

European Union Risk Assessment Report

SODIUM HYPOCHLORITE

CAS No: 7681-52-9

EINECS No: 231-668-3

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Italy

RISK ASSESSMENT

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) 793/93¹ 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) 1488/94², which is supported by a technical guidance document³. 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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SODIUM HYPOCHLORITE RISK ASSESSMENT
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0. OVERALL RESULTS OF THE RISK ASSESSMENT

Environment

- () i) There is need for further information and / or testing**
- (x) ii) There is at present no need for further information and / or testing or for risk reduction measures beyond those which are being applied already**
All scenarios
- () iii) There is a need for limiting the risks; reduction measures which are already being applied shall be taken into account**

Human Health

- () i) There is need for further information and / or testing**
.
- (x) ii) There is at present no need for further information and / or testing or for risk reduction measures beyond those which being applied already**
All scenarios
- () iii) There is a need for limiting the risks ; reduction measures which are already being applied shall be taken into account**

1. GENERAL SUBSTANCE INFORMATION

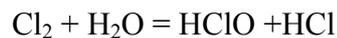
1.1 Chemical identity

CAS No.:	7681-52-9
EINECS No.:	231-668-3
Name:	Sodium hypochlorite
Structural Formula:	Na^+ClO^-
Molecular Formula:	ClO.Na
Molecular Mass (g/mol):	74.4

1.2 Concentration units and purity

Sodium hypochlorite is produced as an aqueous solution, from the reaction of gaseous Cl_2 with water at alkaline pH. Further details, including speciation as a function of pH, are given in Chapter 2 (sections 2.1.1 and 2.4). Ideally, the hypochlorite concentration should be expressed as % NaClO . However, to allow a comparison between this document and legal criteria (which express NaClO solutions in terms of active or available chlorine content) the term “available chlorine” is used in this dossier. (See appendix 4 for detailed explanation.)

Active and available chlorine express the oxidizing power of a chlorine containing solution as if all the chlorine species present were available as Cl_2 , transformed according to reactions such as those given below:



Both active (in practice $\text{Cl}_2 + \text{HOCl}$) and available ($\text{Cl}_2 + \text{HOCl} + \text{ClO}^-$) chlorine are expressed as equivalent content of Cl_2 (molecular weight: 71g). As the molecular weight of Cl_2 is 71 and the molecular weight of NaClO is 74.4, for sodium hypochlorite the equivalent available chlorine measured as the oxidizing power represents 95% of the sodium hypochlorite weight ($\text{M.W. Cl}_2 / \text{M.W. NaClO} \times 100 = 71 \times 100 / 74.4$). The units of available chlorine are g Cl_2 /kg. (See Annex 4 for details)

As produced, sodium hypochlorite solutions generally contain between 12-14% (w/w) available chlorine. However concentrations up to 24% can be produced mainly for industrial uses. A maximum of 1% of sodium hydroxide is left as excess in the hypochlorite solution in order to stabilize the pH value at about 12 and decrease the rate of decomposition; this also allows continuous absorption of carbon dioxide at the air-water interface. The sodium hydroxide is hence transformed into sodium carbonate.

When the solution has just been produced the content of sodium chloride is up to 14%. During storage, the hypochlorite is slowly transformed into chlorate and chloride, and the chloride concentration increases (see 2.4.2.).

Ranges of stabilizers and impurities in the concentrated solution (15% w/w) are typically in the following order:

Sodium hydroxide:	2-6 g/kg (up to 10 g/kg)
Sodium chloride	100-140 g/kg
Sodium carbonate	3-20 g/kg
Sodium chlorate	0.4-1.5 g/kg (up to 7 g/kg)
Sodium bromate	3-45 mg/kg (up to 90 mg/kg)
Iron	0.5-3 mg/kg
Mercury	0.10-0.25 mg/kg (up to 1.2 mg/kg)

1.3 Physico-Chemical Properties

Sodium hypochlorite does not exist as a pure salt at room temperature. It is produced and handled in form of an aqueous solution, which has a yellow colour and a characteristic smell. The following data are valid for an aqueous solution with a content of 15% (w/w) available chlorine (IUCALID, 2001).

Property	Value	References
Physical state	Liquid	
Melting point	- 20 to -30°C	Safety data sheet Hoechst AG 1994
Boiling point	96 – 120 °C	Safety data sheet Hoechst AG 1994
Relative density	1.23 g/cm ³ at 25°C	Sicherheitsdatenblatt der Bayer AG
Vapour pressure	17.4 - 20 hPa at 20°C	Safety Data Sheet Rhone Poulenc
Water solubility	Miscible [29.3 g/100 g (0 deg C) in water]	HSDB
Partition coefficient n-octanol/water (log value)	n.a.	
Granulometry	n.a.	
Conversion factors		
Flash point	n.a.	
Autoflammability		
Flammability		
Explosive properties	Anhydrous sodium hypochlorite is very explosive	HSDB
Oxidizing properties	Strong oxidizing agent usually stored and used in solution	HSDB

Property	Value	References
Viscosity		
Henry's constant	See par. 2.7	

1.4 Classification

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

Current classification according to Annex I (29th ATP):

Classification: C, N

R-sentences: 31-34-50

S-sentences: (1/2)-28-45-50-61

Specific limits:

$C \geq 10\%$: C R31-34

$5\% \leq C < 10\%$: Xi R31-36/38

The C&L Technical Group at the 15-18 March 2005 Meeting, decided to maintain the above classification.

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

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

This classification includes the risk related to the sodium hydroxide always present as a stabilizer in concentrations up to 1% (see Section 1.2).

Theoretical pure sodium hypochlorite should be classified as "very toxic to aquatic organisms" (N, R50) based on aquatic toxicity data, and as "harmful for ingestion" (Xn, R22) on the basis of the oral LD50 data.

This classification does not apply to solutions as their concentration is always below 25%.

1.5 Biocidal properties

When diluted in water, depending on pH value (see 2.4.1), sodium hypochlorite is partly transformed into hypochlorous acid (HOCl). This product is an extremely efficient biocide for prions, viruses, bacteria, parasites and fungi. HOCl reacts actively

by chlorination of nitrogen on compounds like amino acids. So it is very active against proteins. With adapted levels of concentration and contact times it can kill all the micro-organisms. But with much lower concentrations in water (0.1 to 1 mg/l) it is able to inhibit bacterial growth. In this last case the proteins of the membrane are partly destroyed and the bacteria are not able to multiply (Techware Report, 1996; Venkobachar *et al*, 1977)

The use of hypochlorite for pharmaceutical purpose is described in some Pharmacopoeia. It is used directly in contact with tissues for disinfection purpose but also to dissolve necrotic tissues. The solution is also used as a deodorant. The 5% solution is usually not directly used although it is sometimes used in root canal therapy. For therapeutic uses, it is diluted 10 to 30 times, and freshly applied.

1.6 Other starting materials generating available chlorine

Although this risk assessment concerns sodium hypochlorite, it is important to consider that the active fraction of this molecule is the hypochlorite ion, in an equilibrium with hypochlorous acid and chlorine which depends on the pH value (See section 2.4.1). As a consequence, sodium hypochlorite could also be generated from chlorine gas, calcium hypochlorite and chloro-isocyanurates which, in solution, also give rise to HClO and ClO⁻. The choice of available chlorine source involves technical and practical aspects such as, for example, stability for longer periods, higher concentrations of active substance in the product ready for use, or the availability of gaseous or solid product as required. The preparation technique depends on the product type and, as a consequence, different impurities and different degradation products will be found in the different commercial products.

Considering the chemical reactivity of NaClO, it is established that in aqueous solution, for the same pH conditions and available chlorine concentrations, it is not important whether available chlorine is generated from chlorine gas, calcium hypochlorite or sodium hypochlorite. As isocyanuric acid and hypochlorite ion form complexes, the reactivity is slower but the reaction products are the same. The quality and quantity of degradation products formed during the period of storage before use varies depending on the source of hypochlorite used; the reaction products are related to the organic matter content as it will be seen in the different scenarios.

For this assessment only those exposure scenarios in which sodium hypochlorite is (or is still) in use as such will be considered. In addition, available chloride generated from Cl₂ gas will be included in the total available chlorine for applications related to water disinfection. Also, some indication of the existence of other industrial or natural processes which would generate the same products will be given where relevant. However, studies in which molecules other than NaClO have been used as starting products for the generation of HClO-ClO⁻, have been considered in the hazard identification procedure.

2. GENERAL INFORMATION ON EXPOSURE

2.1 Production

2.1.1. Production technologies

Sodium hypochlorite, prepared by Labarraque for the first time in 1820 using chlorine gas and sodium hydroxide and called “Eau de Labarraque”, was used for disinfection (Holleman and Wiberg, 1976). The product was also used for bleaching in paper making. At present sodium hypochlorite is manufactured by the absorption of chlorine in ca. 21% caustic soda solution. The chlorine and the caustic soda are made by electrolysis of brine, and the chlorine is added as gas or liquid.

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. The total Western European production of NaClO in 1995 was estimated to be approximately 303 thousand tonnes, corresponding to 288 thousand tonnes chlorine equivalent. Seen that Switzerland and Norway production is small, this figure can be considered valid for EU production. Import to the EU and export outside the EU are not significant, seen the low cost and the large volume needed for the transportation of sodium hypochlorite solution.

About two thirds of the sodium hypochlorite solutions produced are sold to over 400 companies that formulate, repackage and distribute the products for various end uses including the household market. The other third of the production is used for pulp and paper, cooling water as undiluted form and is not packaged. On-site production is also occurring and these amounts are not taken into account in this risk assessment.

There are three distinct technologies used for chlor-alkali production in the EU and globally. These are mercury cell, diaphragm cell and membrane cell processes. Based on present technology (typically the diaphragm cell process uses asbestos diaphragms at present), membrane cell technology is preferred for new installations, and has been in operation in the EU since the early 1980s.

The industrial production for Europe has been quantified. Major producers in the EU of sodium hypochlorite are found in Table 2.1.

Table 2.1 European Major Producers for Sodium Hypochlorite 1990-1994 (updated 1999) Source: Eurochlor 2006

COMPANY	COUNTRY	LOCATION (process used)
Akzo Nobel BV	Netherlands Sweden Finland Germany	Hengelo (Hg), Rotterdam (M) Skoghall (M) Oulu (Hg) Bitterfeld (M), Ibbenburen (Hg)
Albemarle PPC	France	Thann (Hg)
Albion Chemicals	United Kingdom	Sandbach (Hg)
Associated Octel	United Kingdom	Ellesmere Port (M, Na/Hg)
Atofina	France	Jarrie (Hg)
BASF	Germany	Ludwigshafen (Hg, M)
Bayer AG	Germany	Leverkusen (M, HCl), Dormagen (M, HCl), Uerdingen (Hg, M)
Borregaard Industries	Norway	Sarpsborg (M)
Degussa	Germany	Lulsdorf (Hg)
Electroquímica de Hernani	Spain	Hernani (M)
Ercros	Spain	Flix (Hg), Sabinanigo (Hg), Villaseca (Hg, M)
Finnish Chemicals	Finland	Joutseno (M)
Industrie Chimiche Caffaro	Italy	Torviscosa (Hg)
Ineos Chlor ¹	United Kingdom Germany	Runcorn (Hg) Wilhelmshaven (Hg)
LII Europe	Germany	Frankfurt (Hg)
Metaux Speciaux	France	Plombiere (Na/Hg)
Química del Cinca	Spain	Monzon (Hg)
Rhodia	France	Pont de Claix (D)
Soc. Des Produits Chimiques d'Harbonnières SA	France	Harbonnières (Hg)
Solvay SA/Solvin	Belgium Italy Portugal France Spain Switzerland	Antwerpen (M), Jemeppe sur Sambre (M) Rosignano (Hg), Bussi (Hg) Pova (M) Tavaux (Hg, M) Torrelavega (Hg), Martorell (Hg) Zurzach (Hg)
Syndial	Italy	Assemmini (M), Porto Marghera (Hg)
Tessenderlo Chemie	Belgium France	Tessenderlo (Hg) Loos (Hg)

Hg = mercury cell process, M = membrane process, D = diaphragm process, and Na = variant of the mercury process which utilises a sodium/mercury amalgam.

The data, for 1994, have been provided by Euro Chlor.

¹ The assets originally owned by ICI at Runcorn, Lostock and Wilhelmshaven were purchased by Ineos Chlor in 2001. Subsequently, Ineos Chlor has closed its sodium hypochlorite production facility at Lostock. The Runcorn facility currently only operates mercury cells.

2.1.2. Naturally occurring hypochlorite production

Hypochlorite is also produced naturally in vivo for cell defence processes. The natural production of halo-oxo acids is widespread and related to haloperoxidases, which is well documented in the literature. A good overview of biohalogenation is given by Neidleman and Geigert (1986) and more recently by Winterton (1997). Hypochlorite is produced by chloroperoxidases, which are, among others, produced by mammals (in white blood cells), lichens and in many fungal species (Vollenbroek *et al.*, 1995).

