen(s) in the ring by one or more chlorine atoms, depending on the circumstances and the catalysts used. The reactions are exothermic. The products in this group are chlorobenzenes, chlorotoluenes, aryl chloroalkanes and chlorophenols. HCl is a by-product and chloride and CHCs are waste products (Euro Chlor, 2000).

### *Chloro oxygenated derivatives*

Chlorination of carbonic acids such as acetic acid and propionic acid are the first steps in the production of this chain. Other steps are (a) the formation of MCPA (monochloro phenoxy acetic acid, a phenoxy herbicide), (b) the formation of MCPP (propionic acid instead of acetic acid) and (c) the formation of carboxy methylcellulose (CMC). In the chlorination step, monochloroacetic acid and monochloropropionic acid are products, HCl is a by-product and at steps (a), (b) and (c), chloride is released as a waste product. MCPA and MCPP are chlorine-containing end-products and CMC is a non-chlorine-containing end-product. (Euro Chlor, 2000).

### Inorganic chemicals

In both 2002 and 2003, 16 % of chlorine production was used in the production of inorganic chemicals. Products in this category are synthetic hydrogen chloride (from burning hydrogen and chlorine), sodium hypochlorite, sulphur chlorides, phosphorus chlorides, titanium dioxide, bromine and silicon. Chlorine use for these products has increased by 39% between the early 1980s and 1998, and is still increasing. Most of the chlorine usage leads to the formation of chloride, such as sulphur chlorides, metal chlorides and phosphorus chlorides (Euro Chlor, 2000).

At present sodium hypochlorite is manufactured by the absorption of chlorine in approximately 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. Packed towers containing caustic soda are often used as emergency absorption plants for the gas venting of various chlorine handling operations and this solution is then strengthened with chlorine to provide finished material. Most of the producers are chlor-alkali manufacturers, who produce sodium hypochlorite largely as part of their chlorine production. Further information is available in the Sodium Hypochlorite Risk Assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 2.1.1.)

Chlorine in hypochlorite ends up as chloride, becoming a part of the natural cycle. At OSPAR's request, thorough investigation was carried out of the fate of chlorine after use in water treatment and cleaning. It appeared that the amount of AOX (absorbable organic halogens) was negligible (Euro Chlor, 2000). Further information on hypochlorite may be found in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, with information on AOX by-products in section 3.1.2.2).

For the production of titanium dioxide, make-up chlorine is used to compensate for losses from an essentially closed-loop process (titanium ore + $Cl_2$ $\rightarrow$ titanium tetrachloride $\rightarrow$ titanium dioxide + $Cl_2$) (Euro Chlor, 2000).

Off-site uses of chlorine as an intermediate

In this category, chlorine - supplied in rail tankers, drums and cylinders - has several applications. These include use as an intermediate in the production of dyestuffs and pesticides and also use as an intermediate in small industrial uses. In 1998 just over 2% of the chlorine produced was supplied as elemental chlorine, and this percentage has been assumed to apply in 2003.

Of the 2.2% of the overall chlorine production which was supplied as elemental chlorine in 1998, 39% was used as an intermediate in the production of direct use dyestuff and pesticides and 35% was used in small industry (Euro Chlor, 2000). Elemental chlorine uses include oxidation, chlorination and epoxidation. In certain cases, this can lead to the formation of chlorinated organic pollutants. In most cases, hydrolysis of products formed will result in chloride. In others, additional water treatment will remove the chlorinated compounds (Euro Chlor, 2000).

### 2.2.2.2 Non-Intermediate use of chlorine

Chlorine also has non-intermediate uses, including use in water-based applications including disinfection processes. These include drinking water disinfection (see **section 2.2.2.2.1**), swimming pool disinfection (see section **2.2.2.2.2**), waste water disinfection (see section **2.2.2.2.3**), and use as a biocide in cooling water applications (see section **2.2.2.2.4**). There was almost no use of elemental chlorine in the areas of textile bleaching (see section **2.2.2.2.5**) or in the pulp and paper industry (see section **2.2.2.2.6**).

#### 2.2.2.2.1 Use in drinking water disinfection

Chlorine gas is used as a disinfectant for drinking water supplies, especially in larger facilities. In 2003, approximately 32 thousand tonnes of chlorine were used for this purpose (**Table 2.2**). At environmental pH, the chlorine species responsible for the biocidal action of chlorine are hypochlorous acid, HOCl, and hypochlorite, $OCl^-$ (See **section 1.4**). This use is covered by the Emission Scenario Document on drinking water disinfectants (Herrmann and Wagner, 2003).

The required dosage cannot be determined directly without experimentation. The amount of chlorine added to water depends on the specific content of oxidizable compounds, the amount needed to kill the microorganisms, plus a sufficient reserve to maintain a minimum concentration of "*free available chlorine*" at each point in the water pipe. To maintain this requirement the range for chlorine dosage is about 0.1 $mg.l^{-1}$ for groundwater and up to 0.5 $mg.l^{-1}$ for surface water (Herrmann and Wagner, 2003).

The active biocidal species, hypochlorous acid, HOCl, and hypochlorite, $OCl^-$, are also generated when sodium hypochlorite is used for drinking water disinfection. Disinfection by-products are the same, whether chlorine gas or sodium hypochlorite is the initial source of the active biocide. Disinfection by-products for both chlorine gas and sodium hypochlorite are included in the Sodium Hypochlorite Risk Assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, Sections 3.1.1.7 and 3.1.2.7), which includes the consumption of both chlorine and sodium hypochlorite for this purpose. This risk assessment should be consulted for further information on disinfection by-products.

#### 2.2.2.2.2 Use in swimming pool disinfection

Swimming pools which are not natural pools or small private pools are called circulation baths. Water treatment is needed to obtain and maintain the desired chemical and bacteriological quality of the swimming water. In Europe, four main products are used: hypochlorites of sodium or calcium, chloroisocyanuric salts and chlorine gas. These four products provide a permanent content of hypochlorous acid (HOCl, active chlorine) in the water Chlorine gas is used as a disinfectant in larger, more heavily used swimming pools (WHO, 2000a).

In 2002, approximately seven thousand tonnes of chlorine gas are estimated to have been used in swimming pool water disinfection (see **Table 2.2**). Note that this approximate usage is based on the 1998 usages of chlorine in swimming pool disinfection and in waste water treatment (Euro Chlor, 2000). Chlorine used for these two purposes declined by 6% between 1998 and 2000 (Euro Chlor, 2003b).

Hypochlorous acid is also generated when sodium hypochlorite is used as a swimming pool disinfectant (see **section 1.4**). The Sodium Hypochlorite risk assessment (RAR, Draft of May 2005, section 3.1.1.4) includes chlorine gas among the sources of HOCl (active chlorine) in swimming pools, and covers the HOCl generated from chlorine gas in its calculations of chlorine entering the environment from this use (RAR, Draft of May 2005, section 3.1.2.4). Chlorinated disinfection by-products are also considered in the Sodium Hypochlorite risk assessment (RAR, Draft of May 2005, sections 3.1.1.4 and 3.1.2.4), which should be consulted for further information.

#### 2.2.2.2.3 Use in waste water treatment

Approximately six thousand tonnes of chlorine gas were used in waste water treatment applications in 2003 (see **Table 2.2).** Note that this approximate usage is based on the 1998 usages of chlorine in swimming pool disinfection and in waste water treatment (Euro Chlor, 2000). Chlorine used for these two purposes declined by 6% between 1998 and 2000 (Euro Chlor, 2003b).

This chlorine was used almost exclusively for the post-chlorination of sewage treatment plant effluent before discharge to the marine environment. Details of the treatment process, and of halogenated by-product formation, are included in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.5 and 3.1.2.5). The Sodium Hypochlorite risk assessment includes the chlorine sourced from chlorine gas in the calculation of the total chlorine released to the environment from this use. It should be consulted for further information on the effluent disinfection process, and on halogenated by-product formation.

### 2.2.2.2.4 Use in cooling water treatment

Approximately one thousand tonnes of chlorine gas were used as a biocide in cooling water systems to prevent biofouling in 2003 (see **Table 2.2**). This use declined by 20% between 1988 and 2000 (Euro Chlor, 2003b). A BREF is available which covers the use of both chlorine gas and hypochlorite in industrial cooling applications (European Commission, 2001a). Both chlorine and hypochlorite use are included as recommended techniques.

Chlorine gas used in this application will disassociate in water to produce hypochlorous acid and hypochlorite, which are the active biocides (see **section 1.4**). These are also generated when sodium hypochlorite is used as a biocide in cooling water applications. The sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.1.9), gives details of the different types of cooling water systems in which sodium hypochlorite and chlorine gas can provide the active biocides to prevent biofouling, and the process of biocide administration in each of these systems. Chlorinated disinfection by-products are also considered in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.2.9). The Sodium Hypochlorite risk assessment should be consulted for further information on both the processes used for biocide administration in cooling water systems, and the formation of chlorinated by-products.

### 2.2.2.2.5 Use in textile processing

Although historically hypochlorite has been very widely used in the textile finishing industry, the use of chlorine gas in textile finishing in Western Europe had declined to 300 tonnes per year by 1994, as shown by the Euro Chlor 1994 internal survey. Since 1994 the use of chlorine gas for this purpose is expected to have almost ceased. The Sodium Hypochlorite risk assessment (RAR, Draft of May 2005 section 3.1.1.6) states that today the only use of hypochlorite in textile processing in Europe is for the preshrinking of wool. Hypochlorite has been superseded by other substances in former uses such as stonewashing jeans, whitening of cotton and decolouration of dyed textiles.

Wool chlorination, which prevents further shrinkage of wool fibres, may use chlorine gas, but preferably uses the sodium or calcium salts of the dichloro-isocyanuric acids as these salts are available in solid phase, and allow a slow release of NaClO in water, thus improving the control of operational conditions. Chlorine gas may be produced during this process, as it is carried out under acid conditions and thus requires a high degree of enclosure of the plants, the presence of abatement system of gaseous emission, and a neutralisation stage. The Sodium

Hypochlorite risk assessment (RAR, Draft of May 2005, section 3.1.1.6) gives further information on the process used for wool pre-treatment.

By-products of hypochlorite use in textile processing are discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.6 and 3.1.2.6).

### 2.2.2.2.6 Use in the pulp and paper industry

In the past, chlorine and sodium hypochlorite were used in large amounts in pulp and paper bleaching. However, as discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.1.8), their use in pulp bleaching has been completely been replaced by the Total Chlorine Free (TCF) and Elemental Chlorine Free (ECF) processes in Western Europe. The current uses of hypochlorite are limited to two specific purposes. The first is as a means of disinfection of the paper machine system to discourage the proliferation of unwanted microorganisms. The second is as a means of breaking down the wet strength resins used in some grades of tissue when reject tissue is being processed for use in tissue manufacture.

The use of hypochlorite as a system cleaner occurs during machine shut down, and involves the addition of sodium hypochlorite solution to paper machines partially filled with clean water, followed by vigorous circulation of this solution around the system. It would not be practical to use chlorine gas as a substitute for sodium hypochlorite for this purpose, as the addition process would not be feasible.

## 2.3 TRENDS

Chlorine production increased strongly from the 1950s until the middle of the 1970s. From the mid 1970s, growth levelled off and the chlorine industry in Western Europe is today a mature business. Chlorine production appears to be in a direct relation to GDP (Gross Domestic Product) evolution from the 1980s onwards (**Figure 2.2.**) (Eurochlor, 2000).

***Chlorine production vs GDP***

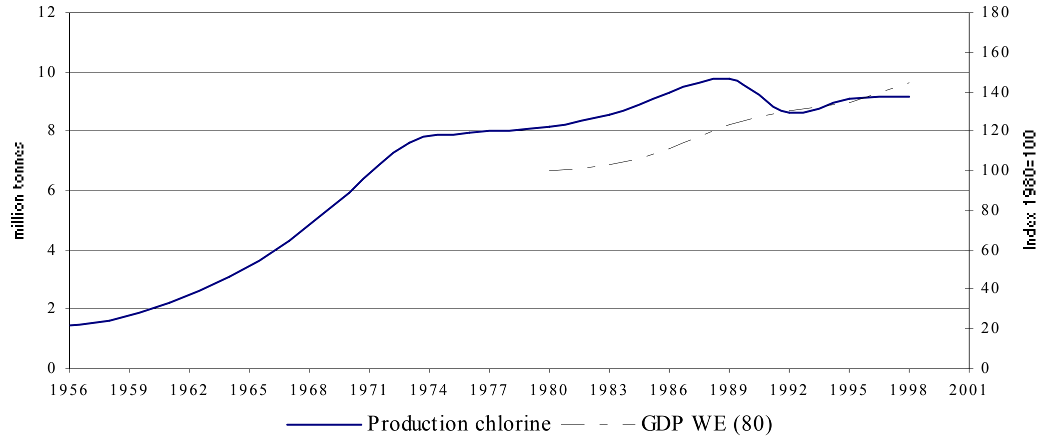


**Figure 2.1 Chlorine Production**

Geographical trends in the production capacity (top graph) and the production (lower graph) of chlorine are shown in figure 2.3. All data is shown relative to the situation in 1970, with both production capacity and production indices set to 100 for that year. It can be seen that production and production capacity have increased most strongly in Spain, Portugal, and Greece, with Germany and Belgium and the Netherlands also showing increases greater than that seen in Europe overall. Production capacity and production in Italy, the UK, and the Nordic countries are similar to, or slightly less than, the levels seen in 1970.

Recently, there was very little change in the proportions of chlorine used in different ways between 2001 and 2002, with a small increase in propylene oxide production being offset by drops in chlorinated solvents and inorganic uses. Sales of the chlorinated solvents trichloroethylene (TRI), perchloroethylene (PER) and methylene chloride declined overall for the seventh successive year. The 2003 and 2002 use data are very similar, with only rounding off errors increasing use in PVC production to 35% of the 101% production total (Euro Chlor 2004c), as compared to 34% of the 100% production total reported for 2002 (Euro Chlor, 2003a)

Use of elemental chlorine in non-intermediate uses has decreased 49% since 1983. This is mainly due to the phase-out of chlorine in pulp bleaching (see **Section 2.2.2.2.6**, and also the Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.1.8) and in textile applications (See **Section 2.2.2.2.5**, and also the Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.1.6). Remaining applications in Europe are for disinfection of drinking water, swimming pools and some chemical reactions. Use in swimming pool water treatment has also decreased, but has been mainly substituted for by sodium hypochlorite (Euro Chlor, 2000). Elemental chlorine now accounts for about 2% of total chlorine use.

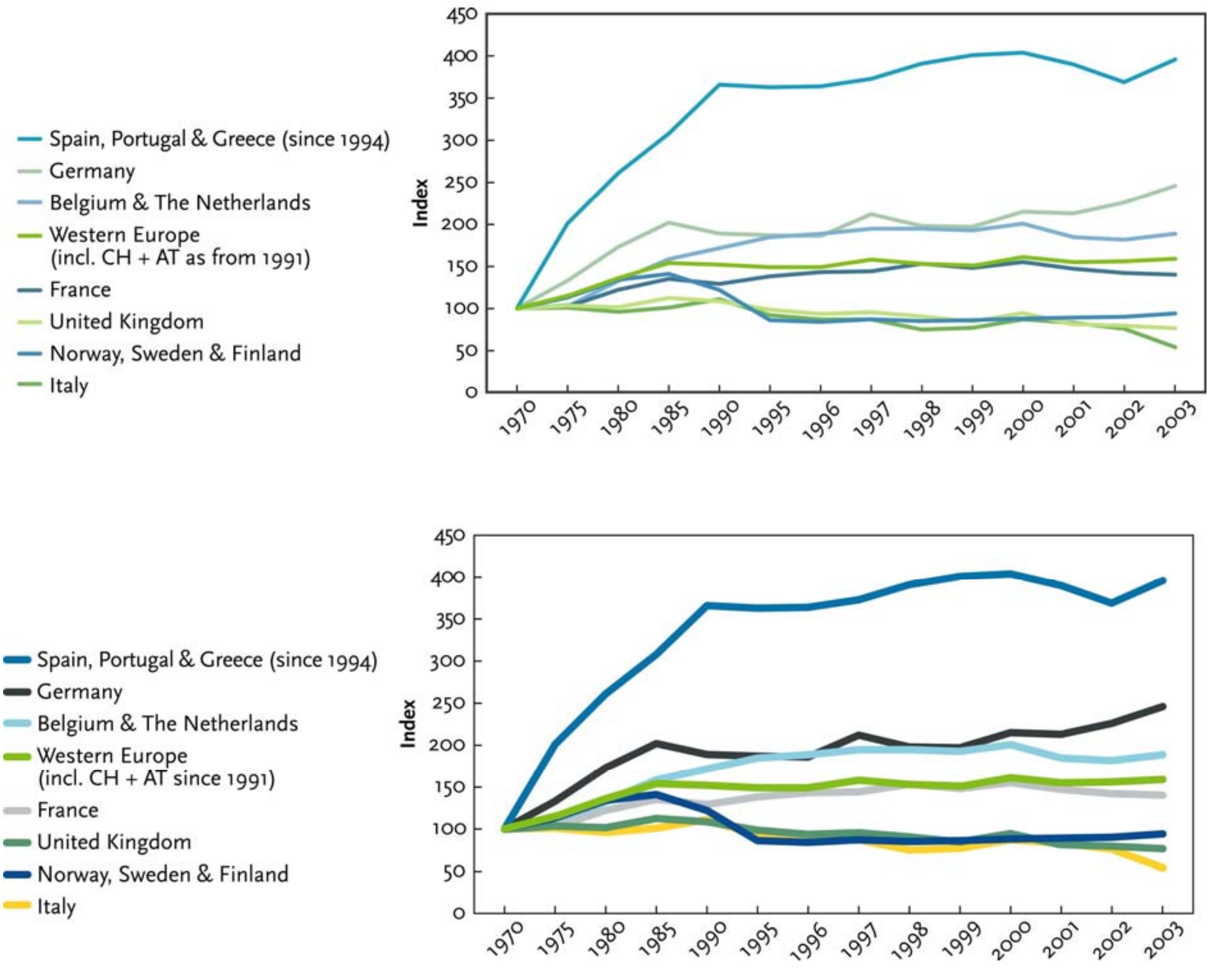


**Figure 2.2 Geographical trends in the production capacity (top) and production (bottom) of chlorine since 1970**

## 2.4 LEGISLATIVE CONTROLS

Chlorine is classified as toxic, irritant, and dangerous to the environment under Directive EEC 67/548. Further details are given in section.1.5. Chlorine production is regulated under the Seveso II directive, Council Directive 96/82/EC, and is also subject to the Integrated Pollution Prevention and Control legislation, Council Directive 96/61/EC. Transport of chlorine is covered by the UN recommendations on the transport of dangerous goods (United Nations, 2001). Occupational exposure to chlorine is regulated, and legislative controls also exist on the uses of chlorine in drinking water disinfection and in the disinfection of swimming pool water.

### 2.4.1 Chlorine Production

Chlorine production is regulated under the Seveso II directive, Council Directive 96/82/EC, which requires the operator to take all measures necessary to prevent major accidents, and to limit their consequences for man and the environment. As part of this directive, production facilities containing 10 tonnes or more of chlorine at any one time are required to notify the appropriate Member State of the existence of the facility and of the processes taking place therein, and to draw up and implement a comprehensive major accident prevention policy. Production facilities containing 25 tonnes or more of chlorine at any one time must prepare a Safety Report, which will contain the necessary information to allow the appropriate Member State to examine and evaluate the processes being carried out, and if necessary, to prohibit their continuation. Each Safety Report must be updated every five years, or more often if necessary.

Chlorine emission, especially to air, from chlorine production facilities is regulated under the Integrated Pollution Prevention and Control legislation, Council Directive 96/61/EC. The IPPC directive lays down measures designed to prevent or, where that is not practicable, to reduce emissions to the air, water and land in order to achieve a high level of protection of the environment taken as a whole, without prejudice to other relevant Community provisions. In accordance with this directive, a reference document on the best available techniques, or BREF, has been prepared for the chlor-alkali manufacturing industry (European Commission, (2001b). This BREF is also concerned with the emission of other substances, including mercury from the mercury cell electrolysis process, one of the processes by which chlorine is produced. In accordance with the IPPC legislation, inventories of chlorine emissions are collected and published regularly.

### 2.4.2 Transport

The UN recommendations on the transport of dangerous goods (United Nations, 2001) state that chlorine should be transported in un-refrigerated portable tanks, with an increased thickness of the tanker shell. Detailed specifications for tank construction and filling procedures are given in the UN recommendations. No other form of chlorine transport is recommended in these recommendations.

### 2.4.3 Occupational Exposure

Short-term (15 minute) indicative occupational exposure limit values for chlorine of 1.5 mg/m$^3$ or 0.5 ppm by volume (ppmV) are proposed in the draft second list of indicative occupational exposure limit values, proposed in implementation of Council Directive 98/24/EC, and in particular Article 3 thereof. The table below shows occupational exposure limits for chlorine in European countries. In almost all countries, the limit for long-term exposure (8 hours time weighted average, or TWA) is 0.5 ppmV or 1.5 mg/m$^3$. The only exception is The Netherlands, where limits are higher. In some cases, a short-term exposure limit (STEL) of 1 ppmV is applied.

**Table 2.3 Occupational exposure limits for chlorine in European Countries**

| Country | Limit | | Reference |
|---|---|---|---|
| | Long term exposure | Short term exposure | |
| Austria | MAK: 0.5 ppmV; 1.5 mg/m3 | Ceiling: 0.5 ppmV; 1.5 mg/m$^3$ | Austria (2003). |

| | | | |
|---|---|---|---|
| Belgium | 8-hour TWA: 0.5 ppmV; 1.5 mg/m$^3$ | 15-minute STEL: 1 ppmV, 2.9 mg/m$^3$ | Belgium (2002). |
| Denmark | TWA: 0.5 ppmV, 1.5 mg/m$^3$ | | Denmark (2002) |
| Finland | 8-hour limit: 0.5 ppmV, 1.5 mg/m$^3$ | 15-minute limit: 1 ppmV, 2.9 mg/m$^3$ | Finland (2002). |
| France | | VLE (valeur limite d'exposition): 1 ppmV, 3 mg/m $^3$ | France (2003). |
| Germany | TRGS 900 limit value: 0.5 ppmV, 1.5 mg/m$^3$ | MAK value should never be exceeded. | Germany (2003). |
| Greece | 8-hour TWA: 1 ppmV, 3 mg/m$^3$ | 15 minute (STEL: 1 ppmV, 3 mg/m$^3$ | Greece (2001). |
| Ireland | 8-hour OEL (TWA): 0.5 ppmV, 1.5 mg/m$^3$ | 15-minute OEL (STEL): 1 ppmV, 3 mg/m$^3$ | Ireland (2002). |
| The Netherlands | MAC ceiling: 1 ppmV, 3 mg/m$^3$ | | Netherlands (2003). |
| Norway | threshold limit value: 0.5 ppmV, 1.5 mg/m$^3$ | ceiling value: 1 ppmV, 3 mg/m$^3$ | Norway (2003). |
| Spain | 8-hour (VLA-ED): 0.5 ppmV, 3 mg/m$^3$ | 15-minute STEL (VLA-EC): 1 ppmV, 3 mg/m$^3$ | Spain (2003). |
| Sweden | Level Limit Value (NGV) 0.5 ppmV, 1.5 mg/m$^3$ | Ceiling Limit Value (TGV): 1 ppmV, 3 mg/ m$^3$ | Sweden (2000). |
| Switzerland | TWA 0.5 ppmV, 1.5 mg/m$^3$ | STEL 0.5 ppmV, 1.5 mg/m$^{3.}$ Freq. X Duration in minutes/shift: 15 min | Switzerland (2003). |
| United Kingdom | TWA 0.5 ppmV, 1.5 mg/m$^3$ | STEL 1 ppmV, 2.9 mg/m$^3$ | UK (2003). |

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

### 2.4.4 Drinking water:

Admissible quantities of free available chlorine in drinking water for different European countries generally vary between 0.1 and 0.5 mg/l. The WHO guideline value is up to 5 mg/l (WHO 2003). Chlorination by-products are also covered by regulation in the EU, with total trihalomethanes being limited to 0.1 mg/l in Council Directive 98/83/EC on the quality of water intended for human consumption (Council of the European Union (1998)). The WHO Guidelines also give values for by-products of chlorine disinfection of drinking water, such as trihalomethanes, halogenated acetonitriles, chlorinated acetic acids, and chloralhydrate, which is formed by reaction of chlorine with humic acids, and has the lowest guideline value (10 µg/l). The WHO Guidelines stress that it is important to optimize treatment processes and to ensure that these remain optimized in order to control residuals of chemicals used in drinking water treatment and the formation of disinfection by-products (WHO 2003).

### 2.4.5 Swimming pool:

National (or regional) legislation sets various parameters in order to guarantee the sanitary quality of water in public swimming pools. Suitable disinfectants include gaseous chlorine (mostly used in large swimming pools), sodium hypochlorite, calcium hypochlorite (mostly used in private swimming pools), and chloroisocyanurated derivatives (OSPAR, 1999; WHO, 2000a). These disinfectants are used in all countries in most cases.

Water used in swimming pools must be drinking water from a public water supply system. The quantity of top-up water is usually regulated at minimum 30 l/swimmer, and filtration is compulsory. Complete and regular emptying of pools is sometimes called for (for example, twice a year). Due to the potential environmental impact of swimming pools, legislation requires the water to be discharged into the natural environment or into the public sewer networks (OSPAR, 1999).

The main regulations relative to swimming pools relate to the minimum content of free available chlorine, and the pH which has to be in the optimum range for hypochlorous acid generation (WHO, 2000b). Some countries give a maximum free available chlorine (1.4 mg/l, France) others a maximum of urea content (Belgium, Netherlands). Other parts of the regulations cover the number of swimmers per m² and the quantities of air and water changes per swimmer or per year (OSPAR 1999). The Spanish regulations originate in the specific Autonomic Communities, several of which specify higher free residual chlorine levels at higher pH values, and some of which give preferred and also admissible values for pH, residual free chlorine, and combined chlorine levels. Some quality parameters for swimming pool water in EU countries are given in **Table 2.4**, with the Spanish regulations (Spain, 2005) grouped and summarised for general comparative purposes.

Disinfection by-products are considered in the WHO report (WHO, 2000a). The WHO report recommends that, for sporadic adult swimmers and pool attendants/lifeguards in chlorine-disinfected pools operated under typical conditions, with low chloroform levels in air and water, the presence of disinfectant by-products is not an issue, and guideline values are not required in indoor or outdoor pools. For worst case exposure scenarios, and for children and competitive swimmers, control of exposure by good ventilation, use of alternative disinfectants, pre-ozonation, effective flushing, and control of precursor addition through pre-swim showering and toilet use are recommended in the WHO report (WHO, 2000a). Some national European regulations include a maximum level of chloramines as lower than 0.6 g/m3 (OSPAR 1999).

**Table 2.4** Quality parameters for swimming pool waters in several European countries

| | France | Spain | Belgium | The Netherlands | Italy | Denmark[1] |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| Filling water | Drinking water | | | | | Drinking water. Surface water if allowed by local council. |
| Daily top-up | 30 l/swimmer | 5% of pool volume | 30 l/swimmer | 30 l/swimmer | 30 l/swimmer | |
| pH | 6.9-7.7 | [2]Maximum range from 6.5 -- 8.5 | 7-7.6 | 6.8-7.8 | | |
| FAC (mg/l) | 0.4-1.4 | [2]lowest: combined or active chlorine 0.3 at pH 7-7.6<br>Typical: 0.4 to 1.5, or 0.5 to 2, at pH up to 8 or even 8.5<br>Highest: 0.8 to 1.4 or 1.5, for pH from 7.6 up to 8 or 8.2 | 0.5-1.5 | 0.5-1.5 | 0.5-1 at pH 6.5-7.5;<br>0.7-2 at pH 7,5-8,5 | 1-3<br>up to 5 mg/l allowed in some pools |
| Combined chlorine (mg/l) | ≤ 0.6 | [2]often less than 0.6 of the FAC. Levels between 0.3 and 0.5 may be specified, with higher levels at higher pH. | ≤ 1 | ≤ 1 | 0,3 at pH 6.5-7.5<br>0.5 at pH 7.5-8.5 | |

1. Denmark (1988). 2. Spain (2005).

# 3 ENVIRONMENT

## 3.1 ENVIRONMENTAL EXPOSURE

### 3.1.1 General discussion

### 3.1.2 Environmental releases

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, as described in **section 1.4.**

### 3.1.2.1 Natural releases

Continuous production of sea-salt aerosols arising from the oceans is considered to be the major source for the presence of a background level of atomic chlorine in the lower atmosphere (Keene, WC, 1999). As part of the chlorine cycling process, Graedel and Keene (1995) estimated a combined average concentration of 75 ± 50 pptv (parts per trillion) chlorine for atmospheric $Cl_2$ and HOCl in the marine boundary layer. Taking the short decay time of less a day into account, they estimated a flux for combined $Cl_2$ and HOCl from sea salt aerosols ranging from 100 to 800 Tg/year (1 Tg = $10^6$ tonnes). Alternatively, chlorine production rates from the oceans are estimated by global circulation models as about 2 billion tonnes per year (Keene, WC, 1999).

Several reaction sequences are postulated as being responsible for the majority of $Cl_2$ generated from sodium chloride in the atmosphere. In a model by Spicer et al (1998), the most important reaction sequence involved reaction with $ClONO_2$, shown below.

$NaCl + ClONO_2 \rightarrow Cl_2 + NaNO_3$

However, the 292 chemical reactions in this model were not able to account for a significant proportion of the atmospheric $Cl_2$ observed. Another potential mechanism, shown to work in the laboratory by Oum et al (1998), involves the photolysis of tropospheric ozone in the presence of sea salt particles above their deliquescence point, with the consequent generation of $OHCl^-$ which then undergoes a series of reactions to generate $Cl_2$. The $Cl_2$ generated due to this additional mechanism is sufficient to account for the $Cl_2$ which is missing when the observed atmospheric levels are compared with the predictions of Spicer et al (1998).

The chemical processes responsible for dechlorinating sea-salt aerosol are not well understood but are believed to involve both acidic and oxidizing species naturally present in the background atmosphere; anthropogenic pollutants enhance rates of volatilization (Keene, WC, 1999). The released gaseous compounds consist of hydrogen chloride (HCl) and probably other inorganic species including molecular chlorine ($Cl_2$), hypochlorous acid (HOCl), and nitryl chloride ($ClNO_2$). The three latter compounds undergo rapid photolysis during the daytime to produce atomic chlorine (Chlorine SIAR 2003; Keene, WC, 1999).

Another natural source of chlorine is the sporadic volcanic release of chloride in the form of hydrochloric acid, which is estimated to be 0.4 to 11 million tons per year (Symonds et al., 1988). Demelle et al. (2001) have shown that 10% of HCl emitted by the Masaya volcano in Nicaragua is deposited locally (57 metric tons) while 90% (510 metric tons) is distributed in the atmosphere (Delmelle et al., 2001).

### 3.1.2.2 Release from production

In 2002, Euro Chlor member companies, representing 97% of chlorine production capacity in Europe, reported the emission to air of approximately 120 metric tonnes of chlorine from 77 production sites in the EU and in nearby countries, including Hungary, Poland, the Czech Republic, Slovakia, Switzerland, and Norway (Euro Chlor, 2004b). The same chlorine production sites reported releases of approximately 19 metric tonnes of chlorine to water sites (Euro Chlor, 2004b). As most chlorine production sites also contain installations which manufacture other chemicals for which chlorine is a production intermediate, these figures cover the releases due to both chlorine production and production of downstream products at the same site, whose manufacture requires chlorine use.

### 3.1.2.3 Release from formulation

Chlorine gas is not generally incorporated into formulated products. Use of chlorine containing products such as sodium hypochlorite, which are found in aqueous solution, is covered in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005.)

### 3.1.2.4 Release from industrial/professional use

The figures given for chlorine release to air and to water from chlorine production (see **section 3.1.2.2**) cover much of the chlorine released in industrial use, in which chlorine is used as an intermediate. As 90% of chlorine manufactured in Western Europe in 2002 was used on site, or moved to adjacent facilities by inter-plant pipelines (Euro Chlor, 2003a), the site release figures should cover approximately 90% of the chlorine released from industrial use. Within these sites, approximately 75% of releases are attributable to chlorine production, while the remaining 25% of releases result from use as an intermediate on site (Euro Chlor, 2004d).

There will be additional releases from the 984,000 tonnes of chlorine, or 10% of the 2002 chlorine production, which was transported by rail, road, or in drums and cylinders in 2002 (Euro Chlor, 2003a). Exact quantitative data for the uses of this chlorine are not available, since this is company owned commercial information, but it is estimated (Euro Chlor, personal communication, 2005) that about 80% of this tonnage is transferred from one chlorine producing site to another, to top up the chlorine availability for sites using more chlorine than they produce (See **section 2.2.1**) or to big industrial customers (all falling under IPPC). The remainder of this tonnage, approximately 20%, goes to smaller users, of which the majority will use quantities less than 25 tonnes per delivery, to stay under the Seveso limit for on-site storage. Examples of such users are cities using the chlorine for water treatment or swimming pools; typical use volumes of such users are one ton (in drums). A relatively small fraction of the smaller users may use higher tonnages per shipment, but normally less than 10000 tonnes per year. Such uses represent other chemical processes where chlorine is normally used as a reactant (Euro Chlor, personal communication, 2005). Thus most of the chlorine used off-site will be used at sites which are covered by the IPPC legislation, where emission control measures will be in force. Users of chlorine which do not fall under IPPC are likely representing very small scale users (tonnages lower than 25 tonnes, but often 1 ton or lower per shipment) using dedicated equipment.

Based on the information given above it is clear that most of the releases from off-site industrial/professional use are covered under IPPC and that other possible local releases will be minor and covered by the detailed realistic worst-case scenario of releases from production sites. In addition, the approximately 46,000 tonnes of chlorine which was used in water applications will have been converted to hypochlorite (see **section 1.4**) and covered within the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005).

As an indication of the total continental release due to use of chlorine transported off-site, a worst case estimate of the entire remaining 938 000 tpa of chlorine could be considered, and assumed to have a similar chlorine release, per tonne of chlorine used, to the losses due to an intermediate on the chlorine production site. This release estimate may not be inappropriate, as most of the release will take place on larger sites where IPPC compliance will be easier to monitor. These assumptions would result in approximately 3.2 metric tonnes of chlorine being released to air, and less than 0.5 metric tonnes of chlorine being released to water, from industrial use due to chlorine which has been transported by road, and which is not covered by the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005).

### 3.1.2.5 Release from private use

Chlorine gas is not used privately.

### 3.1.2.6 Release from disposal

Elemental chlorine is not released from products which contain chlorine, after product disposal (Euro Chlor 2000). Most chlorine is released as chloride from products after disposal. Some chlorine may be released as hydrochloric acid if products are burned, but much of this will be recovered during recycling processes. Any chlorine used in aqueous solution will be converted to hypochlorite **(see section 1.4).** Further information on the fate of hypochlorite is covered in the Sodium Hypochlorite risk assessment. (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005.)

### 3.1.2.7 Summary of releases

The releases of chlorine to the environment from the sources considered above is summarised in **Table 3.1**.

**Table 3.1 Annual chlorine gas releases to the environment in Europe**

| 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. |

The European atmospheric releases from chlorine gas production and from on-site and off-site manufacture of chlorine-containing products are less than 0.0002% of the global $Cl_2$ generated in the marine boundary layer. No chlorine gas will be released from aqueous emissions, as the pH of the waste stream is regulated to ensure that all chlorine is converted to hypochlorous acid and hypochlorite.

### 3.1.3 Environmental fate

In natural water, the $Cl_2$ molecule as well as hypochlorite ions are not stable due to the presence of organic and inorganic matter. The half-life of hypochlorite is estimated to be less than 2 hours due to reduction and photolysis. The free available chlorine reacts to form various chlorinated by-products, e.g. chloramines and chloromethanes. In sewage chlorine is mainly present in the form of chloramines, as hypochlorous acid undergoes a fast decay (SIAR, 2003). Further information is available in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005.section 3.1.2.2 and Appendix 2).

In the atmosphere, chlorine mainly undergoes photolysis: $Cl_2 + h\nu \rightarrow 2Cl°$.

The half-lifetime for that process has been estimated to be in the order of 1–4 hours, depending on the time of the day (Hov, 1985; Peterson, 1976). Calculations described in **Appendix A** show that half-lives for chlorine photolysis can range from less than 5 minutes to several hours, depending on the time of day, with representative values for latitudes $40^{\circ}$N and $55^{\circ}$N given in Table A-1. The resulting chlorine atoms can then react with species present in the atmosphere such as ozone and saturated and unsaturated hydrocarbons. Recombination of chlorine after dissociation can be neglected due to the fast reaction with other species and due to the low concentration of chlorine. Chlorine atoms can also be produced by the reaction of hydrogen chloride with the hydroxyl radical (Hov, 1985). The reaction of chlorine with hydrocarbons gives rise to formation of chlorinated organic compounds (SIAR, 2003). However, on a global scale, the atmospheric burden of chlorine is dominated by natural rather than anthropogenic sources (see **Table 3.1**), and so anthropogenic sources will make only a very small contribution to these processes.

Mobility of chlorine in soil is assumed to be of little relevance as chlorine in an aqueous solution covalently binds to soil organics within the first few millimetres or centimetres of the soil surface. The final target compartment for chlorinated substances, formed from chlorine, will be the hydrosphere. Depending on the inherent properties and the stability of chlorinated products, chlorine may reside in the atmosphere. For example, $NCl_3$ is highly volatile and is found in similar concentrations in air and water (SIAR, 2003).

An octanol/water distribution equilibrium can not be defined for chlorine as it has strong oxidizing properties and will react with the organic phase. A potential for bioaccumulation or bioconcentration of active chlorine species can be disregarded, because of their water solubility and their high reactivity (SIAR, 2003).

### 3.1.3.1 Degradation in the environment

Chlorine is a highly reactive compound, which will react readily in the atmosphere and in soil, and with organic matter. In water, chlorine will form hypochlorous acid and hypochlorite at environmental pH, as discussed in **section 2.1.4**. Chlorine discharged to sewer will react to form chloramines, as discussed in the Sodium Hypochlorite risk assessment, sections 3.1.1.5 and 3.1.2.5 (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005.). These processes are discussed below. As a non-organic compound, chlorine is not biodegradable.

#### 3.1.3.1.1 Atmospheric degradation

If chlorine is emitted in the molecular form to the atmosphere, the main reaction is photolysis, which gives atomic chlorine:

$$Cl_2 + h\nu \rightarrow 2Cl^\circ$$

Photolysis occurs only during daylight hours. The overall half-life for this process has been estimated to be in the order of 1–4 hours, depending on the time of the day (Hov, 1985; Peterson, 1976), and as approximately 2-4 hours (Vetrano, 2001).Both estimates are consistant with an atmospheric lifetime of less than 0.001 year estimated by Graedel and Keene (Graedel & Keen, 1995). Calculations described in **Appendix A** show that half-lives for chlorine photolysis can range from less than 5 minutes to several hours, with representative values for throughout the day for latitudes 40°N and 55°N in summer and winter given in Table A-1. **Appendix A** then uses these half-lives, calculated on a half-hourly basis throughout the day, to show the effect of photolysis on chlorine emitted from specific sites. As shown in **Appendix A,** the chlorine concentration increases with emission during the night, but is rapidly reduced to very close to zero during the daytime hours.

The chlorine atoms formed by photolysis can then react with species present in the atmosphere.

Chlorine atom reactions with saturated hydrocarbons:

Chlorine atoms react with saturated hydrocarbons according to the following reaction:

$Cl^\circ + R\text{-}H \rightarrow HCl + R^\circ$

HCl formed by that process can be washed out by rain water or react with the hydroxyl radical $OH^0$ to regenerate a chlorine atom (DeMore et al 1997):

$HCl + OH^\circ \rightarrow H_2O + Cl^\circ$

The lifetime associated with washout by rain is of the order of 10 days (Giorgi & Chameides, 1985).

Chlorine atom reactions with unsaturated hydrocarbons:

Chlorine atoms can also react with unsaturated organic compounds by addition to unsaturated sites. This reaction can lead to the formation of chloro-organic compounds in the atmosphere.

Chlorine atom reactions with ozone

Chlorine atoms can also react with ozone, as shown below:

$Cl^\circ + O_3 \rightarrow ClO + O_2$

ClO can react with the $HO_2$ radicals to form HOCl and $O_2$.

HOCl can be photolyzed to regenerate Cl°. This corresponds to a catalytic cycle of ozone destruction. There is competition between the reaction of chlorine atoms with hydrocarbons and $O_3$.

It has been estimated ) that 70% of chlorine atoms would react with hydrocarbons on the basis of a 10 ppbv hydrocarbon concentration and a 40 ppbv concentration for ozone.

Monitoring Data

Some data on the monitoring of concentrations of the chlorine molecule in the atmosphere are summarized in **Table 3.2**. Those measurements come from coastal sites. In some work the analytical techniques used measured a combination of HOCl and $Cl_2$, while $Cl_2$ alone is measurable in other work. Diurnal concentration variations are included in the concentration ranges given in the table.

The monitoring data in **Table 3.2** compare well with the estimate of Graedel and Keene (1995) for a combined average concentration of 75 ± 50 pptv chlorine for atmospheric $Cl_2$ and HOCl in the marine boundary layer.

**Table 3.2 Observed atmospheric $Cl_2$ concentrations from coastal sites**

| $Cl_2$ (pptv) | $Cl_2$ + HOCl (pptv) | Location | Reference |
|---|---|---|---|
|  | <26 | Charlotteville Virginia 38°N | Graedel and Keene (1995) |
|  | 13-127 | air near Miami | Graedel and Keene (1995) |
|  | <26-254 | Florida 26° N | Pszenny *et al.* (1993) |
| 10-150 |  |  | Spicer et al (1998) |

### 3.1.3.1.2 Aquatic degradation (incl. sediment)

In water, chlorine is transformed to free available chlorine (gaseous chlorine), hypochlorous acid and hypochlorite ions, whose relative amounts depend on the pH and other physico-chemical properties of the water (see **section 21.4**). At environmental pH, only hypochlorous acid and hypochlorite will be present. The behaviour of these species is described in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, Chapter 2.4) which also takes account of hypochlorous acid and hypochlorite generated from aqueous use of molecular chlorine.

Degradation of $Cl_2$ in water is also influenced by exposure to the UV components of sunlight. (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, Chapter 2.4.2).

### 3.1.3.1.3 Degradation in soil

The high water solubility of chlorine can lead to a high mobility in soil, although chlorine as vapour or as aqueous solution is normally irreversibly combined with soil organics within the first few millimetres or centimetres of the soil surface. (SIAR, 2003))

### 3.1.3.1.4 Summary of 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. The fate of HOCl and $OCl^-$ in the environment, and in the sewer and during sewage treatment, are discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, especially sections 3.1.1.5, 3.1.2.5, 3.1.1.2, and 3.1.2.2). Information is also given in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005) concerning degradation processes when chlorine is used in drinking water purification (sections 3.1.1.7 and 3.1.2.7), swimming pools (sections 3.1.1.4 and 3.1.2.4), and in cooling water purification (sections 3.1.1.9 and 3.1.2.9). In soil, chlorine is normally irreversibly combined with soil organics. The ultimate fate of chlorine in soil is reduction to chloride.

### 3.1.3.2 Distribution

Chlorine gas is soluble in water. It dissolves moderately rapidly forming hypochlorous acid and hypochlorite at environmental pH **(see section 1.4).** In soil, the high water solubility can lead to high mobility, although chlorine as vapour or as aqueous solution is normally irreversibly combined with soil organics within the first few millimetres or centimetres of the soil surface (SIAR, 2003).

Based on water solubility and vapour pressure, the equilibrium distribution of chlorine favours movement towards the atmosphere, but some movement into the aquatic environment is also expected. However, equilibrium conditions are not likely to occur in practice, as molecular chlorine is a strong oxidizer that is consumed by reaction with a wide variety of common environmental materials including most organic substances, e.g. reduced materials such as sulphites and thiosulphates in the soil, and by hydrocarbons in the atmosphere.

In air, at less than percent-level concentrations, chlorine undergoes rapid dilution under turbulent or unstable conditions.

Bioconcentration has not been observed in biota and is not expected for molecular chlorine, as it is chemically reactive and easily ionized in aqueous solution.

#### 3.1.3.2.1 Adsorption

Adsorption to aerosol particles

The fraction of chemical associated with aerosol particles can be estimated from equation 5 in the Technical Guidance:

$$Fass_{aer} = \frac{CONjunge \bullet SURF_{aer}}{VP + CONjunge \bullet SURF_{aer}}$$

With $CONjungeSURF_{aer}$ set to $10^{-4}$ Pa, this gives $Fass_{aer} = 1.5 \times 10^{-10}$.

Thus most atmospheric chlorine gas will not be associated with atmospheric aerosols.

Solids-water:

During production and processing of chlorine no significant releases into the soil are expected. No measured organic carbon-water partition coefficents (Koc) have been found for chlorine. However, chlorine's high water solubility dictates that it will have a low soil adsorption coefficient and thus be very mobile in soil. Chlorine as gas or aqueous solution is normally irreversibly combined with soil organic compounds.

### 3.1.3.2.2 Precipitation

Chlorine is likely to form either hydrochloric acid (HCl) or hypochlorous acid (HOCl) in the atmosphere, either through reactions with hydroxyl radicals or other trace species such as hydrocarbons. These acids are believed to be removed from the atmosphere primarily through precipitation washout, or by dry deposition as gaseous chlorine contacts and reacts with the earth's surface (Vetrano 2001). Chlorine and hydrochloric acid play minor roles in worldwide acid rain deposition, with sulfate, from $SO_2$ emissions, and nitrate, from $NO_x$ emissions, being the major contributors to atmospheric acidity (Vetrano 2001). The major anthropogenic source of HCl to the atmosphere is HCl emitted from combustion, including coal and the incineration of plastics (Vetrano 2001).

### 3.1.3.2.3 Volatilisation from water

As shown in **section 1.4**, chlorine dissolved in water at pH 4 or greater essentially is totally disproportionated, forming $Cl^-$ and $OCl^-$, which have very low volatility. At the conditions T = 20° C, P = 760 mm Hg, and pH = 6.5 - 8.5, after addition of 1.4 mg/l of chlorine gas to water (assuming no other chemicals are present) we have the following reactions:

$$\mathbf{Cl_2 + H_2O = H^+ + Cl^- + HClO \qquad K_1 = 10^{-3.3}}$$

$$\mathbf{HClO = H^+ + ClO^- \qquad K_2 = 10^{-7.3}}$$

Table 3.3 shows the calculated concentrations of the potentially volatile substances $Cl_2$ and HClO, which will remain in the solution (together with $Cl^-$ and $ClO^-$) after reaction. The free chlorine concentration calculated in water at environmentally relevant pH is between $4x10^{-14}$ and $3x10^{-13}$ mg/l.

**Table 3.3 Calculated concentrations of $Cl_2$ and HClO in water at environmentally relevant pH**

| pH | Concentration of free $Cl_2$ in water, mg/l | Concentration of HClO in water, mg/l |
|---|---|---|
| 6.5 | 3.0E-13 | 2.0E-5 |
| 7.0 | 1.2E-13 | 2.0E-5 |
| 7.5 | 6.0E-14 | 1.9E-5 |
| 8.0 | 4.0E-14 | 1.8E-5 |
| 8.5 | 4.0E-14 | 1.9E-5 |

As the concentration of chlorine gas in water is low at environmentally relevant pH, the amount of $Cl_2$ volatilised from water is also expected to be low.

### 3.1.3.2.4 Distribution in wastewater treatment plants

For chlorine production sites, effluent treatment generally includes settlement, pH adjustment, chlorine removal and discharge. There may be combination with effluent from other site processes before or after the treatment. In some cases recycling to brine wells may also be used. Controls on pH, available chlorine concentration, mercury concentration (for mercury process), sodium chloride concentration and suspended solid content (turbidity) are generally applied either on a continuous or discontinuous basis. The BREF for the Chlor-alkali industry (European Commission, 2001b, especially chapter 4.1.5) describes the destruction of any free oxidants in effluents by chemical reduction, by catalytic reduction and by thermal decomposition. All these methods can be applied at existing and new chlor-alkali plants.

Any elemental chlorine present in sewage or used in wastewater treatment will have initially transformed to hypochlorous acid/hypochlorite, as discussed in **section 1.4**, and will then have reacted with organic materials present in the sewage. The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.5 and 3.1.2.5) discusses the use of hypochlorite, including hypochlorite resulting from chlorine use, in wastewater treatment, and shows that chloride is the main product of hypochlorite reactions. By-products of chlorine reaction include trihalo methanes, mainly chloroform (with a predicted $PEC_{Local}$ to water of 7 μg/l) and haloacetic acids (with a predicted $PEC_{Local}$ to water of 3.5 μg/l). In addition, the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.1.2.2 and Appendix 2) discusses the rapid decrease of hypochlorite in the sewer, with calculations showing that essentially no hypochlorous acid/hypochlorite (below $10^{-32}$ ug/l) will remain in the sewer after 1 hour following disposal of a bottle of neat bleach to sewer. The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 2.7) also shows that volatilisation of hypochlorous acid/hypochlorite is not expected during sewage treatment.

### 3.1.3.3 Accumulation and metabolism

Chlorine does not bioaccumulate or bioconcentrate, because of its water solubility and high reactivity. Aqueous chlorine species (see **section 1.4)** 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)

## 3.1.4 Aquatic compartment (incl. sediment)

Distribution of aqueous chlorine species, as described in **section 1.4,** is discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005). Essentially all chlorine discharged to water will be converted into hypochlorous acid (HOCl) and hypochlorite ($OCl^-$). Reaction of these substances with organic matter present in the aqueous environment will also occur.

### 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, as discussed in **section 1.4**. Many of the processes which hypochlorous acid and hypochlorite will undergo in the aqueous environments in which they may be found have been discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005).).

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

The results of the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005) for these uses will be briefly summarised in **section 3.1.4.1.3.**

**Table 2.2** shows that approximately 98% of chlorine produced is used to produce other chemicals, with chlorine often being generated on the same site. **Table 3.1** shows that the initial chlorine generation and the use to produce chemicals on and off the same site will release approximately 19.2 metric tonnes of chlorine per year to an aqueous environment. These releases will be considered together in **section 3.1.4.1.1**.

#### 3.1.4.1.1 Calculation of $PEC_{local}$ for production

**Table 3.1** shows that approximately 19.2 metric tonnes of $Cl_2$ per year are released to the aqueous environment by industrial processes. The component of this emission from sites which combine production and industrial use is 18.7 metric tonnes of $Cl_2$ per year. Although approximately 25% of this emission tonnage is attributable to on-site use, all of the emission from these combined sites will be considered in this section.

As discussed in **section 1.4**, chlorine in aqueous effluent from production sites will be present in the chemical forms of hypochlorous acid (HOCl) and hypochlorite ($OCl^-$). Emission of hypochlorite to water may follow effluent treatment, as was found for approximately one third of production sites reporting information on sewage treatment in 1996-7 (Euro Chlor, 1998). Also, combined site effluents will often contain additional COD, which will be oxidised further in the hypochlorite-containing effluent. In 1996-7, two thirds of responding plants with aqueous effluent reported COD presence in that effluent (Euro Chlor, 1998). Based on these reported characteristics alone, many chlorine production sites are expected to have negligible hypochlorite emissions.

Based on the yearly $Cl_2$ emission reports from all Eurochlor sites for 2002, the median production site had no emission of chlorine via aqueous effluent (Euro Chlor, 2004b). The 90th percentile emission to water was 1111kg/year, which is 3.7 kg/day if chlorine production occurs on 300 days per year. This level of chlorine release, 150 g **chlorine** per hour, is comparable to the realistic worst case scenario for the discharge of swimming pool waste water. In this scenario, the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.4 and 3.1.2.4) assumes a discharge of 100 $m^3$ per hour of wastewater containing a maximum of 1.4 mg/l **available chlorine** to surface water. The model as explained in Appendix 2 of the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005) is then used to predict a hypochlorite concentration lower than $10^{-22}$ µg/l in a standard receiving river. A similar hypochlorite concentration resulting from the 90th percentile production site emission would be expected. 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

**Table 2.2** gives the reported and estimated chlorine use in 2003. The first seven uses listed in this table, for PVC production, non-chlorinated polymer production, the production of inorganic chemicals including sodium hypochlorite, chloromethane production, epichlorohydrin production, the production of solvents, and the production of chlorinated paraffins and other chlorinated compounds, mainly take place on the site of chlorine production. Thus most of the releases for these uses are considered directly as part of the total production site releases in **section 3.1.4.1.3**. Limited information is available concerning the effluent releases for the 10% of chlorine which is transported to other sites for use (European Commission, 2001b). Approximately 1.6 percent of chlorine is used as an intermediate to produce dyestuff and pesticide, or in small industry. Less than 0.5% is used for disinfection. The remaining 7.9% of chlorine is used away from the site of production, for the production of the compounds also produced on-site.

Use of chlorine produced on site

Chlorine used on the site of production is included in the production facility releases discussed in **section 3.1.4.1.3.**

Use of chlorine transported off site, in use category 33

Up to 9.5% of chlorine production is transported from the production site, for use in the Use Category 33 applications given in the top 9 lines of **table 2.2**. The releases from these off site uses are expected to be similar to releases for the same uses which occur on the chlorine production sites. The two uses which generally occur off site, use as an intermediate for the production of dyestuff and pesticide, or in small industry, are assumed to have similar emissions as the other use category 33 uses, per amount of chlorine used. The estimated emissions due to these uses are given in **table 3.1**.

. As discussed in **section 1.4**, any released aqueous chlorine will be present as hypochlorous acid (HOCl) and hypochlorite ($OCl^-$). However, any effluent released to sewer, as may be more usual for small installations, will undergo in-sewer removal as discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, Appendix 2). The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005) gives several scenarios for hypochlorite discharged to sewer, with resulting hypochlorite concentrations in the sewer ranging from $10^{-32}$ to $10^{-23}$ µg/l. The concentration of hypochlorite in the sewer resulting from use in small industry is also expected to be small, as the same reactivity considerations will be applicable.

Use of chlorine for disinfection

Chlorine is used for the disinfection of drinking water, cooling water, and swimming pools, and in waste water treatment. The use of chlorine for these purposes is covered, along with the use of hypochlorite, in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1 and 3.1.2.). A summary of the $PEC_{local}$ information given in that risk assessment report is given below. The full report should be consulted for further detailed information.

*Use of chlorine in waste water treatment*

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.5 and 3.1.2.5) notes that release of treated sewage is always linked to a local permit and controlled by law. Calculations in Appendix 2 of the assessment show that, for pre-chlorination, concentrations may be as low as $10^{-32}$ mg/l freely available chlorine (FAC), which agrees with the measured effluent concentrations being below the limit of detection. Under postchlorination, the total residual chlorine (measured as combined available chlorine, CAC) is kept at concentrations between 1 and 2 mg/l at the point of discharge to effectively control the bacterial contamination of the effluents, as required by local authorities. In general no hypochlorite can be measured after the treatment.

By-products have been measured under sewage treatment conditions. The main species identified was chloride. Additionally monochloramine and to a less extent trihalomethanes and chloroacetic acids have been measured. The $PEC_{Local}$ information for these by-products resulting from both hypochlorite and chlorine use is summarized in **Table 3.4.**

*Use of chlorine in drinking water disinfectants*

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.7 and 3.1.2.7) considers that drinking water treated by chlorine and sodium hypochlorite has a concentration of 0.5 mg/l of available chlorine as worst case. Using standard TGD assumptions and allowing for removal in the sewer (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, Appendix 2) an environmental concentration of sodium hypochlorite in the receiving river of less than $10^{-23}$ µg/l is calculated.

By products resulting from drinking water disinfection include trihalomethanes and haloacetic acids. These will typically be an order of magnitude more abundant than each of the other main types, which include haloacetonitriles, haloaldehydes, haloketones and normally very small quantities of chlorinated phenols. The $PEC_{Local}$ information for by-products resulting from both hypochlorite and chlorine use is summarized in **Table 3.4.**

*Use of chlorine as a swimming pool disinfectant*

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.4 and 3.1.2.4) uses a realistic worst-case scenario for the discharge of swimming pool waste water. Assuming a discharge of 100 $m^3$ per hour of wastewater containing a maximum of 1.4 mg/l available chlorine to surface water, the model as explained in appendix 2 of the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005) can be used, predicting a hypochlorite concentration lower than $10^{-22}$ µg/l in a standard receiving river.

By-products have been evaluated using robust monitoring data from outdoor pools, where disinfectant dosing and haloacetic acid levels are normally significantly higher than in indoor pools. As more haloacetic acids are produced in outdoor situations, and the PNEC for haloacetic acids is much lower than the PNEC for trihalomethane, this represents a realistic worst case. The individual by-product concentrations have then been applied to a standard pool with water make-up and pool emptying rates as per the TGD, to calculate the $PEC_{Local}$ information for by-products resulting from both hypochlorite and chlorine use, as summarized in **Table 3.4.**

*Use of chlorine as a cooling water disinfectant*

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.9 and 3.1.2.9) shows that a PEC value for hypochlorite in a worst-case regular cooling water scenario will rapidly drop to zero when reaching surface water. This is based on the model calculations shown in Appendix 2 of that report, and is supported by experimental measurements (Jenner et al., 1997). The report finds that both concentrations of 0.5 mg/l TRO (maximum value at the condensers, worst-case regular scenario) and concentrations up to 8mg/l (extreme worst-case shock dosing regime) fall below the detection limit within seconds upon reaching the surface water.

The actual formation of inorganic and organohalogen by-products will be highly dependant on specific local conditions and dosing regimes, which are normally under control of local permits. The use of hypochlorite in cooling water is recently described in the reference document on the application of best available techniques (BAT) in industrial cooling systems (European Commission 2001a). Measurements of the main trihalomethane and haloacetic acid formed (bromoform and dibromoacetic acid) in cooling water samples from three power stations showed bromoform levels up to 26.8 ug/l and DBAA levels up to 10.19 ug/l. The $PEC_{Local}$ information for by-products resulting from both hypochlorite and chlorine use is summarized in **Table 3.4.**

*By-products resulting from disinfection*

The Sodium Hypochlorite risk assessment has considered, in sections 3.1.1.and 3.1.2 the by-products that result from hypochlorite use. The hypochlorite considered in the risk assessment includes the hypochlorite transformed from aqueous chlorine use (see **section 1.4**), and the table given below reflects these combined uses.

**Table 3.4** Calculated PEC $local_{water}$ for hypochlorite by-products[1]

| **Scenario** | | **PEC$local_{water}$ (µg/l)** | | |
|---|---|---|---|---|
| | | **AOX**[3] | **THM**[4] | **HAA**[5] |
| 3.1.2.4 | Swimming Pools: | | | |
| | routine | | 0.02 | 0.16 |
| | emptying | | 0.67 | 6.22 |
| 3.1.2.5 | Sewage Treatment | | 7 | 3.5 |
| 3.1.2.6 | Textile bleaching[2] | 1300 | | |
| 3.1.2.7 | Drinking Water: | | | |
| | groundwater | | 0.05 | 0.04 |
| | Surface water | | | |
| | Good quality | | 0.35 | (0.10 – 0.68) 0.17 |
| | DWD compliant | | 0.70 | (0.21 – 1.35) 0.34 |
| | Non-compliant | | 1.70 | (0.51 – 3.30) |
| | Upland, acid | | | (1.08 – 7.80) |
| 3.1.2.8 | Pulp and paper[2] | 1725 | | |
| 3.1.2.9 | 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

Use of chlorine in the pulp and paper industry

Chlorine use in the pulp and paper industry is now very low. Thus the $PEC_{local}$ due to chlorine released to water and transformed to hypochlorite (see **section 1.4**) will be negligible. The use of sodium hypochlorite in the pulp and paper industry, including any hypochlorite resulting from chlorine use, is discussed in The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.8 and 3.1.2.8). By-products are also discussed in the above sections of the sodium hypochlorite risk assessment report. $PEC_{local}$ information for the aqueous environment is shown in **table 3.4.**

Use of Chlorine in the textile industry

Chlorine use in the textile industry is now very low. Thus the $PEC_{local}$ due to chlorine released to water and transformed to hypochlorite (see **section 1.4**) will be negligible. The use of sodium hypochlorite in the textile industry, including any hypochlorite resulting from chlorine use, is discussed in The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, sections 3.1.1.7 and 3.1.2.7). By-products are also discussed in the above sections of the sodium hypochlorite risk assessment report. ). By-products are also discussed in the above sections of the sodium hypochlorite risk assessment report. $PEC_{local}$ information for the aqueous environment is shown in **table 3.4.**

#### 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, as discussed in **section 1.4.** Ultimately, chlorine in the environment will be reduced to chloride (Euro Chlor, 2000).

#### 3.1.4.1.6 Measured levels

Chlorine gas will not be measured in water at environmentally relevant conditions, as chlorine will hydrolyse to form hypochlorous acid (HOCl) and hypochlorite ($OCl^-$) as discussed in **section 1.4.** The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 2.6, discusses the possibility of measuring low levels of hypochlorite.

### 3.1.4.2 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 discussed in **section 3.1.2.1.** As part of the natural chlorine cycle, global chlorine fluxes from 100 million to 2 billion tonnes per year have been estimated (see **Table 3.1**). This natural chlorine is the largest source of chlorine in the atmosphere.

### 3.1.6.1 Calculation of $\mathrm{PEC_{local}}$

Chlorine released to atmosphere due to anthropogenic uses in Europe is given in **Table 3.1**, with further breakdown of use categories provided in **Table 2.2**. **Table 2.2** shows that approximately 98% of chlorine is used to produce other chemicals, with chlorine often being generated on the same site. **Table 3.1** shows that 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, as shown in **section 3.1.3.1.1** and **Appendix A**.

#### 3.1.6.1.1 Calculation of $\mathrm{PEC_{local}}$ for production

As discussed in **section 3.1.2** and following subsections, site releases to atmosphere for chlorine production and for use in the production of chemicals both on site and off site was approximately 126 metric tonnes in Europe in 2002. Europe contains approximately 5% of global population, but only a bit over 1% of the global surface. Therefore this chlorine release is comparable with approximately 1% of the calculated natural chlorine flux of between 100 million and 2 billion tonnes per year. It can be seen that, compared with 1% of the lower global natural chlorine production estimate, or 1 million tonnes of chlorine per annum, the European release of approximately 126 tonnes per year is just over 0.01%. Thus continental and regional risk assessments for the anthropogenic chlorine, which is present at approximately 0.01% of the natural chlorine level, is not appropriate.

The 2004 emission data (see **section 3.1.2.2**) from the 77 production sites which are members of Euro Chlor, and represent 97% of the total chlorine production capacity in the extended EU, have been used to calculate a $\mathrm{PEC_{local}}$ for production. These data are annual emission data, and include releases due to use on site. However, the full site releases have been assumed to be attributable to production in the calculation of $\mathrm{PEC_{local}}$.

As shown in **Appendix A**, photolysis is an important removal mechanism for atmospheric chlorine, which will reduce chlorine levels to close to zero for much of the day. At latitudes below 55°N, up to 90% of chlorine emitted over a 24 hour period can be removed during that 24 hour period by photolysis in summer, while 63% or more will be removed during the winter. 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 as described in **Appendix A**, has been applied to the atmospheric emissions from each site. For the 90% of sites at latitudes below 55°N, with annual averaged reductions in the effective chlorine load emitted due to photolysis ranging between factors of 4 and 5, a factor of 4 reduction has been used. For the 10% of sites above 55°N, the calculated reduction factor of 3.5 for latitude 60°N has been used for sites between 55°N and 60°N, while no reduction due to photolysis has been assumed for sites located above 60°N. 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 $PEC_{local.}$

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 chlorine concentration corresponds to 0.227 μg/m$^3$. Photolysis has already been taken into account in the measurements used in the determination of the average natural chlorine level. Thus the 90th percentile emission site generates a chlorine concentration which is approximately three times the average marine boundary layer chlorine concentration (0.227 μg/m$^3$), and is lower than the maximum reported concentration for chlorine in the marine boundary layer (0.860 μg/m$^3$).

#### 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

The emissions due to chlorine use at the production site have been included in the production site releases, as discussed in **section 3.1.6.1.1**. As discussed in **Section 3.1.2.4,** much of the emission to atmosphere from the approximately 10% of chlorine transported off site will also be included in the production site emission figures, due to transfer of chlorine from one production site to another to top up the chlorine needed for industrial use at the receiving site. It is not possible to quantify the remaining atmospheric emissions from chlorine transported off site, but the fact that many of the sites will be expected to meet IPPC emission standards and the low levels of chlorine delivered to many of the small sites indicates that releases should be smaller than the releases from the major production sites. 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

As discussed in **section 3.1.2.6**, 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).

### 3.1.6.2 Measured levels

Molecular chlorine is a natural constituent of the atmosphere with average concentrations approaching the 100pptv region, as discussed in **section 3.1.2.1.** Monitoring data in **Table 3.2** show a range in chlorine concentrations from below the limit of detection to 254pptv, 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 254pptV to $\mu g/m^3$, then this gives 0.860$\mu g/m^3$.

### 3.1.6.3 Comparison between predicted and measured levels

The calculated $PEC_{local}$ for production, calculated for the 90th percentile production site emission, is 0.628$\mu g/m^3$**.** 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 $\mu g/m^3$, then the average marine boundary layer concentration corresponds to 0.227 $\mu g/m^3$. The naturally occurring photolysis has already influenced the measured natural chlorine level. The highest measured natural chlorine level corresponds to 0.860 $\mu g/m^3$ (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 (see **section 1.4)** 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 Kow value as an input parameter in order to make these calculations, and Kow cannot be measured for a reactive substance such as chlorine. However, as discussed in **section 3.1.2.1** and **Table 3.1,** 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, as discussed in **section 1.4.** 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)

In the aqueous environment at pH levels above 4, chlorine will be present only as hypochlorous acid (HOCl) or hypochlorite ($ClO^-$) (See **section 1.4**). Ecotoxicity due to these species is covered in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1 and following subsections.) In the terrestrial environment, chlorine, as a strong oxidizing agent, will react quickly with organic components in the soil. Thus it is not possible to maintain a constant chlorine concentration in order to carry out testing. Any unreacted chlorine will be present in soil porewater, as hypochlorite or hypochlorous acid, and is discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.4). The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005) should be consulted for information on the effects of hypochlorite and hypochlorous acid in the aquatic and terrestrial environments, but a short summary of the conclusions of that risk assessment are given in the appropriate sections below.

### 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. As discussed in **Section 1.4,** only hypochlorous acid (HOCl), and hypochlorite ($OCl^-$) will be present at environmentally relevant pH.

#### 3.2.1.1.1 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). The data suggest that nitrifying bacteria are somewhat more sensitive to hypochlorite than the average activated sludge organism, with a decrease of nitrifying activity seen at batch doses of 1500 µg NaClO/mg sludge suspended solids. 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).

#### 3.2.1.1.2 Amphibians

No information on toxicity of hypochlorite to amphibians is available in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005).

### 3.2.1.2 Calculation of Predicted No Effect Concentration (PNEC)

#### 3.2.1.2.1 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.). 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. As discussed in **Section 1.4,** only hypochlorous acid (HOCl), and hypochlorite ($OCl^-$) will be present at environmentally relevant pH. The information used to calculate the PNEC for Brackish and Marine water organisms is given in Table 3.7 of the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.3). 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.

#### 3.2.1.2.2 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.

The issue of unidentified halogenated by-products is addressed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.6.2). The raw sewage chlorination process was agreed to represent a 'worst case' for unidentified halogenated by-products in two senses. Firstly, the concentration of by-products in the test effluent is higher, often by orders of magnitude, than those that are discharged to the environment having been created in these other uses. Secondly, the wide range of available substrates in raw sewage would mean that the range of by-products potentially formed would be likely to be wider than those formed in the other scenarios. These factors are relevant for all the chlorine uses discussed in this risk assessment.

Whole effluent tests were carried out on raw sewage with and without chlorination, to establish the additional effect of chlorinated by-products. In summary, the following key conclusions were evident:

- For all the taxa tested the mixture of by-products formed by chlorination of raw settled sewage (C/D-RSS sample) did not increase toxicity relative to that measured in the raw settled sewage (RSS).
- Chlorination of the raw settled sewage did not reduce its biodegradability and showed no evidence of production of additional non-degradable substances to those present in raw settled sewage.
- Chlorination of the raw settled sewage did increase the amounts of lipophilic chlorinated substances capable of being absorbed by SPME fibres prior to biodegradation. However, there was no increased absorption after biodegradation, indicating that any potentially bioaccumulable chlorinated substances formed were biodegradable.

#### 3.2.1.3 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.

#### 3.2.1.4 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 Toxicity test results

Although no data are available for hypochlorite delivered to soil causing toxicity to terrestrial species, **section 3.2.3** contains information concerning the toxicity of gaseous chlorine to terrestrial plants.

#### 3.2.2.1.1 Plants

Although no data are available for hypochlorite delivered to soil causing toxicity to plants, **section 3.2.3** contains information concerning the toxicity of gaseous chlorine to terrestrial plants.

### 3.2.2.2 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). Nevertheless, the available data is summarised below.

Much of the early literature consists of reports of damage to plants during accidental release of chlorine, for example from chlor-alkali manufactories before 1860 which did not have scrubbers for chlorine removal from effluent gasses (Vetrano 2001). No chlorine concentrations were available in these reports, due to the conditions of exposure. Plant leaf damage resembled that caused by sulphur dioxide ($SO_2$). However, Brennan et al (1969) found healthy re-growth after two weeks on the majority of plants affected by one such accidental chlorine release.

A few tests have been carried out which attempted to provide a constant chlorine concentration for a defined exposure period. Vetrano (2001) has reviewed fumigation experiments in which chlorine has been applied to several crops, generally for 4-hour exposure periods. Exposure concentrations ranged from 0.1ppm to 4.67 ppm. Effects, generally leaf damage, depended upon plant species, with some plants being much more sensitive than others. For the most sensitive plants, radish and alfalfa, an exposure threshold for causing damage was established at 0.1 ppm for a 2-hour exposure (Brennan et al 1965). The sensitivity of other plants tested is shown in **Table 3.5**. Those plants which showed no damage from a fourhour exposure to 1 ppm or greater chlorine were classified as resistant by Brennan et al (1965).

**Table 3.5 Sensitivity of plant species to chlorine exposure (data from Brennan et al, 1965, 1996)**

| **Exposure time, hr.** | **Concentration, ppm** | **Plants showing damage** |
|---|---|---|
| 2 | 0.1 | Radish, Alfalfa |
| 4 | 0.1-0.25 | Tobacco, Zinnia, Gromphrena, Onion, Corn, Mustard, Sunflower |
| 4 | 0.5 | Tomato, Cucumber, Dahlia, Nasturtium, Dandelion |
| 4 | 0.8 | Petunia, Pinto Bean, Scotia Bean, Squash, Cowpea, Geranium, Azalea |
| 3 | 0,96 | Shortleaf and Loblolly Pine |
| 3 | 1.0 | Slash Pine |
| 4 | 1.0 | **No Damage shown for** Chenopodium, Polygonium, Oxalis, Begonia, and Pepper |

Brennan et al (1966) also found damage to shortleaf pine, loblolly pine, and slash pine after a three hour exposure to1 ppm chlorine. Damage increased with both chlorine concentration and exposure time. Exposure to 9.6ppm chlorine resulted in damage after only 15 minutes exposure. However, no damage resulted to any of the pines from a 3-hour exposure to 0.72ppm chlorine.

The lowest level giving an effect, 0.1 ppm chlorine for Radish and Alfalfa subjected to a 2-hour exposure (Brennan et al, 1965) has been taken as the exposure threshold for causing damage to plant species. Assuming that the reported measurements express chlorine as ppmV, then this value is more than three orders of magnitude higher than the average natural chlorine level of 75 +/- 50 pptV in the marine boundary layer.

### 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 [5]

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).

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[5] 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.

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 Aquatic compartment (incl. sediment)

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.

The Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of May 2005, section 3.2.1.6.2) uses whole effluent testing from chlorinated raw sewage to show that the halogenated by-products present did not increase the toxicity or reduce the biodegradability of the effluent. As this represents a realistic worst case, there should be no cause for concern for halogenated by-products generated by aqueous use of chlorine.

Conclusions to the risk assessment for the aquatic compartment:

**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 chlorine and its aqueous transformation products hypochlorous acid and hypochlorite, and to halogenated by-products.

### 3.3.2 Terrestrial compartment

Chlorine releases to the terrestrial environment result in no free chlorine, hypochlorous acid, or hypochlorite. Thus there is negligible risk due to these compounds in the terrestrial environment, due to lack of environmental exposure.

Conclusions to the risk assessment for the terrestrial compartment:

**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 chlorine and its aqueous transformation products hypochlorous acid and hypochlorite.

### 3.3.3 Atmosphere

Chlorine release from sites producing and using chlorine is only a small contribution of less than 0.0002% to the global chlorine load, which is dominated by natural chlorine sources.

Local anthropogenic chlorine releases to the atmosphere result in atmospheric chlorine concentrations which are within the range of natural chlorine concentrations measured in the marine boundary layer. Estimates based on the 90th percentile emissions from a chlorine production plant, representing a realistic worst-case, and also assumed to represent a worst-case for on- and off-site uses of chlorine, generate an annual average chlorine concentration of 0.628µg/m$^3$. This is within the range of natural chlorine concentrations measured in the marine boundary layer of 0.227 – 0.860 µg/m$^3$. A full quantitative risk assessment for the atmospheric compartment cannot be carried out because no $EC_{50}$ data for plants is available for chlorine. However, the available information from 29 plant species shows that damage can occur to the most sensitive species at 0.1 ppm, or 0.29 mg/m$^3$, after a 2-hour exposure. This concentration is approximately 1000 times larger than the marine boundary layer concentration. Natural chlorine concentrations vary markedly throughout a 24 hour period as photolysis during the daytime reduces the nightly build-up of chlorine to a very low level again. A similar pattern is predicted for local chlorine releases from production plants, so the short-term (2 to 4 hour) experimental data available may, in general, approximate the environmental exposure pattern.

As the local emission from the 90th percentile production facility is within the experimental range of the natural chlorine concentrations measured in the marine boundary layer, and as the available experimental terrestrial plant data, which indicates an effect on the most sensitive species at concentrations of over 1000 times the natural chlorine level, is of an exposure time which approximates the natural exposure pattern, the available data indicate that local emissions from chlorine production sites do not pose a risk to the atmosphere.

Conclusions to the risk assessment for the atmosphere:

**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 chlorine.

### 3.3.4 Secondary poisoning

Hypochlorous acid and hypochlorite do not bioaccumulate.

Conclusions to the risk assessment for secondary poisoning:

**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 Hypochlorous acid and hypochlorite.

### 3.3.5 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

# 5 RESULTS [6]

## 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.

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[6] 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.

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# ABBREVIATIONS

[update the list to correspond to the substance RAR]

| | |
|---|---|
| ADI | Acceptable Daily Intake |
| AF | Assessment Factor |
| ASTM | American Society for Testing and Materials |
| ATP | Adaptation to Technical Progress |
| AUC | Area Under The Curve |
| B | Bioaccumulation |
| BBA | Biologische Bundesanstalt für Land- und Forstwirtschaft |
| BCF | Bioconcentration Factor |
| BMC | Benchmark Concentration |
| BMD | Benchmark Dose |
| BMF | Biomagnification Factor |
| BREF | Reference document on Best Available Techniques |
| bw | body weight / *Bw*, *b.w.* |
| C | Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| CA | Chromosome Aberration |
| CA | Competent Authority |
| CAS | Chemical Abstract Services |
| CEC | Commission of the European Communities |
| CEN | European Standards Organisation / European Committee for Normalisation |
| CMR | Carcinogenic, Mutagenic and toxic to Reproduction |
| CNS | Central Nervous System |
| COD | Chemical Oxygen Demand |
| CSTEE | Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO) |
| $CT_{50}$ | Clearance Time, elimination or depuration expressed as half-life |
| d.wt | dry weight / dw |
| dfi | daily food intake |
| DG | Directorate General |
| DIN | Deutsche Industrie Norm (German norm) |
| DNA | DeoxyriboNucleic Acid |
| DOC | Dissolved Organic Carbon |
| DT50 | Degradation half-life or period required for 50 percent dissipation / degradation |
| DT90 | Period required for 90 percent dissipation / degradation |
| E | Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |

| | |
|---|---|
| EASE | Estimation and Assessment of Substance Exposure Physico-chemical properties [Model] |
| EbC50 | Effect Concentration measured as 50% reduction in biomass growth in algae tests |
| EC | European Communities |
| EC10 | Effect Concentration measured as 10% effect |
| EC50 | median Effect Concentration |
| ECB | European Chemicals Bureau |
| ECETOC | European Centre for Ecotoxicology and Toxicology of Chemicals |
| ECVAM | European Centre for the Validation of Alternative Methods |
| EDC | Endocrine Disrupting Chemical |
| EEC | European Economic Communities |
| EINECS | European Inventory of Existing Commercial Chemical Substances |
| ELINCS | European List of New Chemical Substances |
| EN | European Norm |
| EPA | Environmental Protection Agency (USA) |
| ErC50 | Effect Concentration measured as 50% reduction in growth rate in algae tests |
| ESD | Emission Scenario Document |
| EU | European Union |
| EUSES | European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment] |
| F(+) | (Highly) flammable (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| FAO | Food and Agriculture Organisation of the United Nations |
| FELS | Fish Early Life Stage |
| GLP | Good Laboratory Practice |
| HEDSET | EC/OECD Harmonised Electronic Data Set (for data collection of existing substances) |
| HELCOM | Helsinki Commission -Baltic Marine Environment Protection Commission |
| HPLC | High Pressure Liquid Chromatography |
| HPVC | High Production Volume Chemical (> 1000 t/a) |
| IARC | International Agency for Research on Cancer |
| IC | Industrial Category |
| IC50 | median Immobilisation Concentration or median Inhibitory Concentration |
| ILO | International Labour Organisation |
| IPCS | International Programme on Chemical Safety |
| ISO | International Organisation for Standardisation |
| IUCLID | International Uniform Chemical Information Database (existing substances) |
| IUPAC | International Union for Pure and Applied Chemistry |
| JEFCA | Joint FAO/WHO Expert Committee on Food Additives |
| JMPR | Joint FAO/WHO Meeting on Pesticide Residues |

| | |
|---|---|
| Koc | organic carbon normalised distribution coefficient |
| Kow | octanol/water partition coefficient |
| Kp | solids-water partition coefficient |
| L(E)C50 | median Lethal (Effect) Concentration |
| LAEL | Lowest Adverse Effect Level |
| LC50 | median Lethal Concentration |
| LD50 | median Lethal Dose |
| LEV | Local Exhaust Ventilation |
| LLNA | Local Lymph Node Assay |
| LOAEL | Lowest Observed Adverse Effect Level |
| LOEC | Lowest Observed Effect Concentration |
| LOED | Lowest Observed Effect Dose |
| LOEL | Lowest Observed Effect Level |
| MAC | Maximum Allowable Concentration |
| MATC | Maximum Acceptable Toxic Concentration |
| MC | Main Category |
| MITI | Ministry of International Trade and Industry, Japan |
| MOE | Margin of Exposure |
| MOS | Margin of Safety |
| MW | Molecular Weight |
| N | Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC |
| NAEL | No Adverse Effect Level |
| NOAEL | No Observed Adverse Effect Level |
| NOEL | No Observed Effect Level |
| NOEC | No Observed Effect Concentration |
| NTP | National Toxicology Program (USA) |
| O | Oxidizing (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| OECD | Organisation for Economic Cooperation and Development |
| OEL | Occupational Exposure Limit |
| OJ | Official Journal |
| OSPAR | Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic |
| P | Persistent |
| PBT | Persistent, Bioaccumulative and Toxic |
| PBPK | Physiologically Based PharmacoKinetic modelling |
| PBTK | Physiologically Based ToxicoKinetic modelling |

| | |
|---|---|
| PEC | Predicted Environmental Concentration |
| pH | logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$ |
| pKa | logarithm (to the base 10) of the acid dissociation constant |
| pKb | logarithm (to the base 10) of the base dissociation constant |
| PNEC | Predicted No Effect Concentration |
| POP | Persistent Organic Pollutant |
| PPE | Personal Protective Equipment |
| QSAR | (Quantitative) Structure-Activity Relationship |
| R phrases | Risk phrases according to Annex III of Directive 67/548/EEC |
| RAR | Risk Assessment Report |
| RC | Risk Characterisation |
| RfC | Reference Concentration |
| RfD | Reference Dose |
| RNA | RiboNucleic Acid |
| RPE | Respiratory Protective Equipment |
| RWC | Reasonable Worst Case |
| S phrases | Safety phrases according to Annex III of Directive 67/548/EEC |
| SAR | Structure-Activity Relationships |
| SBR | Standardised birth ratio |
| SCE | Sister Chromatic Exchange |
| SDS | Safety Data Sheet |
| SETAC | Society of Environmental Toxicology And Chemistry |
| SNIF | Summary Notification Interchange Format (new substances) |
| SSD | Species Sensitivity Distribution |
| STP | Sewage Treatment Plant |
| T(+) | (Very) Toxic (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| TDI | Tolerable Daily Intake |
| TG | Test Guideline |
| TGD | Technical Guidance Document |
| TNsG | Technical Notes for Guidance (for Biocides) |
| TNO | The Netherlands Organisation for Applied Scientific Research |
| UC | Use Category |
| UDS | Unscheduled DNA Synthesis |
| UN | United Nations |
| UNEP | United Nations Environment Programme |
| US EPA | Environmental Protection Agency, USA |
| UV | Ultraviolet Region of Spectrum |

| | |
|---|---|
| UVCB | Unknown or Variable composition, Complex reaction products of Biological material |
| vB | very Bioaccumulative |
| vP | very Persistent |
| vPvB | very Persistent and very Bioaccumulative |
| v/v | volume per volume ratio |
| w/w | weight per weight ratio |
| WHO | World Health Organization |
| WWTP | Waste Water Treatment Plant |
| Xn | Harmful (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| Xi | Irritant (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |

# Appendix A Chlorine Photolysis

During daylight hours chlorine is removed from the atmosphere by photolysis, according to the processes discussed in **section 3.1.3.1.1**. The main process is

$$Cl_2 + h\nu \rightarrow 2\ Cl^{\circ}$$

The rate of photolysis depends upon the time of day and upon the latitude. It is possible to calculate the rate of chlorine photolysis as a function of latitude, longitude, and time of day, using the model developed by Sasha Madronich at the US National Center For Atmospheric Research (Madronich and Flocke, 1999).