Active chlorine species representing chlorine at a formal + 1 oxidation state (HOCl, Cl₂, N-chloroamide, etc.) have been quantified to some extent in one study looking at the rate of conversion of oxygen into polymorphonuclear leukocytes when phagocytosing a micro-organism. It was demonstrated that 28% of the consumed oxygen is converted into active chlorinating agents (Foote *et al.*, 1983). Even chlorine gas species have been identified in neutrophils during phagocytosis (Hazen *et al.*, 1996 a,b).

2.2 Use of sodium hypochlorite

Sodium hypochlorite is used mainly in chemical synthesis, for cleaning, disinfection and sanitation in household, for municipal water and sewage disinfection and for bleaching (see Tables 2.2, 2.3, and 2.4).

In Europe mainly two concentrations are used:

- 12 to 14% available chlorine as generally manufactured
- 3 to 5% available chlorine after dilution

Sodium hypochlorite is increasingly used in a very wide range of formulations for household, institutional or industrial applications (concentrations 1 to 10% available chlorine).

Sodium hypochlorite is used:

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

The main uses of sodium hypochlorite vary considerably from one European country to another. Generally speaking when the main applications are in households, the percentage of this use is between 35 and 60%. Germany has a very special position because it uses more than 70% of its production for the synthesis of other chemicals. When the product is used extensively in households, its range of applications is very large.

Table 2.2 shows the distribution, by country, of the total consumption of sodium hypochlorite among these different uses. The total consumption was estimated to be 288,000tonnes chlorine equivalent in 1994. The total for industrial (*i. e.* non-household) uses is also given in the table. According to SRI International (Stanford Research Institute) the consumption in 1990 was 435 thousand tonnes chlorine equivalent.

Table 2.2. HYPOCHLORITE PRODUCTION AND USE – 1994 (in kt. Cl₂ Equivalent)

REF.	PROD.	TOTAL IND. USES	HOUSE HOLD (**)	PROD. OTHER CHEM.	SWIM. POOL	SEWAGE	TEXTILE BLEACH	DRINK. WATER	P & P	COOL. WATER	OTHERS (*)
FIN+N+S+DK	8.05	6.83	1.22	1.27	0.44	1.46	0.32	0.31	2.40	0.11	0.52
A+D+CH	46.90	43.28	3.62	33.16	2.13	4.73	1.08	0.58	1.11	0.17	0.32
B+NL	35.50	23.07	12.43	14.00	2.80	0.77	0.60	1.30	0.60	1.20	1.80
IRL+GB	50.80	32.10	18.70	23.20	2.25	0.90	1.10	1.50	1.50	1.50	0.15
F	32.40	12.45	19.95	2.23	1.00	0.43	0.35	1.40	0.52	0.16	6.36
EL+I	47.32	27.12	20.20	1.20	1.10	3.04	7.80	3.14	0.30	1.84	8.70
P+E	66.70	24.25	42.45	0.90	6.50	3.85	0.50	1.30	2.10	0.60	8.50
TOTAL	287.67	169.10	118.57	75.96	16.22	15.18	11.75	9.53	8.53	5.58	26.35

(*) Including Institutional and Food industry (Total 12-22.5 ktCl₂ equivalent)
(Source: Euro Chlor - Confidential information - 1996)

(**) Additional data on household discussed in table 2.6 and related text

Table 2.3. CHLORINE USED IN WATER – 1994 (in kt. Cl₂ 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	n.a	0.02	0.02
A+D+CH	12.71	1.85	4.04	6.70	0.02	0.10	/
B+NL	3.52	n.a	n.a	n.a	n.a	n.a	?
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	n.a	/
TOTAL	75.32	32.29	17.43	10.95	9.55	4.80	0.30

(Source: Euro Chlor - Confidential information - 1996)

By comparison, the chlorine (Cl₂) used in these countries for these same purposes is shown in Table 2.3. Available chlorine from both NaOCl and Cl₂ sources have been included in the water-related use scenarios in this assessment. For example, the consumption of hypochlorite and chlorine in European swimming pools in 1994 amounted to 16.22 kt/y and 10.95 kt/y respectively (see Tables 2.2, 2.3). In addition, it is noted that in small swimming pools

chloroisocyanurates are also used. In some applications there is a replacement of sodium hypochlorite by other chemicals. The use of NaClO in commercial bleaching (pulp and paper, textiles) has decreased significantly in the recent past.

The information in Table 2.2 has been used to determine the percentage of the total EU NaOCl production which is used in each of the use scenarios given above. This information is shown in Table 2.4, along with the appropriate Main Category, Industry Category, and Use Category for each exposure scenario, determined in accordance with the TGD.

Table 2.4 : Use Category and Percentages for Sodium Hypochlorite

Use	Main Category	Industrial Category	Use Category	% use of total NaClO
Cleaning and disinfection: Household application	IV	5	9	41
Water treatment (drinking, cooling, sewage water)	III, IV	5, 15	9	11
Swimming pool sanitation	III, IV	5,6	9	6
Production of other chemicals	I	3	37	26
Bleaching: Textile industry	I, IV	13	8	4
Pulp and paper	I	12	8	3
Other (*)	III, IV	15	55	9

(Source: Euro Chlor - Confidential information - 1994)

(*) Including Institutional & Food industry corresponding to 4 to 8% use of total NaClO.

Main Category I:	Use in closed systems
II:	Isolated intermediates Isolated intermediates with controlled transport
III:	Non dispersive use
IV:	Wide dispersive use
Industrial Category	3: Chemical industry: chemicals used in synthesis 5: Personal / domestic 6: Public domain 12: Pulp, paper and board industry 13: Textile processing industry 15: Others
Use Category	8: Bleaching agents 9: Cleaning/washing agents and disinfectants 33: Intermediates 55: Others

As stated previously there are significant differences in the applications of sodium hypochlorite among European countries. The split between total industrial uses and household applications is given for several different countries in Table 2.5.

Table 2.5. Total Industrial and Household Uses (percentage per country)

Countries	Total Industrial Uses	Household Applications
Finland, Norway, Sweden, Denmark	85%	15%
Austria, Germany, Switzerland	92%	8%
Belgium, Netherlands	65%	35%
United Kingdom, Ireland	63%	37%
France	38%	62%
Italy, Greece	57%	43%
Portugal, Spain	36%	64%

(Source: Euro Chlor - Confidential information - 1994)

Sodium hypochlorite has a long history of use in the home for both bleaching of textiles and cleaning and disinfection of household surfaces. The ready availability and cost-effectiveness of the material has ensured that it has taken its place in the repertoire of many households. In textile cleaning the ability to remove stains and to whiten soiled fabrics helps to maintain the life of garments which would otherwise be discarded prematurely. With the move to energy conservation and cooler wash temperatures (e.g. 40 °C), sodium hypochlorite treatment of the laundry load can compensate for the loss of germ kill power obtained in the past from high wash temperatures (Walter and Schillinger, 1975).

In the household hypochlorite is used for cleaning toilet bowls, removing stains from hard surfaces (e.g. tiles in kitchens and bathroom) and as bleaching agent in connection with washing. Hypochlorite is a widely used disinfectant because it is highly effective on fungi, bacteria, spores, and viruses at rather low concentrations (<400 ppm) (FIFE-AIS, 1993). Normally the sodium salt of the hypochlorite acid is used, and therefore the products are strongly basic (pH>7).

Germs in the home are ubiquitous and many can be pathogenic. They can be brought into the home by infected foods (e.g. raw meat), on the person or through domestic animals and insects. The presence of a sick person in the home can also lead to further infection. Under favorable conditions germs and bacteria in particular, can multiply very rapidly and spread across the home. Sodium hypochlorite has proved to be effective against all forms of microbial life (bacteria, virus, fungi, spores) at concentrations which are several orders of magnitude lower than other biocidal systems. This means less emission of chemicals into the environment for the same application. To reduce the risk of infection spreading in the home cleaning with conventional detergents may not be sufficient and disinfection products are required. Sodium hypochlorite has been shown to be the most effective biocidal system and is unique in destroying even the most persistent micro-organisms; its use is recommended in such places as kitchen and bathroom surfaces, in the toilet and wherever hygiene is important (AISE, March 1997).

Country-specific information on the household usage of hypochlorite, including the type of use in the home and the volume of hypochlorite-containing product used is given in Table 2.6.

Table 2.6 - Household Consumption of Hypochlorite Bleach

COUNTRY	FR*	SP ⁺	P	I	GR	UK	IR	NL	B*	D*
PENETRATION (% Households)	77	95	85	76	85	85	82	50	86	11
ALLOCATION (%)										
LAUNDRY	10	30	30	19	15	8	6	5	5	5
HARD SURFACE	84	62	70	80	85	90	88	92	93	93
OTHER	6	8	0	1	0	2	6	3	2	2
CONSUMPTION* (Litres/Year/ Household)	12.5	26.0	15.7	18.6		9.3	7.8	8.0	11.8	2.1
TOTAL VOLUME (kTons/Year of product)	350	450	95	320	50	175	7	26	59	19
TOTAL VOLUME (kTons Cl ₂ ⁴ equivalent/Year of product)	12.6	22.1	4.75	16	2.5	8.75	0.35	1.3	2.15	0.70

Commercial Products (3-5% Hypochlorite)

Source – Confidential market data obtained by AISE and volumes from 1994 based on BEP OSPAR 1999.

* 3.6% active Cl₂

+ 45 Kt at 3.6% active Cl₂

1 All other countries between 4-5%: 5% concentration taken as highest estimate

Table 2.6 is based on accurate Market Research Data which record penetration of household bleaches together with consumption of product per household. The volumes allocated to laundry and hard surface cleaning usage are also known (OSPARCOM, 1999). The tables 2.5 and 2.6 summarize household usage of hypochlorite bleach products in countries of significant penetration (>10 % households). In some countries, depending on the end usage (e.g. laundry, hard surface cleaning), a dosage recommendation is made. If the product is used for disinfection purposes then a dosage recommendation is made which is designed to guarantee the level of microbial life remaining after cleaning is below that which is believed to be dangerous to health. The dosage recommendation will depend on the level of bleach in the product and the end usage.

The total volume of 71.20 kt found from the major formulators for 10 EU countries represents about 25 % of the total tonnage produced in those countries. However the producers' data represent the most conservative estimation, showing 41% of the production is used in household applications.

Under the Dangerous Substances Directive (67/548/CEE) and the dangerous Preparations Directive (88/379/CEE) hypochlorite solutions are classified as “Corrosive” above 10% and “Irritant” between 5-10%. The final classification of the product will also depend on the levels of other materials present such as caustic soda and surfactant.

The volume information in Table 2.6 applies to household hypochlorite preparations, not to sodium hypochlorite reported as active chlorine. These preparations are sold in Europe at concentrations which vary between 0.5-12.5% available chlorine levels, with a prevalence of concentration ranging from 3-5%.

As can be seen from Table 2.2, in some parts of Europe sodium hypochlorite is mainly used for industrial applications (production of other chemicals, water treatment, bleaching), whereas the use of NaClO for household applications is significantly higher in other parts of Europe. Even more significant are the country-specific differences concerning the use as an intermediate (oxidizing agent) in the production of other chemicals, shown in Table 2.7.

Table 2.7: Production of Chemicals Usage (percentage per country)

Countries	Use for the production of other chemicals
Finland, Norway, Sweden, Denmark	16%
Austria, Germany, Switzerland	71%
Belgium, Netherlands	39%
United Kingdom, Ireland	46%
France	7%
Italy, Greece	3%
Portugal, Spain	1%

(Source: Euro Chlor - Confidential information - 1994)

Supporting information for the variation in the main types of hypochlorite use among the different EU member states is provided in Bloemkolk, J.W., 1995. This report estimates that, for some European Countries, the household use of hypochlorite accounts for over 60% of the total hypochlorite production. The consumption varies, however, a great deal among the member countries. In Sweden, for example, the consumption of hypochlorite for cooling water in nuclear power plants represents about 50%, the consumption in swimming baths is 21%, the consumption within the chemical industry and paper industry is about 21% and in the household the consumption is 6%.

2.3 Exposure characterisation

2.3.1 Exposure and release during NaClO production

Sodium hypochlorite is produced by the reaction of chlorine with sodium hydroxide solution in controlled reactors. This production is a waste water free process. Only during occasional cleaning operations (e.g. prior to repair) may small amounts of waste water (2-3 l per tonne of sodium hypochlorite solution produced) occur. This waste water is treated before it is discharged.

Sometimes off-gas from the production of sodium hypochlorite passes through a scrubbing system. All washing solutions are discharged to waste water treatment plants. The final effluent contains mainly chloride. The final product is filled into drums or into bulk containers. Occupational exposure during production may occur in case of sampling, cleaning and filling operations.