The photolysis rate constants and associated chlorine half-lives have been calculated at half hourly intervals for both the longest and the shortest day of the year for latitudes which cover the locations of European chlorine production sites. These half-lives range from less than 5 minutes at mid-day at lower latitudes in summer to several hours at dawn and at sunset. Some representative half-life information is shown in Table A-1. More than 90% of chlorine production sites are located at or below latitude 55°N, and therefore this latitude is considered to represent a reasonable worst case for chlorine removal by photolysis. The calculated chlorine half-lives have been used in a simple spreadsheet model to calculate the average daily chlorine load which remains after photolysis, as a function of latitude.

**Table 6.1 Representative Chlorine half-lives at several latitudes and times of day**

| Time of day | Half-life in hours at Latitude 40° N | | Half-life in hours at Latitude 55° N | |
|---|---|---|---|---|
| | 21 June | 21 December | 21 June | 21 December |
| **04:00** | 4.49 | ∞ | 0.75 | ∞ |
| **06:00** | 0.21 | 22394 | 0.18 | ∞ |
| **09:00** | 0.08 | 0.23 | 0.09 | 0.96 |
| **12:00** | 0.07 | 0.16 | 0.08 | 0.48 |
| **15:00** | 0.11 | 0.69 | 0.11 | 14.07 |
| **18:00** | 0.77 | ∞ | 0.38 | ∞ |
| **21:00** | ∞ | ∞ | 1534 | ∞ |
| **23:00** | ∞ | ∞ | ∞ | ∞ |

The spreadsheet model generates a point source load, suitable as input to the OPS model described in the TGD (2003) and used in EUSES. The spreadsheet model contains 49 columns, each of which represents one-half hour. (The first half hour, beginning at 0:00, and the last half hour, beginning at 24:00, are the same, and this is taken into account in the model.) At the start of each half hour, the entire emission for that half hour, or 1/48 of the daily emission, is released. During the half hour, if there is no light and therefore no photolysis, no diffusion is allowed to take place, and the load emitted remains in the point above the emission stack. If daylight is present and photolysis is possible, the appropriate half-life for chlorine photolysis from the model of Madronich and Flocke (1999) is used in a first order decay model to generate the amount of chlorine remaining at the end of the half hour period. The amount of chlorine remaining at the end of the period is then added to the next half-hourly column of the model, along with the next emission increment (1/48 of the daily emission). This process of emission, photolysis if appropriate, and addition of the amount of chlorine remaining to the next emission continues for each half-hourly increment throughout the 24 hour period. Photolysis is the only process used to reduce the chlorine load. The model is then run for at least two days, until steady state, defined as less than 1% difference between chlorine loads at the ends of the two 24 hour periods, has been reached. Steady state was always reached within 2 days at latitudes of 55°N and below.

As an example, the effect of photolysis on the daily chlorine load resulting from emission of a 10kg/day load as a function of time of year and latitude is shown in figures A-1 (a-d) below. The steady build-up of chlorine during the night and significant reduction by photolysis during the day at both 55°N and 40°N and for the longest and shortest day of the year are noted.

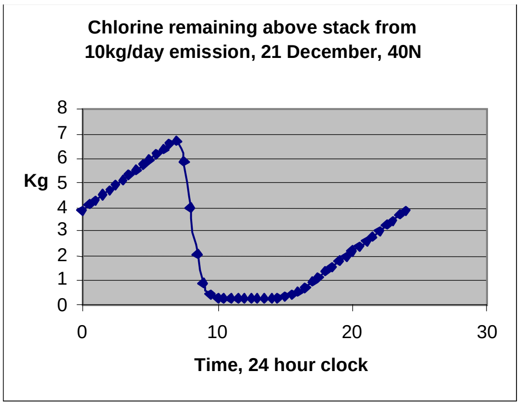

Figure A-1a: 40N, 21 December

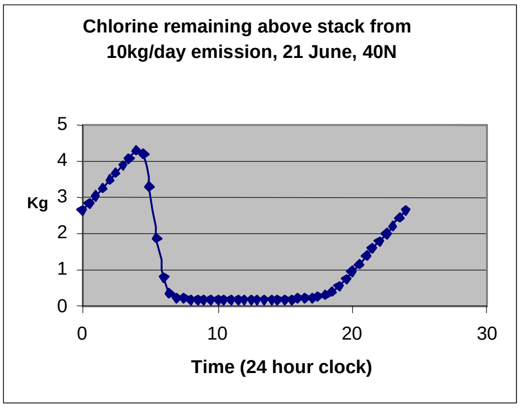

Figure A-1b: 40N, 21 June

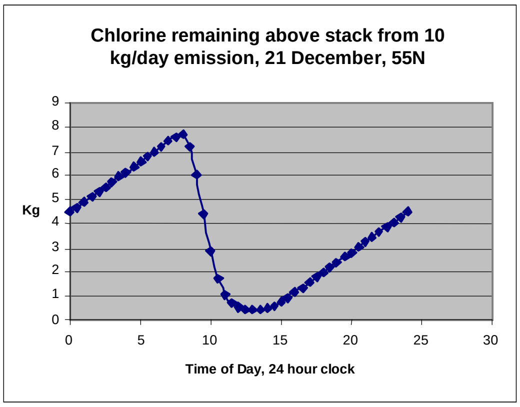

Figure A-1 c: 55N, 21 December

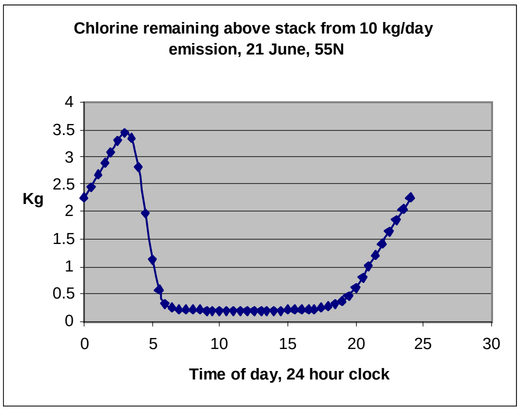

Figure A-1d: 55N, 21 June

The maximum and minimum chlorine loads over the emission stack at the start of a half hourly emission period for the 21 June and 21 December at latitudes 40N and 55N are

**Table 6.2 Chlorine loads remaining after photolysis, from a 10kg/day emission**

| Latitude, Date | 40N, 21 Dec | 40N, 21 June | 55N, 21 Dec | 55N, 21 June |
|---|---|---|---|---|
| **Average chlorine load on the day** | 2.69kg | 1.29 kg | 3.69kg | 0.99kg |
| **Maximum chlorine load** | 6.66kg | 4.29kg | 7.70kg | 3.44kg |
| **Minimum chlorine load** | 0.23kg | 0.21 kg | 0.45kg | 0.21kg |
| **Annual average chlorine load** | 1.99 kg/day | | 2.34kg/day | |

shown in Table A-2, along with the average daily chlorine load for these days and latitudes. In order to be conservative the model takes all maximum, minimum, and daily average data from the start of the half-hourly period, rather than at the end of that period when photolysis may have been operative. Thus the minimum values shown in table A-1 often represent the half-hourly emission of 0.208 kg, as chlorine remaining before the emission will have essentially been eliminated by photolysis. The annual average chlorine daily load from a 10kg/day emission has been calculated from a simple average of the chlorine loads on 21 June and 21 December.

The results in Table A-2 show that, even for latitude 55°N, a 10kg/day chlorine load is reduced to an effective annual load equivalent to 2.34 kg/day. This amounts to a reduction by more than a factor of 4 in annual chlorine load present in the air due to releases from chlorine production sites, for more than 90 percent of sites which produce chlorine.

**Reference :** Sasha Madronich and Siri Flocke. The Role of Solar Radiation in Atmospheric Chemistry. **The Handbook of Environmental Chemistry Vol.2 Part D.Environmental Photochemistry** (ed.by P; Boule)© Springer-Verlag Berlin Heidelberg 1999.

European Commission

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The report provides the comprehensive risk assessment of the substance Chlorine It has been prepared by Italy. in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human populations in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined. The environmental risk assessment concludes that there is no concern for any of the environmental compartments. For human health the scenarios for occupational exposure, consumer exposure and humans exposed via the environment and the possible risks have been examined and no concerns have been identified.

# European Union Risk Assessment Report

# CHLORINE

CAS No: 7782-50-5

EINECS No: 231-959-5

## RISK ASSESSMENT

## (Human Health)

*Final report, December 2007*

Italy

***FINAL APPROVED VERSION***

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# CHLORINE

CAS No: 7782-50-5

EINECS No: 231-959-5

# RISK ASSESSMENT

(Human Health)

*Final version, December 2007*

Italy

***FINAL APPROVED VERSION***

Rapporteur for the risk assessmente of chlorite is Italy.

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| | |
|---|---|
| **Date of Last Literature Search :** | **2004** |
| **Review of report by MS Technical Experts finalised:** | **December 2006** |
| **Final report:** | **[insert year]** |

## Foreword

We are pleased to present this Risk Assessment Report which is the result of in-depth work carried out by experts in one Member State, working in co-operation with their counterparts in the other Member States, the Commission Services, Industry and public interest groups.

The Risk Assessment was carried out in accordance with Council Regulation (EEC) 793/93[1] on the evaluation and control of the risks of "existing" substances. "Existing" substances are chemical substances in use within the European Community before September 1981 and listed in the European Inventory of Existing Commercial Chemical Substances. Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of these substances if they are produced or imported into the Community in volumes above 10 tonnes per year.

There are four overall stages in the Regulation for reducing the risks: data collection, priority setting, risk assessment and risk reduction. Data provided by Industry are used by Member States and the Commission services to determine the priority of the substances which need to be assessed. For each substance on a priority list, a Member State volunteers to act as "Rapporteur", undertaking the in-depth Risk Assessment and recommending a strategy to limit the risks of exposure to the substance, if necessary.

The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94[2], which is supported by a technical guidance document[3]. Normally, the "Rapporteur" and individual companies producing, importing and/or using the chemicals work closely together to develop a draft Risk Assessment Report, which is then presented at a meeting of Member State technical experts for endorsement. The Risk Assessment Report is then peer-reviewed by the Scientific Committee on Health and Environmental Risks (SCHER) which gives its opinion to the European Commission on the quality of the risk assessment.

If a Risk Assessment Report concludes that measures to reduce the risks of exposure to the substances are needed, beyond any measures which may already be in place, the next step in the process is for the "Rapporteur" to develop a proposal for a strategy to limit those risks.

The Risk Assessment Report is also presented to the Organisation for Economic Co-operation and Development as a contribution to the Chapter 19, Agenda 21 goals for evaluating chemicals, agreed at the United Nations Conference on Environment and Development, held in Rio de Janeiro in 1992 and confirmed in the Johannesburg Declaration on Sustainable Development at the World Summit on Sustainable Development, held in Johannesburg, South Africa in 2002.

This Risk Assessment improves our knowledge about the risks to human health and the environment from exposure to chemicals. We hope you will agree that the results of this in-depth study and intensive co-operation will make a worthwhile contribution to the Community objective of reducing the overall risks from exposure to chemicals.

---

[1] O.J. No L 084, 05/04/199 p.0001 – 0075

[2] O.J. No L 161, 29/06/1994 p. 0003 – 0011

[3] Technical Guidance Document, Part I – V, ISBN 92-827-801 [1234]

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# 0 OVERALL RESULTS OF THE RISK ASSESSMENT[4]

| | |
|---|---|
| CAS Number: | 7782-50-5 |
| EINECS Number: | 231-959-5 |
| IUPAC Name: | Chlorine |

## 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.

## Human health

Human health (toxicity)

*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.

*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.

*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.

*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.

*Human health (risks from physico-chemical properties)*

---

[4] 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.

**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.

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# 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 PURITY/IMPURITIES, ADDITIVES

Chlorine is distributed in various stages of purity. The purity ranges from about 99.5 % to almost 100 % for liquid chlorine. The main impurities as a result of production are nitrogen, carbon dioxide, oxygen, bromine and hydrogen, but nitrogen trichloride and halogenated hydrocarbons may also be present. Information on dealing with impurities is given in the BREF for the Chlor-alkali manufacturing industry (European Commission, 2001b, section 2.4.3.1).

Mercury levels in chlorine produced in mercury cell chlor-alkali plants are very low, being about 1 mg of mercury per tonne of $Cl_2$ produced or less (European Commission, 2001b, Annex B, p 129, Euro Chlor 2001, Euro Chlor 2003c). For this reason mercury emissions from the product chlorine will not be discussed further in this risk assessment.

No additives are added to chlorine as produced.

## 1.3 PHYSICO-CHEMICAL PROPERTIES

Chlorine is a greenish-yellow gas having a pungent odour at ambient temperatures and pressures and a density 2.5 times higher than air. In liquid form it is a clear amber colour. Solid chlorine forms yellow crystals.

Chlorine is soluble in water and in salt solutions, the solubility decreasing with salt strength and temperature (above 10 °C). At 25 °C the aqueous solubility is 6.9 g/l

(Budavari et al., 1989); Gerhartz et al 1986, Schmittinger 2000). Chlorine partially hydrolyses in aqueous solution to form HCl and hypochlorous acid:

$Cl_2 + H_2O = HCl + HOCl$

Below 10°C, chlorine forms hydrates which are greenish-yellow crystals. The $Cl_2$-$H_2O$-System has a quadruple point at 28.7°C.

The vapour pressure data of Ambrose et al (1979) from 205.945 to 416.90 K, and Giauque and Powel (1939) from 172.17 to 240.10 K, were used to determine the constants in the Martin-Shin-Kapoor vapour pressure equation (Martin and Longpre, 1984):

$\ln(P) = A + B/T + C^* \ln(T) + D^*T + (E^*(F-T)^*\ln(F-T))/(F^*T)$; P [kPa],

where P is in kilopascals (kPa) and T is in Kelvin (K). The values of the constants are:

$A = 62.402508$ $D = 1.0666308 \times 10^{-2}$

$B = -4343.5240$ $E = 95.248723$

$C = -7.8661534$ $F = 424.90$

The equation fits the measured data well, with an average deviation between the predicted vapour pressure and the experimental values of 0.20 %, giving a standard deviation of 0.29 % (GEST 91/168 (2002d)).

The resultant vapour pressure at 20°C can be converted to 6780 hPa, at 30 °C to 8900 hPa, and at 50 °C to 14550 hPa (Martin and Longpre 1984). Similar values are given in Gerhartz et al (1986), and in Schmittinger (2000).

The density of chlorine gas at 101.3 kPa is a function of temperature, being 3.213. $kg/m^3$ at 0 °C, 2.7 $kg/m^3$ at 50 °C, 2.33 $kg/m^3$ at 100 °C, and 2.051 $kg/m^3$ at 150 °C. (Budavari et al., 1989; Gerhartz et al 1986). The relative density of liquid chlorine at –34 °C is 1.56 $g/cm^3$ (Chim. Oggi, 1999; Budavari et al., 1989). Liquid chlorine is quite compressible, and thus the density of liquid chlorine decreases with increasing temperature, being 1.47 $g/cm^3$ at 0°C and 3698 hPa (Dow Europe SA, 1996), and 1.405 $g/cm^3$ at 20°C and 5690 hPa (Elf-Atochem, 1997).

An octanol-water distribution equilibrium cannot be defined or measured, as both chlorine and hypochlorous acid (formed in water above pH = 4) have oxidising properties, and will react with the organic phase in both the shake flask (OECD, 1995) and the HPLC (OECD, 1989) methods for log Kow determination. In addition, if an octanol water distribution equilibrium of chlorine gas were to be estimated, it would not be appropriate to estimate a bioconcentration factor because of the reactivity of chlorine.

Chlorine generally exhibits a valence of –1 in compounds, but it also exists in the formal positive oxidation states of +1 (NaClO), +3 ($NaClO_2$), + 4 ($ClO_2$), +5 ($NaClO_3$) and +7 ($NaClO_4$). Molecular chlorine is a strong oxidizer and a chlorinating agent, adding to double bonds in aliphatic compounds or undergoing substitution reactions with both aliphatic and aromatic species. Chlorine is very active under specific conditions but it is not explosive or flammable. Chlorine reacts easily with most elements (e.g. S, P, $I_2$, $Br_2$, $F_2$). Reactions with $N_2$, $O_2$ and C are indirect. Chlorine reacts 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 temperatures above 250°C, or in the presence of sunlight or artificial light of ca. 470 nm wavelength, hydrogen and chlorine combine explosively to form HCl (Kroschwitz JI, Grant MH, Howe-Grant M, 1991) Like oxygen, chlorine is able to form flammable mixtures with hydrocarbons and chlorinated hydrocarbons. In general, the range of flammability is somewhat less for chlorine mixtures, compared to oxygen mixtures. (GEST 91/168, 2002c). Detonation of gaseous and liquid mixtures of chlorine with selected hydrocarbons may also occur (GEST 91/168, 2002c). Also, the auto-ignition temperatures of a number of organics in chlorine are known and are found to be much lower than the corresponding value in air or oxygen. Sometimes the auto-ignition temperatures are below 150 °C, but more often values are between 150 °C and 350 °C. This means that, when a mixture of a combustible and chlorine is formed at temperatures of 100 °C and above, a serious thermal explosion hazard or flammability risk is present, when the mixture is allowed to reside for extended periods. (GEST 91/168, 2002c).

Dry chlorine reacts combustively with most metals depending on the temperature. Aluminium, arsenic, gold, mercury, selenium, tellurium, and tin react with dry $Cl_2$ in gaseous or liquid form at ordinary temperatures; steel ignites at about 170°C depending on the physical shape; titanium reacts violently with dry chlorine. Wet chlorine is very reactive because of the hydrochloric acid and hypochlorous acid. Tantalum is resistant to both dry and wet chlorine (Kroschwitz JI, Grant MH, Howe-Grant M, 1991).

The surface tension of liquid chlorine decreases with increasing temperature (GEST 91/168, 2002a). At 20°C, the calculated surface tension is 18.5 $mJ/m^2$.

Table 1.1 Summary of 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<br>3.213 kg/m$^3$ at 0 ºC | Liquid.(Chim. Oggi (1991,) Budavari et al. (1989))<br>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<br>6.9 g/l at 25 ºC | Maximum solubility at 10 ºC. Gerhartz et al (1986), Schmittinger (2000), GEST 2002b.<br>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<br>Viscosity – Gas at 0C | $0.385 \cdot 10^{-3}$ Pa.s<br>$12.4 \cdot 10^{-3}$ Pa.s | Range: 1.032 x $10^{-3}$ Pa.s (–100 C) to 0.249 x $10^{-3}$ Pa.s (100C)<br>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 |

### 1.3.1 Transformation

Addition of chlorine gas to pure water results in the formation of a mixture of hydrochloric acid (HCl) and hypochlorous acid (HOCl) according to law of mass action:

$$k = \frac{[HOCl]x[H^+]x[Cl^-]}{[Cl_2]}$$

The equilibrium constant for this reaction depends upon temperature, as shown in **Table 1.2** below. The proportion of chlorine gas decreases with temperature (Herrmann and Wagner, 2003).

Table 1.2 Equilibrium constant k for chlorine at equilibrium

| Temperature, [°C] | Equilibrium constant, k · $10^4$ |
|---|---|
| 0 | 1.46 |
| 15 | 2.81 |
| 25 | 3.94 |
| 35 | 5.10 |
| 45 | 6.05 |

The following reactions occur when chlorine is added to water (species which are active biocides are in bold letters):

$\mathbf{Cl_2}$ + H2O = **HClO** + HCl (equat. 1)

**HClO** = $H^+$+ $\mathbf{OCl^-}$ (equat. 2)

HCl = $H^+ + Cl^-$ (equat. 3)

$Cl_2$ + 2 $OH^-$= $Cl^-$ + $\mathbf{OCl}^-$ + H2O (equat. 4)

**HClO** = $H^+$ + $Cl^-$ + **O** (equat. 5)

The disproportionation reaction of chlorine in the near-neutral pH region (equation 1) runs in a nearly quantitative manner and is completed within seconds (cf. **Table 1.2)** (Herrmann and Wagner, 2003). There are three species of chlorine in equilibrium in water: gaseous chlorine, HOCl (also a gas at room temperature and pressure), and $ClO^-$. An example of the distribution between them as a function of pH is shown in **Figure 1.1**. For example, at pH 7.5 half of the chlorine is active as HOCl and half is available as $ClO^-$. $Cl_2$ is present in significant quantities only at pH less than 3 (see **Figure 1.1**)

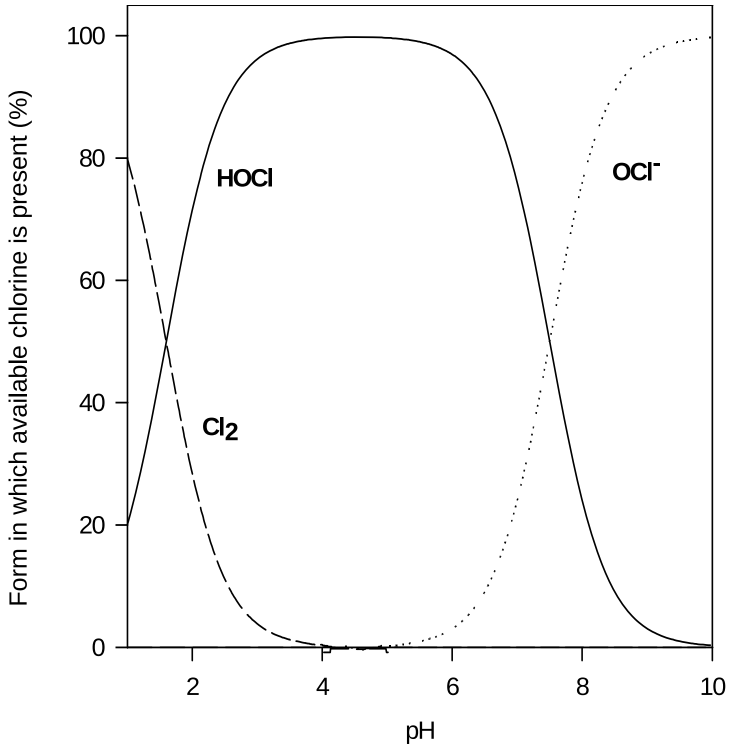


Figure 1.1Calculated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M $Cl_2$ in water at standard temperature and pressure( GEST 91/168, 2002b)

The speciation of chlorine in water is important for all processes in which chlorine is present in an aqueous environment. These processes include chlorine use as a biocide, for example in drinking water disinfection, swimming pool disinfection, sewage effluent disinfection, and cooling water disinfection. Chlorine speciation is also important if chlorine is used in aqueous industrial processes, as was formerly the case in the pulp and paper industry, and in the textile industry. All chlorine discharged to the aqueous environment will be present in speciated form, and this is relevant both for human toxicity and for ecotoxicity studies. In the pH range relevant for both humans and environmental biota, the relevant chlorine species will be hypochlorous acid and the hypochlorite anion.

Hypochlorous acid HClO in its non-dissociated form, predominant in the pH 5-7 region, is a more powerful oxidant than the hypochlorite anion ($OCl^-$) and chlorine. The degree of dissociation is therefore important for disinfection efficacy. It strongly depends on the pH (see **Figure 1.1**) and much less on temperature. Dissociation is poor at pH levels below 6. From pH 6 to 8.5 a nearly complete dissociation of HClO occurs. Thus for disinfection with chlorine control of pH is critical (Herrmann and Wagner, 2003). This is also important for ecototoxicity testing.

Further information concerning aqueous HOCl and its reactions, including reactions in polluted water, are given in the sodium hypochlorite risk assessment report (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, sections 2.4 and 2.5.)

## 1.4 CLASSIFICATION

### 1.4.1 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

### 1.4.2 Proposed classification

Agreed Classification at TC C&L September 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

## 2.1 PRODUCTION

Globally, Western Europe is the second largest chlor-alkali producing region after the US. In 1994, when global chlorine production was 38 million tonnes, the United States produced 11.2 million tones of chlorine. Western Europe, including the EU, Switzerland and Norway, and Hungary, Poland, and the Czech and Slovak republics, produced 10.6 million tonnes of chlorine in 1995, while the third-ranked producing country, Japan, had 4.2 million tonnes production capacity in 1995. (Euro Chlor 2004a, European Commission, 2001b).

In 2004, Euro Chlor represented European chlorine producers in 20 countries, whose 77 production sites account for 97% of the chlorine production capacity in the 25 EU member states. Apart from 32 producers in Western Europe, Euro Chlor has also seven manufacturing members in four Eastern European countries. Full members are producers of chlorine in: Austria, Belgium, the Czech Republic, Finland, France, Germany, Greece, Hungary, Ireland, Italy, the Netherlands, Norway, Poland, Portugal, the Slovak Republic, Slovenia, Spain, Sweden, Switzerland and the United Kingdom (Euro Chlor 2004c, Euro Chlor web site 2004). In addition, chlorine producers who are not members of Euro Chlor have contributed to Euro Chlor statistical publications, such as the chlorine plant and production data available for the 84 plants in Europe (Euro Chlor 2004c).

### 2.1.1 Production processes

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. A short description of these processes is detailed below (European Commission, 2001b).

#### 2.1.1.1 Mercury amalgam electrolysis process

In the mercury electrolyser, mercury flows concurrently with brine along the base of a cell. The mercury acts as the cathode and forms an amalgam with sodium. Chlorine is formed at the anodes, which are suspended in the brine. The anodes are constructed from titanium with a suitable rare metal oxide coating and can be raised or lowered manually or automatically to achieve optimum voltage. The amalgam flows to a reactor (denuder or decomposer) where the amalgam reacts with water in the presence of carbon (graphite) to form caustic soda and hydrogen.

Weirs and water seals in the end sections ensure that hydrogen and chlorine gas streams are contained and isolated from each other and also prevent brine from mixing with the caustic soda. Chlorine gas can leave the cell directly for further treatment and drying or can leave as a two-phase flow with the anolyte. In this case, the anolyte must be dechlorinated before returning to the denuder.

Further information on the mercury amalgam electrolysis process can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b). This includes a discussion of the parts of the process which are responsible for mercury emissions to both air and water (European Commission, 2001b, section 3.1.2.1 and following subsections, and Appendix B). Cumulative mercury emissions to air and water in 1998 are also given (European Commission, 2001, Appendix C). Due to the nature of the process, virtually no mercury is present in the chlorine gas produced.

#### 2.1.1.2 Diaphragm Electrolysis process

In the diaphragm electrolyser an asbestos diaphragm separates the anolyte and catholyte chambers. In some cases polymer modified asbestos is used as the diaphragm. Although asbestos is the most suitable material for diaphragms, new diaphragm materials are under development and are used in some facilities.

The anode is titanium with a suitable rare metal oxide coating and the cathode is steel or nickel-coated steel. The anode and cathode have a fixed position in the cell. In general the distance between the anode and the cathode is arranged for optimum voltage.

Differential hydraulic pressure causes the anolyte to flow through the diaphragm from the anolyte compartment to the catholyte compartment. Chlorine is removed from the vapour space above the anolyte normally under suction. Diaphragm cell liquor containing 9-12% caustic soda and 15-17% sodium chloride overflows from the catholyte chamber to intermediate storage and evaporation, although it can be used directly for other processes. The sodium chloride concentration of NaCl in 50% caustic soda liquor from this process is up to 1%.

Diaphragm cells can have a monopolar (cells in parallel) or bipolar (cells in series) configuration and there is a large variety of types which allows a wide range of current densities to be used. Consequently, a large number of cell designs are in operation.

Further information on the diaphragm electrolysis process can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b).

Until recently, all diaphragm plants used chrysotile asbestos as a separator within the cell. The inherent safety features of this type of separator were acknowledged by legislators and the use of asbestos in such cells remains the only derogation within the Asbestos Directive. Research and development by the industry and its suppliers has resulted in the availability of an alternative non-asbestos separator for certain geometric and electrical designs of cells. Of the nine diaphragm plants in Western Europe at the beginning of 2002, three are in the final stage of conversion to the non-asbestos substitute, one was closed permanently and announcements were made concerning the conversion of a further three to membrane technology (Euro Chlor 2003a).

### 2.1.1.3 Membrane Electrolysis process

Membrane electrolysers can also have a monopolar or bipolar configuration. In the membrane electrolysers the anolyte and catholyte chambers are separated by an ion selective membrane. In comparison with the diaphragm electrolyser there is no physical flow from the anolyte to the catholyte chamber. Instead, sodium ions pass through the membrane and form caustic soda and hydrogen in the catholyte. Caustic soda and hydrogen are produced in the catholyte compartment by the addition of water.

The anodes are made from titanium with a suitable rare metal oxide coating. The cathodes are constructed in steel or nickel and may or may not have a coating. There is some variation in the material used to manufacture of the membrane, which acts as a cation exchange.

The strength of the caustic soda in the membrane process is up to 33 % (with a final NaCl concentration of less than 100 ppm in 50 % caustic solution).

Further information on the membrane electrolysis process can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b).

### 2.1.1.4 Further processing

Generally, before the chlorine can be used, it goes through a series of processes for cooling, cleaning, drying, compression and liquefaction. In some applications, it can be used as a dry gas without need for liquefaction. Very occasionally it can be used directly from the electrolysers. Further information on these processes can be found in the BREF for the chlor-alkali manufacturing industry (European Commission, 2001b).

### 2.1.2 Production capacity

The chlor-alkali industry in Europe is very diversified with producers ranging in size from 6000 t/yr to 1.5 million t/yr chlorine capacity. Twenty percent of the producers manufacture 70% of the chlorine. The largest producer is Dow in Germany; the most geographically spread is Solvay/Solvin with production in seven European countries. Germany outstrips all other European countries in chlorine capacity. Whilst there has been some growth in capacity in Germany, the United Kingdom has seen a substantial drop. Four plants (two membrane, one diaphragm and one mixed membrane/ diaphragm) in the UK out of a total of seven have closed in the last three years. Capacity in the other countries has remained more or less static (Euro Chlor, 2003a). The locations and capacities of chlor-alkali plants in operation in Europe in 2003 can be found in Euro Chlor (2004c), which updates the data given in the BREF for the chlor-alkali manufacturing industry, figure 1.3 and table 1.1, and Appendix A. (European Commission, 2001b).

The volume of chlorine produced in the EU, and also in several nearby countries, is given in **Table 2.1**. The Western European production accounts for 83% of production capacity. Production volume in the EU has increased slightly since 1995, with the 2003 production volume being almost 107% of the 1995 value. There was a small decrease in production volume between 2000 and 2002, but in 2003 production increased to almost the 2000 production level (Euro Chlor, 2004a, Euro Chlor 2004c.)

Table 2.1 Production volume of Chlorine in 2003

| Producing area | Volume of $Cl_2$ produced, in thousands of metric tons[1] |
|---|---|
| Germany | 4 239 |
| Belgium and The Netherlands | 1301 |
| France | 1437 |
| Italy | 506 |
| United Kingdom | 694 |
| Spain, Portugal, and Greece | 741 |
| Norway, Sweden, and Finland | 534 |
| Switzerland and Austria | 135 |
| [2]Poland | 414 |
| Other Eastern European Countries[3] | 181 |
| | |
| Total for EU and nearby countries | 10 180 |

1Production figures for the countries or groups of countries reported have been rounded to the nearest thousand metric tonnes. The Total production figure has been rounded up to the nearest thousand metric tonnes. [2]Data for Poland provided by Poland, 2005. [3]Other Eastern European Countries are Hungary, the Czech Republic, the Slovak Republic, and Slovenia.

### 2.1.3 Transport

Only 7% of the chlorine manufactured in Western Europe is transported by road or rail. Where chlorine needs to be used at adjacent facilities, it is generally moved via inter-plant pipelines (Euro Chlor, 2006). This general chlorine transport by inter-plant pipelines also occurs in Poland (Poland, 2005). Of the 761,000 tonnes transported in 2005 (2004: 925,000 tonnes), 75% was moved in bulk by rail with an average distance of 419 km, 25% by road (average distance 187 km) (Euro Chlor, 2006). Over the last 50 years there have been no fatalities caused by bulk chlorine shipments in Western Europe (Euro Chlor, 2003a).

## 2.2 USES

### 2.2.1 Introduction

Chlorine is mainly used as a chemical intermediate to produce both chlorinated and non-chlorinated compounds. Many of the highest value chlorine chain products – such as polycarbonates, polyurethanes and epoxy resins – do not contain chlorine, but depend on it for their synthesis. 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).

Chlorine use in 2003 is shown in **Table 2.2.** The top six rows of the table are based on the Chlorine Industry Review for 2002-2003 (Euro Chlor, 2003a), and include the 2003 use information described above (Euro Chlor 2004c). Most of this use will be on the same site as production, but the percentage of chlorine used on the production site depends on the individual site. However, some information on the distribution of the percentage of chlorine used at the site of production is available from a Euro Chlor internal survey. This indicates that approximately 10% of sites used more chlorine than was produced on site, and the median site used approximately 96% of the on-site chlorine production. The 10% of sites which need to import chlorine from other sites will account for much of the chlorine transported by road (**Section 2.1.3).** To estimate a further breakdown of the 9% of tonnage in the "other uses" category (Euro Chlor 2004c and Euro Chlor 2003a), the extensive survey of chlorine use carried out in 1998 (Euro Chlor, 2000) has been used. A comparison of the available 2003 and 1998 data showed that the percentages of chlorine used for most applications had not changed appreciably, except for an approximate 20% increase in the amount of chlorine used in the production of inorganic chemicals, and a 20% decrease in the amount of chlorine used in solvent production. Thus the 1998 use percentages were applied to the 2003 production tonnage for the EU and nearby countries, as shown in **Table 2.1,** to estimate the chlorine uses in 2003 for the production of chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, chloro oxygenated derivatives, and as elemental chlorine.

Of the 2.2 % of chlorine production which was supplied as elemental chlorine in 1998, 39% was used as an intermediate in the production of dyestuff and pesticides and 35% was used as an intermediate in small industry. These uses will not normally be on the site of chlorine production. It has been assumed that these uses have retained these use percentages in 2003. In 1998, a further 18% was used for the disinfection of drinking water, while 4.4% was used for swimming pool disinfection. Elemental chlorine was also used, in 1998, in the pulp and paper industry (5% of elemental chlorine production). The replacement of chlorine use in the pulp and paper industry since 1998 by other processes is discussed in **section 2.2.2.2.6.**

A survey made by Euro Chlor in 1994 showed the various uses of elemental chlorine in water-based applications such as drinking water disinfection, use in the pulp and paper industry, swimming pool disinfection, sewage treatment, cooling water disinfection and use in the textile industry. These uses represented 0.8% of the 1994 production figures. The last three uses did not appear in the 1998 survey (Euro Chlor, 2000). However, in 1994 the use of elemental chlorine in the textile industry was small, being 300 tpa. This use is now thought to be negligible, as discussed in **section 2.2.2.2.5**.

There is recent information on the use of elemental chlorine in drinking water disinfection, in cooling water disinfection, and in swimming pool and sewage treatment uses (Euro Chlor 2003b). All uses show a decline in use between 1998 and 2000, with an approximate 20% decrease in the use of chlorine as a cooling water disinfectant, and approximately 6% decrease in the other uses. The 2000 use data have been corrected by the change in total chlorine production to give approximate usage data for 2003. The internal survey (Euro Chlor, 2003b) reports combined data for swimming pool and wastewater treatment use, and it has been necessary to use the 1994 use ratios (47% sewage treatment, 53% swimming pool disinfection) in order to apportion the tonnage used between the two applications. These figures are approximate, but should be considered in the context of the overall decrease in the use of chlorine gas for these purposes, and the small percentage of overall chlorine production which these uses represent. These uses are included in **Table 2.2**. The 1998 study of chlorine flow in Europe (Euro Chlor, 2000) also included 1.5% of chlorine in the category "others", which it is not possible to specify further.

Table 2.2 Reported and estimated chlorine use in 2003

| Use | Type of process (closed, batch)[1] | Industry category | Use category | Quantity used<br>Thousand tonnes per annum | Percentage of total use |
|---|---|---|---|---|---|
| PVC production | Closed | 3 | 33 | 3560[2] | 35[3] |
| Non-chlorinated polymer production | Closed | 3 | 33 | 2440[2] | 24[3] |
| Production of inorganic chemicals, including sodium hypochlorite | Closed | 3 | 33 | 1630[2] | 16[3] |
| Chloromethane production | Closed | 3 | 33 | 810[2] | 8[3] |
| Epichlorohydrin production | Closed | 3 | 33 | 510[2] | 5[3] |
| Production of solvents | Closed | 3 | 33 | 410[2] | 4[3] |
| Production of chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, and chloro oxygenated derivatives | Batch | 3 | 33 | 610[2] | 6[4] |
| Elemental chlorine used offsite as an intermediate in dyestuff and pesticide production | Closed | 3 | 33 | 87[2] | 0.85[4] |
| Small industrial offsite use of elemental chlorine as an intermediate | Closed | 3 | 33 | 77[2] | 0.76[4] |
| Drinking water disinfectants | | 15 | 39 | 33[5,6] | 0.32 |
| Swimming pool disinfectants | | 5,6 | 39 | 7[5,7] | 0.07 |
| Waste water treatment | | 15 | 39 | 6[5,7] | 0.06 |
| Cooling water disinfection | | 15 | 39 | 1[5,9] | 0.01 |
| Pulp and paper industry | | 12 | 8 | Very low[8] | Very low |
| Textile industry | | 13 | 8 | Very low[10] (0.3 in 1994) | negligible |
| | | | | | |
| Total | | | | 10 187[11] | 100.2% |

[1] The definition of closed and batch processes refers only to the steps involving chlorine. [2] These quantities used have been estimated from use percentages. [3] Data from Euro Chlor (2003). [4] Data estimated from 1998 use figures (Euro Chlor, 2000), and 2003 production figures (Euro Chlor 2004c). [5] Data estimated from 2000 information (Euro Chlor, 2003b), updated by the 2003/2000 production ratio. [6] Use in this category declined by approximately 6% between 1998 and 2000 (Euro Chlor, 2003b). [7] The 1994 chlorine use data have been used to estimate the ratio of swimming pool disinfectant to wastewater disinfectant use. [8] The replacement of chlorine use by other processes is discussed in section 2.2.2.2.6. [9] Use in this category declined by approximately 20% between 1998 and 2000 (Euro Chlor, 2003b). [10] The lack of any evidence for continuing use of chlorine gas in the textile industry is discussed in section 2.2.2.2.5. [11] This total is higher than the actual 2003 production total of 10 180 000 tonnes, due to rounding errors in the estimated use percentages.