2.3.2 Exposure and release during Formulation and Use of Products containing NaClO

Producers of cleaning agents use the sodium hypochlorite solution in closed or open systems when formulating their products. **Users** of the resulting formulations are **industrial cleaning** companies and **private households**. Waste water from cleaning operations is usually discharged into public waste water treatment plants where NaClO is reduced or decomposed to sodium chloride. In areas without waste water treatment plants the waste water is discharged to surface water. In household applications, e.g. cleaning of surfaces and soaking of fabrics, exposure and inhalation may occur. If hypochlorite is used in the presence of an acid, chlorine can be released.

Pulp and paper bleaching operations are done in closed systems. The waste water is released into waste water treatment plants where NaClO is mainly converted to sodium chloride. In Northern and Central Europe the amount of sodium hypochlorite that is used for the bleaching of paper and cellulose has decreased.

Sodium hypochlorite is used for **water treatment**, where the hypochlorite oxidizes inorganic or organic compounds in the water and inhibits/destroys microorganisms. The European Guideline for **drinking water** allows the use of NaClO. Treatment of drinking-water containing higher quantity of organic matter can be performed with chlorine dioxide to reduce the formation of halogenated byproducts. For the **disinfection of swimming pools** NaClO can be applied either directly e.g. in form of a 13% aqueous solution or in diluted form. Large public swimming pools use chlorine or chlorine dioxide directly. Small swimming pools also use chloroisocyanurates as they can be handled simply.

Sodium hypochlorite is used for the **disinfection of waste water**. In such a case, the aim is to protect either human or environmental species from bacterial contamination. It may also be used to prevent sewage sludge from bulking before waste water treatment.

In the **production of other chemicals**, sodium hypochlorite is used as an oxidizing agent. Emissions containing sodium hypochlorite do not exist because all NaClO is reduced to sodium chloride.

2.4 Transformation

2.4.1 Species in aqueous solution as a function of pH

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 2.1. For example, at pH 7.5 half of the chlorine is active as HOCl and half is available as ClO⁻. The pH of commercial solutions is above 11 and the only species effectively present is ClO⁻.

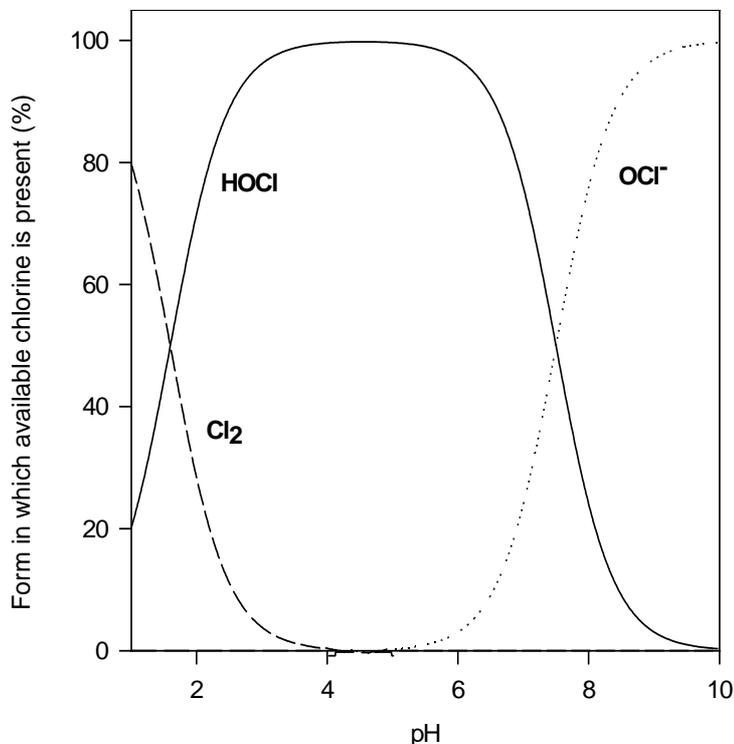


Figure 2.1. Calculated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M Cl₂ in water at standard temperature and pressure (The data in this figure are based on general chemistry handbooks).

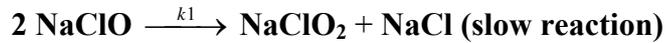
2.4.2 Stability

In concentrated sodium hypochlorite solutions, the content of available chlorine decreases because NaClO tends to disproportionate to chloride and chlorate ions:

The reaction is:



It is the resultant of two reactions: a slow one with formation of chlorite and a fast one with formation of chlorate by reaction between chlorite and hypochlorite.



The first reaction (that produces chlorite) controls the reaction rate producing chlorate.

The formation rate of chlorate, at room temperature and pH = 11, is very slow.

The process is dependant on the time, temperature, impurities, pH and concentration of the sodium hypochlorite solution. Also light can decompose hypochlorite solutions.

Time Dependence

At constant temperature the inverse of the active product concentration is a linear function of the time. A solution dosed at 150 g/l available chlorine which is kept away from sunlight and at constant 15°C, loses 1/6 of its concentration within less than 3 months. In diluted hypochlorite solutions the losses are minor.

pH Dependence

Hypochlorite should not be added to a unbuffered medium, because at low pH, the following secondary reactions could occur:

In acid media under pH 4 hypochlorite will be transformed to gaseous chlorine.

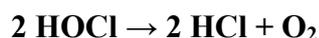


Between pH 4 and 11, both ClO^- and HOCl are present with the latter being much more active. This pH will be obtained when all the sodium hydroxide present in the hypochlorite solution has been carbonated (see chapter 1.2). Degradation of HOCl is more rapid than the degradation of ClO^- .

if pH <6, the main reaction is: $2\text{ HClO} \rightarrow 2\text{ HCl} + \text{ O}_2$

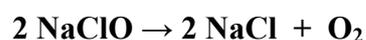
if pH >6, the main reaction is: $3 \text{ NaClO} \rightarrow \text{ NaClO}_3 + 2 \text{ NaCl}$

Hypochlorous acid (HClO) is very unstable and it suddenly decomposes with formation of oxygen:



Dependence upon Impurities

Sodium hypochlorite can decompose to oxygen according to the following reaction:



The decomposition reaction is a bimolecular one and requires an activation energy of 113.3 kJ/mol (26.6 kcal/mol). Although it is slower than the chlorate formation reaction, it is catalysed by trace amounts of metallic impurities.

The strongest decomposition catalysts to oxygen are: Co, Ni and Cu; whereas Fe and Mn are weaker catalysts. To avoid decomposition of commercial hypochlorite solutions, these metals must be reduced as much as possible. Generally, their elimination occurs mechanically by filtering as their solubility is reduced during the hypochlorite production step.

Salts such as sodium chloride, sodium carbonate and sodium chlorate have only a very low influence on reaction rate within the range of concentration where they are normally present. Their influence on reaction rate is only remarkable in some particular cases (e.g. diluted High Grade Sodium Hypochlorite where NaCl content is highly reduced because of the specific production process).

Sodium hydroxide does not influence the reaction rate if its concentration is greater than 10^{-3} M (0.04 g/l).

Light Dependence

The sodium hypochlorite solution is very sensitive to light. Direct sunlight may cause rearrangement and decomposition resulting in the formation of chlorate and oxygen. The presence of isocyanuric acid in solution reduces this sensitivity to a great extent.

Temperature Dependence

The influence of temperature is very high: the decomposition rate doubles if the temperature increases by $\sim 5.5^{\circ}\text{C}$. If temperature is more than 35°C , the decomposition reactions are very rapid:



In every case, the temperature of the solution must be below 55°C in order to prevent a sudden decomposition of the hypochlorite.

The more stable solutions are those of low hypochlorite concentration, with a pH of 11 and low iron, copper, and nickel content, stored in the dark at low temperature.

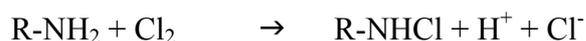
2.5 Chemistry of hypochlorite in polluted water

Chlorine and all of its derived species are oxidative and very reactive compounds. Chlorine gas is a more efficient oxidiser than hypochlorous acid (HOCl), and hypochlorous acid is more efficient than the hypochlorite ion (ClO^-). The balance between HOCl and ClO^- can be studied in polluted water with pH between 4 and 10.

In this case, the kinetic of the reactions and the final products obtained depend for a large extent on the percentage of each of the two species (HOCl, ClO⁻).

The main reaction routes can be described as follows:

- Chlorination with amines R-NH₂ or ammonium NH₄⁺ is very rapid and explains the very fast disappearance of available chlorine in waste water. The chlorine atom linked with a nitrogen atom is expressed as combined chlorine.



If there is, at one point, a large excess of active chlorine over -NH₂, chloramines like R-NCl₂ and NCl₃ are formed. NCl₃ is a very volatile product: the concentration of NCl₃ in air and solution is similar.

- Oxidation reactions occur with many inorganic or organic compounds. Thus, for example, ferrous ion can be transformed into ferric ion, organic radicals can be transformed through hydrolysis, and C-C bonds can be broken. If there are no nitrogen compounds in the solution, this type of reaction is predominant.
- Chlorination of C atoms from organic molecules is easier for molecules with a shorter carbon skeleton. Three typical reactions are: **Reaction with phenol** giving monochlorophenols; **Reaction with molecules containing two carbon atoms**: acetaldehyde, acetonitrile, and acetic acid, which are chlorinated on the CH₃, and give chloroacetaldehydes, chloroacetonitriles and chloroacetic acids; **Reaction with final degradation of the carbon chain** giving THMs and especially CHCl₃ (chloroform).
- AOX is a measure of the number of C-Cl bonds formed in a reaction, expressed as Cl₂ consumed to form these bonds. Part of the AOX content is volatile; the main representative in this case is chloroform. It is very important to distinguish between the volatile and the non-volatile part in order to analyse the AOX. The non-volatile part is of high importance due to the potential stability of some of the components (mainly the chloroacetic and chloroaromatic compounds).

Two different scenarios could be studied separately:

When chlorine is maintained constantly in excess, as in:

- swimming pools
- cooling systems
- drinking water

When chlorine is very rapidly and totally transformed into combined chlorine, as in:

- waste water treatment
- household use
- in contact with soil

In the first scenario, both the rapid and slow reactions can take place and both oxidation and carbon or nitrogen chlorination processes are found. This first type of scenario gives an indication of the AOX formation potential at the equilibrium.

In the second scenario, the main reaction is the nitrogen chlorination with the formation of mainly mono chloramines. The content of the total residual chlorine (TRC) (equal to the available chlorine) disappears within a few minutes. The chemical degradation of combined chlorine in this type of scenario takes a few hours. This second scenario also produces a number of long chain chlorinated molecules (chlorination of C) but to a lesser extent (only 1 or 2% conversion of the available chlorine). These molecules only represent the start of the chemical degradation process. After a certain time, the remaining AOX part will include volatile compounds such as chloroform and more stable molecules such as chloroacetic acids.

The following sections 2.6 and 2.7 are meant to explain possible problems in the analysis of hypochlorite solutions, due to the presence of three species of available chlorine (chlorine gas, hypochlorous acid, hypochlorite anion) and to their volatility.

2.6 Residual Chlorine Analysis

All the research on sodium hypochlorite solutions in water highlights a particular problem of the analysis of the available chlorine remaining in the solution. Given the existence of three species of chlorine in the aqueous compartment (chlorine gas, hypochlorous acid, and hypochlorite anion) and their respective concentration depending on the pH, the total content of these three species has to be measured. This content of available chlorine does not include the concentration of combined chlorine (the heavy chloramines or the mono, di or trichlor- amines). For a very low content of available chlorine (0.2 mg/l), it is impossible to differentiate between free and combined chlorine. Many publications express the content as TRO which is a measure of total residual oxidant, including species like chloramines, bromine, chlorine dioxide.

It is however important to know what the different methods are for determining available chlorine at low concentration in natural or waste waters, fresh or sea water. Generally speaking, these methods were created in the USA or the UK for the analysis of drinking water, and some names are well known: Marks H.C., Palin A.T., Cooper W.J., Dimmock N.A. and Midgley D.

The methods approved by the Standard Methods Committee in 1993 (APHA, 1995) for fresh water use iodine, DPD (N,N-diethyl-p-phenylene-diamine) or syringaldazine. Amongst these three compounds, *iodine* is used for direct or indirect titration of chemicals and in potentiometric or amperometric methods. These four iodine methods can be used for natural or treated fresh or sea water. Only the iodometric back titration can be used for waste water (Whitehouse *et al.*, 1985). The *DPD* methods are used for treated and waste freshwater using ferrous ammonium sulphate or by colorimetry. The *syringaldazine* colorimetric method has been developed specifically for free chlorine

tests in treated fresh water. With colorimetric methods, organic contaminants may produce a false free chlorine reading, and sample colour and turbidity may interfere.

It is obvious that any test method should be used carefully. The method has to be appropriately chosen and adapted for each different matrix. It is particularly difficult to find an accurate method when the solution contains a lot of inorganic or organic compounds.