## 2.2.2 Scenarios

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.

### 2.2.2.1 USE of chlorine as a chemical intermediate

#### 2.2.2.1.1 Use of chlorine in PVC production

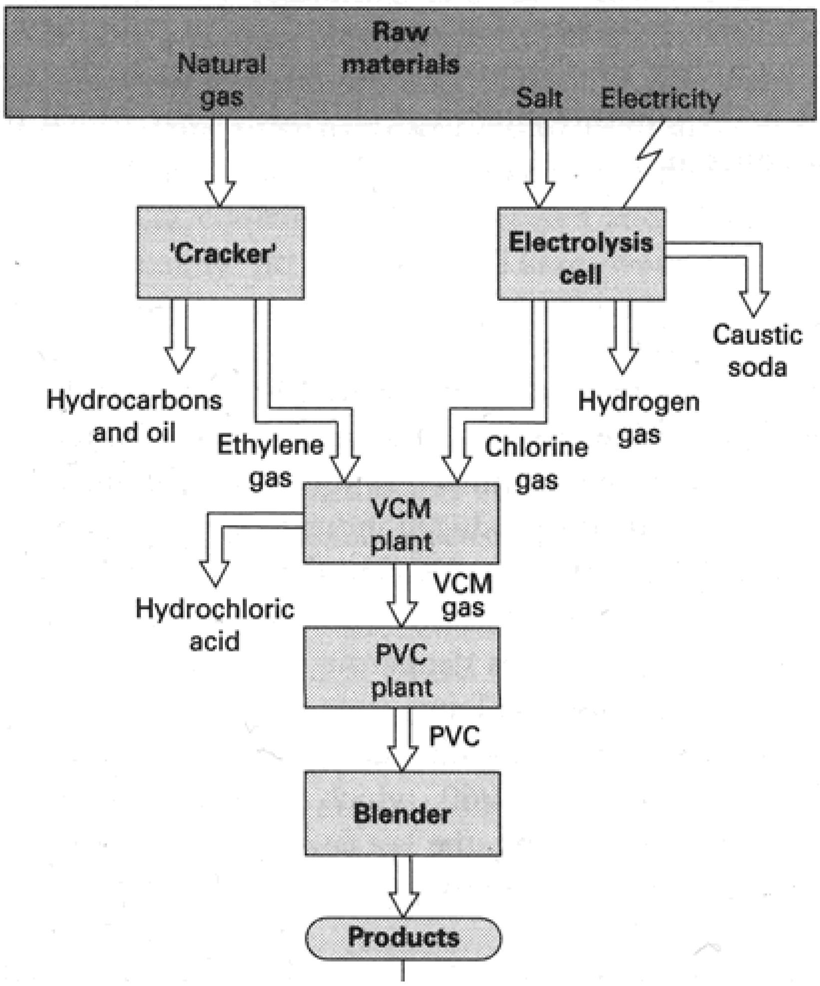
In 2003, 35% of chlorine production was used as an intermediate in the production of Poly Vinyl Chloride, or PVC (Euro Chlor, 2004c). The chemical process for making PVC involves three steps: first, production of the monomer, chloroethane (or vinyl chloride monomer, VCM); then the linking of these monomer units in a polymerisation process; and finally the blending of the polymer with additives. In this process, shown schematically in **Figure 2.1**, ethylene and chlorine are combined to form a liquid, ethylene dichloride (i) which is then heated to give vinyl chloride (or chloroethane) (ii). Chloroethane can also be produced via the oxychlorination route, which is based on ethene, HCl and oxygen. Many plants use a combination of both processes. Chloroethane is then removed, leaving hydrogen chloride gas, which is recovered and recycled in the oxychlorination process. The chemical reaction is:

$$H_2C{=}CH_2 + Cl_2 \rightarrow \underset{(i)}{ClH_2C\text{-}CH_2Cl} \rightarrow \underset{(ii)}{H_2C{=}CHCl} + HCl$$

Chloroethane is the main product, but both HCl and dichloroethane can also be used as end-products. HCl and dichloroethane from outside sources are sometimes fed into the system, serving as intermediates for manufacture of Chloroethane. Chlorinated hydrocarbons are formed as unintentional by-products. Chlorinated hydrocarbons are converted into HCl or are used as feedstock for other products, such as perchloroethylene (also known as PER, tetrachloroethylene or tetrachloroethene.) Some common salt may be formed as waste (Euro Chlor, 2000).

In further stages of the production process, pressure is applied to vinyl chloride (dispersed in water as a suspension or an emulsion) in high pressure chambers at temperatures of 50-70°C. The role of water is to remove and control the heat given off in the polymerisation process. PVC forms as tiny particles which grow and when they reach a desired size the reaction is stopped and any unreacted vinyl chloride is distilled off and re-used. The PVC is separated off and dried to form a white powder (Bristol University website, 2001).

Figure 2.1 Schematic of the PVC production process (Bristol University Website, 2001)



In the PVC production process, chlorine is usually generated on site, and delivered to the required location by pipelines which have been constructed specifically for the purpose of chlorine gas transport. Thus chlorine releases to air are minimal. Any chlorine releases, to air or to water, due to PVC production will have been included in the chlorine releases which are reported as emissions due to chlorine production on the manufacturing site.

### 2.2.2.1.2 Other intermediate uses of chlorine

In most of the larger applications below, chlorine gas will generally be produced on site, as described for PVC production (**section 2.2.2.1.1).** Note that 90% of all chlorine used is produced on site, or transferred to neighbouring installations by pipeline (Euro Chlor, 2003a). Also any chlorine releases, to air or to water, due to production of other chemicals at sites at which chlorine production occurs will have been included in the chlorine releases which are reported as emissions due to chlorine production on the manufacturing site.

### Chloromethanes

In 2003, 8% of chlorine production was used in the production of chloromethanes. These products are principally intermediates in other chemical processes and include methylchloride, methylene chloride, chloroform and carbon tetrachloride. Methylene chloride is mainly used as a solvent. In 1998, this chain consumed 8.4% of the total chlorine available with a recycling index of 30%. Thus 30% of the total chlorine used in these products came from recycled sources (Euro Chlor, 2000).

There are two routes for the production of chloromethanes. One route is based on methane and chlorine, while the other route utilises methanol, hydrogen chloride (HCl) and chlorine, with surplus HCl being recycled (Euro Chlor, 2000).

The main products are monochloromethane (methyl chloride), dichloromethane (methylene chloride), trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride). The principal by-product is hydrochloric acid, an aqueous solution of HCl. Waste products are generated as chlorinated hydrocarbons (CHCs) and salt.

### Other C2 derivatives, solvents and intermediates

This chain contains a number of products, some of which are chlorinated (e.g. the solvents trichloroethylene and perchloroethylene) and others which are not (e.g. ethene amines, polyvinylidenefluoride and some hydrofluorocarbons). Between the early 1980s and 1998 there was a 45% reduction in production of these chemicals, largely due to emission control improvements by dry cleaning units and the phase-out of emissive uses of 1,1,1 trichloroethane under the Montreal Protocol. In 1998, this chain consumed 5% of chlorine production. It did not appear as a separate entry in the 2002 or 2003 use information (Euro Chlor, 2000; Euro Chlor 2003a, Euro Chlor 2004c).

C2 derivatives cover a range of chlorinated compounds made using various production processes. Raw materials (input) can be chlorine, hydrogen chloride, light-end-chlorinated hydrocarbons and dichloroethane. HCl, chlorinated hydrocarbons and tetrachloroethene can be both raw materials and end-products (Euro Chlor, 2000).

The products in this category are: the solvents trichloroethene (TRI), tetrachloroethene (PER) and 1,1,1-trichloroethane and the monomer 1,1-dichloroethene (VDC). There is also a small production of vinyl chloride monomer and tetrachloromethane arising as by-products from some of these processes, which are part of the C2 chain. Additional by-products from all processes are HCl and chlorinated hydrocarbons, with salt as a waste product.

### Allyl chloride-epichlorohydrin (AC-ECH)

Allyl chloride is used for manufacturing pharmaceuticals, pesticides and is the precursor for epichlorohydrin used for epoxy resins. Although only utilising 5% of chlorine production, there has been a 35% increase since 1983(Euro Chlor, 2000).

Epichlorohydrin (ECH), or 1-chloro-2,3-epoxypropane, the main chlorine-containing end-product of this chain, is produced in three steps. The first step (a) is the formation of chloropropene-1 (allyl chloride, AC) by chlorination of propene-1. In the second step (b) conversion of AC with hypochlorite into 1,2- and 1,3-dichlorohydroxy-propene (dichlorohydrin, DCH) takes place. In the final step (c) DCH is converted into ECH with either sodium hydroxide or calcium hydroxide (Euro Chlor, 2000).

Epichlorohydrin is a liquid at room temperature and pressure. Other end-products in these processes are allyl chloride, 1,3-dichloropropene (DCP) and 1,2,3-trichloropropane (TCP). HCl is a by-product, with CHCs and chloride as waste products.

Polyurethanes, epoxides and polycarbonates

In 2002 and 2003, 24 % of chlorine produced was used in the production of non-chlorinated products, including isocyanates and oxygenates, which are used in the production of polyurethanes, epoxides and polycarbonates. Polyurethanes themselves do not contain chlorine and the di-isocyanate production process yields large amounts of HCl which is variously used in ethylene dichloride (dichloroethane) production, the merchant hydrochloric acid market or neutralised to common salt. The precursors for polyurethanes are propene oxide and diisocyanates. Polycarbonates are versatile engineering plastics. There is no chlorine in the end product and chlorine is discharged from this chain in the form of innocuous inorganic chloride. Methylene chloride is also used as a reaction medium (Euro Chlor, 2000).

*Propene oxide production*

Production of propylene oxide (propene oxide, PO) by the chlorohydrin route takes place in two main steps: (a) hydrochlorination of propene into 1-chloro-2-hydroxypropene (propylene chlorohydrin) and (b) conversion of 1-chloro-2-hydroxypropene into 1,2-epoxypropene (propene oxide, PO). Non-chlorine based production can use peroxidate of isobutene or ethylbenzene in co-production with 1,1-dimethylethanol or styrene. In the mid-1990s, half of total European capacity was based on the chlorine route (Euro Chlor, 2000).

The end-product of this production process is almost exclusively propene oxide. By-products are dichloropropene and chlorinated hydrocarbons, and chloride is the main waste product (Euro Chlor, 2000).

The chlorinated hydrocarbons are incinerated to HCl or are used as feedstock for the chemical industry. Chloride is a waste stream and enters the natural environment. Chlorine in chlorinated hydrocarbons appears as chloride in HCl, chlorine in chlorinated compounds or, when neutralised, inorganic chloride (Euro Chlor, 2000).

*Phosgene derivatives*

Phosgene is used as a precursor in the production of di-isocyanates, which are precursors of polyurethanes. This is its largest use, in terms of chlorine volume. It is also used to produce polycarbonates, which are second in volume of chlorine use. The third type of phosgenation product, in volume of chlorine use, is the isocyanates, which are intermediates for manufacture of crop protection agents and pharmaceuticals. This group of products is an important supplier of recycled hydrogen chloride in the chlorine industry, either as feedstock for oxychlorination or hydrogen chloride electrolysis (Euro Chlor, 2000). These groups will be described below.

*Phosgene derivatives: Diisocyanate production:*

Production of most isocyanates is based on phosgenation of primary amines. Toluene diisocyanate (TDI) production is based on the raw materials toluene diamine (a mixture of 2,4- and 2,6- isomers) and phosgene, and either monochlorobenzene or orthodichlorobenzene is used as solvent/reaction medium. The resulting diisocyanate isomers are separated by distillation or crystallisation. During diisocyanate formation, chlorine is converted into HCl (Euro Chlor, 2000).

Diphenylmethane diisocyanate (MDI) production is based on the raw materials diphenylmethane diamine and phosgene, whilst monochlorobenzene is the reaction medium. The phosgenation step yields an aromatic diisocyanate mixture, similar in composition to the polyamine. Typically, a mixture of MDI and its dimer and trimer is produced. Polymeric MDI is formed after phosgenation of a polymethylphenyl amine. Also, in the case of MDI, HCl is formed as a by-product. Other diisocyanates formed by phosgenation processes are the aliphatic diisocyanates (ADI), which consist of hexamethylene diisocyanate (HDI), hydrogenated MDI, isophoron diisocyanate (IPDI) and trimethylhexamethylene diisocyanate (TMDI). In all cases, HCl is released during phosgenation, which takes place in a solvent (Euro Chlor, 2000).

The only chlorine-containing by-product of these production processes is HCl. The end-products are diisocyanates. Where no HCl is recovered, chlorine appears as waste chloride from neutralisation of the HCl (Euro Chlor, 2000).

*Phosgene derivatives: Polycarbonate production*

In a two-phase process, phosgene reacts with bisphenol-A (BPA) to yield the acid chloride of diphenyl propane dicarbonate. Polymerisation and polycondensation gives polycarbonate. The two phases are methylene chloride (MC) and an aqueous solution of sodium hydroxide. During the process, enrichment of polycarbonate takes place in the MC phase. Hydroxide in the other phase neutralises the HCl released by the reaction at the water-MC interface. A small amount of chain terminator is added (phenol or p-tertiary butylphenol) and triethyl amine is used as a catalyst. Water/organic solution separation and washing of the MC solution gives polycarbonate (Euro Chlor, 2000).

The process yields polycarbonate, an amorphous thermoplastic material with interesting characteristics for many technical applications. Polycarbonates do not contain chlorine, and chlorine flow ends at the stage of polymerisation and polycondensation: chlorine, phosgene, and chloride in solution. During production, methylene chloride (sometimes monochlorobenzene) is used and losses lead after a certain period to chloride by physical degradation (in nature or by incineration). In Germany, a polycarbonate recycling process is in use for recovering used CDs to make products such as computer housing (Euro Chlor, 2000).

Chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, and chloro oxygenated derivatives

In 2003, approximately 6% of chlorine production was used to produce chlorinated paraffins, chlorinated acyclic derivatives, chloro aryl derivatives, and chloro oxygenated derivatives.

### *Chlorinated paraffins*

Chlorinated paraffins are a group of chemicals manufactured by chlorination of liquid n-paraffins or paraffin wax and contain 30-70% chlorine. During production, HCl is formed as a by-product. For a given feedstock, increasing chlorine content results in products with higher viscosity and density. Chlorinated paraffins are grouped into a number of distinct families, depending on the chain-length of the feedstock. These are short-chain, $C_{10}$ to $C_{13}$ paraffins, medium-chain, $C_{14}$ to $C_{17}$ paraffins, long-chain, $C_{18}$ to $C_{20}$ paraffins, and wax, with a $C_{25}$ average chain length (Euro Chlor, 2000).

### *Chlorinated acyclic derivatives*

Production of higher alkanes and alkenes - excluding chlorinated paraffins - takes place by chlorination of the corresponding alkanes and alkenes, where chlorine is the only chlorine-containing raw material. The products are chlorinated rubbers, chlorinated polyolefins (Cl-PVC, Cl-PE), chlorobutenes (chloroprenes) and linear alkylbenzenesulfonate (LAS), made by sulfonation of linear alkylbenzene. HCl is a by-product and chlorinated hydrocarbons are waste products (Euro Chlor, 2000).

### *Chloro aryl derivatives*

Chlorination of arenes (such as benzenes and toluenes) gives substitution of hydrogen(s) in the ring by one or more chlorine atoms, depending on the circumstances and the catalysts used. The reactions are exothermic. The products in this group are chlorobenzenes, chlorotoluenes, aryl chloroalkanes and chlorophenols. HCl is a by-product and chloride and CHCs are waste products (Euro Chlor, 2000).

### *Chloro oxygenated derivatives*

Chlorination of carbonic acids such as acetic acid and propionic acid are the first steps in the production of this chain. Other steps are (a) the formation of MCPA (monochloro phenoxy acetic acid, a phenoxy herbicide), (b) the formation of MCPP (propionic acid instead of acetic acid) and (c) the formation of carboxy methylcellulose (CMC). In the chlorination step, monochloroacetic acid and monochloropropionic acid are products, HCl is a by-product and at steps (a), (b) and (c), chloride is released as a waste product. MCPA and MCPP are chlorine-containing end-products and CMC is a non-chlorine-containing end-product. (Euro Chlor, 2000).

### Inorganic chemicals

In both 2002 and 2003, 16 % of chlorine production was used in the production of inorganic chemicals. Products in this category are synthetic hydrogen chloride (from burning hydrogen and chlorine), sodium hypochlorite, sulphur chlorides, phosphorus chlorides, titanium dioxide, bromine and silicon. Chlorine use for these products has increased by 39% between the early 1980s and 1998, and is still increasing. Most of the chlorine usage leads to the formation of chloride, such as sulphur chlorides, metal chlorides and phosphorus chlorides (Euro Chlor, 2000).

At present sodium hypochlorite is manufactured by the absorption of chlorine in approximately 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. Packed towers containing caustic soda are often used as emergency absorption plants for the gas venting of various chlorine handling operations and this solution is then strengthened with chlorine to provide finished material. Most of the producers are chlor-alkali manufacturers, who produce sodium hypochlorite largely as part of their chlorine production. Further information is available in the Sodium Hypochlorite Risk Assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 2.1.1.)

Chlorine in hypochlorite ends up as chloride, becoming a part of the natural cycle. At OSPAR's request, thorough investigation was carried out of the fate of chlorine after use in water treatment and cleaning. It appeared that the amount of AOX (absorbable organic halogens) was negligible (Euro Chlor, 2000). Further information on hypochlorite may be found in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, with information on AOX by-products in section 3.1.2.2).

For the production of titanium dioxide, make-up chlorine is used to compensate for losses from an essentially closed-loop process (titanium ore + $Cl_2$ → titanium tetrachloride → titanium dioxide + $Cl_2$) (Euro Chlor, 2000).

Off-site uses of chlorine as an intermediate

In this category, chlorine - supplied in rail tankers, drums and cylinders - has several applications. These include use as an intermediate in the production of dyestuffs and pesticides and also use as an intermediate in small industrial uses. In 1998 just over 2% of the chlorine produced was supplied as elemental chlorine, and this percentage has been assumed to apply in 2003.

Of the 2.2% of the overall chlorine production which was supplied as elemental chlorine in 1998, 39% was used as an intermediate in the production of direct use dyestuff and pesticides and 35% was used in small industry (Euro Chlor, 2000). Elemental chlorine uses include oxidation, chlorination and epoxidation. In certain cases, this can lead to the formation of chlorinated organic pollutants. In most cases, hydrolysis of products formed will result in chloride. In others, additional water treatment will remove the chlorinated compounds (Euro Chlor, 2000).

### 2.2.2.2 Non-Intermediate use of chlorine

Chlorine also has non-intermediate uses, including use in water-based applications including disinfection processes. These include drinking water disinfection (see **section 2.2.2.2.1**), swimming pool disinfection (see section **2.2.2.2.2**), waste water disinfection (see section **2.2.2.2.3**), and use as a biocide in cooling water applications (see section **2.2.2.2.4**). There was almost no use of elemental chlorine in the areas of textile bleaching (see section **2.2.2.2.5**) or in the pulp and paper industry (see section **2.2.2.2.6**).

#### 2.2.2.2.1 Use in drinking water disinfection

Chlorine gas is used as a disinfectant for drinking water supplies, especially in larger facilities. In 2003, approximately 32 thousand tonnes of chlorine were used for this purpose

(**Table 2.2**). At environmental pH, the chlorine species responsible for the biocidal action of chlorine are hypochlorous acid, HOCl, and hypochlorite, $OCl^-$ (See **section 1.4**). This use is covered by the Emission Scenario Document on drinking water disinfectants (Herrmann and Wagner, 2003).

The required dosage cannot be determined directly without experimentation. The amount of chlorine added to water depends on the specific content of oxidizable compounds, the amount needed to kill the microorganisms, plus a sufficient reserve to maintain a minimum concentration of "*free available chlorine*" at each point in the water pipe. To maintain this requirement the range for chlorine dosage is about 0.1 $mg.l^{-1}$ for groundwater and up to 0.5 $mg.l^{-1}$ for surface water (Herrmann and Wagner, 2003).

The active biocidal species, hypochlorous acid, HOCl, and hypochlorite, $OCl^-$, are also generated when sodium hypochlorite is used for drinking water disinfection. Disinfection by-products are the same, whether chlorine gas or sodium hypochlorite is the initial source of the active biocide. Disinfection by-products for both chlorine gas and sodium hypochlorite are included in the Sodium Hypochlorite Risk Assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, Sections 3.1.1.7 and 3.1.2.7), which includes the consumption of both chlorine and sodium hypochlorite for this purpose. This risk assessment should be consulted for further information on disinfection by-products.

#### 2.2.2.2.2 Use in swimming pool disinfection

Swimming pools which are not natural pools or small private pools are called circulation baths. Water treatment is needed to obtain and maintain the desired chemical and bacteriological quality of the swimming water. In Europe, four main products are used: hypochlorites of sodium or calcium, chloroisocyanuric salts and chlorine gas. These four products provide a permanent content of hypochlorous acid (HOCl, active chlorine) in the water Chlorine gas is used as a disinfectant in larger, more heavily used swimming pools (WHO, 2000a).

In 2002, approximately seven thousand tonnes of chlorine gas are estimated to have been used in swimming pool water disinfection (see **Table 2.2**). Note that this approximate usage is based on the 1998 usages of chlorine in swimming pool disinfection and in waste water treatment (Euro Chlor, 2000). Chlorine used for these two purposes declined by 6% between 1998 and 2000 (Euro Chlor, 2003b).

Hypochlorous acid is also generated when sodium hypochlorite is used as a swimming pool disinfectant (see **section 1.4**). The Sodium Hypochlorite risk assessment (RAR, Draft of November 2005, section 3.1.1.4) includes chlorine gas among the sources of HOCl (active chlorine) in swimming pools, and covers the HOCl generated from chlorine gas in its calculations of chlorine entering the environment from this use (RAR, Draft of November 2005, section 3.1.2.4). Chlorinated disinfection by-products are also considered in the Sodium Hypochlorite risk assessment (RAR, Draft of November 2005, sections 3.1.1.4 and 3.1.2.4), which should be consulted for further information.

#### 2.2.2.2.3 Use in waste water treatment

Approximately six thousand tonnes of chlorine gas were used in waste water treatment applications in 2003 (see **Table 2.2).** Note that this approximate usage is based on the 1998 usages of chlorine in swimming pool disinfection and in waste water treatment (Euro Chlor, 2000). Chlorine used for these two purposes declined by 6% between 1998 and 2000 (Euro Chlor, 2003b).

This chlorine was used almost exclusively for the post-chlorination of sewage treatment plant effluent before discharge to the marine environment. Details of the treatment process, and of halogenated by-product formation, are included in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, sections 3.1.1.5 and 3.1.2.5). The Sodium Hypochlorite risk assessment includes the chlorine sourced from chlorine gas in the calculation of the total chlorine released to the environment from this use. It should be consulted for further information on the effluent disinfection process, and on halogenated by-product formation.

### 2.2.2.2.4 Use in cooling water treatment

Approximately one thousand tonnes of chlorine gas were used as a biocide in cooling water systems to prevent biofouling in 2003 (see **Table 2.2**). This use declined by 20% between 1988 and 2000 (Euro Chlor, 2003b). A BREF is available which covers the use of both chlorine gas and hypochlorite in industrial cooling applications (European Commission, 2001a). Both chlorine and hypochlorite use are included as recommended techniques.

Chlorine gas used in this application will disassociate in water to produce hypochlorous acid and hypochlorite, which are the active biocides (see **section 1.4**). These are also generated when sodium hypochlorite is used as a biocide in cooling water applications. The sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.1.9), gives details of the different types of cooling water systems in which sodium hypochlorite and chlorine gas can provide the active biocides to prevent biofouling, and the process of biocide administration in each of these systems. Chlorinated disinfection by-products are also considered in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.2.9). The Sodium Hypochlorite risk assessment should be consulted for further information on both the processes used for biocide administration in cooling water systems, and the formation of chlorinated by-products.

### 2.2.2.2.5 Use in textile processing

Although historically hypochlorite has been very widely used in the textile finishing industry, the use of chlorine gas in textile finishing in Western Europe had declined to 300 tonnes per year by 1994, as shown by the Euro Chlor 1994 internal survey. Since 1994 the use of chlorine gas for this purpose is expected to have almost ceased. The Sodium Hypochlorite risk assessment (RAR, Draft of November 2005 section 3.1.1.6) states that today the only use of hypochlorite in textile processing in Europe is for the preshrinking of wool. Hypochlorite has been superseded by other substances in former uses such as stonewashing jeans, whitening of cotton and decolouration of dyed textiles.

Wool chlorination, which prevents further shrinkage of wool fibres, may use chlorine gas, but preferably uses the sodium or calcium salts of the dichloro-isocyanuric acids as these salts are available in solid phase, and allow a slow release of NaClO in water, thus improving the control of operational conditions. Chlorine gas may be produced during this process, as it is carried out under acid conditions and thus requires a high degree of enclosure of the plants, the presence of abatement system of gaseous emission, and a neutralisation stage. The Sodium Hypochlorite risk assessment (RAR, Draft of November 2005, section 3.1.1.6) gives further information on the process used for wool pre-treatment.

By-products of hypochlorite use in textile processing are discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, sections 3.1.1.6 and 3.1.2.6).

#### 2.2.2.2.6 Use in the pulp and paper industry

In the past, chlorine and sodium hypochlorite were used in large amounts in pulp and paper bleaching. However, as discussed in the Sodium Hypochlorite risk assessment (Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.1.8), their use in pulp bleaching has been completely been replaced by the Total Chlorine Free (TCF) and Elemental Chlorine Free (ECF) processes in Western Europe. The current uses of hypochlorite are limited to two specific purposes. The first is as a means of disinfection of the paper machine system to discourage the proliferation of unwanted microorganisms. The second is as a means of breaking down the wet strength resins used in some grades of tissue when reject tissue is being processed for use in tissue manufacture.

The use of hypochlorite as a system cleaner occurs during machine shut down, and involves the addition of sodium hypochlorite solution to paper machines partially filled with clean water, followed by vigorous circulation of this solution around the system. It would not be practical to use chlorine gas as a substitute for sodium hypochlorite for this purpose, as the addition process would not be feasible.

## 2.3 TRENDS

Chlorine production increased strongly from the 1950s until the middle of the 1970s. From the mid 1970s, growth levelled off and the chlorine industry in Western Europe is today a mature business. Chlorine production appears to be in a direct relation to GDP (Gross Domestic Product) evolution from the 1980s onwards (**Figure 2.2.**) (Eurochlor, 2000).

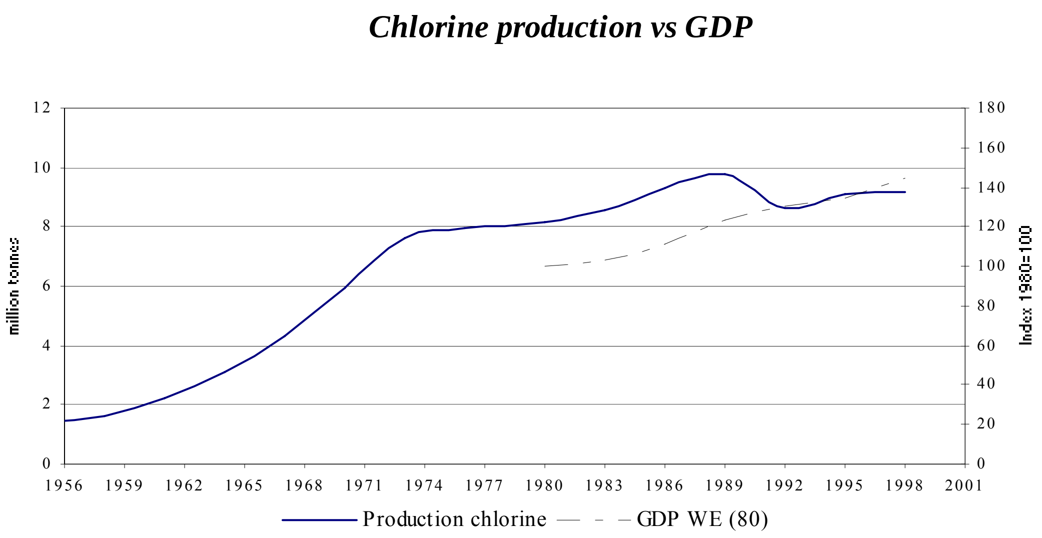


Figure 2.2 Chlorine Production

Geographical trends in the production capacity (top graph) and the production (lower graph) of chlorine are shown in figure 2.3. All data is shown relative to the situation in 1970, with both production capacity and production indices set to 100 for that year. It can be seen that production and production capacity have increased most strongly in Spain, Portugal, and Greece, with Germany and Belgium and the Netherlands also showing increases greater than that seen in Europe overall. Production capacity and production in Italy, the UK, and the Nordic countries are similar to, or slightly less than, the levels seen in 1970.

Recently, there was very little change in the proportions of chlorine used in different ways between 2001 and 2002, with a small increase in propylene oxide production being offset by drops in chlorinated solvents and inorganic uses. Sales of the chlorinated solvents trichloroethylene (TRI), perchloroethylene (PER) and methylene chloride declined overall for the seventh successive year. The 2003 and 2002 use data are very similar, with only rounding off errors increasing use in PVC production to 35% of the 101% production total (Euro Chlor 2004c), as compared to 34% of the 100% production total reported for 2002 (Euro Chlor, 2003a)

Use of elemental chlorine in non-intermediate uses has decreased 49% since 1983. This is mainly due to the phase-out of chlorine in pulp bleaching (see **Section 2.2.2.2.6**, and also the Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.1.8) and in textile applications (See **Section 2.2.2.2.5**, and also the Risk Assessment Report for Sodium Hypochlorite, Draft of November 2005, section 3.1.1.6). Remaining applications in Europe are for disinfection of drinking water, swimming pools and some chemical reactions. Use in swimming pool water treatment has also decreased, but has been mainly substituted for by sodium hypochlorite (Euro Chlor, 2000). Elemental chlorine now accounts for about 2% of total chlorine use.

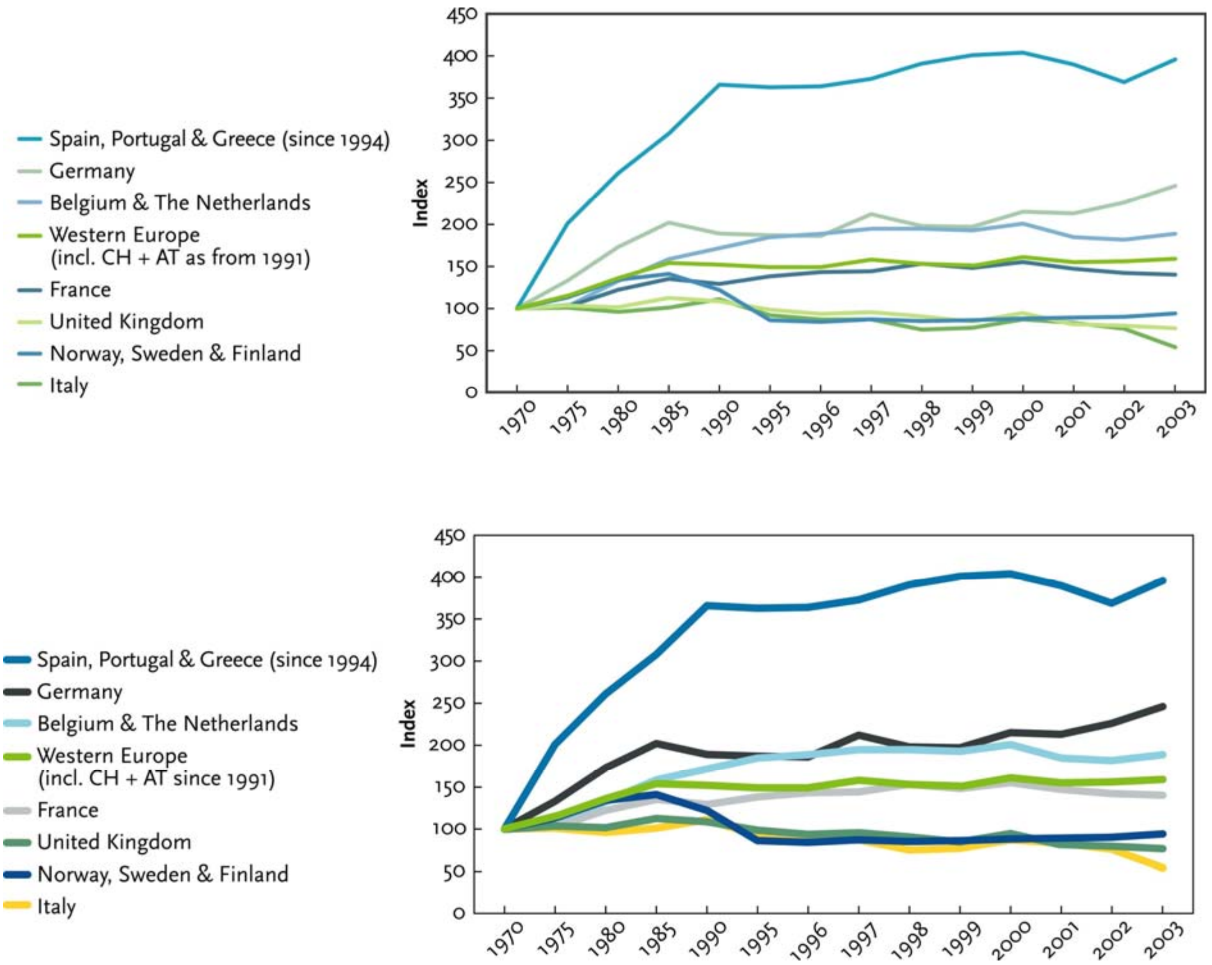


Figure 2.3 Geographical trends in the production capacity (top) and production (bottom) of chlorine since 1970

## 2.4 LEGISLATIVE CONTROLS

Chlorine is classified as toxic, irritant, and dangerous to the environment under Directive EEC 67/548. Further details are given in section.1.5. Chlorine production is regulated under the Seveso II directive, Council Directive 96/82/EC, and is also subject to the Integrated Pollution Prevention and Control legislation, Council Directive 96/61/EC. Transport of chlorine is covered by the UN recommendations on the transport of dangerous goods (United Nations, 2001). Occupational exposure to chlorine is regulated, and legislative controls also exist on the uses of chlorine in drinking water disinfection and in the disinfection of swimming pool water.

### 2.4.1 Chlorine Production

Chlorine production is regulated under the Seveso II directive, Council Directive 96/82/EC, which requires the operator to take all measures necessary to prevent major accidents, and to limit their consequences for man and the environment. As part of this directive, production facilities containing 10 tonnes or more of chlorine at any one time are required to notify the appropriate Member State of the existence of the facility and of the processes taking place therein, and to draw up and implement a comprehensive major accident prevention policy. Production facilities containing 25 tonnes or more of chlorine at any one time must prepare a Safety Report, which will contain the necessary information to allow the appropriate Member State to examine and evaluate the processes being carried out, and if necessary, to prohibit their continuation. Each Safety Report must be updated every five years, or more often if necessary.

Chlorine emission, especially to air, from chlorine production facilities is regulated under the Integrated Pollution Prevention and Control legislation, Council Directive 96/61/EC. The IPPC directive lays down measures designed to prevent or, where that is not practicable, to reduce emissions to the air, water and land in order to achieve a high level of protection of the environment taken as a whole, without prejudice to other relevant Community provisions. In accordance with this directive, a reference document on the best available techniques, or BREF, has been prepared for the chlor-alkali manufacturing industry (European Commission, (2001b). This BREF is also concerned with the emission of other substances, including mercury from the mercury cell electrolysis process, one of the processes by which chlorine is produced. In accordance with the IPPC legislation, inventories of chlorine emissions are collected and published regularly.

### 2.4.2 Transport

The UN recommendations on the transport of dangerous goods (United Nations, 2001) state that chlorine should be transported in un-refrigerated portable tanks, with an increased thickness of the tanker shell. Detailed specifications for tank construction and filling procedures are given in the UN recommendations. No other form of chlorine transport is recommended in these recommendations.

### 2.4.3 Occupational Exposure

Short-term (15 minute) indicative occupational exposure limit values for chlorine of 1.5 mg/m$^3$ or 0.5 ppm by volume (ppmV) are proposed in the draft second list of indicative occupational exposure limit values, proposed in implementation of Council Directive 98/24/EC, and in particular Article 3 thereof. The table below shows occupational exposure limits for chlorine in European countries. In almost all countries, the limit for long-term exposure (8 hours time weighted average, or TWA) is 0.5 ppmV or 1.5 mg/m$^3$. The only exception is The Netherlands, where limits are higher. In some cases, a short-term exposure limit (STEL) of 1 ppmV is applied.

Table 2.3 Occupational exposure limits for chlorine in European Countries

| Country | Limit | | Reference |
|---|---|---|---|
| | Long term exposure | Short term exposure | |
| Austria | MAK: 0.5 ppmV; 1.5 mg/m3 | Ceiling: 0.5 ppmV; 1.5 mg/m$^3$ | Austria (2003). |
| Belgium | 8-hour TWA: 0.5 ppmV; 1.5 mg/m$^3$ | 15-minute STEL: 1 ppmV, 2.9 mg/m$^3$ | Belgium (2002). |
| Denmark | TWA: 0.5 ppmV, 1.5 mg/m$^3$ | | Denmark (2002) |
| Finland | 8-hour limit: 0.5 ppmV, 1.5 mg/m$^3$ | 15-minute limit: 1 ppmV, 2.9 mg/m$^3$ | Finland (2002). |
| France | | VLE (valeur limite d'exposition): 1 ppmV, 3 mg/m $^3$ | France (2003). |
| Germany | TRGS 900 limit value: 0.5 ppmV, 1.5 mg/m$^3$ | MAK value should never be exceeded. | Germany (2003). |
| Greece | 8-hour TWA: 1 ppmV, 3 mg/m$^3$ | 15 minute (STEL: 1 ppmV, 3 mg/m$^3$ | Greece (2001). |
| Ireland | 8-hour OEL (TWA): 0.5 ppmV, 1.5 mg/m$^3$ | 15-minute OEL (STEL): 1 ppmV, 3 mg/m$^3$ | Ireland (2002). |
| The Netherlands | MAC ceiling: 1 ppmV, 3 mg/m$^3$ | | Netherlands (2003). |
| Norway | threshold limit value: 0.5 ppmV, 1.5 mg/m$^3$ | ceiling value: 1 ppmV, 3 mg/m$^3$ | Norway (2003). |
| Poland | 1.5 mg/m$^3$ | 9 mg/m$^3$ | Poland ( 2005) |
| Spain | 8-hour (VLA-ED): 0.5 ppmV, 3 mg/m$^3$ | 15-minute STEL (VLA-EC): 1 ppmV, 3 mg/m$^3$ | Spain (2003). |
| Sweden | Level Limit Value (NGV) 0.5 ppmV, 1.5 mg/m$^3$ | Ceiling Limit Value (TGV): 1 ppmV, 3 mg/ m$^3$ | Sweden (2000). |
| Switzerland | TWA 0.5 ppmV, 1.5 mg/m$^3$ | STEL 0.5 ppmV, 1.5 mg/m$^{3.}$ Freq. X Duration in minutes/shift: 15 min | Switzerland (2003). |
| United Kingdom | TWA 0.5 ppmV, 1.5 mg/m$^3$ | STEL 1 ppmV, 2.9 mg/m$^3$ | UK (2003). |

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

### 2.4.4 Drinking water:

Admissible quantities of free available chlorine in drinking water for different European countries generally vary between 0.1 and 0.5 mg/l. For example, in Poland the drinking water limit for chlorine is 0.3 mg/l. The WHO guideline value is up to 5 mg/l (WHO 2003). Chlorination by-products are also covered by regulation in the EU, with total trihalomethanes being limited to 0.1 mg/l in Council Directive 98/83/EC on the quality of water intended for human consumption (Council of the European Union (1998)). The WHO Guidelines also give values for by-products of chlorine disinfection of drinking water, such as trihalomethanes, halogenated acetonitriles, chlorinated acetic acids, and chloralhydrate, which is formed by reaction of chlorine with humic acids, and has the lowest guideline value (10 µg/l). The WHO Guidelines stress that it is important to optimize treatment processes and to ensure that these remain optimized in order to control residuals of chemicals used in drinking water treatment and the formation of disinfection by-products (WHO 2003).

### 2.4.5 Swimming pool:

National (or regional) legislation sets various parameters in order to guarantee the sanitary quality of water in public swimming pools. Suitable disinfectants include gaseous chlorine (mostly used in large swimming pools), sodium hypochlorite, calcium hypochlorite (mostly used in private swimming pools), and chloroisocyanurated derivatives (OSPAR, 1999; WHO, 2000a). These disinfectants are used in all countries in most cases.

Water used in swimming pools must be drinking water from a public water supply system. The quantity of top-up water is usually regulated at minimum 30 l/swimmer, and filtration is compulsory. Complete and regular emptying of pools is sometimes called for (for example, twice a year). Due to the potential environmental impact of swimming pools, legislation requires the water to be discharged into the natural environment or into the public sewer networks (OSPAR, 1999).

The main regulations relative to swimming pools relate to the minimum content of free available chlorine, and the pH which has to be in the optimum range for hypochlorous acid generation (WHO, 2000b). Some countries give a maximum free available chlorine (1.4 mg/l, France) others a maximum of urea content (Belgium, Netherlands). Other parts of the regulations cover the number of swimmers per m² and the quantities of air and water changes per swimmer or per year (OSPAR 1999). The Spanish regulations originate in the specific Autonomic Communities, several of which specify higher free residual chlorine levels at higher pH values, and some of which give preferred and also admissible values for pH, residual free chlorine, and combined chlorine levels. Some quality parameters for swimming pool water in EU countries are given in **Table 2.4**, with the Spanish regulations (Spain, 2005) grouped and summarised for general comparative purposes.

Disinfection by-products are considered in the WHO report (WHO, 2000a). The WHO report recommends that, for sporadic adult swimmers and pool attendants/lifeguards in chlorine-disinfected pools operated under typical conditions, with low chloroform levels in air and water, the presence of disinfectant by-products is not an issue, and guideline values are not required in indoor or outdoor pools. For worst case exposure scenarios, and for children and competitive swimmers, control of exposure by good ventilation, use of alternative disinfectants, pre-ozonation, effective flushing, and control of precursor addition through pre-swim showering and toilet use are recommended in the WHO report (WHO, 2000a). Some national European regulations include a maximum level of chloramines as lower than 0.6 g/m3 (OSPAR 1999).

Table 2.4 Quality parameters for swimming pool waters in several European countries

| | France | Spain | Belgium | The Netherlands | Italy | Denmark[1] |
|---|---|---|---|---|---|---|
| Filling water | Drinking water | | | | | Drinking water. Surface water if allowed by local council. |
| Daily top-up | 30 l/swimmer | 5% of pool volume | 30 l/swimmer | 30 l/swimmer | 30 l/swimmer | |
| pH | 6.9-7.7 | [2]Maximum range from 6.5 -- 8.5 | 7-7.6 | 6.8-7.8 | | |
| FAC (mg/l) | 0.4-1.4 | [2]lowest: combined or active chlorine 0.3 at pH 7-7.6<br>Typical: 0.4 to 1.5, or 0.5 to 2, at pH up to 8 or even 8.5<br>Highest: 0.8 to 1.4 or 1.5, for pH from 7.6 up to 8 or 8.2 | 0.5-1.5 | 0.5-1.5 | 0.5-1 at pH 6.5-7.5;<br>0.7-2 at pH 7,5-8,5 | 1-3<br>up to 5 mg/l allowed in some pools |
| Combined chlorine (mg/l) | ≤ 0.6 | [2]often less than 0.6 of the FAC. Levels between 0.3 and 0.5 may be specified, with higher levels at higher pH. | ≤ 1 | ≤ 1 | 0,3 at pH 6.5-7.5<br>0.5 at pH 7.5-8.5 | |

1. Denmark (1988). 2. Spain (2005).

# 4 HUMAN HEALTH

## 4.1 HUMAN HEALTH (TOXICITY)

### 4.1.1 Exposure assessment

#### 4.1.1.1 General discussion

Chlorine is essentially (99%) produced by one of the three electrolysis processes described in **section 2.1.1**., i.e. mercury amalgam, diaphragm and membrane processes, which are all closed systems. The chlorine gas stream is contained, isolated and can leave the electrolysis cells directly for further treatment and drying or can leave the cells as a two phase flow with the anolyte. In this case, the anolyte must be dechlorinated normally by suction before returning to the denuder, the chlorine stream going then into further treatment and drying.

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. The main uses of chlorine are described under **section 2.2**.and the proportions of chlorine used in the various applications are given in **Table 2–2** under the same section.

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.

#### 4.1.1.2 Occupational exposure

For each scenario, occupational exposure to chlorine is described in as much detail as possible. 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. Exposure to hypochlorite in water has been discussed in the Risk Assessment Report for this sodium hypochlorite and references are made to the relevant chapters.

#### 4.1.1.2.1 Occupational exposure from production

**Description of workers' tasks**

In a chlor-alkali plant, workers can generally perform one of the following tasks: production work, maintenance, sampling or packaging of the end product.

Production work consists of process control: operation of manual valves; adjustment of anode level, control of process parameters, loading or unloading, preparation of maintenance activities; doing rounds including visual checks of piping, pumps, valves, etc. In many plants remote control devices are used but an on-site survey is made by operators.

Maintenance consists in control, revision, repair of mechanic or electronic components, including replacement of fittings, valves, instruments and cleaning of the electrolysis cells. Coupling and decoupling of pipelines can also take place for maintenance purposes. The opening of the chlorine system takes place only after it has been emptied, purged, shut-off via blind flange and disconnected.

Sampling generally consists in the analysis of organics, water and gaseous impurities in liquid chlorine. The sample is taken from the tank of a road or rail tanker, and from sampling stations in the plant. Special sampling devices are used. The analysis is made in the laboratory in a hood or in a vented area. Because the analytical controls are made automatically during the production process, the sampling procedure is only used to check the quality and reliability of the system and consequently, chlorine analyses in the laboratory are not very frequent.

As far as the packaging is concerned, chlorine generally leaves the production plant via pipeline in the gaseous or liquid form. Chlorine is always compressed and liquefied when it is transported via rail or road tankers or, in a few cases, via small containers. In all cases, the transfer of chlorine is done through loading stations adapted to the size of the tank or vessel. The main elements of these stations for road trucks or rail tankers are articulated arms or flexible hoses. All precautions are taken to avoid the movement of the container during the course of loading. As the tank is in right position, workers achieve the connection between the fixed and the mobile storage with bolts and nuts, the connecting section being sucked off through a chlorine absorption unit and flushed with dried air. Then the loading can start. The operation can take up to two hours. Two operators are always present.

**Safety procedures**

*Production*

Chlorine is produced in a closed system, and during normal working procedures, exposure to chlorine is possible only in case of leaks. Liquefaction, storage and loading areas are equipped with detectors. All workers in the plant receive specific training to react in a safe way in case of leaks. Personal Protective Equipment (PPE) is always used: safety glasses, safety shoes, long sleeved shirt, long pants, escape mask. In case of chlorine leaks, detection and monitoring are performed as described hereafter. Self-contained breathing apparatus are used for emergency operations.

*Maintenance*

Exposure could be possible during some specific maintenance activities. In most plants, maintenance personnel have to follow written procedures dictated by the plant supervisor. In general, maintenance work is carried out only if a "work permit" from the plant supervisor is issued when the status of the plant has been checked. Safety procedures and PPE to be used to prevent exposure are dictated by the plant supervisor and documented in the work permit. In general, PPE used for handling of the product is: goggles, face shield, gloves, safety shoes, long sleeved shirt, long pants and gas-mask. In case of opening of the system, PPE used is goggles, face shield, gloves, rubber overall, rubber boots, gas mask or self-contained breathing apparatus. Of course, the opening of chlorine system takes place only after it has been emptied, purged, shut-off via blind flange and disconnected. Because chlorine is in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently, no dermal exposure is to be expected. The only possible exposure is by inhalation but use of PPE prevents this.

*Sampling*

The sampling of chlorine is made by trained personnel with sufficient knowledge of all aspects of chlorine handling. Protective equipment (safety shoes, long sleeved shirt, long pants, safety goggles, escape respirator) is used. In the laboratory, similar precautions are used and the analyses are made in a hood or in a vented area.

*Packaging*

All personnel who enter the area of a chlorine loading installation have available personal respiratory protection. A line diagram of the pipe-work and advice concerning the method of operation is permanently available. Safety devices exist to prevent overpressure and, in some cases, water spraying systems are placed both at the loading station and in the storage area. A plant log of the loading operations is maintained by the operating personnel. This plant log indicates in particular the identification of the transport containers, their tare weight, their laden weight, their pressure and their general physical state, as well as any major item of maintenance. An emergency plan and precise instructions in case of emergency are permanently available and brought to the knowledge of the personnel involved. Self-contained breathing sets and protective clothing suitable for dealing with a chlorine leak are generally available in lockers located near the discharge point, and accessible at all times in case of emergency.

Safety procedures and the use of appropriate protective equipment limit the exposure to chlorine to accidental events. Potential for exposure to chlorine exists as a result of leaks. Chlorine leaks are readily detected by smell. The threshold of smell is, based on controlled exposure studies in humans, in the range of 0.03-0.3 ppm (0.15-1.5 mg/m$^3$) (see **section 4.1.2.3.3**). However the ability to detect chlorine by odour is lost after brief exposure. Plants are equipped with chlorine detectors in different locations. They can generally detect 0.1 ppm (0.3 mg/m$^3$) as a theoretical minimum. They have a pre-alarm level of 0.25 ppm – 0.30 ppm (0.75-0.90 mg/m$^3$) and an alarm level of 0.5 ppm (1.5 mg/m$^3$). In case of a leak, the presence of chlorine in the atmosphere is detected either by smell or by alarm detectors and workers shall evacuate or put on the appropriate PPE. All personnel normally carry a mask on or with them when executing tasks that could lead to exposure to chlorine gas. Most of the plants perform TWA analysis and some of them STEL analysis on a regular basis. Data are provided in the following paragraphs.

### Protection efficacy

Clothing: because chlorine is in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently no dermal exposure is to be expected. Workers wear protective clothing made of materials (PVC, nitrile rubber, neoprene rubber, PE, natural rubber) that have a breakthrough time of more than 8 hours during performance test (Forsberg/Mansdorf) in emergency cases in which a task with expected long term exposure is performed. In some cases, dermal PPE are also used in case of opening the chlorine system, as an additional protective measure to the de-gassing of the system.

Respirators: respirators efficacy is defined by an Assigned Protection Factor (APF), which reflects the level of protection that a properly functioning respirator is expected to provide to a population of properly fitted and trained users. For example, an APF of 10 means that the user of the respirator will not inhale more than one tenth of the airborne contaminant present in the air. APF for some models of respirators are presented below (UK and NL).

| | |
|---|---|
| Mask with B-filter, half-mask | 10 – 20 |
| Mask with B-filter, full face | 20 – 40 |
| Self contained breathing apparatus | 100 – 2000 |

The type of respirator is chosen according to the possible chlorine concentration level and the duration of the operation in the presence of chlorine. For example, the use of simple filter masks is prohibited where there is a risk of a high concentration of chlorine.

Inhalation exposure

**OELs**

Existing regulations in European countries impose Occupational Exposure Limits (OEL) for chlorine on a short and long term basis.

**Table 2–3** under **section 2.4.3** shows occupational exposure limits for chlorine in European countries. In almost all countries, the limit for long term exposure (8 hours TWA) is 0.5 ppm (1.5 mg/m$^3$), with the only exception of The Netherlands, where limits are higher. In some cases, a short term exposure limit (15 minutes STEL) of 1 ppm (3 mg/m$^3$) is applied. A draft proposal of European Directive on occupational exposure limits establishes an indicative limit of 0.5 ppm (1.5 mg/m$^3$) for short term exposure (15 minutes) to chlorine.

*Measured data*

Measured data are available on chlorine atmospheric concentration in the workplace in different parts of the chlor-alkali plant and for different tasks.

The measuring device used for chlorine monitoring is an electrochemical sensor, which is sensible not only to chlorine, but also to other chlorinated substances present in the air (Euro Chlor Code of Practice, Monitoring chlorine exposure to workers, 2000). We can then assume that the chlorine concentration measured in the atmosphere of a chlor-alkali plant is a worst case for inhalation exposure, because

- The measured value takes into account the exposure coming from several production plants (chlorine and other chlorinated chemicals)
- The measured level is the sum of chlorine and other chlorinated substances
- The sensors are also measuring exposure when the operators are using PPE (they are indeed wearing a mask if the alarm threshold of 0.5 ppm (1.5 mg/m$^3$) is exceeded).

**Table 4-1, Table 4-2 and Table 4-** present the concentrations of chlorine in the atmosphere measured in chlor-alkali plants. Data in **Table 4-1** and **Table 4-** refer to all functions in the plants while **Table 4-2** provides information on different activities in the plant (normal cell room operations, laboratory, filling activities, maintenance). They are representative for typical exposure of workers during the different tasks and provide an overall picture of worker's exposure in chlor-alkali plant. As explained above, they can be considered as worst case exposures.

It has to be pointed out that chlorine concentrations used to calculate STEL and TWA values have been measured also when the workers are wearing a mask or PPE. Workers shall indeed wear a mask or PPE as soon as chlorine is detected either by smell or by alarm detector. In these conditions, it should be considered that the maximum exposure level is the highest threshold value of smell as described in **section 4.1.2.3.3**, the detector threshold being generally set at a lower value. The value of 0.5 ppm (1.5 mg/m$^3$) is therefore used as conservative threshold value. Consequently, even if **Table 4-1, Table 4-2** and **Table 4-** represent the full range of raw data, when calculating the 90th percentile of the maximum detected values to define the reasonable worst case exposure levels, only values equal or lower than 0.5 ppm (1.5 mg/m$^3$) are retained.

*Short-term exposure*

**Table 4-1** and **Table 4-2** present STEL data, obtained following the Euro Chlor code of practice "Monitoring Chlorine Exposure to Workers" (2000). In most cases, the instrument used was an electrochemical sensor with a data logger worn by an operator. Samples are taken continuously over a defined time period and the mean chlorine concentration is calculated every 15 minutes. The number of samples in **Table 4-2** corresponds to the number of 15 minutes periods for which the chlorine concentration has been measured. The measurement campaign took place in 1991. A "quality check" of the database was made and very high values measured when workers were using PPE were not considered.

In some cases, the proposed STEL limit (0.5 ppm, 1.5 mg/m$^3$) was exceeded. However, as the operators were wearing their sensor all the time during the survey, it has to be stressed that most of values exceeding 0.5 ppm (1.5 mg/m$^3$) were measured in very specific situations (filling operations, coupling and uncoupling of pipelines, etc) and that in all these cases it's compulsory to wear PPE (including masks with filters or, for higher or longer exposure risk, self-contained breathing apparatus) and to follow specific safety procedures.

Table 4-1 Workers exposure to chlorine in the atmosphere during chlorine production.
Summary of measured STEL data (Euro Chlor, 2001)

| Function | Number of workers | Number of samples | Range | Average | Median | 90th percentile |
|---|---|---|---|---|---|---|
| Operators, maintenance, filling, laboratory | 931 | 9345 | 0 – 5 ppm<br>[0 – 15 mg/m$^3$] | 0.075 ppm<br>[0.225 mg/m$^3$] | 0.050 ppm<br>0.15 mg/m$^3$] | 0.167 ppm<br>0.501 mg/m$^3$] |

Table 4-2 Workers exposure to chlorine in the atmosphere during chlorine production.
Measured STEL data specific for function (Euro Chlor, 2001).

| Function | Number of workers | Number of samples | Range | Average | Median | 90th percentile |
|---|---|---|---|---|---|---|
| Operators | 705 | 6732 | 0 – 5 ppm<br>[0 – 15 mg/m$^3$] | 0.072 ppm<br>[0.216 mg/m$^3$] | 0.040 ppm<br>[0.216 mg/m$^3$] | 0.180 ppm<br>[0.540 mg/m$^3$] |
| Maintenance | 131 | 166 | 0 – 1 ppm<br>]0 – 3 mg/m$^3$] | 0.082 ppm<br>[0.246 mg/m$^3$] | 0.050 ppm<br>[0.150 mg/m$^3$] | 0.160 ppm<br>[0.480 mg/m$^3$] |
| Filling | 77 | 291 | 0 – 5 ppm<br>[0 – 15 mg/m$^3$] | 0.077 ppm<br>[0.231 mg/m$^3$] | 0.057 ppm<br>[0.171 mg/m$^3$] | 0.166 ppm<br>[0.498 mg/m$^3$] |
| Laboratory | 18 | 2156 | 0 – 0.3 ppm | 0.046 ppm | 0.050 ppm | 0.084 ppm |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | [0 – 0.9 mg/m$^3$] | [0.138 mg/m$^3$] | [0.150 mg/m$^3$] | [0.252 mg/m$^3$] |

The analysis of the statistical data shows that the median is lower than the average for all functions. This means that the average is dominated by few, higher values and that most of the values are below the average. The 90-percentile value is high, because of the presence of peaks values.

In order to better evaluate the influence of peaks values on the statistics, a limited survey was carried out in July 2006. Some companies were asked to provide short term exposure data, in order to be able to identify peaks of exposure and to establish their duration.

**Table 4-3** presents the result of a survey on 5 cell room operators in one chlorine production plant. STEL measures were taken during 5 hours with an electrochemical sensor couples with a data logger worn by an operator.

Table 4-3 Measured STEL data and peaks duration (Euro Chlor, 2006)

| | Maximum exposure (peak) | Duration of the peak | Average exposure | Average exposure excluding peak | Notes |
|---|---|---|---|---|---|
| 1 | 0.06 ppm [0.18 mg/m$^3$] | 75 minutes | 0.02 ppm [0.06 mg/m$^3$] | 0 ppm [0 mg/m$^3$] | |
| 2 | 0.27 ppm [0. 81 mg/m$^3$]<br>0.23 ppm [0. 81 mg/m$^3$] | 15 minutes<br>15 minutes | 0.05 ppm [0.15 mg/m$^3$] | 0 ppm [0 mg/m$^3$] | |
| 3 | 0.25 ppm [0. 75 mg/m$^3$] | 15 minutes | 0.02 ppm [0.06 mg/m$^3$] | | |
| 4 | No peak registered | | 0 ppm | | |
| 5 | 0.70 ppm [2.10 mg/m$^3$]<br>1.25 ppm [3.75 mg/m$^3$] | 15 minutes<br>15 minutes | 0.1 ppm [0.3 mg/m$^3$] | 0 ppm [0 mg/m$^3$] | 15 minutes following the peaks the exposure was 0 and 0.02 respectively |

**Table 4.4** presents personal monitoring measures from 1990 to 2005 in two chlorine production units. Data reported are TWA from 1990 to 2003 and STEL from 2004 onwards. The personal measuring device was equipped with a data logger, which allowed to registered data during a full shift and to identify peaks. We can see that peaks of exposure are not so frequent and that their duration is always short (about a minute).

Table 4-4 Number of peaks measured in two chlorine production units from 1990 to 2005 (Euro Chlor, 2006)

| Year | Number of Measurements | Number of peaks ( ppm [mg/m$^3$]) | Number of Measurements | Number of peaks ( ppm [mg/m$^3$]) |
|---|---|---|---|---|
| | Production unit n. 1 | | Production unit n. 2 | |
| 1990 | 37 | 35 * not detectable<br>1 * 0.1 [0.3]<br>1 * 0.4 [1.2] | 21 | 20 * not detectable<br>1 * 0.2 [0.6] |
| 1991 | 45 | not detectable | 24 | 23 * not detectable,<br>1 * 0.1 [0.3] |
| 1992 | 34 | not detectable | 20 | not detectable |
| 1993 | 33 | 30 * not detectable,<br>3 * 0.1 [0.3] | 20 | 19 * not detectable<br>1 * 0.1 [0.3] |
| 1994 | 39 | 36 * not detectable<br>2 * 0.1 [0.3]<br>1* 0.3 [0.9] | 20 | 19 * not detectable<br>1 * 0.1 [0.3] |

| | | | | |
|---|---|---|---|---|
| 1995 | 18 | 13 * not detectable<br>5 * 0.1 [0.3] | 20 | 14 * not detectable<br>5 * 0.1[0.3]<br>1 * 0.2 [0.6] |
| 1996 | 24 | 21 * not detectable,<br>3 * 0.1 [0.3] | 20 | 20 * not detectable |
| 1997 | 21 | 19 * not detectable,<br>3 * 0.1 [0.3] | 24 | 23 * not detectable<br>1 * 0.1 [0.3] |
| 1998 | 22 | 20 * not detectable<br>1 * 0.1 [0.3]<br>1 * 0.2 [0.6] | 26 | 26 * not detectable |
| 1999 | 18 | 15 * not detectable<br>3 * 0.1 [0.3] | 22 | 22 * not detectable |
| 2000 | 16 | 15 * not detectable<br>1 * 1.6 [4.8] (1) | 20 | 17 * not detectable<br>0,1 [0.3] |
| 2001 | 4 | 4 * not detectable | 14 | 14 * not detectable |
| 2002 | 10 | 10 * not detectable | 19 | 18 * not detectable<br>1 * 0.1 [0.3] |
| 2003 | 8 | 8 * not detectable | 24 | 21 * not detectable<br>1 * 0.1 [0.3]<br>2 * 0.2 [0.6] |
| 2004 | 19 | 17 * not detectable<br>1 * 0.1 [0.3]<br>1 * 0.5 [1.5] | 21 | 18 * not detectable<br>1 * 0.1 [0.3]<br>1 * 0.3 [0.9]<br>1 * 0.5 [1.5] |
| 2005 | 13 | 10 * not detectable<br>1 * 0.1 [0.3]<br>1 * 0.3 [0.9]<br>1 * 0.4 [1.2] | 10 | 9 * not detectable<br>1 * 0.1 [0.3] |

* = Measurements

(1) =During this measurement the employee was wearing a breathing apparatus which is fed with compressed air.

(

The data presented in tables 4-3 and 4-4 show that high exposure peaks can be present, but their duration is limited. In most cases, they do not represent real exposure because workers wear PPE when they expect they can 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.

*Long-term exposure*

**Table 4-5** presents data on long term exposure as TWA. The data stems from 27 plants in many countries in Europe and from 5271 workers dealing with various functions in the plants. As most of the workers cover different functions in the plants over a long range period, it is not possible to split the TWA values into the various functions as it is done for the short term STEL values. They provide however an overall picture of worker's exposure in chlor-alkali plant. Being an old database, it was not possible to conduct a "quality check" to eliminate outliers.

Table 4-5 Workers exposure to chlorine in the atmosphere during chlorine production.
Summary of measured TWA data (Euro Chlor, 1997).

| Function | Number of workers | Range | Average | Median | 90th percentile |
|---|---|---|---|---|---|
| Operators, maintenance, filling, laboratory | 5271 | 0 – 6.5 ppm<br>[0 – 19.5 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.103 ppm<br>[0.309 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |

In some cases, the limit of 0.5 ppm (1.5 mg/m$^3$) was exceeded. However, as the operators were wearing their sensor all the time during the survey, it has to be stressed that most of the values exceeding 0.5 ppm (1.5 mg/m$^3$) were measured in very specific situations (filling operations, coupling and uncoupling of pipelines, etc) and that in all these cases it is compulsory to wear PPE (including masks with filters or, for higher or longer exposure risk, self-contained breathing apparatus) and to follow specific safety procedures. Moreover, as the various locations have alarm systems with a pre-alarm level at 0.25-0.30 ppm (0.75-0.90 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, in practice, not exposed to concentrations higher than 0.5 ppm (1.5 mg/m$^3$). Additionally, as the threshold of smell is normally below 0.5 ppm (1.5 mg/m$^3$). We can conclude that there is no exposure level higher than 0.5 ppm (1.5 mg/m$^3$), the workers being obliged to wear a mask as soon as chlorine is detected either by smell or by detector.

*Modelled data*

Four different scenarios are used: normal production work in cell room, maintenance, loading-filling and laboratory work. The EASE model is used for assessing the possible inhalation exposure to chlorine gas. The conditions considered for the four scenarios and the corresponding results of the modelling are presented in the **Table 4-6** hereafter.

Table 4-6 EASE modelled exposure to chlorine in production plant

| | Scenario 1<br>Work in production cell-rooms | Scenario 2<br>Maintenance work | Scenario 3<br>Loading-filling work | Scenario 4<br>Laboratory work |
|---|---|---|---|---|
| Temperature of the process, °C | 90 | 25 | 25 | 25 |
| Physical state | gas/vapour | gas/vapour | gas/vapour | gas/vapour |
| Exposure type | gas/vapour | gas/vapour | gas/vapour | gas/vapour |
| Aerosol formation | no | no | no | no |
| Ability to become airborne | high | high | high | high |
| Use pattern | closed system | closed system | closed system | closed system |
| Pattern of control | full containment | LEV | LEV | LEV |
| Significant breaching | false | true | true | true |
| EASE EXPOSURE RANGE | 0- 0.1 ppm<br>[0 – 0.3 mg/m$^3$] | 100-200 ppm<br>[300 – 600 mg/m$^3$] | 100-200 ppm<br>[300 – 600 mg/m$^3$] | 100-200 ppm<br>[300 – 600 mg/m$^3$] |

*Summary/statement of the exposure level*

It appears that for scenario 1, work in production cell-rooms, the results of the modelling are well in line with the measured data as given in **Table 4-2** and **Table 4-**. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the Short Term Exposure Level (STEL) is indeed varying in the range 0 to 0.5 ppm (0 - 1.5 mg/m$^3$) for cell-room operators. The average is 0.072 ppm (0.216 mg/m$^3$) and the 90th percentile value of 0.180 ppm (0.54 mg/m$^3$), while the long term exposure (TWA) value is calculated with an average of 0.102 ppm (0.306 mg/m$^3$) and a 90th percentile of 0.235 ppm (0.705 mg/m$^3$). Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 1 is 0.180 ppm (0.54 mg/m$^3$), while the long term exposure is 0.235 ppm (0.705 mg/m$^3$).

For scenarios 2, 3 and 4, maintenance, loading-filling and laboratory works, the results of the modelling are indicating a potential exposure in the range 100-200 ppm (300 – 600 mg/m$^3$), while the measured values are much lower. The reasons of these differences are linked to the rough and simple character of the hypotheses considered in modelling. We should indeed consider that, during maintenance and filling processes, there is a breaching of the process in the presence of a LEV (local exhaust ventilation). But there is no possibility to include in the model the fact that the systems are degassed before opening, which significantly reduces the possible exposure. In the laboratory work, the analyses are made in a hood or a vented area and, additionally the special sampling device is directly connected to the analytical instrument, drastically reducing the possible exposure. Moreover, the model does not consider the existence of personal protection equipment (PPE) while these are generally used in practice. In these conditions, the experimental measured data are more reliable than the modelled values. Chlorine concentration measured in the atmosphere of a chlor-alkali plant is indeed a worst case for inhalation exposure, because

- the measured value takes into account the exposure coming from several production plants (chlorine and other chlorinated chemicals)
- the measured level is the sum of chlorine and other chlorinated substances
- the sensors are also measuring exposure when the operators are using PPE; they are wearing mask if the alarm threshold of 0.5 ppm (1.5 mg/m$^3$) is exceeded.

For scenario 2, the measured data as given in **Table 4-2** and **Table 4-** are used. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the Short Term Exposure Level (STEL) value for maintenance operators is varying in the range 0 to 0.5 ppm (1 - 1.5 mg/m$^3$) with an average of 0.082 ppm (0.246 mg/m$^3$) and a 90th percentile value of 0.160 ppm (0.480 mg/m$^3$), while the long term exposure (TWA) value, covering all functions, is calculated with an average of 0.102 ppm (0.306 mg/m$^3$) and a 90th percentile of 0.235 ppm (0.705 mg/m$^3$). Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 2 is 0.160 ppm (0.480 mg/m$^3$), while the long term exposure is 0.235 ppm (0.705 mg/m$^3$).

For scenario 3, the measured data as given in **Table 4-2** and **Table 4-** are used. If, as explained, the maximum exposure value is limited to the threshold of smell, the Short Term Exposure Level (STEL) value for filling operators is varying in the range 0 to 0.5 ppm (0 - 1.5 mg/m$^3$) with an average of 0.077 ppm (0.231 mg/m$^3$) and a 90th percentile value of 0.166 ppm (0.498 mg/m$^3$) while the long term exposure (TWA) value, covering all functions, is calculated with an average of 0.102 ppm (0.306 mg/m$^3$) and a 90th percentile of 0.235 ppm (0.705 mg/m$^3$). Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 3 is 0.166 ppm (0.498 mg/m$^3$)while the long term exposure is 0.235 ppm (0.705 mg/m$^3$).

For scenario 4, the measured data as given in **Table 4-2** and **Table 4-** are used. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the Short Term Exposure Level (STEL) value for laboratory operators is varying in the range 0 to 0.3 ppm (0 – 0.9 mg/m$^3$) with an average of 0.046 ppm (0.138 mg/m$^3$)and a 90th percentile value of 0.084 ppm (0.252 mg/m$^3$), while the long term exposure (TWA) value, covering all functions, is calculated with an average of 0.102 ppm (0.306 mg/m$^3$) and a 90th percentile of 0.235 ppm (0.705 mg/m$^3$). Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 4 is 0.084 ppm (0.252 mg/m$^3$), while the long term exposure is 0.235 ppm (0.705 mg/m$^3$).

Using as a reasonable worst case the 90th percentile of the distribution of the exposure levels observed at each location, the short term and long term inhalation exposure to chlorine in the four scenarios considered (cell-room operators, maintenance operators, filling and laboratory operators) are summarised in **Table 4-7**.

Table 4-7 Short term and long term exposures in chlorine production and handling

| | Short term inhalation exposure | | Long term inhalation exposure | |
|---|---|---|---|---|
| | Typical average | 90th percentile | Typical average | 90th percentile |
| Scenario 1 | 0.072 ppm<br>[0.216 mg/m$^3$] | 0.180 ppm<br>[0.540 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |
| Scenario 2 | 0.082 ppm<br>[0.246 mg/m$^3$] | 0.160 ppm<br>[0.480 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |
| Scenario 3 | 0.077ppm<br>[0.231 mg/m$^3$] | 0.166 ppm<br>[0.498 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |
| Scenario 4 | 0.046 ppm<br>[0.138 mg/m$^3$] | 0.084 ppm<br>[0.252 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |

These values are very conservative for the following reasons:

- the measured value takes into account the exposure coming from several production plants (chlorine and other chlorinated chemicals)
- the measured level is the sum of chlorine and other chlorinated substances
- the sensors are also measuring exposure when the operators are using PPE, including a mask

Moreover, as the various locations have alarm systems with a pre-alarm level at 0.25-0.30 ppm (0.75-0.90 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.

As most of the workers cover different functions in the plants over a long range period, it is not possible to split the long term exposure values into the various functions as it is done for the short term ones.

Comparing the two sets of data, we can see that STEL and TWA values are in the same order of magnitude (STEL values are even lower than TWA ones). Considering that

- the TWA database is older and of a lower quality,
- in the TWA it is not possible to distinguish between the different functions,
- the STEL data always represent personal monitoring, while the TWA data in some cases are derived from stationary monitoring systems

it is proposed to take forward to the Risk Characterisation the STEL data only, for all the endpoints.

The relevance of typical values vs 90-percentile will be further discussed in the Risk Characterisation section.

Dermal exposure

Because chlorine is not liquid but in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently no dermal exposure is to be expected. Moreover, the processes are closed and in case of opening of the system for maintenance purposes, safety procedures are applied in such a way that the opening of the system always takes place after complete degassing of the chlorine. On the basis of a precautionary approach, the use of protective equipment such as face shield, goggles and gloves is mandatory in production area. This clearly indicates that there is no direct contact with liquid chlorine and, consequently, no dermal exposure.

*Summary/statement of the exposure level*

There is no dermal exposure.

#### 4.1.1.2.2 Occupational exposure from formulation

There is no formulation of chlorine neither in production nor for uses.

#### 4.1.1.2.3 Occupational exposure from end uses

**General discussion**

Chlorine is mainly used as a chemical intermediate to produce both chlorinated as well as non-chlorinated compounds. Details concerning sector applications are mentioned in **Table 2–2**. A special survey prepared by Euro Chlor in January 2000 showed that in 1998, 35.5% of chlorine was used in the production of PVC/PVDC/Rubber, 30.5% in the production of non-chlorinated polymers (polyurethanes, epoxides and polycarbonates), 18% in the production of organic chemistry and solvents, 13.5% for the inorganic chemistry. Only 2.2% of $Cl_2$ production finds its end-use in the elemental form, mainly for disinfection of water.

Chlorine gas leaving the electrolysers is approximately 80-90°C and saturated with water vapour. In general chlorine goes through a series of processes for cooling, cleaning, drying, compressing and liquefying. In some applications it can be used directly from the electrolysers.

Chlorine is supplied in gaseous form to the consuming industries mainly by pipeline. To a minor extent, it is distributed in liquefied form in bottles or tankers (road and railway). In all applications, occupational exposure to chlorine gas may occur during handling (filling) operations and/or production of chemicals. In all processes, chlorine gas wastes are treated by absorption systems (alkaline scrubbers) at various stages from the production to the storage. Various systems are in place in the different plants. The overall objective is obviously to avoid chlorine emission to the atmosphere in order to respect workplace and emission regulations.

To assess the exposure to chlorine in end uses, two types of applications are considered: the use as intermediate in chemicals production and the use in bleaching and water disinfection.

##### 4.1.1.2.3.1 Chlorine as intermediate in production of chemicals

As indicated in the general discussion, chlorine is used as intermediate in the production of polymers (chlorinated or non-chlorinated), in the production of organic chemicals and solvents and in the production of inorganic chemicals. It is used as a chlorinating and oxidizing agent of organic intermediates. These applications usually take place in the production plant and gaseous chlorine is transferred via pipelines to on-site users. Chlorine is filled into the reaction vessel through closed systems, while off-gases from the reactor are treated (generally by alkaline scrubbers) before release in the atmosphere. Most of the productions are continuous processes (like dichloroethane production) but some are using batch processes (like chlorinated paraffin production). The proportions of chlorine used as intermediate in the various productions of chemicals are given in **Table 2–2**.

**Description of worker’s tasks and safety procedures**

Production work consists of process control: operation of manual valves; control of process parameters, loading or unloading, preparation of maintenance activities; doing rounds including visual checks of piping, pumps, valves, etc. The processes are closed and during normal work, exposure to chlorine is possible only in case of accident. In batch processes, the chlorine is vaporised from storage on an “on-demand” basis and fed into the batch reactors via a closed system. Unreacted chlorine at the end of the reaction is vented through an alkaline scrubber. Chlorine detectors are placed in the loading and in the degassing areas. Personal

Protective Equipment (PPE) is always used: safety glasses, safety shoes, long sleeved shirt, long pants, escape mask. In case of chlorine leaks, detection and monitoring are performed. Self-contained breathing apparatus are used for emergency operation.

Maintenance consists in control, revision, repair of all mechanic or electronic components. Coupling and decoupling of pipelines can take place for maintenance purposes. The opening of chlorine system takes place only after it has been emptied, purged, completely degassed, shut-off via blind flange and disconnected. Maintenance and repairs of pumps, dosing systems and automatic control systems is only carried out by specialised companies or trained workers after complete degassing of the system. In most plants, maintenance personnel have to follow written procedures dictated by plant supervisor. In general maintenance work is carried out only if a “work permit” from the plant supervisor is issued when the status of the plant has been checked. Safety procedures and personal protective equipment to be used to prevent exposure are dictated by the plant supervisor and documented in the work permit. In general, PPE used for handling of the product is: goggles, face shield, gloves, safety shoes, long sleeved shirt, long pants and gas mask. In case of opening of the system, PPE used is goggles, face shield, gloves, rubber overall, rubber boots, gas mask or self-contained breathing apparatus.

Sampling generally consists in the analysis of organic, aqueous or gas phases in reaction medium. The sample is taken from the system at well identified sampling stations in the plant. Special sampling devices are used by trained persons with sufficient knowledge of all aspects of chlorine handling. Manual sampling is only done to check the reliability of the automated remote control systems. Protective equipment (safety shoes, long sleeved shirt, long pants, safety goggles, escape respirator) is used.

Loading and unloading: Gaseous chlorine is transferred via pipelines to on-site users and chlorine is filled into the reaction vessel through closed systems, while off-gases from the reactor are treated before release to the atmosphere. When tankers or cylinders are used for smaller productions, the transfer of chlorine is done through loading stations adapted to the size of the vessel. All personnel who enter the area of a chlorine loading installation receive a special training and have available personal respiratory protection. A line diagram of the pipe-work and advice concerning the method of operation is permanently available. An emergency plan and precise instructions in case of emergency are permanently available and brought to the knowledge of the personnel involved. Self-contained breathing sets and protective clothing suitable for dealing with a chlorine leak are generally available in lockers located near the discharge point, and accessible at all times in case of emergency.

For information on the efficacy of PPE, see **section 4.1.1.2.1**.

Exposure scenarios

As in the case of chlorine production, four main scenarios are considered to assess the exposure to chlorine in processes using chlorine as intermediate:

- The normal production activities
- The maintenance work
- The loading-unloading operation
- Laboratory work

In all cases, safety procedures and the use of appropriate protective equipment limit the exposure to chlorine to accidental events. Potential for exposure to chlorine exists as a result of leaks. Chlorine leaks are readily detected by smell. The threshold of smell is in the range of

0.03 – 0.3 ppm (0.09 – 0.9 mg/m$^3$). Plants are equipped with chlorine detectors in different locations. They can generally detect 0.1 ppm (0.3 mg/m$^3$) as a theoretical minimum and have a pre-alarm level of 0.25-0.30 ppm (0.75-0.90 mg/m$^3$) and an alarm level of 0.5 ppm (1.5 mg/m$^3$). In case of a leak, the presence of chlorine in the atmosphere is detected by smell or by alarm detectors and workers shall wear the appropriate PPE. All personnel normally carry a mask on or with them.

Most of the plants perform TWA analysis and some of them STEL analysis on a regular basis.

Inhalation exposure

The same Occupational Exposure Levels (OEL) apply to all productions using chlorine. Consequently the OEL values reported in **Table 2–3** are also applicable to these chlorine uses.

Similarly, the measured data provided in **Table 4-1** and **Table 4-** under **section 4.1.1.2.1** are covering exposure levels in production plants using chlorine as intermediate. As explained before, these measured values are indeed reflecting exposure to chlorine and chlorinated substances coming from several production plants (chlorine and other chlorinated chemicals). The data in **Table 4-2**, which are specific to the chlorine production, are not used here. Only the data covering all functions are considered because they are more representative of the multi-functional tasks carried out by the workers.

These measured values can then be seen as covering the four scenarios considered (normal work, maintenance, loading-unloading operations as well as laboratory work).

The modelled data have been obtained by applying the EASE model for assessing the possible inhalation exposure to chlorine gas. The conditions considered for the four scenarios and the corresponding results of the modelling are presented in **Table 4-8** hereafter.

Table 4-8 EASE modelled exposure to chlorine in plant using chlorine as intermediate

| | Scenario 1 Work in production | Scenario 2 Maintenance work | Scenario 3 Loading-filling work | Scenario 4 Laboratory work |
|---|---|---|---|---|
| Temperature of the process, °C | 90 | 25 | 25 | 25 |
| Physical state | gas/vapour | gas/vapour | gas/vapour | gas/vapour |
| Exposure type | gas/vapour | gas/vapour | gas/vapour | gas/vapour |
| Aerosol formation | no | no | no | no |
| Ability to become airborne | high | high | high | high |
| Use pattern | closed system | closed system | closed system | closed system |
| Pattern of control | full containment | LEV | LEV | LEV |
| Significant breaching | false | true | true | true |
| EASE EXPOSURE RANGE | 0- 0.1 ppm<br>[0 – 0.3 mg/m$^3$] | 100-200 ppm<br>[300 – 600 mg/m$^3$] | 100-200 ppm<br>[300 – 600 mg/m$^3$] | 100-200 ppm<br>[300 – 600 mg/m$^3$] |

It appears that for scenario 1, work in production, the results of the modelling are well in line with the measured data as given in **Table 4-2** and **Table 4-**. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the Short Term Exposure Level (STEL) is indeed varying in the range 0 to 0.5 ppm (0 – 1.5 mg/m$^3$) for cell-room operators.