Hypochlorous acid in solution is particularly unstable. As shown in section 2.4, exposure to sunlight or strong light will accelerate the transformation of hypochlorous acid into chloride. Agitation of the sample also accelerates this reduction process. Therefore, samples have to be analysed immediately after sampling, while avoiding light and agitation, and cannot be stored.

In the best conditions, the lowest accurate limit is 10 µg/l. In reality, in environmental aqueous media for ecotoxicology research, it would certainly be justifiable to restrict the lowest accurate limit to 100 µg/l for available chlorine.

The complexity of hypochlorite chemistry shown in this and the preceding two sections must be taken into account when measurements are carried out to determine the amount and type of chlorine-containing material present in environmental matrices or derived from environmental processes. In particular, the limits imposed upon possible measurements by the constraints of stability and by the limits of analytical detection must be considered. The loss due to volatility of some species of available chlorine and of some chlorine reaction products must also be considered, and consideration given to complete mass balance determinations when necessary.

2.7 Volatility of HOCl and ClO⁻

The volatility of the species of available chlorine in water and of three main species of combined chlorine have been studied by Holzwarth et al (1984),. Blatchley et al (1992), published the Henry's constant of HOCl. These references expressed this information with different units and using different forms of Henry's law. Currently Henry's law constant is expressed in atm and is the ratio between partial pressure in the air divided by a mole fraction in water. The figure given by Blatchley is expressed in atm and is 0.06 atm. The figures calculated by Holzwarth are without unit and expressed in mole fraction in the air divided by mole fraction in the water (for HOCl at pH 5.5 and at a temperature of 20°C, 0.076). These two expressions of Henry's law constant are not very easy to interpret. It is proposed to use a figure without unit expressing mg/l in air divided by mg/l in water. After correction of Holzwarth figures in this new unit (1 mole of air weighing 28 g and 1 mole of water 18 g; 1 m³ of air weighing 1.2 kg and 1 litre of water weighing 1 kg), we have new figures of a Henry's coefficient for the different products at a temperature of 20°C:

ClO ⁻	pH = 8.5	H = 0.07 10 ⁻⁴
HOCl	pH = 5.5	H = 0.4 10 ⁻⁴
NH ₂ Cl	pH = 9	H = 2.4 10 ⁻⁴
NHCl ₂	pH = 6.4	H = 8 10 ⁻⁴

NCl_3 $\text{pH} = 1.8$ $H = 2300 \cdot 10^{-4}$

The volatility of NCl_3 is about one thousand times the volatility of the 3 other compounds. The ClO_2^- Henry's coefficient is about five times lower than the coefficient of HOCl . At 40°C and $\text{pH} = 1.8$ the Henry's coefficient for NCl_3 is 0.6, very close to the maximum possible figure which is 1.

These figures make clear that NCl_3 is completely extracted by stripping and that ClO_2^- is extremely difficult to extract. For HOCl , Holzwarth et al (1984) has measured that 10% of the product present in a cooling tower could be flashed off if the water is at 40°C and with a $\text{pH} = 6.5$. Some measurements above the surface of a swimming pool taken by the French INRS (Institut National de Recherche sur la Sécurité) have made clear that even with very low content of NCl_3 in the pool the large majority of inorganic chlorinated species in the air is composed of NCl_3 (Héry *et al.*, 1994)

The "smell of chlorine" gives an idea of the total content of inorganic chlorinated species present in the atmosphere. In a swimming pool atmosphere the public is able to smell "chlorine" at a content of 0.1 mg/m^3 of equivalent NCl_3 ; a comfort limit is 0.5 mg/m^3 (Massin *et al.*, 1998).

For a generalised approach to the presence of inorganic chlorine species in the atmosphere, a content of above 0.05 mg/m^3 of total (available and combined) chlorine would be smelt by people (Massin *et al.*, 1998). This total content could be in two forms : gaseous mainly as NCl_3 or aerosol as a mixing of all the species (available and combined chlorine) in the droplets of water.

2.8 Exposure Control

Controls exist on the content of active chlorine in drinking water which is generally between 0.1 to 0.5 ppm. For example, for Italian legislation the maximum content of active chlorine in drinking water is 0.2 ppm; in waste waters it is 0.2 ppm; in swimming pools it is 1.2 ppm.

Although there is no occupational exposure limit (OEL) for sodium hypochlorite most countries adopted the OEL (or MAK or TLV) for chlorine in Germany, i.e. 1.5 mg/m^3 in air.

3. ENVIRONMENT

3.1 Environmental exposure

3.1.1 Introduction

Environmental exposure may occur through the production and uses of sodium hypochlorite and additionally through the formation of hypochlorite through the use of chlorine in water. These sources of hypochlorite are all included in this risk assessment. Due to the instability and highly reactive nature of hypochlorite it will disappear very rapidly when entering the environment. This means that a regional background concentration of hypochlorite cannot exist and therefore a regional exposure scenario is not realistic and will not be considered here. It can be concluded that any potential impact of hypochlorite will be restricted to local conditions.

The actual local impact of hypochlorite depends very much on the specific conditions for each application. Therefore specific exposure scenarios will be used to estimate the local risks.

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

A more appropriate and detailed characterisation in terms of specific chlorinated by-products and overall composition of AOX for each specific scenario has thus been provided for most scenarios. This includes PEC/PNEC calculations at least for chloroform and trichloroacetic acid, two important identifiable by-products for which formal risk assessments already exist. In each case, these calculations have then been extended to estimate PEC/PNEC ratios for all trihalomethanes and haloacetic acids, because they may have similar toxic modes of action. Evidence about the likelihood of formation of high hazard molecules such as dioxins are also included. This is further supplemented by a qualitative overview of the nature of other chlorinated by-products and a quantification where possible of exposure. For most scenarios, conclusions about risks for the environment from organo-halogen by-products are also drawn from a 'whole effluent' testing programme conducted as a worst case model on chlorinated raw sewage as agreed with the Technical Meeting.

As regards polychlorinated dioxins and furans, these can be formed by electrophilic chlorination in acid solution where chlorine (Cl₂) is present, but not in neutral or alkaline solution where the only species are hypochlorous acid and hypochlorite (cf Figure 2.1). For example, polychlorinated dioxins form during acid chlorination of wood pulp at pH 3, but above pH 6 the amounts become undetectable (Hise et al., 1989), Berry et al, 1989). Similarly, polychlorinated compounds are not formed at or above pH 5 when 0.3 mM dibenzo-*p*-dioxin or dibenzofuran is mixed with 60 mM

hypochlorous acid (4,470 mg/L as sodium hypochlorite) for 24 hours (Onodera et al, 1989).

In most use scenarios the pH will be maintained around neutral (typically >6) or on the alkaline side for a variety of reasons, but largely to avoid any possibility of chlorine evolution: dioxin formation would thus also not be expected. In some scenarios there are specific studies which have investigated dioxin formation directly. The evidence from studies and pH conditions are reviewed case-by-case for each scenario in the following section.

3.1.1.1. Production

Sodium hypochlorite is generally produced alongside with chlorine in the chlor-alkali industry. It is manufactured by the absorption of chlorine in a 20 to 23 % caustic soda solution. Chlorine and caustic soda are produced by electrolysis of brine and the chlorine is added to caustic as a gas to obtain hypochlorite. The concentrated hypochlorite solutions obtained (usually 13.5% but sometimes up to 24 % active chlorine) are then transported as bulk material to the user. The European production was 287.67 kt in 1994 (see Table 2.2).

The emissions of hypochlorite to the environment from the production processes are minor. The available chlorine in effluent is measured as TRC (Total Residual Chlorine), but it cannot be distinguished to what extent this TRC value in the final effluent is related to hypochlorite or to other oxidative compounds that are present in the same effluent. Final effluents of production plants are usually a combination of effluents from different processes and may for example also include sewage. Measurements from production sites have shown that many plants discharge measurable quantities of COD and any available chlorine, which is a strong chemical oxidizer and will normally react rapidly and disappear in effluent or immediately after reaching the receiving water.

Halogenated organic by-products

Because no organic materials are involved in this process, halogenated organic by-products do not arise.

3.1.1.2. Household use

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

Household hypochlorite preparations are sold in Europe at concentration, which vary between 0.5-12.5% available chlorine levels, with a prevalence of concentration ranging from 3-5%. The dosage recommendation will depend on the level of bleach in the product and the end usage.

By-products

In formulated bleach solutions there is a small conversion of hypochlorite to chlorate and chloride: 10 to 20% hypochlorite is broken down in domestic products after storage for 1 year at 20°C. In use/sewage/environment where organic and nitrogenous materials are present, sodium hypochlorite acts as a highly reactive oxidizing agent. It reacts rapidly with organic matter and most ($\approx 99\%$) of the available chlorine is converted to inorganic chloride (Jolley and Carpenter, 1975). If nitrogen-containing compounds are present chloramines will be formed, the specific species formed depends upon the conditions. A minor reaction that also occurs is the chlorination of organic matter - in domestic uses of hypochlorite about 1.5% of the initial available chlorine is incorporated into Organohalogen By-Products (OBPs) (Schowanek et al., 1996).

The range of organohalogen by-products (OBPs) formed from domestic use of hypochlorite can, in theory, be extremely large and dependent on the organic compounds present during use and in the sewer. The most common OBP's identified during laundry use are trihalomethanes, haloacetic acids, and haloacetonitriles, analogous to those formed during the chlorination of drinking water (Smith, 1994). These, plus halogenated aldehydes and ketones, are also the main expected by-products during other cleaning and disinfection uses, including reactions in the sewer (TNO Delft, 1991).

It is inevitably impossible to identify all the different chemical species formed during reaction of an oxidizing agent such as hypochlorite with complex mixtures of proteins, carbohydrates, fats and various other substances encountered during cleaning. A risk assessment of these by-products must then necessarily rely at least partly on consideration of the environmentally relevant properties of the mixtures.

Many of the unidentifiable components measured as AOX will be chlorinated versions of complex substrates that would be equally hard to identify in the original matrix. These larger molecules tend to be very sparsely chlorinated (often 1 carbon atom), rather than polychlorinated, such that their properties are not radically different from the substrate molecule. It is likely that a significant fraction will be of high molecular weight (>600 – 1000 Dalton) and thus of low bioavailability (AISE, 1997).

It was found that the formation of the various OBPs is dependent on the NaClO:COD ratio (AISE;1997). The formation of smaller reaction products (CO₂, THM, chlorinated acetic acid derivative) is stimulated by a high ratio. THM, halogenated acetic acid derivatives, and halogenated aldehydes are primarily formed from humic, carboxylic and amino acids. In general, the formation of OBP will increase concurrently with the prolonged contact time and rise in temperature. Elevated pH will generally stimulate the formation of THM. It has also been found that more OBPs are produced when hypochlorite reacts with proteins than with fats or carbohydrates (AISE, 1997).

In a field-study programme directly monitoring domestic effluent from apartment blocks housing around 420 people, Schowanek et al. (1996) found that the degree of NaClO to AOX conversion (when using hypochlorite in the household) varied between 0.54% and 2.6% (1.5% on average).

Effluents from laundry bleaching have been studied most extensively because they are generated in a controllable closed system. Laundry bleaching also produces some of the highest Cl to AOX conversion rates and, because of the potential substrates present, an effluent that is relatively complex compared with those from other cleaning tasks with lower organic loads.

In other studies using various laundry detergents and hypochlorite during washing the degrees of conversion of NaClO to OBP were measured to be approx. 0.7-4% (6.2% in one sample) (Smith, 1994). In addition it was found that chloroform represented 5-13% of OBP, with an average of 10.3%. In a similar study between 0.3 and 3.3% of the chlorine, added as hypochlorite, was converted into AOX, of which approx. 17% could be identified as chloroform (IVL, 1990a). It was found that washing of dirty laundry without laundry detergents gave the highest levels of AOX. Furthermore, the degradability of AOX in the wash water was measured (OECD 301c) to be between 27 and 67% in 28 days (48% on average).

Smith (1994) reported 59-73% removal of AOX from washing machine effluent in semi-continuous activated sludge (SCAS) tests with very little adsorbed onto the sludge. Degradation rates of up to 85-90% have been reached after acclimation of the biomass in prolonged tests, which is comparable with rates for other organics in the effluent indicating the chlorinated species are not more recalcitrant than the substrate molecules. (AISE 1997). Similarly high rates of removal (87-94%) were obtained in experiments over 20 weeks passing bleached laundry effluent through simulated domestic septic tanks, again with insignificant adsorption onto the sludge (Braidia et al 1998).

Studies to explore whether the by-product mixtures generated during laundry bleaching might contain significant quantities of potentially bioaccumulative species after sewage treatment, have been reported by Ong et al. (1996). These used a combination of HPLC according to draft EPA methods (USEPA 1991) to isolate a potentially bioaccumulative fraction. Capillary gas chromatography with full scan electron impact ionization mass spectrometry at a detection limit of 10 ng/l provided no positive or tentative identifications of chlorinated substances in the potentially bioaccumulative fraction. Similarly, there were no peaks corresponding to any of the compounds of 'highest concern' as listed by the USEPA. Comparison with unbleached laundry effluents indicated that the range of other potentially bioconcentrable compounds present was similar irrespective of the use of bleach. The authors concluded that use of hypochlorite in laundering is unlikely to generate persistent bioconcentrable compounds.

When using NaClO hard-surface and toilet cleaning, the formation of OBPs during five different common tasks has been measured as ranging from 0.06% (as AOX) of the active chlorine for toilet cleaning to 0.12% for floor cleaning (Josa et al., 1997). This comparatively low conversion rate reflects the fact that OBP formation is limited during use by the level and nature of organic matter present, and by the contact time, though the types of by-products can be influenced by chlorine concentrations and pH.

Most of the OBPs are thus formed after spent cleaning solutions are released to mix with sewage when they are poured down the drain or when the toilet is flushed.

All household uses of hypochlorite take place at alkaline to neutral pH. Formation of polychlorinated dioxins and furans is thus not expected. However, because dioxins are found in both municipal sewage sludge and household wastewater, several studies have looked directly for possible formation of such compounds but have concluded that this does not happen (Office of Nature Conservancy, Sweden, 1992; Rappe C. 1992; Horstmann and McLachlan 1995). These studies examined hypochlorite use in laundry and machine dishwashing, which represent the most aggressive conditions of household use. In each case dioxins were detected but the levels were similar whether hypochlorite was used or not. Through a series of studies, Horstmann, McLachlan and colleagues came to the conclusion that the dioxins that can be found in household wastewater do not originate in detergents, bleaching agents, or from the washing process, but come from certain contaminated textiles, (cf Section 3.1.1.6) and are redistributed by wearing, bathing and laundering over numerous washing and bathing cycles (Horstmann et al, 1992, 1993; Horstmann and McLachlan 1994, 1995)

3.1.1.3. Production of other chemicals

Sodium hypochlorite acts as a chlorinating and oxidizing agent towards organic compounds. In addition to its use in the preparation of carboxylic acids by haloform oxidation and amines by the Hoffmann rearrangement it has numerous interesting and useful synthetic applications. Most reactions are used in the manufacturing of organic intermediates:

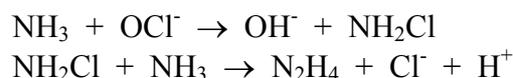
- Aromatically bound methylene groups in acetyl substituted aromatics are oxidized by NaClO to carboxylic acids.
- Acetylenic protons are displaced to give chloroacetylenes.
- Cyclopentadiene and indene are readily chlorinated by hypochlorite to perchloro cyclo penta diene and 1,1,3-trichloroindene, respectively.
- Aliphatic oximes and primary and secondary nitro compounds are converted to geminal chloro nitro alkanes.
- Symmetrical dialkyl hydrazines and methylenediamine sulfate are oxidized to azo compounds and diaziridine, respectively. O-nitroanilines are oxidized in good yields by hypochlorite to benzofuran oxides.
- 2,4-dinitroaniline, on treatment with NaClO, in alkaline methanol, is converted to 5-chloro-4-methoxy-benzofuran-1-oxide via a haloalkyl substitution reaction; the haloalkoxy reaction has been applied to additional heterocycles, eg, 6-nitroanthroxanic acid.
- Unsaturated aldehydes, ketones and nitrile are epoxidized in one step in high yield via nucleophilic attack by hypochlorite ion.
- Hypochlorite readily chlorinates phenols to mono-, di, and tri-substituted compounds.
- Production of carboxymethylcellulose (CMC).
- Production of chlorinated trisodium phosphate, a bleaching agent.

- The production of hydrazine by the “Bayer Process”.

This latter process shall be presented as an example for the use of sodium hypochlorite in chemical synthesis in Germany. In this process hydrazine is produced by reaction of ammonia and sodium hypochlorite in the presence of acetone. NaClO oxidizes ammonia via monochloramine finally to hydrazine. Thereby it is completely reduced to sodium chloride (NaCl).



Chloramine appears as an intermediate product which reacts with ammonia under formation of hydrazine:



Because of the alkalinity of the reaction mixture all monochloramine is transformed completely into hydrazine, so that no monochloramine will remain in the final product (Holleman and Wiberg, 1976).

In 1994, the total production of sodium hypochlorite in Western Europe was estimated to be 287.67 thousand metric tons as chlorine equivalent (Euro Chlor data, 1994 as in Tables 2.2, 2.4). 26% of the total consumption was estimated to be used as a chemical intermediate (75.96 kt/y chlorine equivalent). In this application there are significant differences between the individual European countries as shown in Table 2.2. Whereas the use of sodium hypochlorite for the production of chemicals is significantly high in the northern and western parts of Europe, its use is very low in Southern Europe, where sodium hypochlorite is mainly used for household applications.

Sodium hypochlorite reacts with organic intermediates in controlled closed systems. A solution of sodium hypochlorite is filled into the reaction vessels through closed systems. Emissions to the environment will not occur as NaClO is reduced completely to sodium chloride during the process. Because of the alkalinity of the reaction mixture the formation of chlorine is excluded. Off-gas from the reactor is usually treated in a thermal exhaust air decontaminator before release into the atmosphere. The waste water is usually treated because of the organic compounds and at the same time any left available chlorine is destroyed.

Halogenated organic by-products

Formation of halogenated organic by-products will be entirely dependent on the reaction substrate and risks should be assessed in risk assessments of those products.

3.1.1.4. Swimming pool

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 (see section 2.4.1).

Polluted water is discharged outside the swimming pool, when the filters are cleaned. A certain quantity of water is also consumed for maintaining the humidity of the atmosphere of the swimming pool. The total consumption of water varies substantially from one pool to another, according to the way the pool is managed. An average figure could be 50 l/swimmer (Legube, 1996). In many countries it is compulsory to completely empty the pool 2 times/year.

Outdoor swimming pools consume higher quantities of disinfectant because it is destroyed by sunlight and because the sweat which is dissolved in the water is greater per swimmer during the summer. The consumption of hypochlorite and chlorine in European swimming pools in 1994 amounted to 16.22 kt/y and 10.95 kt/y respectively (see Tables 2.2, 2.3).

The main regulations relate to the minimum content of FAC (free available chlorine) in the swimming pool, which is always around 0.4 mg/l, and the pH which has to be in a range of 6.5 to 8.5. Some countries give a maximum of FAC (1.4 mg/l in France). The only potential contact with soil is for open swimming pools where a small quantity of water could overflow onto the sides of the pool.

Halogenated organic by-products

The principal halogenated by-products formed when swimming pool water is chlorinated are trihalomethanes (THMs, predominantly chloroform), haloacetic acids (mainly dichlor- and trichloroacetic acid, chloral hydrate (CCl₃CH(OH)₂) and dichloroacetonitrile (WHO 2002).

After formation, the THMs tend to evaporate, and dichloroacetonitrile and chloral hydrate undergo hydrolysis to DCA and chloroform or TCA respectively, such that the dominant compounds in pool effluents are DCA and TCA. The amounts of chlorinated by-products discharged (measured as AOX) have been shown to be typically of the order of 0.5% of the available chlorine applied (Legube, 1996).

Swimming pool pH is controlled between 6.5 and 8.5 as noted above. Formation of dioxins is thus not expected.

3.1.1.5. Sewage treatment

Hypochlorite or chlorine can be used in two different ways to treat sewage waters. Treatment occurs either before (prechlorination) or after (postchlorination) the waste water treatment plant.

Prechlorination

Hypochlorite is sometimes used for chlorinating sewage immediately before waste water treatment. This treatment serves to prevent sludge from bulking. When unwanted filamentous organisms or protozoans become abundant, activated sludge starts bulking (i.e. it does not settle). This leads to reduced performance of the plant and produces turbid effluent. Addition of hypochlorite to the sewage eliminates to a certain extent the filamentous organisms which are primarily responsible for bulk formation and thus provides better sludge settling characteristics. It also reduces the number of protozoans, which are predators of the effective sewage treatment bacteria and thus if present in excess may reduce the removal capacity of the treatment plant. The use of hypochlorite to eliminate filamentous organisms or protozoans is not very common, is not a continuous process and is only done on a need basis. Hypochlorite will be eliminated during the treatment process and will normally not enter the effluent or the receiving surface water.

Postchlorination

In some countries located near the sea, effluents of certain waste water treatment plants are chlorinated before release into the marine environment (Abarnou *et al*, 1990). The aim is to protect the shellfish farms and recreational zones from bacterial contamination by lowering the total coliforms below 1000CFU/100 ml. It may also serve to reduce the amount of organic matter in the effluent and can be used to reduce malodour.

European consumption of hypochlorite and chlorine for sewage treatment are respectively 15.18 and 9.55 kt/y (data from 1994 as in Tables 2.2 and 2.3).

Postchlorination processes used for disinfection of wastewater require a chlorine dose of 5 - 40 mg Cl₂/l. Both hypochlorite and chlorine are used. Usually a contact time between 30 and 60 minutes is allowed. Chlorine dosages are designed to match the composition of the waste water in order to minimise the chlorine discharges in the environment. Free available chlorine (FAC) will undergo a rapid reaction with reaction partners (carbon, reduced metals amines, etc.) and transform all hypochlorite (FAC) to combined available chlorine (CAC). This CAC will not act as effective disinfection product. In general no hypochlorite can be measured after the treatment. The CAC consists mainly of chloramines depending on the pH and on the ratio of hypochlorite to ammonium. However in conditions realistic for waste water (pH 6.6 to 8) and an excess of ammonia, only monochloramine is formed (Abarnou and Miossec, 1992). About 50% of the total combined chlorine is composed of organic chloramines.

Halogenated organic by-products

Given the range of substrates available, the range of chlorinated by-products that may be formed is potentially wide, and the presence of many different individual compounds in chlorinated sewage effluents has been demonstrated. There have been relatively few attempts to identify and quantify these in relation to typical operating conditions, however. Overall incorporation rates of applied available chlorine into chlorinated by-products, measured as AOX or DOX (dissolved organic halogen) are of the order of 0.5 –

2% depending for example on contact time and Cl:DOC ratio (Davis *et al* 1993, Rebhun *et al.* 1997).

Trihalomethanes, particularly chloroform, and haloacetic acids are formed, and it seems likely that most of the classes of by-products produced during drinking water chlorination (see 3.1.1.7) are also found in sewage. At low Cl:DOC ratios the presence of ammonia in the effluent appears to widen the range of compounds formed, but reduces the overall amounts formed including the haloforms and halo acetic acids for example (Rebhun *et al.* 1997).

Small quantities of chlorinated phenols have been seen to be formed in sewage chlorination experiments, of the order of 0.01% of the available chlorine dose. The phenols formed were predominantly 2-chloro- and 2,4-dichlorophenols with some formation of 2,4,6-trichlorophenol only at high (100mg/l) applied doses (Davis *et al* 1993). These studies showed no increase in pentachlorophenol levels following chlorination, and possibly a there was a decrease at lower doses (20 and 40 mg/l av.Cl₂).

Dioxins appear in nearly all sewage sludge samples, whether chlorinated or not, and the levels and congener profiles vary widely. As chlorination takes place at neutral to slightly alkaline pH, no dioxin formation is to be expected. Sources of the dioxin in sludge will vary between locations with specific industrial operations making a contribution in industrial areas. Although the possible sources of these dioxins have been extensively researched, and household wastewater (conveying dioxins originating in contaminated textiles) has been identified as an important source for sewage works serving residential areas, there are no reports suggesting sewage chlorination makes a contribution.

3.1.1.6. Textiles

Hypochlorite for textile finishing has been very widely used during the last two centuries. EURATEX states that today the only use of hypochlorite in textile processing in Europe is for the preshrinking of wool. Hypochlorite has been superceded by other substances in former uses such as stonewashing jeans, whitening of cotton and decoloration of dyed textiles.

Textile finishing as a whole is a very complex process, which needs a wide range of chemical products. Textile finishers try to reject a minimum of total waste water per kilo of treated textile; from 1000 l/kg in 1950, discharged effluent is now in a range of 5-50 l/kg.

Available data show that 12.05 kt of Cl₂ equivalent have been used in Europe in 1994 (300 t as chlorine gas and 11.75 kt as bleach) (see Tables 2.2, 2.3).

The treatment of wool with hypochlorite is generally performed in order to pre-shrink the fibres, avoiding further shrinking after production. Wool chlorination is normally performed in an acid environment, in which gaseous chlorine formation is unavoidable. This requires a high degree of enclosure of the plants, the presence of abatement system of gaseous emission, and a neutralisation stage. The sodium or

calcium salts of the dichloro-isocyanuric acids are generally used for wool chlorination; these salts are available in solid phase, and allow a slow release of NaClO in water, thus improving the control of operational conditions.