The average is 0.072 ppm (0.216 mg/m$^3$) and the 90th percentile value of 0.180 ppm (0.540 mg/m$^3$), while the long term exposure (TWA) value is calculated with an average of 0.102 ppm (0.306 mg/m$^3$) and a 90th percentile of 0.235 ppm (0.705 mg/m$^3$).

Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 1 is 0.180 ppm (0.540 mg/m$^3$), while the long term exposure is 0.235 ppm (0.705 mg/m$^3$).

For scenarios 2, 3 and 4, maintenance, loading-filling and laboratory work, the results of the modelling are indicating a potential exposure in the range 100-200 ppm (300 - 600 mg/m$^3$), while the measured values are much lower. The reasons of these differences are linked to the rough and simple character of the hypotheses considered in modelling. We should indeed consider that, during maintenance and filling processes, there is a breaching of the process in the presence of LEV. But there is no possibility to include in the model the fact that the systems are degassed and purged before opening, reducing significantly the possible exposure. Moreover, the model does not consider the existence of personal protection equipment (PPE) while these are generally used in practice. In these conditions, the experimental measured data are more reliable than the modelled values. Chlorine concentration measured in the atmosphere of a chlor-alkali plant is indeed a worst case for inhalation exposure, because

- the measured value takes into account the exposure coming from several production plants (chlorine and other chlorinated chemicals)
- and the measured level is the sum of chlorine and other chlorinated substances
- the sensors are also measuring exposure when the operators are using PPE; they are wearing a mask when the alarm threshold of 0.5 ppm (1.5 mg/m$^3$) is exceeded

For scenarios 2, 3 and 4, the measured data, as given in **Table 4-1** and **Table 4-** are used. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the maximum Short Term Exposure Level (STEL) value, covering all functions, is varying in the range 0 to 0.5 ppm (1.5 mg/m$^3$) with an average of 0.075 ppm (0.225 mg/m$^3$) and a 90th percentile value of 0.167 ppm (0.501 mg/m$^3$), while the long term exposure (TWA) value, covering all functions, is calculated with an average of 0.102 ppm (0.306 mg/m$^3$) and a 90th percentile of 0.235 ppm (0.705 mg/m$^3$).

Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenarios 2, 3 and 4 is 0.167 ppm (0.501 mg/m$^3$), while the long term exposure is 0.235 ppm (0.705 mg/m$^3$).

*Summary/statement of the exposure level*

Using as a reasonable worst case the 90th percentile of the distribution of the exposure levels observed at each location, the short term and long term inhalation exposure to chlorine in the four scenarios considered (production operators, maintenance operators, filling operators and laboratory workers) are summarised in **Table 4-9** hereafter.

These values are very conservative for the following reasons:

- the measured value takes into account the exposure coming from several production plants (chlorine and other chlorinated chemicals)
- the measured level is the sum of chlorine and other chlorinated substances
- the sensors are also measuring exposure when the operators are using PPE, including a mask

Moreover, as the various locations have alarm systems with a pre-alarm level at 0.25-0.30 ppm (0.75-0.90 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 exposed to concentrations higher than 0.5 ppm (1.5 mg/m$^3$) even when the personal monitor is indicating higher values.

Table 4-9 Short term and long term exposures when chlorine is used as intermediate

| Scenarios | Short term exposure | | Long term exposure | |
|---|---|---|---|---|
| | average | 90th percentile | average | 90th percentile |
| Production | 0.072 ppm<br>[0.216 mg/m$^3$] | 0.180 ppm<br>[0.540 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |
| Maintenance | 0.075 ppm<br>[0.225 mg/m$^3$] | 0.167 ppm<br>[0.501 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |
| Filling | 0.075 ppm<br>[0.225 mg/m$^3$] | 0.167 ppm<br>[0.501 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |
| Laboratory | 0.075 ppm<br>[0.225 mg/m$^3$] | 0.167 ppm<br>[0.501 mg/m$^3$] | 0.102 ppm<br>[0.306 mg/m$^3$] | 0.235 ppm<br>[0.705 mg/m$^3$] |

Dermal exposure

Because chlorine is not liquid but in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently no dermal exposure is to be expected. Moreover, the processes are closed and in case of opening of the system for maintenance purposes, safety procedures are applied in such a way that the opening of the system always takes place after complete degassing of chlorine. On the basis of a precautionary approach, the use of protective equipment such as face shield, goggles and gloves is mandatory in production area. This clearly indicates that there is no direct contact with liquid chlorine and, consequently, no dermal exposure.

*Summary/statement of the exposure level*

There is no dermal exposure.

### 4.1.1.2.3.2 Chlorine used in bleaching and water disinfection

### 4.1.1.2.3.2.1 General discussion

A survey made by Euro Chlor in 1994 showed the various applications of elemental chlorine in water applications such as drinking water, swimming pool, sewage treatment, cooling water, pulp and paper and textile industry. These uses represent about 1% of the chlorine production. Details are given in **Table 4-10** hereafter.

Table 4-10 Chlorine used in bleaching and water disinfection – 1994 (in kt of chlorine)

| COUNTRY/USES | TOTAL | DRINKING WATER | PULP & PAPER | SWIMMING POOL | SEWAGE | COOLING WATER | TEXTILE |
|---|---|---|---|---|---|---|---|
| FIN+N+S+DK | 1.89 | 0.99 | 0.61 | 0.25 | / | 0.02 | 0.02 |
| A+D+CH | 12.71 | 1.85 | 4.04 | 6.70 | 0.02 | 0.10 | / |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| B+NL | 3.52 | ? | ? | ? | ? | ? | ? |
| IRL+GB | 22.11 | 16.50 | 0.10 | 0.35 | 0.80 | 4.16 | 0.20 |
| F | 5.18 | 2.40 | 0.45 | 1.45 | 0.46 | 0.42 | / |
| EL+I | 4.37 | 1.35 | 2.67 | 0.02 | 0.15 | 0.10 | 0.08 |
| P+E | 29.06 | 9.20 | 9.56 | 2.18 | 8.12 | / | / |
| TOTAL | 75.32 | 32.29 | 17.43 | 10.95 | 9.55 | 4.80 | 0.30 |

(Source: Euro Chlor - Confidential information - 1996)

The values reported in **Table 4-10** are more detailed than those given in **Table 2–2** and provide a better view of the applications of chlorine in water. They are however too high for bleaching use in pulp and paper and textile. The tonnages used in these two applications have strongly decreased over the last ten years because of environmental concerns due to by-products formation. Chlorine has been substituted by other bleaching agents both in textile finishing and in pulp bleaching processes. More information is provided in chapters 4.1.1.2.3.2.6 and 4.1.1.2.3.2.7.

#### 4.1.1.2.3.2.2 Chlorine distribution

Inhalation exposure

As indicated in 4.1.1.2.3.2.1, the quantities used in bleaching and water disinfection are small compared to the production levels and the uses of chlorine as intermediate. The large chlorine producers are not directly supplying the small and medium users but are using specialised distributors who are conditioning the chlorine in drums and cylinders starting from tankers. The water disinfection market is essentially covered by these distributors who provide cylinders and/or drums to the end users, according to their needs.

The handling operations in distribution companies are essentially the loading-unloading of tankers and/or drums and cylinders. The workers are filling tankers at suppliers' sites, unloading these tankers in drums or cylinders and supplying the drums/cylinders to the end-users. Except for the varying size of the vessels the loading unloading operations are quite similar to those used on production sites. Both the full and empty containers are closed when connected. The empty container and the connecting circuit are then placed under vacuum or depression before the opening of the full container. The loading can start. When the empty container is filled the two containers are closed and the connecting circuit sucked off through a chlorine absorption unit as described under **section 4.1.1.2.1**. Escape masks are at hand and alarm systems are placed in the room where the filling is done and where the vessels are stored. The chlorine detectors used can generally detect 0.1 ppm (0.3 mg/m$^3$) as a theoretical minimum and have a pre-alarm level of 0.25-0.30 ppm (0.75-0.90 mg/m$^3$). In case of a leak, the presence of chlorine in the atmosphere is detected, turning red light and buzzer are switched on and workers shall wear the appropriate PPE. All personnel normally carry a mask.

The only possible exposure to chlorine could take place during the "loading-unloading" of chlorine. Safety procedures and the use of appropriate protective equipment limit the exposure to chlorine to accidental events. Consequently, the only scenarios to be considered here are the storage of chlorine and the connection - disconnection of cylinders/drums to each other.

*Measured data*

The measured data are scarce because the potential of exposure is only linked to the connection – disconnection of chlorine vessels to each other, operations which are done at a relatively low frequency and for short periods of time (15 to 30 minutes). In the best practices, chlorine detectors are set in the storage/loading area to initiate alarm (turning red light and buzzer) in case of a leak or levels higher than 0.25 – 0.30 ppm (0.75 – 0.90 mg/m$^3$). The workers are not wearing personal detector and consequently, no measured exposure data is available.

As the operations, the safety measures and the procedures are similar to those used in production plants for the filling of tankers, it is possible to use the measured data reported in **Table 4-2** for the filling operation and **Table 4-** covering all functions. Due to the low frequency of operations, only short term exposure should be considered.

*Modelled data*

The modelled data have been obtained by applying the EASE model for assessing the possible inhalation exposure to chlorine gas for the two scenarios considered. The conditions used for modelling and the corresponding results are presented in the **Table 4-11** hereafter.

Table 4-11 EASE modelled exposure to chlorine in the distribution chain

| | Scenario 1<br>Work in storage area | Scenario 2<br>Connection–disconnection operations |
|---|---|---|
| Temperature of the process, °C | 25 | 25 |
| Physical state | gas/vapour | gas/vapour |
| Exposure type | gas/vapour | gas/vapour |
| Aerosol formation | no | no |
| Ability to become airborne | high | high |
| Use pattern | closed system | closed system |
| Pattern of control | full containment | LEV |
| Significant breaching | false | true |
| EASE EXPOSURE RANGE | 0- 0.1 ppm (0 - 0.3 mg/m$^3$) | 100-200 ppm (300 – 600 mg/m$^3$) |

The scenario 1 was not considered in chlorine production because there is no storage in cylinders or drums. The storage is a purely closed system with full containment. As there is no measured data, the result of the EASE model will be used that indicate a worst case exposure of 0.1 ppm (0.3 mg/m$^3$).

For scenario 2, the results of the modelling are indicating a potential exposure in the range 100-200 ppm (300-600 mg/m$^3$), while the measured values in **Table 4-2** are much lower. The reason of these differences is linked to the rough and simple character of the hypotheses considered in modelling. We should indeed consider that, during the filling process, there is a breaching of the system in the presence of LEV. But there is no possibility to include in the model the fact that the system is degassed and purged before opening, significantly reducing the possible exposure. Moreover, the model does not consider the existence, in practice, of an alarm at 0.25-0.30 ppm (0.75-0.90 mg/m$^3$), which initiates safety procedures and the wearing of personal protection equipment (PPE). In these conditions, the experimental measured data are more reliable than the modelled values. As explained before, the chlorine concentration measured in the atmosphere of a chlor-alkali plant is indeed a worst case for inhalation exposure.

The measured data, as given in **Table 4-2** are used. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the maximum Short Term Exposure Level (STEL) value for filling operators is varying in the range 0 to 0.5 ppm (0 to 1.5 $mg/m^3$) with an average of 0.077 ppm (0.231 $mg/m^3$) and a 90th percentile value of 0.166 ppm (0.498 $mg/m^3$). As indicated before the occasional character of these operations does not request to consider long term exposure.

Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 2 is 0.166 ppm (0.498 $mg/m^3$). There is no need to consider long term exposure.

*Summary/statement of the exposure level*

In scenario 1, storage area, the worst case, short term inhalation exposure as calculated by EASE model is 0.1 ppm (0.3 $mg/m^3$).

Using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 2, (connection-disconnection operators) is 0.166 ppm (0.498 $mg/m^3$). This value is very conservative as explained before. There is no need to consider a long term exposure due to the occasional character of the operations: the distributors deal with chlorine only occasionally and connection-disconnection of chlorine vessels normally take 15-30 minutes (low frequency and short time operation).

Dermal exposure

Because chlorine is not liquid but in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently no dermal exposure is to be expected. Moreover, the processes are closed and in case of opening of the system for maintenance purposes, safety procedures are applied in such a way that the opening of the system always takes place after complete degassing of chlorine. On the basis of a precautionary approach, the use of protective equipment such as face shield, goggles and gloves is mandatory in the working area. This clearly indicates that there is no direct contact with liquid chlorine and, consequently, no dermal exposure.

*Summary/statement of the exposure level*

There is no dermal exposure.

#### 4.1.1.2.3.2.3 Drinking water

Admissible quantities of free available chlorine in drinking water for different European countries generally vary between 0.1 and 0.5 mg/l. The WHO guideline value is up to 5 mg/l. Chlorination by-products are also covered by regulation in EU in the revised Directive 98/83/EC on the quality of water intended for human consumption. Chlorine is used not only in the water treatment plant at abstraction point, but also at different stations placed on the adduction circuit, if the purified water is transported over long distance. The chlorine content is adjusted to maintain the bacteriological quality of the water along the water distribution system.

Representative handling process

When chlorine is used as disinfection agent for production of drinking water, it is supplied either in cylinders containing 60 to 100 kg chlorine or in special drums containing 600 to 1000 kg chlorine, depending on the size of the treatment plant. These containers are provided by specialised distributors (see **section 4.1.1.2.3.2.2** on chlorine distribution). The cylinders or drums are kept in a well ventilated area, protected from rain, and access is limited to authorised and well trained personnel (locked zone). In most cases, an escape mask is at hand in the area.

The replacement of an empty cylinder/drum by a full one is the key operation where exposure to chlorine could happen. Other occupational exposure to chlorine for workers handling the product in drinking water plants does not normally occur, as the product is added to water via closed circuits. The empty container is closed and the connecting circuit is placed under depression because the system is under chlorine demand. A pressure manometer is placed on the connecting circuit to ensure that it is under depression before the connection takes place. The change of cylinder/drum is only done when the system is under depression to avoid chlorine emission. The new cylinder/drum is connected to the system through a flexible, stainless steel pipe and a new crushable join to ensure a good tightness. The new cylinder/drum is then progressively opened and checked for possible leaks with an ammonia "detector". To reduce discontinuity in chlorine feeding during the change of cylinders/drums, they are connected to the system by pair, one being in use, while the other remains in standby. When the container in use is empty, a special valve system allows a quick change to the container in standby. The change of cylinders/drums occurs at a mean frequency of about once per week and the operation takes between 20 and 30 minutes.

The loading area is equipped with chlorine detectors. They can generally detect 0.1 ppm and have a pre-alarm level of 0.25-0.30 ppm (0.75-0.90 mg/m$^3$). In case of a leak, the presence of chlorine in the atmosphere is detected, an alarm (turning red light and buzzer) is switched on and workers shall wear the appropriate PPE including a mask.

Introduction of chlorine into the water is done through rigid, stainless steel pipes, equipped with pumps and control systems. Chlorine is sucked in by a water flow into a gas-water mixer called "chlorinator", which is placed on a secondary water circuit, not directly on the main stream. All pipes are rigidly secured and the length is kept as short as possible. Several "chlorinators" can work in parallel depending on the chlorine demand. The introduction circuit and the operating conditions are automatically regulated via remote control systems.

When replacing or changing the chlorine cylinders, workers are not wearing protective personal equipment but, if necessary, an approved gas mask is on hand. Adequate ventilation of the storage local is generally assured. Maintenance and repairs of pumps, dosing and automatic control systems are carried out only by specially trained workers or specialised companies. Regular training for the safe handling of chemicals and of chlorine in particular are organised in the plants.

Inhalation exposure

As indicated in **section** 1.3.1 in water, chlorine is transformed to free available chlorine (gaseous chlorine), hypochlorous acid and hypochlorite ions (see **figure 1.1**), their ratios depending on the physical-chemical properties of the water (mainly pH). For example, at pH 7.5 half of the chlorine is present as HOCl and half as $ClO^-$. In all the uses of chlorine in water disinfection, the pH value is higher than 7.0. This means that chlorine does not exist anymore in its $Cl_2$ (gaseous) form. The scenarios considering human exposure to solutions containing hypochlorous acid and hypochlorite ions have been treated extensively in the Risk Assessment Report of sodium hypochlorite.

Consequently, the only scenarios to be considered here are the storage of chlorine and the connection - disconnection of cylinders/drums to each other or to the water systems. The main differences between the applications of chlorine in water are linked to the size of the operation and the size of the vessels used. In all cases, the chlorine gas is delivered by specialized distributors who provided the cylinders or the drums to the end-users.

*Measured data*

The measured data are scare because in all these applications the potential of exposure is only linked to the connection – disconnection of chlorine vessels to each other or to the water systems, operations which are done at a relatively low frequency, i.e. about once per week for a short period of time 15 to 30 minutes. In the best practices, chlorine detectors are set in the storage/loading area to initiate alarm (turning red light and buzzer) in case of leak or level higher than 0.25-0.30 ppm (0.75-0.90 mg/m$^3$). The workers are not wearing personal detector and consequently, no measured exposure data is available.

As the operations, the safety measures and the procedures are similar to those used in production plants for the filling of tankers, it is possible to use the measured data reported in **Table 4-2** for the filling operation. Due to the occasional character of the operations, there is no need to consider long term exposure.

*Modelled data*

The modelled data have been obtained by applying the EASE model for assessing the possible inhalation exposure to chlorine gas for the two scenarios considered. The conditions used for modelling and the corresponding results are presented in the **Table 4-12** hereafter.

Table 4-12 EASE modelled exposure to chlorine in drinking water disinfection

| | Scenario 1<br>Work in storage area | Scenario 2<br>Connection–disconnection operations |
|---|---|---|
| Temperature of the process, °C | 25 | 25 |
| Physical state | gas/vapour | gas/vapour |
| Exposure type | gas/vapour | gas/vapour |
| Aerosol formation | no | no |
| Ability to become airborne | high | high |
| Use pattern | closed system | closed system |
| Pattern of control | full containment | LEV |
| Significant breaching | false | true |
| EASE EXPOSURE RANGE | 0- 0.1 ppm (0 – 0.3 mg/m$^3$) | 100-200 ppm (300 – 600 mg/m$^3$) |

The scenario 1 was not considered in chlorine production because there is no storage in cylinders or drums. The storage is a purely closed system with full containment. As there is no measured data, the result of the EASE model will be used that indicate a worst case exposure of 0.1 ppm (0.3 mg/m$^3$).

For scenario 2, the results of the modelling are indicating a potential exposure in the range 100-200 ppm (300 – 600 mg/m$^3$), while the values measured in chlorine production plants for similar tasks are much lower. The reasons of these differences are linked to the rough and simple character of the hypotheses considered in modelling. We should indeed consider that, during the filling process, there is a breaching of the system in the presence of LEV. But there is no possibility to include in the model the fact that the system is degassed and purged before opening, significantly reducing the possible exposure. Moreover, the model does not consider the existence, in practice, of an alarm at 0.25 ppm (0.75 mg/m$^3$), which initiates safety procedures and the wearing of personal protection equipment (PPE). In these conditions, the experimental measured data are more reliable than the modelled values. As explained before, chlorine concentration measured in the atmosphere of a chlor-alkali plant is indeed a worst case for inhalation exposure.

The measured data from **Table 4-2** is used. If, as explained, the maximum exposure value is limited to the level detected by the alarm, the maximum Short Term Exposure Level (STEL) value for filling operators is varying in the range 0 to 0.5 ppm (0 to 1.5 mg/m$^3$) with an average of 0.077 ppm (0.231 mg/m$^3$) and a 90th percentile value of 0.166 ppm (0.498 mg/m$^3$). Due to the occasional character of the operations, there is no need to consider long term exposure.

Consequently, using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 2 is 0.166 ppm (0.498 mg/m$^3$); no long term exposure is considered.

*Summary/statement of the exposure level*

In scenario 1, storage area, the worst case, short term inhalation exposure as calculated by EASE model is 0.1 ppm (0.3 mg/m$^3$).

Using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 2, (connection-disconnection operators) is 0.166 ppm (0.498 mg/m$^3$). This value is very conservative as explained before. No long term exposure needs to be considered.

Dermal exposure

Because chlorine is in the gaseous form at room temperature and normal pressure, no contact with liquid chlorine and consequently no dermal exposure is to be expected. Moreover, the processes are closed and when chlorine is introduced in water, it is transformed into hypochlorite. Exposure to hypochlorite in water has been reviewed in the Risk Assessment Report of sodium hypochlorite (chapter 4.1.1.3.5).

*Summary/statement of the exposure level*

There is no dermal exposure.

#### 4.1.1.2.3.2.4 Waste water treatment

The operations linked to the use of chlorine in waste water treatment are very similar to ones described in the use of chlorine for drinking water disinfection (**section 4.1.1.2.3.2.3**) and the scenarios are the same (storage and connection – disconnection). Consequently, the same results can be used and are summarised hereafter.

*Summary/statement of the exposure level*

In scenario 1, storage area, the worst case, short term inhalation exposure as calculated by EASE model is 0.1 ppm (0.3 mg/m$^3$).

Using the 90th percentile as a reasonable worst case, the short term inhalation exposure to chlorine in scenario 2, (connection-disconnection operators) is 0.166 ppm (0.498 mg/m$^3$). This value is very conservative as explained before. No long term exposure needs to be considered.

#### 4.1.1.2.3.2.5 Swimming pool disinfection

The disinfection of swimming pool water with chlorine is submitted to several regulations. Most of them relate to the minimum content of free available chlorine (FAC) in water, which is generally around 0.4 mg/l, and the pH which has to be in a range of 6.5 to 8.5. Some regulations include a maximum level of chloramines as low as 0.6 g/m$^3$. Some countries give a maximum FAC (1.4 mg/l, France) others a maximum of urea content (Belgium, Netherlands). Other aspects of the regulations cover the number of swimmers per m$^2$ and the quantities of air and water changes per swimmer or per year.

When swimmers enter the pool, they transfer into the water soluble chemical products (soap residues, cosmetics, oils) and a large number of micro-organisms present on their skin. While they are in the pool, swimmers produce sweat, and may expel urine and saliva. All these products have to be chemically destroyed, in order to limit their concentration, by adding to the water a certain dose of an oxidising and disinfecting agent and by permanently maintaining a minimum content of this agent in the pool.

In Europe, four main products are used:

- sodium hypochlorite,
- calcium hypochlorite,
- chloroisocyanuric salts (used mainly in small swimming pools) or
- chlorine gas.

These four products provide a permanent content of hypochlorous acid (HOCl, active chlorine) in the water. Other chemicals used in swimming pools are acid (HCl, $H_2SO_4$ or $CO_2$) to decrease the pH, and flocculants ($Al^{3+}$, $Fe^{3+}$ or polyelectrolytes) to help clarify the water. The presence of filters is absolutely necessary to stop the suspended matters circulating in the water circuit.

Outdoor swimming pools consume higher quantities of disinfectant because it is destroyed by sunlight and because the sweat dissolved in the water per swimmer is greater in summer.

According to the French Ministry of Health, the quantity of disinfection agent introduced in water is between 3 and 5 g of $Cl_2$ equivalent per $m^3$ of water per day in indoor pools, between 7 and 16 g of $Cl_2$ equivalent per $m^3$ of water per day in outdoor pools.

Representative handling process

When chlorine is used as disinfection agent for swimming pool water, it is generally supplied in cylinders containing 40 to 100 kg chlorine by specialised distributors. The cylinders are kept in a well ventilated area, protected from rain, and the access of which is limited to authorised persons (locked zone). In most cases, an escape mask is at hand in the area. The replacement of an empty cylinder by a full one is the key operation where an exposure to chlorine could happen, because other occupational exposure to chlorine for workers handling the product in swimming pools does not normally occur, as the product is added via closed circuits. The change of cylinder is only done when the system is under chlorine demand, placing the connecting pipe under depression and consequently avoiding chlorine emission. The empty cylinder is then closed and the new one connected to the pipe with a new crushable join to ensure a good tightness. The new cylinder is then opened. This operation takes about 20 minutes time and is done at a frequency of about once per week.

The loading area is generally equipped with chlorine detectors which can detect 0.1 ppm (0.3 $mg/m^3$) and have a pre-alarm level of 0.25-0.30 ppm (0.75-0.90 $mg/m^3$). In case of a leak, the presence of chlorine in the atmosphere is detected, an alarm (turning red light and/or buzzer) is switched on and workers shall wear the appropriate PPE including a mask.

Introduction of chlorine into swimming pools is done through PE pipes, equipped with pumps and control systems. Chlorine is introduced in a main water mixer and header placed on the water circuit but not directly in the swimming pool. All pipes have to be rigidly secured, while keeping the length as short as possible. In order to prevent reaction with acids and the production of gaseous chlorine when the chlorine has been transformed into hypochlorite ions, acid pipes are clearly labelled and the acid is introduced via dosing pumps controlled by automatic pH measurements. The pH value is generally maintained at about 7.5.

When replacing or changing the chlorine cylinders, workers are not wearing protective personal equipment but, if necessary, an approved gas mask is on hand. Adequate ventilation of the storage room is generally assured. Maintenance and repairs of pumps, dosing and automatic control systems are carried out only by specialised companies.

Detailed safety procedures to be followed when chlorine is used in swimming pools are described in Euro Chlor document “Safe use of chlorine at swimming pools” (1998).

The paper describes safe use of liquid chlorine delivered in cylinders to non-domestic swimming pools. The objective is to eliminate any risk to the public at the swimming pool due to use of chlorine gas. This document describes the safe handling when chlorine is delivered in liquid phase in cylinders of a capacity not exceeding 100 kg. The flow rate from chlorine cylinders is generally sufficient to treat most swimming pools. The maximum chlorine gas flow rate is dependent on temperature. In Germany the recommended flow rate is 1% of cylinder content per hour and in Austria, recommended flow rate is 2% of cylinder content per hour, at 20°C. Chlorine cylinders should not be subjected to ambient temperatures in excess of 40°C.

As soon as chlorine is introduced to water and the pH regulated, it is converted to hypochlorite and reference should be made to the Risk Assessment Report of sodium hypochlorite (chapter 4.1.1.3.3). The only scenarios of possible exposure to chlorine are similar to those one described under “storage” and connection-disconnection” of chlorine under drinking water disinfection here above. The same conclusions and exposure levels should then be considered as in **section 4.1.1.2.3.2.3**.

#### 4.1.1.2.3.2.6 Chlorine in pulp and paper industry

Since the survey made in 1994 by Euro Chlor on the uses of chlorine in water applications, (see **Table 4-10**), the pulp and paper application disappeared, the use of chlorine having been replaced by the use of chlorine dioxide ($ClO_2$) as a bleaching agent. It should indeed be noted that in past years, in order to minimize the production of by-products, the European pulp and paper industry has been switching from chlorine-based bleaching to chlorine dioxide or hydrogen peroxide based bleaching processes. This has lead to the current situation in Europe, where the use of chlorine-based bleaching processes is minimal. This is confirmed by a 1998 review from CEPI (Confederation of European Paper Industries), which, though not complete, suggests that chlorine is no longer used for bleaching purposes in Western Europe. Similarly, a pulp and paper company in Norway made some measurements of chlorine concentrations in the atmosphere around the vacuum filter where the pulp is washed and no chlorine could be detected. Therefore we can conclude that human exposure to chlorine in the pulp and paper industry in Western Europe is insignificant.

#### 4.1.1.2.3.2.7 Chlorine in textile industry

The application of chlorine in the textile industry is also very minor, chlorine being more and more replaced by sodium hypochlorite as bleaching agent. The users prefer sodium hypochlorite because it is easier to handle and to store; in these applications indeed, the chlorine itself has always been introduced in water and used as sodium hypochlorite solution. Therefore we can conclude that human exposure to chlorine in the textile industry in Western Europe is insignificant.

#### 4.1.1.2.3.2.8. Chlorine for cooling water disinfection

The disinfection of cooling water is essential to avoid accumulation of micro-organism and algae in cooling towers and heat exchangers in industrial processes and, in particular, in large power plants. These are closed processes with no possible contact of human with chlorine, except during the unloading of chlorine from the storage vessel and its loading into the water system. Chlorine content and pH are monitored to avoid corrosion of the cooling system.

As soon as chlorine is introduced into water and the pH regulated, the exposure to chlorine gas is insignificant since it is converted to hypochlorite. The risk of occupational exposure for workers to cooling water and disinfection water of big aqueducts is very similar and referable to accidental exposures in occasion of filling or displacement of the storage tanks of sodium hypochlorite. This case having been considered in the corresponding Risk Assessment Report (chapter 4.1.1.3.5), the only scenarios of possible exposure to chlorine are similar to those describing “storage” and “connection-disconnection” of chlorine under drinking water disinfection. The same conclusions and exposure levels should then be considered as in **section 4.1.1.2.3.2.3**.

### 4.1.1.2.4 Summary of occupational exposure

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.

Table 4-13 Conclusions of the occupational exposure assessment

| | | Inhalation | | | | Dermal | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Reasonable worst case | | Typical concentration | | Reasonable worst case | | Typical concentration | |
| Scenario | Activity [1] | Unit: ppm [mg/m³] | Method[2] | Unit: ppm [mg/m³] | Method [2] | Unit | Method [2] | Unit | Method [2] |
| **Production** | | | | | | | | | |
| Subscenario 1<br>Cell-room operators | Long term | 0.235 [ 0.705] | Measured | 0.102 [ 0.756] | Measured | NONE | | NONE | |
| | Short term | 0.180 [0.540] | Measured | 0.072 [ 0.216] | Measured | NONE | | NONE | |
| Subscenario 2<br>Maintenance operators | Long term | 0.235 [0.705] | Measured | 0.102 [ 0.306] | Measured | NONE | | NONE | |
| | Short term | 0.160 [0.480] | Measured | 0.082 [ 0.246] | Measured | NONE | | NONE | |
| Subscenario 3<br>Filling operators | Long term | 0.235 [ 0.705] | Measured | 0.102 [0.756] | Measured | NONE | | NONE | |
| | Short term | 0.166 [0.498] | Measured | 0.077 [0.231] | Measured | NONE | | NONE | |
| Subscenario 4<br>Laboratory | Long term | 0.235 [0.705] | Measured | 0.102 [0.756] | Measured | NONE | | NONE | |
| | Short term | 0.084 [0.252] | Measured | 0.046 [0.138] | Measured | NONE | | NONE | |
| **Formulation** | | | | | | | | | |
| Subscenario 1<br>No Formulation | Long term | NA | | NA | | NA | | NA | |
| | Short term | NA | | NA | | NA | | NA | |
| USES : CHLORINE AS CHEMICAL INTERMEDIATE | | | | | | | | | |
| Subscenario 1<br>Production operator | Long term | 0.235 [0.705] | Measured | 0.102 [0.756] | Measured | NONE | | NONE | |
| | Short term | 0.180 [ 0.540] | Measured | 0.072 [0.216] | Measured | NONE | | NONE | |
| Subscenario 2<br>Maintenance operator | Long term | 0.235 [ 0.705] | Measured | 0.102 [0.306] | Measured | NONE | | NONE | |
| | Short term | 0.167 [0.501] | Measured | 0.075 [ 0.225] | Measured | NONE | | NONE | |
| Subscenario 3<br>Filling operators | Long term | 0.235 [0.705] | Measured | 0.102 [0.306] | Measured | NONE | | NONE | |
| | Short term | 0.167 [0.501] | Measured | 0.075 [0.225] | Measured | NONE | | NONE | |
| Subscenario 4<br>Laboratory operators | Long term | 0.235 [0.705] | Measured | 0.102 [0.306] | Measured | NONE | | NONE | |
| | Short term | 0.167 [0.501] | Measured | 0.075 [0.225] | Measured | NONE | | NONE | |
| USES: CHLORINE IN WATER DISINFECTION | | | | | | | | | |
| Subscenario 1<br>Storage | Long term | NONE | | NONE | | NONE | | NONE | |
| | Short term | 0.1 [0.3] | EASE | 0 [0] | EASE | NONE | | NONE | |
| Subscenario 2<br>Connection-disconnection | Long term | NONE | | NONE | | NONE | | NONE | |
| | Short term | 0.166 [0.498] | Measured | 0.077 [ 0.231] | Measured | NONE | | NONE | |

### 4.1.1.3 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. See chapter 4.1.1.4.1 of sodium hypochlorite RAR for further information on accidental exposure to chlorine.

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). Exposure to sodium hypochlorite in swimming pool and via drinking water has been discussed in sodium hypochlorite RAR (chapters 4.1.1.4.2 and 4.1.1.4.3).

#### 4.1.1.3.1 Summary of consumer exposure

No consumer exposure is expected.

### 4.1.1.4 Humans exposed via the environment

Chlorine emissions on a European level are summarised in **Table 3.1**. 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. The fate and effects of these emissions to the environment on a local scale have been dealt with in **sections 3.1.4 and 3.1.6**.

Due to the properties of chlorine the substance will only remain in the water compartment for a very short period of time (see **section** Error! Reference source not found.). 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 (see **sections 1.3 and 1.4**). 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 (chapter 3.1.6.1.1). 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”.

#### 4.1.1.5 Combined exposure

No such exposure is thought to occur.

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

As chlorine is a gaseous substance, the most significant route of exposure is by inhalation. However, especially from its use in drinking water disinfectant, exposure of residual chlorine by the oral route can occur. Under physiological conditions (37°C, pH 7.4), chlorine reacts with water in the tissues to give nascent oxygen, hydrogen chloride and hypochlorous acid.

The following reactions can take place (CEC, 1992):

$Cl_2 + H_2O \Leftrightarrow HCl + HClO$ (Equilibrium; predominant species is pH-dependent)
$2Cl_2 + 2H_2O \Leftrightarrow 4HCl + O_2$
$3Cl_2 + 3H_2O \Leftrightarrow 5HCl + HClO_3$

The primary available chlorine species in solution in water are not different from those coming from hypochlorous acid at similar pH. Therefore tests using solutions of chlorine prepared by bubbling chlorine gas into water and adjusting pH (to slightly basic conditions) are comparable to those using hypochlorite solutions with pH adjusted.

Chlorine, as chlorine gas, chlorite ion or hypochlorite, is a strong oxidant that readily reacts with organic molecules to produce a variety of chlorinated compounds. This reactivity in biological systems makes it difficult to study the pharmatoxicokinetics of chlorine and to separate the effects of chlorine from those of the chlorinated derivatives and their metabolites.

#### 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.

The primary available chlorine species in aqueous solution are not different from those coming from hypochlorous acid at similar pH. 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.)

#### 4.1.2.1.1 Studies in animals

*Inhalation*

Effects of chlorine exposure in rats and mice are depending on concentration. At moderate to high concentrations chlorine can exert its effect over the whole respiratory tract. In a 6 week inhalation study at 9 ppm in rats hyperplasia and hypertrophy of epithelial cells was observed in bronchioles, alveolar tracts and alveoli (Barrow et al., 1979). On the other hand, at low concentrations ($\leq$ 2.5 ppm, 7.5 mg/m$^3$) effects of chlorine exposure occur only in the upper airways as was demonstrated by the results of a 2-year inhalation study in rats and mice, in which lesions were confined to the nasal passage (Wolf DC et al.).

*Dermal*

Due to the gaseous nature, no specific studies are available. Also no toxicokinetic information following dermal exposure studies of chlorine solutions in water is available.

*Oral*

A series of pharmacokinetic studies using $^{36}$Cl-labelled hypochlorous acid were conducted (Abdel-Rahman et al., 1983) in rats. These studies are of limited value as the form of $^{36}$Cl could not be determined in various body compartments. Three groups of 4 Sprague-Dawley rats were orally administered with different quantities of HO$^{36}$Cl solution. A peak of radioactivity in rat plasma occurred 2 hours after HO$^{36}$Cl administration in fasted rats and 4 hr after administration in non-fasted rats. $^{36}$Cl radioactivity was distributed throughout the major tissues, 96 hr after HO$^{36}$Cl administration. The highest levels were found in plasma, whole blood, bone marrow, testis, skin, kidney and lung. The lowest levels were found in the liver, carcass and fat tissue. HO$^{36}$Cl-derived radioactivity was not detected in expired air throughout the 96 hr study. During the same period, 36.43% + 5.67 (mean + S.E.) of the administered dose was excreted through the urinary route, while 14.8% + 3.7 was recovered in the faeces, giving a poor total recovery of 51.23% + 1.97 (Abdel-Rahman et al., 1983).

Vogt et al. (1979) reported that chloroform could be measured in the blood, brain, liver, kidneys and fat of rats to which sodium hypochlorite was administered by gavage at doses of 20, 50 or 80 mg in 5 ml of water. Thus, the by-product chloroform can be formed by the reaction of chlorine with stomach contents.

Other by-products formed in vivo by the interaction of chlorine and stomach content that have been reported are dichloroacetonitriles (DCAN), dichloroacetic acid (DCA) and trichloroacetic acid (TCA) (Mink et al., 1983). Fasted and non-fasted rats received 7 ml of an 8 mg/ml solution of sodium hypochlorite at pH 7.9 (about 140 mg/kg bw) by gavage. TCA was found in the gut contents and in the plasma 1 hour after the treatment, suggesting the formation of trichloroacetic acid independently from foreign organic material in the gut.

Chloroform and DCA were also detected, generally associated with TCA. DCAN was also detected in some of the non-fasted rats (Mink, 1983).

Scully and co-workers reported on the formation of organic chloramines in stomach contents by chlorination of free amino acids. The chlorine demand of free amino acids in stomach contents was found to be only about 4% of the total. Consequently, this process may be substrate-limited at concentrations of chlorine found as residuals in drinking-water. However, use of higher concentrations of chlorine would also lead to breakdown of proteins present in the stomach fluid. Thus, as concentrations are increased to levels that would be used in animal studies, these products would be formed at a much higher concentration, similar to the phenomena noted with trihalomethanes (THM) and haloacetic acids (HAA) by-products (Scully et al., 1990).

No chlorination reaction products were observed in urinary extracts of rats after ingestion of 8 and 16 mg/day sodium hypochlorite solution for 8 days (Kopfler, 1985).

#### 4.1.2.1.2 Studies in humans

Although the possible effects of human exposure via different routes to chlorine, whether as chlorine gas, chlorite ion or hypochlorite, are well-known, few data are available on quantitative rates of by-products formed, distributed, metabolised and excreted.

*Inhalation*

Also in humans effects of chlorine will primarily be confined to the upper airways.

Groups of 5 men and 5 women were exposed to various concentrations of a bolus peak concentration of 3 ppm (9 mg/m$^3$) chlorine at respiratory flows of 150, 250 and 1000 ml/sec. Differences in uptake between mouth and nasal breathing were examined. Because $Cl_2$ rapidly and reversibly hydrolyses in aqueous solution, increasing the respiratory flow does not increase the $Cl_2$ that reaches the respiratory air spaces during either nasal or oral breathing. Less than 5% of the inspired $Cl_2$ penetrated beyond the upper airways and none reached the respiratory air spaces. In all cases, more than 95% of the chlorine inhaled was absorbed in the upper airways (Nodelman and Ultman, 1999).

*Dermal*

No specific studies available. There is also no toxicokinetic information available from human exposure studies with chlorine solutions in water by dermal route.

*Oral*

There is no specific data available on oral exposure to chlorine gas. Also no toxicokinetic information is available from human oral exposure studies with chlorine solutions in water.

#### 4.1.2.1.3 Summary of toxicokinetics, metabolism and distribution

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.

Although only moderately soluble in the epithelial lining fluid, its fast reaction to surface material and tissue of the respiratory tract causes it to be a potential toxic gas. Mice and rats are obligate nose breathers and have a more complex nasal structure then humans, and develop more severe nasal responses to inhalation toxicants then humans. However, available data indicate that in both humans and rodents at low concentrations (below 2.5 ppm, 7.5 mg/m$^3$) almost all chlorine is absorbed in the upper airways and does not reach the lower airways.

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

Many animal studies on the acute inhalation toxicity of chlorine gas have been conducted in the past. Furthermore a significant amount of human data is available.

Solutions of chlorine in water contain hypochlorous acid and/or hypochlorite. The acute toxicity of these solutions is described in the EU RAR of Sodium Hypochlorite.