EURATEX have described the process, known as the Chlorine Hercoset process, as follows. The continuous Chlorine Hercoset process for wool top features five sequential chemical operations, namely chlorination under acidic conditions, antichlor treatment to remove residual/unreacted chlorine, neutralisation, rinsing, Hercoset application, softener application and drying.

Chlorination is carried out using cold water (10-15 deg C) and a wetting agent (2.5 g/l) and features either chlorine gas dissolved in water or a mixture of sulphuric acid mixed with sodium hypochlorite, both of which generate hypochlorous acid and a pH of around 1.5 -2.0. The mechanics of the chlorination stage can vary depending on the manufacturer, but regardless of this the objective is simply to apply approximately 2% chlorine on weight of wool and this is calculated on the basis of the chlorine concentration of the solution feed into the first bowl and the amount of wool passing through the line. The rate of reaction of chlorine under these conditions is very rapid and the reaction of chlorine with the wool is virtually quantitative, but any residual, unreacted chlorine is effectively neutralised in the antichlor bowl which contains sodium sulphite (5g/l) and is adjusted to a pH of 9.0 and a temperature of 40 degrees C.

The role of the chlorination stage is to prepare the wool for the subsequent application of the Hercoset resin (2% solids on weight of wool), which is applied immediately after the rinsing stage, and the bowl operates at a pH of 7.5 and a temperature of 35 degrees C. The reaction of chlorine with the wool achieves two objectives, namely a partial degradation of the surface scale structure to produce negatively charged proteins at the surface of the fibre and the generation of a hydrophilic surface as a result of the removal of a chemically bound fatty acid. The Hercoset polymer, which is cationically charged, has no affinity for untreated wool, but following chlorination it readily reacts with the wool, and imparts a uniquely high degree of shrink-resistance due to its ability to swell when wet and mask the remaining scale structure.

An estimate of waste flow from wool bleaching of 8 – 25 m³t⁻¹ is reported in the European Commission; Technical Guidance Document.

As no detailed information is available, the estimate provided by TGD of 1.5 t day⁻¹ for wool for processed goods per day are applied for the emission calculation. PEC for NaClO in the bleaching effluent can be assumed to be negligible given dechlorination with sulphite is part of the process

Halogenated organic by-products

Halogenated by-products arising from the pre-shrinking of wool can be estimated from studies reported by Augustin et al (1991). They observed AOX in the combined effluent of shrinkproofing lines at levels up to 39mg/l, representing an AOX load of 350 g/tonne wool processed. They also established that 23% of this AOX arose after the hypochlorite stage from the application of a epichlorhydrin-based processing

resin which itself contributes some AOX including manufacturing by-products. This leaves 77%, i.e. 30 mg/l or 270 g/tonne wool as arising from hypochlorite use.

Wool is a natural protein structure containing amino acids and polyamide linkages. The amino nitrogens would be expected to provide a favoured reaction site for hypochlorite resulting in N-chloro derivatives i.e. non-organochlorines containing C-Cl bonds. During acid chlorination of wool in continuous top treatment the reaction with chlorine occurs principally in the exocuticular region of the fibre and results in the following chemical modifications

- Formation of partial oxidation states of cystine
- Oxidation of cystine to cysteic acid
- Hydrolysis of peptide bonds at tyrosine residues, and
- Formation of N-chloro derivatives (N-chloroamines, N-chloroamides)

As a consequence of these reactions soluble proteinaceous material is formed in the exocuticle being removed from the fibre in the antichlorination stage which is essential for stopping the chlorination reaction. The release of chlorinated proteins in the sulphite antichlorination stage is mainly responsible for the AOX load of the complete process effluent.

Augustin et al report that 30% of the AOX in the final effluent (i.e.39% of the hypochlorite derived AOX) of wool shrinkproofing lines consisted of mono- and dichloro-tyrosine. Volatiles accounted for less than 5% of AOX in the total effluent.

Because the former hypochlorite bleaching of cellulose took place at slightly alkaline pH, no dioxin formation would be expected. Studies by Horstmann et al (1993) confirm this: they investigated polychlorinated dioxin and furan levels on cotton cloth through 16 different stages of textile processing and finishing. The dioxin levels on the samples after hypochlorite treatment, both with and without peroxide, were marginally lower than prior to those treatment steps.

As wool bleaching takes place at acid pH, the possibility of dioxin formation arises, though wool is protein rather than cellulose based, and the complex lignin structures rich in phenolic dioxin precursors that are present in wood-pulp are not present in wool. Some amino acids in wool proteins such as tyrosine do have aromatic rings. Information supplied by EURATEX indicates that analysis of a combined sample of the chlorination and antichlorination baths from a wool shrinkproofing line, taken as a worst case example at the end of the 12 hour operating period before replenishment, detected a total amount of 1.1 ng/l TEQ dioxins in the 2 x 400 l baths, Following dilution during rinsing etc. this was calculated to represent a load of 28.5 pg/l TEQ in the chlorination line effluent. Note that it is not established whether the dioxins were formed during chlorination or whether they arose from some other source.

3.1.1.7. Drinking water

Sodium hypochlorite is widely used for water supplies - particularly in smaller systems - as the source of chlorine species for primary disinfection and in aqueducts to maintain the efficacy of disinfection in the entire network. Chlorine gas may be used similarly, generally in larger installations.

The use of NaClO for disinfection is generally considered easy, safe and cheap, although its efficacy is reduced with time. Formation of different by-products by reaction between chlorine species and organic matter in the treatment of surface water also occurs to a small extent.

Sodium hypochlorite is used as liquid solution, with a maximum active chlorine level of 15% and 10% a more general level. The solution is pumped directly into the treatment plant or injected into the water pipeline.

The use of NaClO in drinking water is regulated by rules which cover three main items: the microbiological water quality or the maintenance of disinfection (no pathogens), the quantity of remaining chlorine in tap water and the quality of the water in terms of by-product content.

Different treatment pathways may occur in the potabilization process, depending on the quality of the raw-water. Generally when groundwater, with its low content of suspended solids and low DOC (dissolved organic carbon) is used, NaClO is added as a unique step before the filtration. Where the water is more turbid, NaClO is added at two different points: firstly in a pre-disinfection step followed by flocculation, sedimentation and filtration and secondly in a post-disinfection step before entering water in the network pipes for the distribution to end-users. In the case of surface waters, the pathway to be followed becomes longer because the quality of the water is poorer than in the previous case.

It is advisable to insert an additional disinfectant dosage point after the secondary sedimentation before the final filtration step. In the most complicated situation three disinfectant dosage points along the treatment pathways may be necessary.

The consumption of sodium hypochlorite and chlorine for water disinfection were 9.53 and 32.29 kt/y of Cl₂ equivalent respectively in EU in 1994 (See Tables 2.2 and 2.3).

The legally permissible quantity of available chlorine in the water is set at values between 0.1-0.5 mg/l in many European countries. These values are in agreement with the concentration of 5 mg/l of available chlorine indicated by the WHO as a guideline value. The value of 0.5 mg/l is taken as a worst case scenario as it is only applied when bad conditions (temperature and contamination e.g.) are occurring. Actual figures are not available for Europe but are estimated to be below 0.1 mg/l.

Halogenated organic by-products

The principal types of chlorinated by-products formed during chlorination of drinking water are the haloforms or trihalomethanes (THMs), principally chloroform, and haloacetic acids. Though the levels vary according to parameters such as raw water quality, pH, temperature, dose, contact time, treatment methods and sequence, and

chlorination agent, THMs and HAAs will typically be an order of magnitude more abundant each of the other main types, which include haloacetonitriles, haloaldehydes, haloketones and normally very small quantities of chlorinated phenols. These by-products are formed by reaction with humic, and fulvic acid derivatives and other natural organic matter in the raw water. Various attempts have been made to derive predictive equations for OBP formation based on the above parameters and DOC or UV absorbance at 254nm as measures of organic matter, but their practical applicability is very limited. As a broad guide, something of the order of 1% to 5% of the dosed available chlorine will be converted to AOX (Premazzi *et al.*, 1997b), rather higher than in other applications of hypochlorite because of the low doses used and long contact times.

Since the discovery of the presence of THMs by Rook in 1974, controlling levels of chlorinated by-products has become a preoccupation for water companies and is increasingly tightly regulated to protect human health, though the focus varies in different geographical regions. Methods of reducing OBP formation are now well developed, and include improving raw water quality before chlorination, use of chloramination, and use of alternative disinfectants such as ozone, chlorine dioxide or UV. In most countries, the nature of the water distribution system demands a 'chlorine residual' is maintained to the consumer's tap, and this is often required by law.

Because chlorination takes place at pH close to neutral, dioxin formation is not expected, nor is there good evidence to suggest that chlorination makes a significant contribution to the normally low dioxin levels in drinking water. In drinking water plants, raw water pH will normally be close to neutral. For example, in a study of by-product formation in Finnish drinking water where much surface water is regarded as 'acid', raw water pH across 35 plants ranged from 6 to 7.5 (Nissinen *et al.*, 2002). Adjustment of pH is a standard part of water treatment practice: in the distribution system, acidity can lead to problems such as corrosion and lead solubilisation, so water is rarely distributed at acid pH. For example, the pH of distributed water in the above study ranged from 7.6 to 9.1 (excepting one works at 6.6).

3.1.1.8. Pulp and Paper

In the past sodium hypochlorite as well as chlorine have been used in large amounts in the pulp and paper industry in Europe as a bleaching agent. Currently this is no longer the case. The use of these bleaching agents gave rise to serious environmental concerns due to its by-products and has triggered many investigations and regulations. The conditions of P&P bleaching with this former technology, i.e. the wood pulp as a broad range of organic precursors rich in phenolic molecules, long contact times with the oxidising agent and low pH conditions, were favouring the formation of chlorinated aromatic by-products and even dioxins were formed.

Although much could be done to reduce or eliminate problematic emissions by effluent treatment or partial oxidant substitution, the environmental concern has strongly pushed industry to find alternative processes. Nowadays the P&P production in Europe is using either the elemental chlorine free (ECF) process, using ClO₂ as oxidant or totally chlorine free (TCF) using hydrogen peroxide as oxidant (CEPI, 2003). Further information on these alternative technologies can be found elsewhere and the main parameters are outlined for reference in an Annex to of this report.

Again according to CEPI the current use of hypochlorite in the P&P industry is now limited to two specific applications. 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 always occurs during a machine shutdown and involves the partial filling of the paper machine system with clean water to which is added a quantity of sodium hypochlorite. The water is circulated vigorously around the system for up to one hour, and is then discharged into the normal effluent treatment processes, prior to subsequent discharge. The concentration of hypochlorite in the system is low, and quantities are determined so that there is near zero residual free hypochlorite at the end of the cleaning process. Any high level of residual hypochlorite would also encourage corrosion of the machine system. Once discharged to the effluent plant any residual hypochlorite is quickly neutralised by exposure to the paper mill's effluent treatment processes.

Hypochlorite is also traditionally used to break down broke (rejected tissue which is recirculated within the mill's production processes) or other waste tissue to which has been added wet strength resin to improve its effectiveness as a facial tissue or towel. Hypochlorite is the only known chemical which effectively breaks down certain types of these resins, notably epichlorhydrin-modified polyamide/amine resins. Broke and waste treatment is at the beginning of the tissue making process, and involves slushing tissue in a batch pulper where it will be pulped at around 4% consistency in water. A quantity of hypochlorite calculated in relation to the broke content is added to the water to achieve wet strength breakdown as necessary: typical dosage would give an initial solution of below 100 ppm hypochlorite. (It also bleaches any unwanted colours in the waste tissue). Once the pulping process is complete the fibre slurry is pumped into the stock preparation system of the tissue machine before going forward to the machine. The machine will often be making coloured product, and the residual hypochlorite levels in the broke or waste must be sufficiently low to ensure that it does not affect the colour of the product being made in any way. Any high level of residual hypochlorite would also encourage corrosion of the machine system. There are therefore cogent reasons for ensuring that no significant residual hypochlorite enters the tissue machine system, and therefore the likelihood of any residual hypochlorite reaching the environment via the machine system and effluent treatment systems is very remote.

Due to the developments illustrated above, consumption of hypochlorite and chlorine in the pulp and paper industry has been reduced drastically in recent years. Consumption for the year 1994 was 17.43 and 8.53 kt/y for chlorine and hypochlorite respectively (Tables 2.2 and 2.3).but it is expected that the current use is still lower.

Hypochlorite consumption in the pulp bleaching process.

Pulp production in Europe in 1997 was $36.1 \cdot 10^6$ t (CEPI, 1998).

The overall hypochlorite consumption reported by Euro Chlor in 1994 is 8.53 kt/year as available chlorine. On the basis of the current limited application of hypochlorite as detailed above it is not expected that any reactive chlorine will be discharged into the environment.

Halogenated organic by-products

Details on potential by-products arising from current P&P processes due to the application of hypochlorite as described above are not detailed by CEPI, but it may be expected that the formation of by-products in the machine cleaning use will closely parallel those formed in Industrial and Institutional Cleaning and are covered by that scenario as well as under the worst-case approach followed in the WET testing.

The wet-strength resins that hypochlorite is currently employed to remove are primarily epichlorhydrin-modified polyamides. The process takes place at alkaline pH, not just for maximum effectiveness but because this also minimises degradation of the cellulose fibre which would prejudice its usability. The hypochlorite may be expected to break down the resin by disrupting the polyamide linkages, but it also appears to act by oxidising and chlorinating azetidinium ring structures via a classic haloform reaction to form first alpha-haloketones and then chloroform (Chung 2003). There are thus two facile processes to consume the hypochlorite, and chloroform and N-chloroamino- compounds could be expected to be the dominant by-products.

Lignin levels in broke, being fully processed and bleached pulp, would be expected to be low, so the level of phenolic substrates present which could potentially be chlorinated should also be low. Since pH is always alkaline no formation of dioxins would be expected, and any chlorination of phenols would give mono- or dichlorinated compounds rather than higher chlorinated analogues (Hise et al 1997). Hypochlorite can also react with cellulose to form chloroform, but this reaction is much slower than its reaction with lignin (Hise 1995) a factor which was critical in allowing its long former use in pulp bleaching without degrading the fibre. There is no mention in the literature of formation of haloacetic acids in this system but this will probably be minor compared to chloroform. It must also be borne in mind that the wet-strength resins themselves both contain, and are a source of chlorinated organics, including chloroform, which is released when they are repulped. This, of course, is a feature of the resin, not a specific consequence of the use of hypochlorite.

3.1.1.9. Cooling Water

Hypochlorite is applied as biocide in cooling water systems to prevent biofouling. Other compounds are also used (e.g. ClO₂, quaternary ammonium compounds), but hypochlorite is very effective and of relatively low cost and therefore a major biocide for this application.

Due to the potential of by-product formation many studies have been carried out to evaluate the impact of various biocides, including hypochlorite. A useful overview of biofouling prevention methods in cooling water applications is given by Jenner et al. (1998). In France, UK and The Netherlands extensive studies have been done by

power companies (Jenner et al., 1997, Jenner et al., 1998) and water management authorities (e.g. Baltus and Berbee, 1996 and Berbee, 1997). Renewed attention has now been generated by the need to control the *Legionella* disease.

Recently an IPPC reference document on the application of best available techniques (BAT) to industrial cooling systems was issued (European Commission, 2001). This extensive BAT states that it has ‘met a high level of support from the Technical Working Group, despite the complexity of the issue. An important conclusion with respect to this risk assessment is that ‘industrial cooling processes are very site- and process-specific’. So site-specific conditions determine the actual practices applied. Both chlorine and hypochlorite are included as recommended techniques in the BAT document.

Based on the extensive information available, this section will describe the most important types of cooling systems and their treatment requirements, the fate of hypochlorite in such systems, and also the measured concentrations of by-products for the sea- and freshwater situation will be summarized.

Cooling water systems are used in electrical power generation, chemical industry, refineries, base metal industry and the food industry. These industries are the largest users of cooling waters in the Netherlands, according to a recently published report (Van Donk and Jenner, 1996). Recent developments have been focusing on the economy of dosing, which combines the advantages of cost-effective operation and a minimal impact on the environment. The report summarizes the state-of-the-art practices of hypochlorite application in cooling water systems (CWS), which is used as a basis to develop a generic scenario for risk assessment purposes. The basic principles of CWS are similar, but different types exist. These can be divided into *once-through* and *recirculating* systems. In once-through systems hypochlorite is the major biocide since it is essential to use a fast reacting chemical. More than 90% of recirculating systems also use hypochlorite.

Power plants represent well studied examples of the application of hypochlorite in CWS, concerning both the current dosing practices and the formation of by-products (Van Donck and Jenner, 1996, Jenner *et al.*, 1997). By-products of the chlorination of cooling water (seawater) are summarized afterwards.

The consumption of hypochlorite produced by the chemical industry for cooling water applications is estimated at 5.58 kt/y as Cl₂ equivalents. The use of gaseous chlorine is rather similar with 4.80 kt/y for the year 1994 (tables 2.2 and 2.3). Furthermore chlorine is sometimes produced electrochemically on site for cooling water applications in electrical power plants.

Three major dosing systems for hypochlorite into cooling water systems can be distinguished, which will be described shortly to define the worst-case scenario to be used in risk assessment. The dosing regimes described are a “clean once-through CWS”, a “fouled once-through CWS” and an “open recirculating CWS”.

In once-through types of CWS such as in power plants mussels are the major fouling organisms. These are preferably treated preventively, because this is the most cost-effective practice. Mussel larvae can be treated with much lower doses than adult

organisms, since adults can close their valves and survive long periods of high dosage living anaerobically. This means that the 'clean' scenario should be considered as the regularly applied one, while the scenario for 'fouled CWS' is exceptional.

Clean once-through CWS

A clean once-through type of CWS will react as a tube reactor, with a complex of reactions taking place between hypochlorite and both inorganic and organic matter. A minimal dosage is required to satisfy this 'chlorine demand', i.e. the fast oxidation of the inorganic and organic oxidizable fractions. In this process secondary oxidizing compounds such as chloramines are also formed which are also included in TRO (total residual oxidant). Dosing should be high enough to have sufficient FO (free oxidant) in the cooling system. Dosing can also be based on TRO. A typical dosage, for an estuarine or coastal scenario, ranges from 1.5-3 mg/l expressed as Cl₂ at the intake, which will result in a concentration of 0.25-0.35 mg/l TRO at the heat exchanger (i.e. after approximately 4-8 minutes of reaction time).

During the spat fall (release of the larvae) period, for example which takes place in The Netherlands for about 4-6 weeks in June/July), hypochlorite will be dosed continuously. After the spat fall period until surface water temperatures have fallen below 12 °C, dosing will be discontinuously 4 hours on (as a maximum) and 4 hours off. For exceptional conditions, higher hypochlorite dosing may be necessary, up to 0.5 mg/l TRO.

In freshwater clean once-through CWS, macrofouling can be controlled by dosing hypochlorite at a level of at least 0.35 mg/l continuously during 2-3 weeks in autumn, when temperatures are still higher than 12 °C. The rest of the year no dosing is required for macrofouling control. For microfouling in clean freshwater once-through systems a minimum level of 0.4 mg/l TRO for 30 min/day is required.

Fouled once-through CWS

For microfouling control the procedure is similar to the clean situation, because microfouling can always be controlled. For macrofouling chlorination is usually applied preventively, which means that it will be exceptional.

For successful control of macrofouling high dosages are required. Adult bivalves will close their valves and switch to a slow anaerobic metabolism. Two week periods of 5 mg/l can be survived, as well as continuous levels of 0.5 mg/l for two months.

Open recirculating CWS

In recirculating CWS usually shock-dosing is applied. The application regime may vary from once or twice a year at levels > 10 mg/l, as has been reported for France, to dosing for 1 hour/day, but more intervals per day or continuous dosing are also employed. The high dosing described for France is applied with the cooling system closed. The effluent is not released until TRO drops below 0.1 mg/l to prevent by-product formation and release. This treatment aims at reducing pathogens. A shock-dose of 1-2 mg/l TRO can be as effective as continuous dosing of 0.5 mg/l. The first option is much more cost-effective and preferred in practice.

Relevant risk assessment scenario

The practices described above represent the currently applied dosing strategies for biofouling control in the UK, France and The Netherlands. For PEC derivation in risk assessment the concentrations at the outlet should be considered. Since these are not well known, the concentrations prevailing at the condensers can be taken as a worst-case approach. When regular use is considered, the worst-case situation is continuous dosing at 1-3 mg/l TRO at the inlet, resulting in 0.35 mg/l TRO at the condensers for periods of several weeks during the spat fall period (June/July), but occasionally 0.5 mg/l TRO at the condensers may be necessary. For the UK either continuous dosing at 0.2 mg/l TRO at the condensers or discontinuous treatment with 0.5 mg/l TRO at the inlet of 10 min/h or 1h/d or the equivalent is applied. The treatment season is when the seawater is above 10°C (April-November).

The 0.5 mg/l TRO at the condensers is the highest concentration in regular applications, which represents the realistic (regular) worst-case situation. Peak dosing only occurs exceptionally, since the good operation of power plants is best safeguarded by preventive treatment of fouling. This can be achieved at relatively low dosing as described above. Exceptionally, when fouled systems have to be treated, higher doses for shorter periods can be applied. In that case, doses of 2 mg/l at the condensers may be necessary for relatively short periods of several hours per day. A worst-case shock injection dosing regime for controlling slime has been described, requiring 2-10 mg/l at the inlet for 10-20 minutes every 4-8 hours (Whitehouse *et al.*, 1985), which can be assumed to generate up to a maximum of 8 mg/l TRO at the condensers.

The information above is used to determine PEC_{local} for TRO for the aqueous environment. Results for this, and separate estimates for by-products are given in section 3.1.2.9.

Halogenated organic by-products

The halogenated organic by-products formed during cooling water chlorination will broadly parallel those forming in drinking water chlorination. The principal families detected are thus the trihalomethanes, which are normally the most prevalent, followed by haloacetic acids and haloacetonitriles. Small quantities of halophenols are sometimes detected.

Some of the largest cooling water chlorination installations are at coastal power stations where the water intake is seawater. While the broad families of by-products formed are similar, in seawater, as in freshwaters of high bromide content, the applied active chlorine is rapidly converted to bromine species so brominated by-products predominate.

Seawater used in the largest cooling systems has a natural pH between 8.0 and 8.2. The pH of freshwaters used for cooling will be kept close to neutral or alkaline to avoid corrosion problems or chlorine formation. In each case, dioxin formation is not expected.

3.1.1.10. Institutional and food industry

The following are a list of those industries which exploit the cleansing and disinfecting properties of sodium hypochlorite:

Food and catering industry

- Dairy industry
- Meat industry
- Catering industry
- Poultry industry
- Food and beverage industries

Institutional

- Hospitals
- Care homes
- Industry/offices
- Water treatment (waste/air conditioning)
- Industrial laundries

Products containing sodium hypochlorite are frequently commercialized as concentrated solutions (up to 12.5%) and can be used neat, though they are almost always used diluted. They can be obtained as single products or as part of a “system approach” to hygienic cleaning. In this case the user will purchase the product, the equipment and the recommended procedures for carrying out a particular task. Strong sodium hypochlorite solution BP is defined as an aqueous solution containing not less than 8% w/w of available chlorine. Sodium hypochlorite solutions of differing concentrations are commonly used for the rapid disinfection of hard surfaces, food and dairy equipment, and also of babies feeding bottles and for the disinfection of drinking water (Martindale, 1982).

These products are generally used by qualified and trained staff who are made aware of the regulations and special conditions to be used when handling the products. The products are commercialized by specialist companies who will also provide the necessary procedures and training.

Institutional usage of sodium hypochlorite will be similar to that occurring in the Household Scenario.

In the Food industry where it is necessary to clean food processing equipment, for example, a solution of hypochlorite is circulated around the equipment (CIP = Cleaning in place, see Figure 4.1 in chapter 4.1.1.3.6.1) and no human exposure occurs. However, in many instances when it is necessary to clean large surfaces such as floors, walls or other vertical surfaces, the product is applied (from a spray) in the form of a foam or gel. In this instance the operators are supplied with protective clothing such as boots, overalls and face visor including a nasal and mouth mask.

The European consumption of sodium hypochlorite through Food, Catering and Institutional usage is not a precise figure but is believed to be of the order of 250-

450,000 tonnes (Personal Communication to the author from Diversey-Lever) expressed as a 5% solution of sodium hypochlorite.

Many large industries will have their own waste water treatment plant. Any subsequent discharge to the municipal sewers will have to conform to local guidelines and effluent permits will frequently be required. In many cases the industries will possess the complete waste water treatment procedures and in this instance final discharge will be directly to surface waters. Local authorities carefully monitor the situation.

Should any hypochlorite ever reach the sewage system it will rapidly decompose, as is demonstrated for release due to household usage in Appendix 2. The factors covering the fate of sodium hypochlorite in the environment from Institutional usage and small industries can also be considered to be similar to those arising from the Household Scenario.

Halogenated organic by-products

The range of chlorinated by-products formed in industrial and institutional cleaning operations will be similar to those formed in household use since the soils with which the hypochlorite reacts will be similar mixtures of proteins, carbohydrates, fats and other organic matter. Particularly in institutional cleaning, the concentrations and methods of use closely parallel household use.

Since these uses are also invariably at alkaline pH, especially to avoid chlorine formation, no dioxin formation is to be expected.