#### 4.1.2.2.1 Studies in animals

In vivo studies

*Inhalation*

The acute inhalation toxicity of chlorine gas has been investigated in a great number of animal species including rodents, rabbits, guinea pigs, dogs, cats and pigs.

***Lethality***

Rat and mouse

Weedon et al. (1940) found a LT$_{50}$ of 28 minutes for mice and of 53 minutes for rats exposed to 1000 ppm (3000 mg/m$^3$). For rats and mice the available lethality data (individual mortality data, LC$_{50}$) for up to 60 minutes chlorine exposure are presented in **Table A-1, Table A-2, Table A-3 and Table A-4 (Appendix)**.

Limited data on lethality are available for exposures longer than 60 minutes.

In mice and rats exposed to 250 ppm (750 mg/m$^3$) the LT$_{50}$ was 440 minutes. The first rat died at 6.4 hours, the last one 16 hours after start of exposure (Weedon et al. 1940).

Mice exposed to 170 ppm (510 mg/m$^3$) for 85 to 160 minutes showed a mortality of 57-71% after 30 days of observation (Bitron and Aharonson, 1978). Exposure of female mice to chlorine for 3 hours at 22 ppm (66 mg/m$^3$) resulted in 100% mortality. At 10 ppm (30 mg/m$^3$) 80% mortality was observed after 3 hours and 90% after 6 hours of exposure (Schlagbauer and Henschler, 1967).

Dog

For dogs exposed to chlorine a 3 minute $LC_{50}$ of 7500 ppm (22500 mg/m$^3$) was reported (NRC, 1976). Exposure of dogs for 30 min to 800-900 ppm (2400-2700 mg/m$^3$) chlorine resulted in more than 85% mortality (Barbour, 1919). For the same exposure period the $LC_{50}$ in dogs is 636 ppm (1908 mg/m$^3$) after 5 days observation (**Table 4-13**; Underhill, 1920).

Table 4-13 Acute inhalation toxicity dog (mortality)

| Concentration (ppm – mg/m$^3$) | Animal number | Exposure time (minutes) | Mortality % (Observation days) | Reference |
|---|---|---|---|---|
| 1583 - 4749 | 14 | 30 | 93 (5) | Underhill, 1920 |
| 928 - 2784 | 23 | 30 | 91(5) | Underhill, 1920 |
| 819 - 2417 | 18 | 30 | 61(5) | Underhill, 1920 |
| 710 - 2130 | 21 | 30 | 67(5) | Underhill, 1920 |
| 600 - 1800 | 10 | 30 | 40(5) | Underhill, 1920 |
| 491 - 1473 | 17 | 30 | 30(5) | Underhill, 1920 |
| 164 - 492 | 9 | 30 | 11(5) | Underhill, 1920 |

Rabbit

An exposure to 1000 ppm (3000 mg/m$^3$) for 30 minutes was lethal to rabbits within one hour. Hundred percent mortality was also observed in a 2-day observation period among rabbits exposed for 30 minutes to 500 ppm (1500 mg/m$^3$), but all animals survived at 250 ppm (750 mg/m$^3$) (Barrow and Smith, 1975). Mortality was observed among rabbits exposed for 280 to 630 ppm (840 to 1890 mg/m$^3$) for 65 minutes (Lehmann, 1887).

Cat

Mortality was observed among cats exposed for 15 minutes to 400 to 1430 ppm (1200 and 4290 mg/m$^3$) (Hill, 1915).

Cats exposed to 268 to 630 ppm (804 to 1890 mg/m$^3$) died within 65 minutes (Lehmann, 1887).

Pig

In anaesthetised and mechanically ventilated pigs, exposure to 110 and 140 ppm (330 and 420 mg/m$^3$) chlorine for 10 minutes resulted in mortality in five out of six animals in 6 hours (Gunnarsson et al., 1998).

Guinea pig

Among guinea pigs exposed for 30 minutes mortality was observed above 3300 ppm (9900 mg/m$^3$) (Zeehuisen, 1922). Guinea pigs exposed to 280-810 ppm (840 – 2430 mg/m$^3$) died between 50 and 190 minutes (Lehmann, 1887).

### Conclusions (acute inhalation, mortality)

- No 4-hour inhalation $LC_{50}$ in rats is available. In rats, the 60 minutes $LC_{50}$ is 448 ppm (1.3 mg/l, 1344 mg/m$^3$). The EU classification for acute toxicity by inhalation is Toxic. (T, R23).
- Between species the variation in lethality ($LC_{50}$) is given in **Table 4-14**:

Table 4-14 Acute inhalation toxicity (LC50)

| Species | 10 min | 30 min | 60 min |
|---|---|---|---|
| mouse | 290-1033 ppm [870-3099 mg/m$^3$] | 127-496 ppm [381-1488 mg/m$^3$] | 137-170 ppm [411-510 mg/m$^3$] |
| rat | 1913 ppm, 5739 mg/m$^3$ | 689 ppm [2067 mg/m$^3$] | 448 (-689) ppm [1344 (-2067) mg/m$^3$] |
| dog | | 636 ppm [1908 mg/m$^3$] | |
| rabbit | | 250-500 ppm [750-1500 mg/m$^3$] | |

- The Toxicity Working Party of Major Assessment Panel (UK, 1985) used a selected set of eight experiments (*) to arrive at a reasonable representative overall value for a 30 minutes $LC_{50}$ for animals of about 300-400 ppm (900-1200 mg/m$^3$). This conclusion was based on experiments with exposure times up to 2 hours of which a substantial amount were mouse data (overall average 30 min $LC_{50}$ of about 250 ppm, 750 mg/m$^3$) together with some rat data (400 ppm, 1200 mg/m$^3$) and one set of dog data (600 ppm, 1800 mg/m$^3$).
  (*) Bitron and Aharonson (1978), Schlagbauer and Henschler (1967), Underhill (1920), Weedon (1940), Silver and Mc Grath (1942), Alarie (1980).
- Lethality thresholds for animals can be derived from dose response relationships. $LC_{01}$ values calculated by Zwart (1987) and Ten Berge et al. (1986) for 30-minute exposures are 112 ppm (336 mg/m$^3$) for mice and 424 ppm (1272 mg/m$^3$) for rats.
- The individual mortality data for all species for up to 60-minute exposures show no lethality below 62 ppm (186 mg/m$^3$) (**Table A-1**). In female mice exposed to chlorine for 3 hours at 22 ppm (66 mg/m$^3$) resulted in 100% mortality, while at 10 ppm (30 mg/m$^3$) 80% mortality was observed (Schlagbauer and Henschler, 1967).

### *Effects*

Mouse

Mice exposed to 2000 ppm (6000 mg/m$^3$) chlorine for 10 minutes showed hyperplasia in the epithelium of the conductive airways at day 4. The relative lung weights of mice that survived (450-1181 ppm, 1350-3543 mg/m$^3$) were still increased at the end of the 14-day observation period. Increase in relative lung weight (> 10 g/kg bw.) showed a positive correlation with exposure time and concentration (Zwart, 1987).

Mice exposed to 1000 ppm (3000 mg/m$^3$) were subdued. Later moderate dyspnea, foamy secretion at the nostrils and marked lachrymation were noticed. All mice died within 50 min showing prostration and terminal convulsions. In mice exposed to 250 ppm (750 mg/m$^3$) very few effects other than lachrymation were observed during the first hour of exposure. (Weedon et al., 1940).

Silver et al (1942) reported that death among mice exposed to 380-842 ppm (1140-2526 mg/m$^3$) (measured) chlorine for 10 minutes occurred from oedema, lung congestion and secondary pneumonia. The lungs of animals killed at day 14 after exposure were practically free from pathological changes.

Mice exhibited lachrymation, rhinorrha and gasping after exposure to 122-193 ppm (366-579 mg/m$^3$) chlorine for 1 hour. Mice that survived at the lowest exposure level had subnormal weight gains during the post exposure observation period (MacEwen and Vernot, 1972).

Schlagbauer and Henschler (1967) mainly observed increased lung weight and lung damage in mice that died after a 30 minutes exposure to 62-179 ppm (186-537 mg/m$^3$). The lung damage was characterised by severe necrotic damage of the tracheal epithelium, desquamation of bronchi and bronchioli, and alveolar oedema. In animals surviving eight to ten days after exposure to 55-160 ppm (165-480 mg/m$^3$) chlorine only minor residual damage was observed in the respiratory epithelium.

Mice (and also rats) exposed to 9 ppm (27 mg/m$^3$) chlorine for 6 hours exhibited lesions mainly in the nasal passage including epithelial necrosis, cellular exfoliation, erosion, ulceration and squamous metaplasia (Jiang et al., 1983)

<u>Rat</u>

Rats exposed to chlorine (317-5695 ppm, 951-17085 mg/m$^3$) (Zwart, 1987; Weedon et al., 1940) responded with rapid shallow breathing, which lasted only a few seconds. Thereafter the animals showed laboured breathing characterised by a low respiration rate, a maximal inspiration and a long inspiratory pause. Expiration was rapid and was directly followed by inspiration. Near the end of the exposure period (60 min) the respiration pattern changed to gasping, probably induced by the developing oedema. During exposure rats were restless and showed signs of irritation (eyes closed, wet nares, nasal discharge and bubble formation). After exposure (565-585 ppm, 1695-1755 mg/m$^3$, 30-60 min), effects on the respiratory tract were absent in early deaths (less than 1 day). No effects on the nasal epithelium were registered, while slight hyperplasia of the larynx and trachea epithelium (occasionally accompanied by squamous metaplasia) was observed in animals sacrificed 2 days after exposure. Effects on the lung were present at 2 and 14 days after exposure and consisted of:

- focal disorganisation of bronchiolar epithelium occasionally accompanied by squamous metaplasia
- focal (perivascular and peribronchiolar) aggregates of poly and/or mono morphonuclear inflammatory cells
- focal increased septal cellularity
- focal pneumonitis, oedema.

All these changes were generally described as slight. Following exposure to high concentration and short exposure time, e.g. 5700 ppm (17100 mg/m$^3$) for 5 min, effects in the nose and larynx/trachea were still present at 14 days after exposure. Relative lung weight of rats, exposed to chlorine at levels higher than the $LC_{01}$ (424 ppm, 1272 mg/m$^3$, 30 min), were still increased at the end of the 14-day observation period. The increase showed a positive correlation with exposure concentration and time.

Exposure for 2 minutes to 1500 ppm (4500 mg/m$^3$) resulted in mild perivascular oedema and occasional small clusters of polymorphonuclear leukocytes in the mucosa of large airways. Rats exposed for 5 minutes to 1500 ppm (4500 mg/m$^3$) showed increased lung resistance and an inflammatory response (neutrophils in the BAL fluid) up to 3 days and enhanced responsiveness to methacholine up to 7 days after exposure. In rats exposed for 5 and 10 minutes, 1500 ppm (4500 mg/m$^3$) chlorine caused severe effects (moderate perivascular and intra-alveolar oedema, epithelial necrosis and detachment) in the lungs within one day after exposure, followed by an inflammatory reaction for three days. At 72 hours after exposure the lung epithelium showed signs of regeneration, which was still significant after 7 days. Full recovery took about 30 days. (Demnati et al., 1995; Demnati et al., 1998ab).

Rats exhibited lachrymation, rhinorrha and gasping after exposure to 213-427 ppm (639-1281 mg/m$^3$) chlorine for 1 hour. Depressed growth rates were seen in rats surviving 268 ppm (804 mg/m$^3$) chlorine. Most common finding at necropsy was mottling of the liver tissue. (MacEwen and Vernot, 1972)

Lungs from rats exposed to 50 to 100 ppm (150-300 mg/m$^3$) for 2 minutes were normal within 72 hours after exposure. Only slight perivascular oedema was observed at 200 and 500 ppm (600-1500 mg/m$^3$) and 2 to 5 minutes exposure (Demnati et al., 1995).

Exposure of rats to 9.1 ppm (27,3 mg/m$^3$) chlorine for 6 hours resulted in moderate to severe lesions in the respiratory tract confined to the upper airways (Jiang et al., 1983).

Dog

Exposure of dogs to chlorine (Underhill, 1920; Winternitz et al., 1920; Barbour, 1919) for 30 minutes induced general excitement (restlessness, barking, urination and defecation), irritation (blinking of eyes, sneezing), salivation, retching, vomiting and laboured-distressed breathing. After exposure, the symptoms continued in those animals exposed to the highest concentrations (up to 2000 ppm, 6000 mg/m$^3$) In addition, loss of appetite, depression, weakness and changes in body-temperature and pulse rate were observed. Dogs dying within 24 hours following exposure showed severe injury of the mucous membranes of the upper respiratory tract with irregular dilation and contraction of the bronchi resulting in alternating patches of acute emphysema and atelectasis occurred. In those dying later (2-5 days), there was an increased intensity of inflammation and development of lobular pneumonia; abscess formation, gangrene and bronchiolar spasm. Pulmonary infection, pneumonia, bronchitis were indicated as the cause of death in late deaths (5-15 days). Survivors (exposed to 164-200 ppm, 492-600 mg/m$^3$ for 30 minutes after15-193 days) showed residual effects of exposure (fibrosis, chronic bronchitis, emphysema and bronchiolitis obliterans).

Acidosis was observed in dogs exposed to chlorine to 80-90 ppm (240-270 mg/m$^3$) for 30 minutes (Hjort and Taylor, 1919).

Dogs exposed to 24-30 ppm (72-90 mg/m$^3$) chlorine for 30 minutes had an increased body temperature showed signs of irritation, salivation, retching and vomiting. All effects returned to normal directly after exposure (Babour, 1919).

Rabbit

Acute lung injury was studied in the isolated rabbit lung exposed to 500 ppm (1500 mg/m$^3$) chlorine for 10 minutes. Following exposure, an increase in lung weight was observed within 30 minutes caused by pulmonary oedema as a result of increased permeability of the pulmonary micro-circulation. Microscopic changes varied from discrete congestion of the alveolar capillaries to large areas of intra-alveolar oedema. Necrosis and desquamation of the bronchial epithelium was also observed (Menaouar et al., 1997).

Post-mortem examination showed that lungs from rabbits exposed to 100 and 200 ppm (300 and 600 mg/m$^3$) for 30 minutes appeared mildly haemorrhagic at day 3 and 14 (chronic pneumonitis, anatomic emphysema bronchitis, bronchiolitis). At day 60 effects on pulmonary compliance were still present in these rabbits. Rabbits exposed to 50 ppm (150 mg/m$^3$) chlorine for 30 min showed reversible effects in pulmonary compliance (Barrow and Smith, 1975).

Rabbits exposed to 33-66 ppm (99-198 mg/m$^3$) for several hours were restless, and showed dyspnea. Three to four days after exposure, bronchitis, bronchiolitis, emphysema and haemorrhagic spots were found in rabbits exposed to 66 ppm (198 mg/m$^3$). The effects seen following exposure to 33 ppm (99 mg/m$^3$) were less dramatic (atelectasis, foamy secretion) (Lehmann, 1887).

Cat

Cats exposed to 18-66 ppm (54-198 mg/m$^3$) of chlorine for 3-5 hours showed salivation, dyspnea, and signs of irritation and were frequently vomiting during exposure. After exposure, the major symptom was coughing. Effects on the lung (oedema haemorrhage, emphysema) were present directly and up to 3 days after exposure (Lehmann, 1887).

Pig

Anaesthetised and mechanically ventilated pigs exposed to 110 or 140 ppm (330 or 420 mg/m$^3$) chlorine for 10 minutes developed severe pulmonary dysfunction (increased pulmonary vascular resistance, decrease in Pa02. Microscopic examination showed sloughing of the bronchial epithelium, interstitial oedema and early infiltration with leukocytes, but largely intact alveoli 6 hours after exposure (Gunnarsson et al., 1998; Gunnarsson et al., 2000).

Guinea pig

Exposure of guinea pigs to 33-66 ppm (99-198 mg/m$^3$)of chlorine for 3.5-6.5 h resulted in dyspnea, signs of irritation and respiratory depression. Directly after exposure, the lungs showed oedema, haemorrhage and signs of emphysema (Lehmann, 1887).

### Conclusions (acute inhalation, effects)

Inhalation of chlorine gas induces effects on the lung. Brief exposures in rats and mice did not induce significant histological changes up to 500 ppm (1500 mg/m$^3$). Exposures up to 60 minutes to 50-500 ppm (150-1500 mg/m$^3$) induced effects on the respiratory system, which were reversible in two weeks. After several hours exposure to 18-33 ppm (54-198 mg/m$^3$) chlorine effects, other than signs of irritation and respiratory depression, like increased body temperature, salivation, foamy secretion, vomiting, haemorrhage, necrotic damage of the tracheal epithelium, desquamation of bronchi and bronchioli, alveolar oedema, atelectasis and emphysema, were observed in all animal species studied. In rats and mice after 6 hours exposure to 9 ppm (27 mg/m$^3$) chlorine moderate to severe lesions in the respiratory tract were reported.

*Dermal*

No specific studies available. However, chlorine is a gas and therefore the target organ for acute exposure is the lung, which explains why dermal studies with chlorine gas are not available. When added to water, chlorine reacts to form hypochlorous acid and/or hypochlorite (see chapter 2.2.2). The acute dermal toxicity of these solutions is described in the EU RAR of Sodium hypochlorite (chapter 4.1.2.2).

*Oral*

No specific studies available. However, chlorine is a gas and therefore the target organ for acute exposure is the lung, which explains why oral studies are not available. Acute oral exposure to chlorine gas is not a realistic exposure scenario. When added to water, chlorine reacts to form hypochlorous acid and/or hypochlorite (see chapter 2.2.2). The acute dermal toxicity of these solutions is described in the EU RAR of Sodium hypochlorite (chapter 4.1.2.2).

In vitro studies

Cralley (1942) examined the effects of chlorine on mucociliary activity of sections of excised rabbit trachea. The excised tracheal tissue was maintained in a constant temperature-humidity chamber and observed microscopically. 30 ppm (90 mg/m$^3$) of chlorine for 5 minutes and 18-20 ppm (54-60 mg/m$^3$) for 10 minutes caused cessation of ciliary activity without recovery. It was reported that the concentration necessary to produce ciliostasis is of the same order as that which produces immediate irritation of the throat, i.e. 15 ppm (45 mg/m$^3$). Concentrations ranging from 200 ppm (600 mg/m$^3$) for less than one minute to 20 ppm (60 mg/m$^3$) for about 2.5 minutes caused reversible ciliostasis.

#### 4.1.2.2.2 Studies in humans

In vivo studies

*Inhalation*

Despite mortality was observed among people exposed to chlorine gas either during warfare or due to accidental release of the gas no exact data on lethal concentrations and exposure times are reported. The available case reports on accidental exposure, in which some indication of the extent of exposure and its effect on the persons involved is given, are the following:

- Large volume of chlorine gas escaped from railroad car resulting in a few seconds/few minutes exposure to more than 1000 ppm (3000 mg/m$^3$) of 19 persons. No deaths occurred (Charan et al., 1985).
- Near Bombay 88 people, aged 21 to 60 years, were exposed at a chemical plant to 66 ppm (198 mg/m$^3$) chlorine for nearly one hour. They all presented dyspnea and coughing, as well as irritation of the throat and eyes, headache, giddiness, chest pain and abdominal discomfort. Radiological investigation in the hospital revealed in some persons hilar congestion and prominent bronchial vasculature markings. Respiratory incapacity was observed in 62 persons 48 hours after the exposure. A bronchoscopy after 5 days revealed tracheobronchial congestion in 56 persons and chronic bronchitis in 12 persons. In 28 persons scattered hemorrhagic spots were noted under the bronchial mucosa. Seven persons showed evidence of bronchial erosion and had persistent cough and respiratory distress. Cytopathological features were observed in bronchial brushings up to 25 days after exposure (Shroff et al., 1988).
- Mjondalen, Norway, 7-8 tons of chlorine released, 85 people hospitalized, 3 of whom died (2 immediately, 1 after 5 days), 30-60 ppm (90-180 mg/m$^3$) estimated exposure (Romcke and Evensen, 1940; Hoveid, 1956).
- Rupture of railroad tank, 30 tons of liquid chlorine, 100 persons treated, and exposure 10 ppm (30 mg/m$^3$) after 3 hours, 400 ppm (1200 mg/m$^3$) after 7 hours, 1 death (infant) (Joyner and Durel, 1962; Weill et al., 1969).
- In a submarine 47 persons were exposed mostly at levels above the odour thresholds, some to levels equal or higher than 34 ppm (102 mg/m$^3$) for about 15 minutes, of them 26 persons were seriously affected (Tatarelli, 1946).
- Six tons of chlorine leaked from Erkimia's site at Flix resulting in an average atmospheric chlorine concentration of 5 ppm (15 mg/m$^3$), though for short periods concentrations reached 20 ppm (60 mg/m$^3$). Twelve people were injured - six plant workers and six

residents - close to the plant; all were released from the hospital within a few days. (Chemical Week 31 January 1996)
- Two employees from a Dow Chemical plant in Pittsburg were treated at a Medical Center for chlorine vapour inhalation. They complained of light-headedness and sore throats after about 75 pounds (34 kg) of chlorine leaked from a pipe. The chlorine vapour registered at 2 ppm (6 mg/m$^3$) (San Francisco Chronicle, 3 February 1998).

The cause of death after chlorine exposure is almost always recorded as pulmonary oedema. Other causes of death that relate to exposure to very high concentrations of chlorine over very short periods of time are:
- broncho-constriction,
- shock,
- immediate respiratory arrest,
- cardiac complications.

Overall after acute chlorine exposure, the following signs and symptoms are described:
- In very severe cases: nausea, vomiting with syncope and coma, as well as convulsions;
- In severe cases in addition cyanosis, decreased body temperature, muscle pain, pink sputum, rales and pulmonary oedema are observed;
- In mild to severe exposures symptoms start within 10 minutes of exposure and dysfunction cleared within 1 to 3 months (Kaufman and Burkons, 1971; Beach et al., 1969; Ploysongsang et al., 1982).

In cases where no pulmonary oedema was evident, symptoms resolved within 1 week in subjects whose chief complaint was cough. A slower resolution was noted in subjects whose initial chief complaint was dyspnea. In these subjects pulmonary function was still impaired 2 weeks after exposure (Hasan et al., 1983).

More general symptoms of chlorine exposure, also occurring at low concentrations, are:
- Cough
- Dyspnea
- Dizziness
- Headache
- Irritation (lung, skin)
- Dryness of the oropharyngeal mucosa
- Irritation of the conjunctiva and nasopharynx
- Lacrimation,
- Chest pain,
- Fever,
- Fatigue on exertion.

Even though chlorine at low concentrations does not produce any serious subjective symptoms, it adversely affects pulmonary function.

Exposure of volunteers at 1 ppm (3 mg/m$^3$) for 4 to 8 hours resulted in sensory irritation and changes in pulmonary functions, resolving within 1 day. At 0.5 ppm (1.5 mg/m$^3$) for up to 8 hours only trivial changes were observed (Rotman et al., 1983).

Anglen (1980) obtained similar results. In this study, pulmonary function measurements showed increased mucous secretion from the nose and increased mucus in the hypopharinx after 4-hour exposure to 2.0 ppm (6 mg/m$^3$) and after 8 hour to 1.0 ppm (3 mg/m$^3$). No effects on pulmonary function were observed after exposure to 2.0 ppm (6 mg/m$^3$) for 2 hours and to 0.5 ppm (1.5 mg/m$^3$) for 8 hours.

Further evidence that 0.5 ppm (1.5 mg/m$^3$) is a NOAEL in humans is provided by a study of Emmen and Hoogendijk (1997), which was published by Schins et al. (2000). The study was well documented and was done according to Good Clinical Practice. The objectives of this study were:

1) to determine if chlorine exposure at low levels induces nasal effects in humans as it does in rodents; and
2) to establish a possible occurrence of respiratory effects in human volunteers exposed to chlorine vapour at concentrations of 0, 0.1, 0.3 and 0.5 ppm (0, 0.3, 0.9 and 1.5 mg/m$^3$).

The 8 male volunteers were exposed for 6 hour per day on 3 consecutive days to each of the 4 exposure conditions. Data analysis was limited to 7 subjects since one volunteer decided to stop participating for reasons not related to the study.

Some adverse effects were reported by the volunteers and registered by the physician. Most of them were classified as “impossible” or “unlikely” to be treatment related. The following effects were judged as “possible” to be treatment related: sinus tension (1 case), eye irritation (5 cases), coughing (2 cases), nose congestion (2 cases), dry throat (1 case), dry mouth (1 case), throat irritation (1 case), expiratory wheeze (1 case), mucus production in nasal cavity (1 case).

The study concluded that nasal lavage measurements did not support an inflammatory response or irritant effects on the nasal epithelium. Furthermore no significant effect on lung function parameters was found. The study did not support an inflammatory effect in the nose nor shows changes in the respiratory function at repeated exposure up to 0.5 ppm (1.5 mg/m$^3$). Also Shusterman et al. (1998) did not find any significant change in nasal airway resistance in persons exposed to 0.5 ppm (1.5 mg/m$^3$) for 15 minutes.

D’Alessandro et al (1996) exposed normal and hyper-responsive individuals to chlorine at 0.4 or 1.0 ppm (1.2 or 3 mg/m$^3$) for 60 minutes. No significant changes were seen in hyper-responsive individuals exposed to 0.4 ppm (1.2 mg/m$^3$). At 1.0 ppm (3 mg/m$^3$) a significant fall in FEV1 was recorded, which was greater in hyper-responsive individuals.

Recently, one case was reported by Benjamin and Pickles (1997) of chlorine-induced anosmia. The person inhaled three or four breaths of chlorine over 20 seconds. He developed acute dyspnea and pains in the chest. He was diagnosed as having pulmonary oedema and was hospitalized for four days. The person had a reduced sensation of taste and complete lack of smell, the latter remaining for at least two years.

There is very limited evidence in the literature for chronic adverse neurological effects following acute chlorine exposure. Kilburn (2000) evaluated twenty-two persons, 7 to 48 months after an acute chlorine exposure at home and at work, with a battery of neurobehavioral and visual tests. Each test for each person was compared with individually predicted test values calculated with equations derived from nearly 300 individuals who were unexposed to chemicals from two communities. These subjects completed questionnaires related with health complaints and occupational and other exposures to chemicals and a standard respiratory questionnaire was also completed. The exposed subjects were exposed accidentally to chlorine but in no instance was the chlorine concentration in air measured. Chronic effects observed after acute exposure included memory loss, hearing loss, impaired balance, decreased vibration sensitivity, decreased colour discrimination, decreased reaction time, decreased grip strength and decreased verbal recall.

Apart from the author of this study, it is generally not accepted that chlorine is directly causing neurological effects.

A syndrome, defined by Brooks et al (1985) as Reactive Airways Dysfunction Symptom (RADS) has also been related to acute chlorine exposure. This syndrome is a sudden onset type of asthmatic illness occurring in responsive subjects, with normal pulmonary physiology and with no bronchial hyper-reactivity, following acute inhalation of high-dose irritant gases.

Several cases of respiratory hyper-responsiveness following acute exposure to high concentration of chlorine have been reported in the literature:

A number of studies have shown that chronic obstructive changes (decreased FEV1 and FEV1/FVC) can occur in workers who had been exposed previously to high levels of chlorine. Changes in airway reactivity (measured by challenge testing, such as methacholine challenge testing) among workers exposed to chlorine have also been assessed. These studies suggest that bronchial hyper-responsiveness appears to be a chronic effect of chlorine among exposed workers:

- Schwartz et al (1990), after an average of 8.5 years follow-up, noted airflow obstruction in exposed workers, but suggested it was probably not due to exposure. However, they also noted airway hyper-reactivity in 5 of 13 individuals, 12 years after exposure, that appeared to be directly related to the degree of airflow obstruction and air trapping observed immediately after exposure, and hence may be related to exposure.
- In a longitudinal study (1992-94) in 239 workers of a metal production plant accidental chlorine exposure could be related to increase in airway responsiveness in 19 workers (Gautrin et al., 1999). In addition, chronic rhinitis in these workers was significantly associated with acute exposure to chlorine (Leroyer et al., 1998).

In addition to studies of workers exposed to chlorine, where there may be more than one exposure over a period of time, there have been reports of individuals with one acute exposure to chlorine who appear to be suffering chronic respiratory effects from the exposure:

- A restrictive defect with a decrease in lung diffusing capacity has been described 2 to 3 years after chlorine exposure in a study by Kowitz et al (1967).
- Boulet (1988) reported on two cases of exposed individuals, one exposed to hydrochloric acid and the other to a bleaching agent which contained chlorine, with bronchial hyper-responsiveness present one and six years after exposure, respectively. The presence of mild pre-existing asthma in the first case may have exacerbated the effects of exposure.
- Schonhofer et al (13) followed-up three exposed individuals, and noted bronchial hyper-responsiveness and reactive airways dysfunction syndrome more than 2.5 years post exposure.

Besides the research mentioned above, there has been some work that suggest no chronic effects of chlorine exposure. Weill et al (1969) and Jones et al (1986) did not find abnormalities up to 6 years after accidental chlorine exposures that could not be attributed to other underlying lung diseases or smoking. Also Leroyer et al (1998), in their 4-year follow-up of 13 workers with accidental chlorine exposure, showed complete recovery in three months for the individual who had decreased FEV1 and two individuals with decreased PC20. Hasan et al (18) found improvement in respiratory symptoms, FVC, and FEV1 within 5 months. In this study, however, the bronchial hyper-responsiveness was not assessed.

*Dermal*

No specific studies available with chlorine gas.

*Oral*

No specific studies available with chlorine gas.

#### 4.1.2.2.3 Summary of 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 $C^n \times t = k$. 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 $C^n \times t = k$, '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 $\leq$ 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

Chlorine is an irritant gas that produces immediately severe irritant or corrosive effects at the site of first contact. Low concentrations result in injuries primarily to the ocular and rhino-pharyngeal mucosa. At higher concentrations and increased respiration rate, the tracheo-bronchial mucosa and the pulmonary parenchymal tissue are also affected (Beach et al., 1969).

#### 4.1.2.3.1 Skin

Studies in animals

Standard guideline studies to determine the irritation/corrosivity potential of chlorine can not be done because chlorine is a gas at ambient temperature. Acute dermal toxicity studies with animals are also not possible/available. Although many animal experiments studied the short term effects of chlorine exposure, skin effects have not been described in most cases because the main target organ is the respiratory tract. Solutions of chlorine in water contain hypochlorous acid and/or hypochlorite. These solutions have shown to be irritating or corrosive to the skin of animals (see sodium hypochlorite RAR, chapter 4.1.2.3).

Studies in humans

No specific studies available.

#### 4.1.2.3.2 Eye

Studies in animals

Standard guideline studies to determine the eye irritation/corrosivity potential of chlorine can not be done because chlorine is a gas at ambient temperature. However, acute inhalation toxicity studies with chlorine gas clearly showed that chlorine is irritating to the eyes (see section 4.1.2.2.1). Solutions of chlorine in water contain hypochlorous acid and/or hypochlorite. These solutions can be irritating or corrosive to the eyes (see EU RAR sodium hypochlorite).

Studies in humans

Matt reported already in 1889 that 3.5-4 ppm chlorine produced an immediate burning sensation of the eyes while severe burning in eyes was observed at 2.5 ppm (7.5 $mg/m^3$) after 5-16 minutes. The direct effects of chlorine exposure to humans are described in **Table 4-15**. In many cases the reported effects included effects on the eyes, like “burning of conjuctiva” or “irritation of the eyes”. These irritating effects on the eyes were reported at a chlorine concentration range of 0.2 to 4 ppm (0.6 to 12 mg/m$^3$).

### 4.1.2.3.3 Respiratory tract

Studies in animals

*Mice*

To evaluate the degree of sensory irritation of chlorine in mice, the measurement of the percentage decrease in respiratory rate was utilised.

Mice were exposed for 10 minutes to concentrations from 0.7 to 38.4 ppm (2.1 to 115.2 mg/m$^3$). At 38.4 ppm (115.2 mg/m$^3$) the maximum response (80-85% decrease) was observed. Recovery from exposure was delayed at levels higher than 10 ppm (30 mg/m$^3$). The $RD_{50}$ for male mice was calculated to be 9.30 ppm (27.9 mg/m$^3$) for 10 minutes exposure, while at 19 ppm (57 mg/m$^3$) a 50% decrease in respiratory rate was reached within 2 minutes (Barrow et al., 1977; Chang and Barrow, 1984).

Gagnaire et al (1994) observed a 10-minute $RD_{50}$ for chlorine of 8 ppm (24 mg/m$^3$) and a 60-minute $RD_{50}$ of 3.5 ppm (10.5 mg/m$^3$) in mouse. Recovery was rapid and complete after exposures up to 4.6 ppm (13.8 mg/m$^3$) for 120 minutes.

In mice no sensory irritation response appeared at 0.7 ppm (2.1 mg/m$^3$) (Barrow et al., 1977).

Recently the acute respiratory responses of the mouse to chlorine were studied by Morris et al. (2005). Respiratory physiological responses were measured in female C57Bl/6J mice exposed to 0.8 to 4.0 ppm (2.4 to 12 mg/m$^3$) chlorine gas. Chlorine was a potent sensory irritant with an $RD_{50}$ of 2.3 ppm (6.9 mg/m$^3$). The gas induced airway obstruction as indicated by a concentration-dependent increase in specific airways resistance (sRaw) during the 15-min exposure. At 0.8 ppm (2.4 mg/m$^3$), chlorine produced only mild sensory irritation (<20% change in breathing frequency) and a 65% increase in sRaw.

*Rats*

For male rats 10 minutes $RD_{50}$ values of 10.9 ppm (32.7 mg/m$^3$) (Chang and Barrow, 1984) and 25 ppm (75 mg/m$^3$) (Barrow and Steinhagen, 1982) were reported. Delayed recovery was also observed at exposures above 10 ppm (30 mg/m$^3$).

Exposure of rats to 0.4 ppm (1.2 mg/m$^3$) (4 hours) was the irritation threshold and raised the neutrophil levels in washings from lungs, bronchi and nasal cavity, whereas the levels of polynucleoli were lower (Ponomereva, 1980).

*Cats, rabbits and guinea pigs*

Cats exposed to 1 ppm (3 mg/m$^3$) chlorine for 7.5 hours showed only sneezing and some salivation. Rabbits and guinea pigs showed to be less sensitive with first effects appearing at 18 ppm (54 mg/m$^3$) during a 5-h exposure (Lehmann, 1887).

Studies in humans

Matt (1889) noted that 3.5-4 ppm (10.5-12 mg/m$^3$) chlorine produced an immediate burning sensation of eyes and nasal congestion while severe burning in eyes, itching in mouth and throat, nasal congestion, heavy coughing and breathing pains were observed at 2.5 ppm after 5-16 minutes.

Joosting and Verberk (1975) reported on an experiment with human volunteers exposed to chlorine for two hours to 0.5, l, 2 and 4 ppm (1.5, 3, 6 and 12 mg/m$^3$). No effects on respiration rate and ventilatory capacity where observed. Subjective phenomena (smell, taste, cough, irritation of eyes, nose, throat) showed a dose-related response. Irritation was clearly detected at 2 ppm (6 mg/m$^3$), while for eye irritation and cough at 1 ppm (3 mg/m$^3$) some subjects turned out more responsive than the others did. The exposure to 0.5 ppm (1.5 mg/m$^3$) revealed only borderline effects. It was concluded that 2 ppm (6 mg/m$^3$) for 2 hours was reasonably bearable for healthy subjects.

A chlorine study performed on 30 students disclosed some sensation of odour, throat irritation and urge to cough in subjects exposed for 4 hours at 0.5 and 1.0 ppm (1.5 and 3 mg/m$^3$). Exposure at 2 ppm (6 mg/m$^3$) was reported to be much more irritating than that at 0.5 and 1.0 ppm (1.5 and 6 mg/m$^3$) for the same period. Neither 8 hour exposures to 0.5 ppm (1.5 mg/m$^3$) nor 15 min exposures to 2 ppm (6 mg/m$^3$) produced significant effects (pulmonary function) other than recognition (Anglen et al., 1980).

Additional studies on respiratory irritation of chlorine were reported by Beck (1959) and by Rupp and Henschler (1967). The results of these studies are summarised in **Table 4-15**.

Further evidence that 0.5 ppm (1.5 mg/m$^3$) is a NOAEL in humans is provided by a study of Emmen and Hoogendijk (1997), which was published by Schins et al. (2000). The study was well documented and was done according to Good Clinical Practice. The objectives of this study were:

1) to determine if chlorine exposure at low levels induces nasal effects in humans as it does in rodents; and
2) to establish a possible occurrence of respiratory effects in human volunteers exposed to chlorine vapour at concentrations of 0, 0.1, 0.3 and 0.5 ppm (0, 0.3, 0.9 and 1.5 mg/m$^3$).

The human male volunteers were exposed for 6 hour per day on 3 consecutive days to each of the 4 exposure conditions. The total number of volunteers was 8 (data analysis was limited to 7 subjects since one volunteer decided to stop participating for reasons not related to the study) and their age was 20-50 years. Furthermore they were considered healthy, as determined by medical and laboratory examination, and they had a normal lung function. Nasal lavage measurements were conducted during the study and the results did not support an inflammatory response or irritant effects on the nasal epithelium. Furthermore no significant effect on lung function parameters was found. The study did not support an inflammatory effect in the nose nor shows changes in the respiratory function at repeated exposure up to 0.5 ppm (1.5 mg/m$^3$).

### *Odour perception and irritation threshold*

Chlorine has a characteristic pungent odour. A brief summary of studies in humans on odour perception, compared with irritation and tolerance of chlorine exposure is given in **Table 4-16**, highlighting the considerable range of values obtained. The odour threshold seems to range from about 0.1 to about 1 mg/m$^3$ (0.03 – 0.3 ppm). The ability to detect chlorine by odour is lost after brief exposure.

Table 4-15 Direct effects in humans of controlled exposure to chlorine

| Concentration (exposure time) | Number exposed | Effect (cases observed) | Reference |
|---|---|---|---|
| 3.5-4.0 ppm<br>10.5-12 mg/m$^3$] | 1 | Immediate burning of eyes, nasal congestion | Matt (1889) |
| 2.3 ppm [6.9 mg/m$^3$] (5 - 16 min) | 1 | Severe burning in eyes, itching in mouth and throat, nasal congestion, heavy coughing, breathing pains | Matt (1889) |
| 2 ppm [6 mg/m$^3$] (2 hr) | 31 | Itching or burning of the throat, urge to cough | Anglen (1981) |
| 2 -4 ppm [6 – 12 mg/m$^3$] (2 hr) | 8 | No change in pulmonary function. Cough, irritation of eyes, nose and throat | Joosting & Verberk (1975) |
| 1.4 ppm [4.2 mg/m$^3$ ] (concentrations increasing from 0-1.8 ppm ]0- 5.4 mg/m$^3$], 30 min) | 4 | Neck pain, substernal pain conjunctival irritation (1), headache (1) | Beck (1959) |
| 1.3 ppm [3.9 mg/m$^3$] (7 min) | 1 | Burning sensation in eyes and nose | Matt (1889) |
| 1.0-1.3 ppm , 3-3.9 mg/m$^3$] (increasing from 0 to 1.3 ppm [0 to 3.9 mg/m$^3$], 35 min) | 1 | Severe shortness of breath and cough with violent headache | Rupp & Henschler (1967) |
| 1.0 ppm [3.0 mg/m$^3$] (2 hrs) | 8 | Eye irritation and cough in some individuals | Joosting & Verberk (1975) |
| 1.0 ppm [3.0 mg/m$^3$] | 10 | Tickling and stinging in the nose (6), scratchiness and dryness in the throat (4), dull sensation in the teeth and a slight metallic taste (1), headache and pressure, burning of ocular conjunctiva/ outer skin, coughing, constriction of breathing(1) | Beck (1959) |
| 1.0 ppm [3 mg/m$^3$] (increasing from 0 to 1.0 ppm, 0 to 3 mg/m$^3$, 35 min) | 3 | Headache | Rupp & Henschler (1967) |
| 0.1-0.5 ppm [0.3-1.5 mg/m$^3$] (6 hrs per day, 3 days) | 7 | No inflammatory effect in the nose, no changes in respiratory function (FVC, FEV1 and FVC/FEV1), no indication of irritant effect on the nasal epithelium | Emmen & Hoogendijk (1997); Schins et al. (2000) |
| 0.5 ppm [1.5 mg/m$^3$] (increasing from 0 to 1.3 ppm, 0 to 3.9 mg/m$^3$, 50 min) | 5 | Cough, stinging | Rupp & Henschler (1967) |
| 0.45 ppm [1.35 mg/m$^3$] (ranging from 0.35 to 0.72 ppm, [1.05 to 2.16 mg/m$^3$]) | 19 | Burning of conjuctiva, pain after 15 min | Rupp & Henschler (1967) |
| 0.36 ppm [1.08 mg/m$^3$] | 4 | Sensation of choking (1) | Beck (1959) |
| 0.3 ppm [0.9 mg/m$^3$] | 4 | Stinging in the throat (3) | Beck (1959) |
| 0.2 ppm [0.6 mg/m$^3$] | 13 | Slight tickling in the nose and throat (7), cough (1), sensations in the ocular conjunctiva (3) | Beck (1959) |
| 0.09 ppm [0.27 mg/m$^3$] | 10 | Tickling and stinging in the nose (4), cough (1), dryness in throat (1) | Beck (1959) |
| 0.06-0.2 ppm [0.18-0.6 mg/m$^3$] | 3 | Itching in the nose | Rupp & Henschler (1967) |
| 0.058 ppm [0.174 mg/m$^3$] (ranging from 0.04 to 0.097 ppm [0.12 to 0.291 mg/m$^3$]) | 20 | Tickling in throat | Rupp & Henschler (1967) |
| 0.027 ppm [0.081 mg/m$^3$] (ranging from 0.014 to 0.054 ppm [0.042 to 0.162 mg/m$^3$]) | 20 | Tickling of nose | Rupp & Henschler (1967) |

Table 4-16 Odour and irritation thresholds

| Odour threshold | | Threshold of irritation | | Intolerable concentration | | Reference |
|---|---|---|---|---|---|---|
| mg/m³ | ppm | mg/m³ | ppm | mg/m³ | ppm | |
| 3.8 | 1.3 | 3.8-8.7 | 1.3-2.3 | 11.6 | 4.0 | Matt (1889) |
| 1.5 | 0.5 | 2.9-5.8 | 0.9-1.7 | 11.6 | 4.0 | Joosting & Verberk et al. (1975) |
| 0.6-1.5 | 0.2-0.5 (100%) | | | | | Rupp and Henschler (1967) |
| 0.9 | 0.3 (100%) | | | | | Leonardes et al. (1969) |
| 0.8-1.3 | 0.24-0.39 | 1.3-2 | 0.39-0.6 | | | Takirev (1967) |
| 0.7-0.75 | 0.24-0.26 | | | | | Styazkin (1963) |
| 0.3 | 0.09 | | | | | Ugryomova-Spaznikova (1952) |
| 0.23 | 0.8 | | | | | Dixon & Ikels (1977) |
| 0.12-0.29 | 0.04-0.09<br>0.05-0.10<br>(70-90%) | 0.9 | 0.3 | 2.9-4.1 | 0.9-1.4 | Beck (1959) |
| 0.06-0.15 | 0.02-0.06 (50%) * | 0.06-0.15 | 0.02-0.06 | 1.45 | 0.4 | Rupp & Henschler (1967) |

* recognisable over the first 5 to 10 min: 0.02 ppm; 5 to 15 min: 0.05 ppm; 5 to 20 min: 0.1 ppm; 5 to 30 min: 0.2 ppm; 5 > 60 min: 1 ppm

#### 4.1.2.3.4 Summary of 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 Corrosivity

Based on a recently approved international hazard assessment (SIDS Initial Assessment Profile, SIAP), chlorine is corrosive to the skin (OECD, 2003).

Direct contact with liquid chlorine or concentrated vapour can cause severe chemical burns and frostbite, leading to cell death and ulceration.

Secondary references and also internal documentation of chlorine producers shows that gaseous chlorine (and liquid chlorine) can be corrosive to the skin and eyes (e.g. it can result in blindness). The corrosive effects on skin and eyes are supported by the observed acute respiratory effects for animals and humans.

Based on the available data it is proposed to classify and label chlorine as Corrosive (C) with R35 (Causes severe burns). Currently chlorine is classified as Irritant (Xi) with R36/37/38 (Irritating to eyes, respiratory system and skin).

### 4.1.2.5 Sensitisation

#### 4.1.2.5.1 Studies in animals

Skin

No specific studies available with chlorine gas.

Respiratory tract

No specific studies available with chlorine gas.

#### 4.1.2.5.2 Studies in humans

Skin

No specific studies available with chlorine gas.

Respiratory tract

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.

#### 4.1.2.5.3 Summary of 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.

### 4.1.2.6 Repeated dose toxicity

#### 4.1.2.6.1 Studies in animals

In vivo studies

As pointed out in **section 4.1.2**, chlorine reacts with water in aqueous solutions to hypochlorous acid and/or hypochlorite. The toxicity of sodium hypochlorite following repeated or continuous administration has been extensively studied in a number of species following exposure through chlorinated water and by the dermal route. The oral and dermal toxicity studies with hypochlorite in aqueous solution are described in the EU RAR of Sodium Hypochlorite and will not be further discussed in this report.

*Inhalation*

Rat

In a 6-week study, groups of 10 male and 10 female F344 rats were exposed to 0, 1, 3 or 9 ppm (0, 3, 9 or 27 mg/m$^3$) chlorine gas for 6 hours/day, 5 days/week, whole body (Barrow et al., 1979). Exposure-related decreases in body weights were noted at 1 (females only), 3 and 9 ppm (3, 9 and 27 mg/m$^3$). Three females in the 9 ppm (27 mg/m$^3$) group died before the end of the study. Inflammation was observed throughout the respiratory tract with hyperplasia and hypertrophy of epithelial cells of the respiratory bronchioles, alveolar ducts and alveoli of male and female 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 (Barrow et al., 1979).

Groups of approximately 70 female and male F344/N rats were exposed whole body to 0, 0.4, 1.0 or 2.5 ppm (0, 1.2, 3 or 7.5 mg/m$^3$) chlorine gas for 6 hours/day 5 days/week (male rats) or 3 alternate days/week (female rats) for 2 years, with an interim necropsy performed at 12 months (10 rats/sex/concentration group). A complete necropsy was performed on all animals. Exposure-dependent lesions were confined to the nasal passage in all sex and species groups.

Chlorine-induced lesions, which were most severe in the anterior nasal cavity, included 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. Intracellular accumulation of eosinophilic proteinaceous material was also a prominent response involving the respiratory transitional and olfactory epithelia and in some cases the squamous epithelium of the nasal vestibule. Many of these nasal lesions exhibited an increase in incidence and/or severity that was related to chlorine exposure concentrations and were statistically-significantly increased at all chlorine concentrations studied. Inhaled chlorine in rodents is an upper respiratory tract toxicant; the LOAEL for respiratory irritation was 0.4 ppm (CIIT 1993; Wolf et al., 1995). The incidence of neoplasia will be discussed in **section 4.1.2.8** (carcinogenicity).

Mouse

Groups of approx. 70 female and male B6C3F1 mice each were exposed whole body to 0, 0.4, 1.0 or 2.5 ppm (0, 1.2, 3 or 7.5 mg/m$^3$) chlorine gas for 6 h/d, 5 d/week for 2 years, with an interim necropsy performed at 12 months. Exposure-dependent lesions were confined to the nasal passage, most severe in the anterior nasal cavity including respiratory and olfactory epithelial degeneration, septal fenestration, mucosal inflammation, respiratory epithelial hyperplasia, squamous metaplasia, goblet cell hypertrophy and hyperplasia, and secretory metaplasia of the transitional epithelium of the latera meatus. Many of these nasal lesions exhibited a statistically-significantly increase in incidence and/or severity related to chlorine exposure concentration (Wolf et al., 1995). The LOAEL for lesions in the upper respiratory tract was 0.4 ppm (1.2 mg/m$^3$). A NOAEL could not be established.

Monkeys

To investigate the chronic effects of chlorine inhalation, Rhesus monkeys (Macaca mulatta) were exposed whole body to concentrations of 0, 0.1, 0.5, or 2.3 ppm (0, 0.3, 1.5 or 3.9 mg/m$^3$) chlorine for 6 hr per day, 5 days per week for 1 year (Klonne et al., 1987). Pulmonary physiology, body weights, urinalysis, electrocardiographs, hematology and clinical chemistry were evaluated monthly during the study. Blood gas evaluations were performed at 3-month intervals during the study. Histopathologic, ophthalmologic and neurologic parameters were evaluated after the 1-year exposure period. Monkeys exposed to 2.3 ppm (3.9 mg/m$^3$) chlorine exhibited signs of ocular irritation during the daily exposures and a superficial conjunctival irritation was present in the 2.3 ppm (3.9 mg/m$^3$) group after the 1-year exposure regimen. Treatment-induced lesions revealed by histopathology were confined to the respiratory tract. These were found in the respiratory epithelium of the nasal passages and trachea and were limited to focal, concentration-related epithelial hyperplasia with loss of cilia and decreased numbers of goblet cells in affected areas. These changes in the nose and trachea were focal and mild in monkeys exposed to 2.3 ppm (3.9 mg/m$^3$) and were not found in all animals in this exposure group. Tracheal lesions were confined to the 2.3 ppm (3.9 mg/m$^3$) group. At the lower chlorine concentrations, similar though less prominent respiratory epithelial lesions were observed. The results of this study indicate that 2.3 ppm (3.9 mg/m$^3$) chlorine acts as an upper respiratory irritant in monkeys, while 0.5 and 0.1 ppm (1.5 and 0.3 mg/m$^3$) induce changes of questionable clinical significance. Furthermore, the monkey appears to be less sensitive than the rat to chlorine toxicity.

Ibanes et al. (1996) compare Klonne et al. study and the rodent cancer bioassay (Wolf et al., 1995) and conclude that chlorine-induced lesions, which were confined to the respiratory tract, exhibit both similarities and differences among rodents and primates. At equivalent airborne concentrations (around 2.5 ppm, 7.5 mg/m$^3$), chlorine-induced responses were less severe in monkeys , but extended more distally in the respiratory tract to involve the trachea, while treatment-induced lesions were confined to the nose in rats and mice. In both rodents and monkeys, airflow-driven regional dosimetry patterns were considered to play a major role in lesions distributions.

#### 4.1.2.6.2 Studies in humans

In vivo studies

No indications of chronic toxicity in humans have been reported in the literature. Several epidemiological studies of the effects of the consumption of chlorinated drinking water on the health of the general population have been reported. No causal link between any long term health effect (including increased cancer risk) and consumption of chlorinated drinking water was established in these studies (IARC, 1991). For more details, see the EU RAR for sodium hypochlorite, chapter 4.1.2.7.

*Inhalation*

No specific studies available.

*Dermal*

No specific studies available.

#### 4.1.2.6.3 Summary of 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) (chapter 4.1.2.2.2) 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 (chapter 4.1.2.5), 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.

### 4.1.2.7 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*.

### 4.1.2.8 Carcinogenicity

As pointed out in **section 4.1.2** chlorine reacts with water in aqueous solutions to hypochlorous acid and/or hypochlorite. The toxicity of sodium hypochlorite following repeated or continuous administration has been extensively studied in a number of species following exposure through chlorinated water. The oral studies with hypochlorite in aqueous solution are described in the EU RAR of Sodium Hypochlorite and will not be further discussed in this report.

#### 4.1.2.8.1 Studies in animals

*Inhalation*

Groups of approximately 70 female and male F344/N rats and B6C3F1 mice were exposed to 0, 0.4, 1.0 or 2.5 ppm (0, 1.2, 3 or 7.5 mg/m$^3$) chlorine gas for 6 hours/day 5 days/week (mice and male rats) or 3 alternate days/week (female rats) for 2 years, with an interim necropsy of rats performed at 12 months (10 rats/sex/concentration group). A complete necropsy was performed on all animals. Exposure-dependent lesions were confined to the nasal passage in all sex and species groups. Chlorine-induced lesions, which were most severe in the anterior nasal cavity, included 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. Intracellular accumulation of eosinophilic proteinaceous material was also a prominent response involving the respiratory transitional and olfactory epithelia and in some cases the squamous epithelium of the nasal vestibule. 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. The incidence of neoplasia was not increased by exposure indicating that inhaled chlorine in rodents is an upper respiratory tract toxicant but not a carcinogen (CIIT 1993; Wolf et al., 1995). The LOAEL for respiratory irritation was 0.4 ppm.

*Dermal*

No studies available.

#### 4.1.2.8.2 Studies in humans

*Inhalation*

The human carcinogenicity of chlorine was not fully evaluated in the available long-term exposure studies in the workforce of chlorine production or processing plants.

*Dermal*

No specific studies available.

#### 4.1.2.8.3 Summary of 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, chapter 4.1.2.7. 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.

#### 4.1.2.9 Toxicity for reproduction

No developmental or fertility studies in rodents are available with chlorine for the inhalation route.

As pointed out in **section 4.1.2** chlorine reacts with water in aqueous solutions to hypochlorous acid and/or hypochlorite. The toxicity of sodium hypochlorite following repeated or continuous administration has been extensively studied in a number of species following exposure through chlorinated drinking water.

The potential teratogenic and reproductive effects of chlorine have been examined mainly in 3 studies:

- in Long-Evans rats following oral administration of chlorine by gavage (Carlton et al., 1986)
- in Sprague-Dawley rats given chlorinated drinking water prior to and throughout gestation (Abdel-Rahman et al., 1982)
- in BDII rats given chlorinated drinking water in a "multigeneration study" (Druckrey, 1968).

In the Carlton study (1986), potential reproductive effects were assessed in Long-Evans rats. The protocol was in good compliance with actual current standards.

Males (12 per group) were administered doses of 0, 1, 2, and 5 mg/kg body weight of aqueous chlorine, (as HOCl). Administration by gavage started 56 days prior to breeding and continued throughout the 10 day breeding cycle. Female rats (24 per group) received the same concentrations by gavage for 14 days prior to breeding and throughout breeding, gestation and lactation, until the pups were weaned on day 21. Following the breeding period, males were bled for complete blood count and thyroid hormone levels determination and then were subject to a complete gross necropsy and histopathological examination of the reproductive tract.

Dams were observed for fertility, gestation duration, body weight gain, maternal behaviour and at day 21 of lactation bled for complete blood count and then sacrificed for gross necropsy and histopathology of the reproductive tract.

Litters were observed for viability, litter size, day of eye opening (this day was considered for all pups of a same litter i.e. when all pups of a same litter had open eyes, this day was considered for the whole litter), bodyweight gain, gross external abnormalities, day of vaginal opening (for selected pups).

No clinical signs of toxicity, haematological changes or body weight depression were observed in the treated adult male and female rats. No alterations in sperm count, sperm motility or sperm morphology were seen and there were no histopathological lesions in the reproductive tract of adult male and female rats exposed to 1 to 5 mg/kg/d of aqueous chlorine. There were no dose-related effects on fertility, foetal viability, litter size, foetal body weight, day of eye opening or day of vaginal patency.

It is noteworthy that the doubtful effect observed in the sperm-head abnormalities assay in mice (Meier, 1985) was not found in the Carlton study in rats (see above) at similar doses and with treatment duration of 56 days against 5 days in the Meier study.

In the Abdel-Rahman study (1982), female SD rats (6 per group) were administered chlorine, as hypochlorous acid (HOCl), in drinking water at concentrations of 0, 0.1, 10 and 100 mg/l per day for 2.5 months prior to conception and throughout gestation. Doses expressed in mg/kg of hypochlorous acid can be estimated as about 0.1, 1 and 10 mg/kg/day according to the specified rat bodyweight (225-250 g) and a default value of 20 ml/day/animal for water consumption (actual consumption not specified in the publication). Rats were killed on day 20 of gestation and the foetuses were examined, half for soft tissue abnormalities and half for skeletal abnormalities. No information was given on possible maternotoxic effect at any exposure concentration.

All foetuses were found viable and normal in external appearance. There was no statistical difference between control and treated groups for the number of resorptions and foetal weights. There was no statistical difference between control and treated groups in % of skeletal defects and in % of soft tissue anomalies. There were no statistically significant changes in incidences of skeletal variants observed in treated groups versus controls. Incompletely ossified or missing sternebrae or rudimentary ribs changes that were not dose-related cannot be considered as attributable to treatment.

Some rare soft tissue defects were observed in the high dose group 100 mg HOCl /l as in the control group while the lower concentrations of hypochlorous acid (1 and 10 mg/l) did not produce any defects. In the 100 mg/l group, the authors found 3 cases of adrenal agenesis, 1 case of dextrocardia, 1 case of improper orientation of the apex and 1 case of atrio ventricular valve enlargement. The distribution of these cases among the litters and foetuses were not presented but the authors reported similar defects in the control group although they do not specify the number of cases. Furthermore, the difference in incidence between the treated group and the control group was not statistically significant using the fœtus as the unit for the statistical analysis. The choice of the fœtus as unit rather than the litter certainly maximizes the power of the statistical analysis and thus counterbalances the low number of dams and subsequent litters per group. Because similar tissue defects were observed in the control and high dose groups and none in the lower treated groups and because the difference in incidence was not statistically significant, these findings strongly indicate that these soft tissue defects were spontaneous in origin rather than treatment-related.

Moreover, no indication of toxic developmental effects was seen in the Carlton study (no abnormal offspring, no effect on litter size, perinatal mortality, pup growth and neonatal weight) which was supported by the US-EPA (1986).

In the Druckrey study (1968), a group of 60 male and female BDII rats (sex ratio not specified) was given tap water containing 100 mg/l available chlorine prepared with chlorine gas (fresh preparation was repeated each week, in compliance with stability data). The animals were mated and the treatment was continued for life span through the following generations from 1955 to 1964, with the exception of F3 and F4 animals which were treated during the weaning period only. All together, 236 animals in five generations were exposed

(Parental, F1, F2, F5 and F6). Two control groups were used (sex and age not specified), one starting in 1955 (n = 20) and the other in 1962 (n = 36).

The results are poorly documented but no toxic effects were reported on fertility, growth, survival or at histological examination of the main organs.

#### 4.1.2.9.1 Summary of 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. For more details on the epidemiological studies, see chapter 4.1.2.8.2 of 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.

Chlorine reacts with water in aqueous solutions to hypochlorous acid and/or hypochlorite. The toxicity of sodium hypochlorite following repeated or continuous administration has been extensively studied in a number of species following exposure through chlorinated water. The oral studies with hypochlorite in aqueous solution are described in the EU RAR of Sodium Hypochlorite and the risk characterisation for the oral route will not be further discussed in this report.

The endpoints considered in the risk characterisation and their N(L)OEAL have been listed in **Table 4-17**.

Table 4-17 Summary of effects (NR: Not Relevant)

| 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

*Inhalation exposure*

In chlorine manufacturing, four exposure scenarios have been considered (cell-rooms operators, maintenance operators, filling operators and laboratory). As explained in chapter, 4.1.1.2.1, 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 (see chapter 4.1.1.2.1).

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.

*Dermal exposure*

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 4-189** for summary of results of the risk characterisation.

Table 4-18 Occupational risk assessment for acute toxicity

| | 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 NOAEL of 0.5 ppm (1.5 mg/m$^3$) is compared with the exposure estimates. When using the 90th percentile of the distribution of the maximum exposure levels, 3 out 4 scenarios used in production of chlorine, all scenarios for the use of chlorine as chemical intermediate and one scenario for the use of chlorine in water disinfection show a MOS of less than 5, which thus would lead to a conclusion (iii). However, using the more typical average concentrations, which is - in view of the high level of adequate protecting measures already in place in plants manufacturing or using chlorine and of the influence of short duration exposure peaks on the 90th percentile values - a much more realistic approach, the MOS values are higher than 5 in all scenarios.

Even if a worst case approach (the use of 90th percentile) would lead to a conclusion iii in some scenarios, we would not recommend Risk Reduction Measures additional to those already in place (use of alarm sensors and use of Personal Protective Equipments for tasks that could lead to chlorine exposure).

Therefore, the overall conclusion for all occupational scenarios is:

**Conclusion (ii)**

#### 4.1.3.1.2 Irritation and corrosivity

Chlorine is a corrosive gas that can produce immediately severe effects at the site of first contact (skin, eyes and/or respiratory tract). Exposure of workers to chlorine gas is well-controlled and the use of PPE is obligatory. 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 4-1820** for summary of results of the risk characterisation.

Table 4-20 Occupational risk assessment for irritation

| | 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 NOAEL of 0.5 ppm (1.5 mg/m$^3$) is compared with the exposure estimates. When using the 90th percentile of the distribution of the maximum exposure levels, 3 out 4 scenarios used in production of chlorine, all scenarios for the use of chlorine as chemical intermediate and one scenario for the use of chlorine in water disinfection show a MOS of less than 5, which thus would lead to a conclusion (iii). However, using the more typical average concentrations, which is - in view of the high level of adequate protecting measures already in place in plants manufacturing or using chlorine and of the influence of short duration exposure peaks on the 90th percentile values - a much more realistic approach, the MOS values are higher than 5 in all scenarios.

Even if a worst case approach (the use of 90th percentile) would lead to a conclusion iii in some scenarios, we would not recommend Risk Reduction Measures additional to those already in place (use of alarm sensors and use of Personal Protective Equipments for tasks that could lead to chlorine exposure).

Therefore, the overall conclusion for all occupational scenarios 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 used for risk characterisation is based on human studies. As explained in the conclusions of the repeated dose toxicity chapter (4.1.2.6.3), human repeated exposure to chlorine is not expected to lead to effects other than the irritation observed in the study by Schins et al. (2000). The effects appear to be related to concentration in air and not to duration of exposure (SCOEL, 1998). According to the TGD, the minimal MOS for workers therefore only needs to take into account an intra-species factor of 5. See **Table 4-21** for summary of results of the risk characterisation.

The NOAEL of 0.5 ppm is compared with the exposure estimates. When using the 90th percentile of the distribution of the maximum exposure levels, 3 out 4 scenarios used in production of chlorine, all scenarios for the use of chlorine as chemical intermediate and one scenario for the use of chlorine in water disinfection show a MOS of less than 5, which thus would lead to a conclusion (iii). However, using the more typical average concentrations, which is - in view of the high level of adequate protecting measures already in place in plants manufacturing or using chlorine and of the influence of short duration exposure peaks on the 90th percentile values - a much more realistic approach, the MOS values comparable to the minimal MOS (5) for production and use as intermediate. No exposure is foreseen for the drinking water disinfection scenario.

Even if a worst case approach (the use of 90th percentile) would lead to a conclusion iii in some scenarios, we would not recommend Risk Reduction Measures additional to those already in place (use of alarm sensors and use of Personal Protective Equipments for tasks that could lead to chlorine exposure).

Therefore, the overall conclusion for all occupational scenarios is:

**Conclusion (ii)**

Table 4-21 Occupational risk assessment for repeated dose toxicity

| | 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] | $\infty$ | ii | 0 [0] | 0.5 [1.5] | $\infty$ | ii |
| Connection-disconnection | 0 [0] | 0.5 [1.5] | $\infty$ | ii | 0 [0] | 0.5 [1.5] | $\infty$ | 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. When chlorine is used for disinfection purposed (in swimming pools and in drinking water treatment), it is added to water and is transformed into hypochlorite and hypochlorous acid. The possible consumer exposure to these chemicals has been evaluated in sodium hypochlorite Risk Assessment (chapters 4.1.1.4.2 and 4.1.1.4.3) and it has been concluded that no risk is expected (chapter 4.1.3.3).

Consumers can be exposed to chlorine gas in case of accidental mixing of bleach and acids. More information on the frequency of these accidents is presented in chapter 4.1.1.4.1 of sodium hypochlorite Risk Assessment.

### 4.1.3.3 Humans exposed via the environment

Chlorine emissions on a European level are summarised in **Table 3.1**. 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. The fate and effects of these emissions to the environment on a local scale have been dealt with in **sections 3.1.4 and 3.1.6**.

Due to the properties of chlorine the substance will only remain in the water compartment for a very short period of time (see **section 1.3**). 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 (see **sections 1.3 and 1.4**).

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 µg/m$^3$ has been calculated (chapter 3.1.6.1.1). 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”.

#### 4.1.3.4 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

Exposure of workers to chlorine is discussed in **section 4.1.1**.

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 4.1.3.3**.

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 4.1.3.3**.

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

# 5 RESULTS [5]

## 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.

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[5] 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.

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# ABBREVIATIONS

| | |
|---|---|
| ADI | Acceptable Daily Intake |
| AF | Assessment Factor |
| ASTM | American Society for Testing and Materials |
| ATP | Adaptation to Technical Progress |
| AUC | Area Under The Curve |
| B | Bioaccumulation |
| BBA | Biologische Bundesanstalt für Land- und Forstwirtschaft |
| BCF | Bioconcentration Factor |
| BMC | Benchmark Concentration |
| BMD | Benchmark Dose |
| BMF | Biomagnification Factor |
| bw | body weight / *Bw*, *b.w.* |
| C | Corrosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| CA | Chromosome Aberration |
| CA | Competent Authority |
| CAS | Chemical Abstract Services |
| CEC | Commission of the European Communities |
| CEN | European Standards Organisation / European Committee for Normalisation |
| CMR | Carcinogenic, Mutagenic and toxic to Reproduction |
| CNS | Central Nervous System |
| COD | Chemical Oxygen Demand |
| CSTEE | Scientific Committee for Toxicity, Ecotoxicity and the Environment (DG SANCO) |
| $CT_{50}$ | Clearance Time, elimination or depuration expressed as half-life |
| d.wt | dry weight / dw |
| dfi | daily food intake |
| DG | Directorate General |
| DIN | Deutsche Industrie Norm (German norm) |
| DNA | DeoxyriboNucleic Acid |
| DOC | Dissolved Organic Carbon |
| DT50 | Degradation half-life or period required for 50 percent dissipation / degradation |
| DT90 | Period required for 90 percent dissipation / degradation |
| E | Explosive (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| EASE | Estimation and Assessment of Substance Exposure Physico-chemical properties [Model] |

| | |
|---|---|
| EbC50 | Effect Concentration measured as 50% reduction in biomass growth in algae tests |
| EC | European Communities |
| EC10 | Effect Concentration measured as 10% effect |
| EC50 | median Effect Concentration |
| ECB | European Chemicals Bureau |
| ECETOC | European Centre for Ecotoxicology and Toxicology of Chemicals |
| ECVAM | European Centre for the Validation of Alternative Methods |
| EDC | Endocrine Disrupting Chemical |
| EEC | European Economic Communities |
| EINECS | European Inventory of Existing Commercial Chemical Substances |
| ELINCS | European List of New Chemical Substances |
| EN | European Norm |
| EPA | Environmental Protection Agency (USA) |
| ErC50 | Effect Concentration measured as 50% reduction in growth rate in algae tests |
| ESD | Emission Scenario Document |
| EU | European Union |
| EUSES | European Union System for the Evaluation of Substances [software tool in support of the Technical Guidance Document on risk assessment] |
| F(+) | (Highly) flammable (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| FAO | Food and Agriculture Organisation of the United Nations |
| FELS | Fish Early Life Stage |
| GLP | Good Laboratory Practice |
| HEDSET | EC/OECD Harmonised Electronic Data Set (for data collection of existing substances) |
| HELCOM | Helsinki Commission -Baltic Marine Environment Protection Commission |
| HPLC | High Pressure Liquid Chromatography |
| HPVC | High Production Volume Chemical (> 1000 t/a) |
| IARC | International Agency for Research on Cancer |
| IC | Industrial Category |
| IC50 | median Immobilisation Concentration or median Inhibitory Concentration |
| ILO | International Labour Organisation |
| IPCS | International Programme on Chemical Safety |
| ISO | International Organisation for Standardisation |
| IUCLID | International Uniform Chemical Information Database (existing substances) |
| IUPAC | International Union for Pure and Applied Chemistry |
| JEFCA | Joint FAO/WHO Expert Committee on Food Additives |
| JMPR | Joint FAO/WHO Meeting on Pesticide Residues |
| Koc | organic carbon normalised distribution coefficient |

| | |
|---|---|
| Kow | octanol/water partition coefficient |
| Kp | solids-water partition coefficient |
| L(E)C50 | median Lethal (Effect) Concentration |
| LAEL | Lowest Adverse Effect Level |
| LC50 | median Lethal Concentration |
| LD50 | median Lethal Dose |
| LEV | Local Exhaust Ventilation |
| LLNA | Local Lymph Node Assay |
| LOAEL | Lowest Observed Adverse Effect Level |
| LOEC | Lowest Observed Effect Concentration |
| LOED | Lowest Observed Effect Dose |
| LOEL | Lowest Observed Effect Level |
| MAC | Maximum Allowable Concentration |
| MATC | Maximum Acceptable Toxic Concentration |
| MC | Main Category |
| MITI | Ministry of International Trade and Industry, Japan |
| MOE | Margin of Exposure |
| MOS | Margin of Safety |
| MW | Molecular Weight |
| N | Dangerous for the environment (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC |
| NAEL | No Adverse Effect Level |
| NOAEL | No Observed Adverse Effect Level |
| NOEL | No Observed Effect Level |
| NOEC | No Observed Effect Concentration |
| NTP | National Toxicology Program (USA) |
| O | Oxidizing (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| OECD | Organisation for Economic Cooperation and Development |
| OEL | Occupational Exposure Limit |
| OJ | Official Journal |
| OSPAR | Oslo and Paris Convention for the protection of the marine environment of the Northeast Atlantic |
| P | Persistent |
| PBT | Persistent, Bioaccumulative and Toxic |
| PBPK | Physiologically Based PharmacoKinetic modelling |
| PBTK | Physiologically Based ToxicoKinetic modelling |
| PEC | Predicted Environmental Concentration |

| | |
|---|---|
| pH | logarithm (to the base 10) (of the hydrogen ion concentration $\{H^+\}$ |
| pKa | logarithm (to the base 10) of the acid dissociation constant |
| pKb | logarithm (to the base 10) of the base dissociation constant |
| PNEC | Predicted No Effect Concentration |
| POP | Persistent Organic Pollutant |
| PPE | Personal Protective Equipment |
| QSAR | (Quantitative) Structure-Activity Relationship |
| R phrases | Risk phrases according to Annex III of Directive 67/548/EEC |
| RAR | Risk Assessment Report |
| RC | Risk Characterisation |
| RD50 | Concentration expected to elicit a 50% decrease in respiratory rate |
| RfC | Reference Concentration |
| RfD | Reference Dose |
| RNA | RiboNucleic Acid |
| RPE | Respiratory Protective Equipment |
| RWC | Reasonable Worst Case |
| S phrases | Safety phrases according to Annex III of Directive 67/548/EEC |
| SAR | Structure-Activity Relationships |
| SBR | Standardised birth ratio |
| SCE | Sister Chromatic Exchange |
| SCOEL | Scientific Committee on Occupational Exposure Limits |
| SDS | Safety Data Sheet |
| SETAC | Society of Environmental Toxicology And Chemistry |
| SNIF | Summary Notification Interchange Format (new substances) |
| SSD | Species Sensitivity Distribution |
| STP | Sewage Treatment Plant |
| T(+) | (Very) Toxic (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| TDI | Tolerable Daily Intake |
| TG | Test Guideline |
| TGD | Technical Guidance Document |
| TNsG | Technical Notes for Guidance (for Biocides) |
| TNO | The Netherlands Organisation for Applied Scientific Research |
| UC | Use Category |
| UDS | Unscheduled DNA Synthesis |
| UN | United Nations |
| UNEP | United Nations Environment Programme |
| US EPA | Environmental Protection Agency, USA |

| | |
|---|---|
| UV | Ultraviolet Region of Spectrum |
| UVCB | Unknown or Variable composition, Complex reaction products of Biological material |
| vB | very Bioaccumulative |
| vP | very Persistent |
| vPvB | very Persistent and very Bioaccumulative |
| v/v | volume per volume ratio |
| w/w | weight per weight ratio |
| WHO | World Health Organization |
| WWTP | Waste Water Treatment Plant |
| Xn | Harmful (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |
| Xi | Irritant (Symbols and indications of danger for dangerous substances and preparations according to Annex III of Directive 67/548/EEC) |

# Appendix A

Table A-1 Acute inhalation toxicity mice (mortality)

| Concentration (ppm) | 6 min | 9 min | 10 min | 14 min | 15 min | 17 min | 18 min | 25 min | 29 min | 30 min | 40 min | 44 min | 50 min | 58 min | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1626 |  |  | 100% |  |  |  |  |  |  |  |  |  |  |  | Zwart, 1997 |
| 1297 |  |  | 100% |  |  |  |  |  |  |  |  |  |  |  | Zwart, 1997 |
| 1181 |  |  | 40% |  |  |  |  |  |  |  |  |  |  |  | Zwart, 1997 |
| 842 |  |  | 40% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 801 |  |  | 30% |  |  |  |  |  |  |  |  |  |  |  | Zwart, 1997 |
| 794 |  |  | 75% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 745 |  |  | 70% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 741 |  |  | 0% |  |  |  |  |  |  |  |  |  |  |  | Zwart, 1997 |
| 711 |  |  | 55% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 707 |  |  | 60% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 690 |  |  | 15% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 638 |  |  | 45% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 633 |  |  |  |  |  |  |  |  |  | 70% |  |  |  |  | Zwart, 1997 |
| 631 |  |  | 40% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 596 |  |  |  |  |  |  |  |  |  | 90% |  |  |  |  | Zwart, 1997 |
| 593 |  |  | 5% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 569 |  |  | 0% |  |  |  |  |  |  |  |  |  |  |  | Zwart, 1997 |
| 564 |  |  |  |  |  |  |  |  |  | 60% |  |  |  |  | Zwart, 1997 |
| 549 |  |  | 35% |  |  |  |  |  |  |  |  |  |  |  | Silver et al., 1942 |
| 537 |  |  |  |  |  |  |  |  |  | 70% |  |  |  |  | Zwart, 1997 |

| Concentration (ppm) | 6 min | 9 min | 10 min | 14 min | 15 min | 17 min | 18 min | 25 min | 29 min | 30 min | 40 min | 44 min | 50 min | 58 min | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 450 | | | | | | | | | | 40% | | | | | Zwart, 1997 |
| 380 | | | 10% | | | | | | | | | | | | Silver et al., 1942 |
| 290 | 0% | | | | | | | | | | | | | | Bitron + Aharonson, 1978 |
| 290 | | 40% | | | | | | | | | | | | | Bitron + Aharonson, 1978 |
| 290 | | | | | 80% | | | | | | | | | | Bitron + Aharonson, 1978 |
| 290 | | | | | | | | 100% | | | | | | | Bitron + Aharonson, 1978 |
| 290 | 0% | 40% | | | 80% | | | 100% | | | | | | | Bitron + Aharonson, 1978 |
| 179 | | | | | | | | | | 100% | | | | | Schlagbauer + Henschler, 1967 |
| 170 | | | | 0% | | | | | | | | | | | Bitron + Aharonson, 1978 |
| 170 | | | | | | 29% | | | | | | | | | Bitron + Aharonson, 1978 |
| 170 | | | | | | | 7% | | | | | | | | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | 7% | | | | | | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | | | 25% | | | | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | | | | 64% | | | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | | | | | 71% | | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | | | | | | 21% | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | | | | | | 28% | Bitron + Aharonson, 1978 |
| 170 | | | | 0% | | 29% | 7% | | 7% | | 25% | 64% | 71% | 21-28% | Bitron + Aharonson, 1978 |
| 170 | | | | | | | | | | | | | | 92% | Bitron + Aharonson, 1978 |
| 160 | | | | | | | | | | 80% | | | | | Schlagbauer + Henschler, 1967 |
| 143 | | | | | | | | | | 60% | | | | | Schlagbauer + Henschler, 1967 |
| 132 | | | | | | | | | | 60% | | | | | Schlagbauer + Henschler, 1967 |
| 125 | | | | | | | | | | 30% | | | | | Schlagbauer + Henschler, 1967 |

| Concentration (ppm) | 6 min | 9 min | 10 min | 14 min | 15 min | 17 min | 18 min | 25 min | 29 min | 30 min | 40 min | 44 min | 50 min | 58 min | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 110 | | | | | | | | | | 30% | | | | | Schlagbauer + Henschler, 1967 |
| 65 | | | | | | | | | | 10% | | | | | Schlagbauer + Henschler, 1967 |
| 55 | | | | | | | | | | 0% | | | | | Schlagbauer + Henschler, 1967 |

Table A-2 Acute inhalation toxicity mice ($LC_{50}$)

| Concentration (ppm) | Animal sex (number) | Exposure time (min) | Observation time (days) | References |
|---|---|---|---|---|
| 1033 | M(30) F(30) | 10 | 14 | Zwart, 1987 |
| 674 | M(300) | 10 | 10 | Silver et al., 1942 |
| 628 | MF(20?) | 10 | 10 | Lipton + Rotariu, 1941 |
| 597 | MF(?) | 10 | 10 | Silver + Mc Grath, 1942 |
| 524 | MF(?) | 10 | 10 | Silver + Mc Grath, 1942 |
| 302 | MF(?) | 10 |  | Alarie, 1980 |
| 290 | MF(?) | 11 | 30 | Bitron + Aharonson, 1978 |
| 496 | M(30) F(30) | 30 | 14 | Zwart, 1987 |
| 127 | F(80) | 30 | 10 | Schlagbauer + Henschler, 1967 |
| 170 | MF(?) | 55 | 30 | Bitron + Aharonson, 1978 |
| 137 | MF(?) | 60 | ? | Vernot et al., 1977 |

Table A-3 Acute toxicity, rat (mortality)

| Concentration (ppm) | 2 min | 5 min | 10 min | 30 min | 60 min | References |
|---|---|---|---|---|---|---|
| 5695 |  | 70% |  |  |  | Zwart, 1987 |
| 3300 |  |  |  | 0% |  | Zeehuisen, 1922 |
| 2843 |  | 0% |  |  |  | Zwart , 1987 |
| 2210 |  |  | 60% |  |  | Zwart, 1987 |
| 1626 |  | 0% | 10% |  |  | Zwart, 1987 |
| 1500 | 0% |  | 12.5 % |  |  | Demnati, 1995 |
| 1181 |  | 0% | 0% |  |  | Zwart, 1987 |
| 813 |  | 0% |  |  |  | Zwart, 1987 |
| 801 |  |  | 0% |  |  | Zwart, 1987 |
| 746 |  | 0% |  |  |  | Zwart, 1987 |
| 741 |  |  | 0% |  |  | Zwart, 1987 |
| 634 |  |  |  | 60% |  | Zwart, 1987 |
| 602 |  |  |  | 50% |  | Zwart, 1987 |
| 585 |  |  |  |  | 100% | Zwart, 1987 |
| 569 |  |  | 0% |  |  | Zwart, 1987 |
| 564 |  |  |  | 30% |  | Zwart, 1987 |
| 561 |  | 0% |  |  |  | Zwart, 1987 |
| 560 |  |  |  |  | 80% | Zwart, 1987 |
| 537 |  |  |  | 0% |  | Zwart, 1987 |
| 500 |  |  |  |  | 60% | Zwart, 1987 |

| Concentration (ppm) | 2 min | 5 min | 10 min | 30 min | 60 min | References |
|---|---|---|---|---|---|---|
| 500 | 0% | 0% | 0% | | | Demnati 1995 |
| 450 | | | | | 40% | Zwart, 1987 |
| 317 | | | | | 0% | Zwart, 1987 |

Table A-4 Acute inhalation toxicity rat ($LC_{50}$)

| Concentration (ppm) | Animal sex (number) | Exposure time (min) | Observation time (days) | References |
|---|---|---|---|---|
| 5406 | M F (30) | 5 | 14 | Zwart, 1987 |
| 1913 | M F (30) | 10 | 14 | Zwart, 1987 |
| 689 | M F (20) | 30 | 14 | Zwart, 1987 |
| 448 | M F (25) | 60 | 14 | Zwart, 1987 |
| 293 | M | 60 | ? | Vernot et al., 1977 |

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The report provides the comprehensive risk assessment of the substance Chlorine. It has been prepared by Italy in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances, following the principles for assessment of the risks to man and the environment, laid down in Commission Regulation (EC) No. 1488/94.

The evaluation considers the emissions and the resulting exposure to the environment and the human populations in all life cycle steps. Following the exposure assessment, the environmental risk characterisation for each protection goal in the aquatic, terrestrial and atmospheric compartment has been determined. The environmental risk assessment concludes that there is no concern for any of the environmental compartments. For human health the scenarios for occupational exposure, consumer exposure and humans exposed via the environment the possible risks have been examined and no concerns have been identified.