3.1.2. Aquatic compartment (incl. sediment)

Releases of hypochlorite to the aquatic compartment are generally low (below the detection limit of current analytical methodology) due to the rapid decay of hypochlorite as demonstrated in Appendix 2. However, direct discharges may occur under certain local circumstances for some sewage treatment uses. Predicted environmental concentrations (PEC) for the aquatic compartment for various uses are estimated in Cl₂ equivalent (measured as TRO or TRC).

Halogenated by-products

Estimates of by-product releases, including PEC calculations for haloforms and haloacetic acids, are provided for most scenarios below. For scenarios where effluents pass through sewage treatment plants, standard removal rates for THMs and haloacetic acids have been derived as follows. Any other removal rates used are explained in the specific scenario:

i. THMs

Chloroform is extensively removed in sewage treatment, probably primarily by volatilisation as well as by degradation. In some scenarios, removal by volatilisation in sewers en route to the treatment plant will also be extensive.

Removal rates in excess of 90% have been reported (Chloroform RAR, 2007). In many scenarios small amounts of the other THMs are also present and except in high bromide environments they normally decrease in the order $\text{CHCl}_3 > \text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$. All trihalomethanes are volatile, the volatility decreasing in the same order: for example estimated half-lives in a model river are CHCl_3 1.3 hrs; CHBrCl_2 2.0 hrs; CHBr_2Cl 2.6 hrs and CHBr_3 7.3 hrs (HSDB) Consequently, a removal rate of 90% has been used for THMs.

ii. Haloacetic Acids

For trichloroacetic acid, the OECD SIDS risk assessment uses a degradation rates in STPs of 66%, and that is adopted for these scenarios. Dichloroacetic acid is treated in the EU risk assessment for trichloroethylene as readily biodegradable [Trichlorethylene risk assessment R018_0109] so a removal rate of 87% as per the PGD is adopted here. For simplicity, the same removal rate is adopted for MCA, which is generally a minor by-product, even though MCA has been shown to be more than 99% removed in STPs as per the risk assessment for that substance. [MCA risk assessment]

Brominated acetic acids are generally more biodegradable than their chlorinated counterparts. Hashimoto et al (1998) incubated samples of chloro and bromoacetic acids in river water for 30 days at 20 deg C in the dark. Apart from TCA all had essentially disappeared at the end of the test, and levels for MCA and the 6 bromine containing acids were lower than for DCA where 6% remained. Tribromoacetic acid spontaneously decomposes in aqueous solution to form bromoform (Heller-Grossman 1993).

In the PEC calculations which follow, on the basis of the above it has been decided for simplicity to use a removal rate of 66% for TCA and 87% for all other haloacetic acids.

3.1.2.1. Production:

As explained in 3.1.1.1. initial plant discharges containing oxidising substances such as hypochlorite measured as TRC will include other oxidising substances. In most cases final discharges from production sites contain measurable chemical oxygen demand (COD) which would have consumed any residual oxidant present from the production process, such that there would be none released in the final effluent. Based on the results of a questionnaire on TRC releases from production sites (see Appendix 6) tentative $\text{PEC}_{\text{local}}$ values could be estimated for 44 sites. Of these, three-quarters would have no residual oxidant in the effluent because of the presence of COD. .. For the sites that reported levels of TRC in the effluent as well as dilution factor information for the receiving surface waters tentative initial $\text{PEC}_{\text{local}}$ values ranging from <0.000006 to 0.07 mg/l could be calculated.

Halogenated organic by-products

Because no organic materials are involved in the production process, chlorinated organic by-products do not arise.

3.1.2.2. Household

Irrespective of the household use of hypochlorite (i.e. cleaning/disinfection/laundry) the waste hypochlorite solution is likely to be discharged to sewer where the high levels of organic and nitrogenous material will consume virtually all the hypochlorite. Taking a worst-case of neat formulated bleach product going to sewer (8 mg/l available chlorine assumed), and a residence time of 1 hour, then the concentration of hypochlorite at the end of the sewer will be below 10^{-32} $\mu\text{g/l}$ (Appendix 2). Hence effectively no hypochlorite will reach sewage treatment plants nor the aquatic environment. Any monochloramine formed will continue to act as an oxidant, and undergo extensive degradation during sewage treatment, such that the calculated level in the river will be below 5×10^{-10} $\mu\text{g/l}$ (Appendix 2).

Halogenated organic by-products

A field monitoring approach, involving the active participation of the inhabitants of a small community in the Italian town of Parma, was used to assess the effect of the use of household hypochlorite bleach on the formation of organohalogen (AOX) in domestic sewage under realistic usage conditions. The study showed a very good correspondence between *predicted* and *measured* AOX concentration and hypochlorite-to-AOX conversion rate in domestic sewage.

Schematically, the study consisted of three phases, each one lasting three weeks: 1. an "*undisturbed period*," to record baseline values on AOX concentration in domestic sewage (referred to in the study as phase IIA); 2. a "*no bleach period*" during which the site inhabitants were requested to stop any use of hypochlorite bleach (phase IIB); and 3. a "*controlled bleach usage period*," during which the inhabitants were provided with a bleach of known hypochlorite concentration to measure the degree of hypochlorite-to-AOX conversion (phase IIC). Before the conduction of the study, a "pilot phase" lasting one week was carried out to characterize the experimental site, and to identify and solve any relevant logistic/experimental issue.

The results of the study can be summarized as follows:

1. for all periods of the day, the average AOX value in Phase IIB (the "no-bleach period") is lower than for either of the two bleach use phases.
2. the average AOX values are the highest during the 8:00 - 16:00 day part, with the effect being less pronounced for the IIB period.
3. the variability of the AOX readings in Phase IIA and IIC is higher than in Phase IIB. This can probably be explained by the effect of bleach usage as an additional and variable AOX source.

The above observations suggest an effect of bleach usage on the average AOX levels, with the majority of the AOX being formed during the day. When taken together, these day part differences translate into statistically significant differences ($\alpha = 5\%$) between

Phase IIB and the two bleach use phases. The latter were not significantly different. In the no-bleach period (IIB) the mean AOX value is $106 \mu\text{g.l}^{-1}$, versus $143 \mu\text{g.l}^{-1}$ in the "undisturbed bleach use period" (IIA). Hence the difference in AOX level is about $37 \mu\text{g.l}^{-1}$. The fact that in phase IIC the AOX level ($158 \mu\text{g.l}^{-1}$) returned to a level comparable to that in phase IIA, can be seen as an internal control for the experiment.

The emission of AOX, expressed as a total daily AOX emission per inhabitant, was around 22 mg. Of this amount, 7.0 - 7.5 mg can be attributed to the use of domestic bleach. The contribution of bleach to the total AOX emission is therefore in the range of 30 - 35% at this particular site (Schowanek D et al., 1996).

The results of this field monitoring of actual household use fit well with laboratory and simulated use measurements which range broadly between 0.1 – 4% across the spectrum of different household uses and situations.

Two scenarios can be considered:

Scenario 1 (Realistic European Average)

In our local scenario we have hypothesized for 10,000 inhabitants (3 persons per family unit) a consumption of 1 liter of 4% (P) hypochlorite solution (mean concentration on the market is around 4) per month per each family unit. This leads to an overall local consumption (Qd) of 136.67 kg of hypochlorite solution per day ($111.11 \text{ l/d} \times \text{density of } 1.23 \text{ kg/l}$). (This equates to 4.99 kg /person/year which is close to a European average – range 0.2 – 11.8 kg/person/year expressed as 3 – 5 % product). Further, it was considered that a fraction (50%) of the used NaClO is not discharged (Fc). An NaClO-to-AOX conversion factor of 1.5 % (T) is used as obtained from direct field monitoring measurements (Schowanek et al, 1996). A removal of AOX (degradation and volatilization) of 60% in the sewers and sewage treatment system was assumed. As in the TGDs, the per capita wastewater flow was set to 200 L/day and the dilution factor (DF) is 10.

Using these assumptions, the local contribution of AOX emission ($E_{\text{localwater}}$) can be calculated as follows:

$$E_{\text{localwater}} = P * Qd * (1 - Fc) * T$$

$$E_{\text{localwater}} = 0.04 * 136.67 * (1 - 0.5) * 0.015 = 0.041 \text{ kg/d of AOX}$$

$$C_{\text{localinf}} = E_{\text{localwater}} / \text{waste water flow}$$

$$C_{\text{localinf}} = 0.041 \text{ kg/day} * 10^6 \text{ mg/kg} / (200 \text{ L/cap. day} * 10000 \text{ cap}) = 0.0205 \text{ mg/l}$$

$$C_{\text{localeff}} = C_{\text{localinf}} * F_{\text{stpwater}}$$

Considering a value of 0.4 for F_{stpwater} (i.e. 60% removal) the C_{localeff} value is 0.0082 mg/l

$$C_{\text{localwater}} = C_{\text{localeff}} / DF = 0.00082 \text{ mg/l considering a dilution factor of 10.}$$

This latter value of 0.00082 mg/l could be assumed to be equivalent to the **PEC_{local water}** considering negligible the **PEC_{regional water}** level.

This leads to an extra AOX PEC **local** of 0.8 µg/l.

Scenario 2 Worst case

This scenario is based on the Spanish consumption of 11.8 kg/person/year (expressed as 3 – 5 % product), which is the highest in Europe. Considering that all by-products are discharged to sewer ($F_c = 0$), a NaClO-to-AOX conversion factor of 1.5 % (T) from direct field monitoring measurements (Schowanek et al., 1996), and assuming 60% removal (degradation and volatilization) in the sewers and sewage treatment system, ($F_{stp\ water} = 0.4$) the local contribution of AOX emission ($E_{local\ water}$) can be calculated as follows:

$$Q_d \text{ (for 10,000 inhabitants)} = 11.8 \text{ kg/person/year} * 10,000 / 365 = 323.29 \text{ kg/d}$$

$$E_{local\ water} = P * Q_d * (1 - F_c) * T$$

$$E_{local\ water} = 0.04^5 * 323.29 * (1 - 0) * 0.015 = 0.194 \text{ kg/d of AOX}$$

$$C_{local\ inf} = E_{local\ water} / \text{waste water flow}$$

$$C_{local\ inf} = 0.194 \text{ kg/day} * 10^6 \text{ mg/kg} / (200 \text{ L/cap.day} * 10000 \text{ cap}) = 0.097 \text{ mg/l}$$

$$C_{local\ eff} = C_{local\ inf} * F_{stp\ water}$$

Considering a value of 0.4 for $F_{stp\ water}$ (i.e. 60% removal) the $C_{local\ eff}$ value is 0.0388 mg/l

$$C_{local\ water} = C_{local\ eff} / DF = 0.00388 \text{ mg/l considering a dilution factor of 10.}$$

This latter value of 0.00388 mg/l could be assumed to be equivalent to the **PEC_{local water}** considering negligible the **PEC_{regional water}** level.

This leads to an extra AOX PEC **local** of 3.9 µg/l.

An assessment of the risk posed by these chlorinated by-products collectively measured as AOX can be made under the following headings:

a) Identifiable reaction products

For emission calculation purposes, domestic cleaning and disinfection uses can be considered in two categories: laundry and other uses, which are mainly hard surface cleaning and toilet cleaning. Laundry use accounts for approx 15% of total hypochlorite usage in Europe (calculated ex Table 2.6). Smith (1994) found that an average of 2.6% of active chlorine was converted to OBP (as AOX) during use. Chloroform accounted on average for 10.3% of the AOX, TCA for 5.2% and DCA for 6.2% of the AOX. On the

⁵ 4% represents an average on the market.

basis of ratios seen in other scenarios other THMs would be likely to be around 10% of the chloroform level making total THMs 11.3% of AOX. Similarly, other HAAs would be likely to be around 10% of combined TCA and DCA levels i.e. 5.7% of AOX, making DCA plus other HAAs total 7.3% of AOX.

For the other uses, which account for 85% of hypo consumption, there are data on total chlorinated by-product formation (measured e.g. as AOX). However, there is little quantitative data on individual by-products and it is thus necessary to estimate the amounts of chloroform and TCA that will be formed from data on analogous reaction situations.

During use, the Cl:COD ratio will be relatively high, and Peters (1991) estimated that concentrations of trihalomethanes generated in the cleaning solution would be of the order of 15 – 75 µg/l for chloroform and 3 – 10 µg/l for bromodichloromethane. For the haloacetic acids he estimated concentrations of 15 - 75 µg/l TCA, 7 – 20 µg/l DCA and 3 – 5 µg/l DBA. He listed other by-products totalling around 5 - 30 µg/l. Studies of by-products formed in cleaning, drinking water and sewage disinfection with hypochlorite typically find that such identifiable small molecules (i.e. a total of 70 – 215 µg/l here) make up roughly between 25 – 50% of total AOX.(e.g. Smith 1994; Reckhow and Singer 1990). Assuming the same applies here, a total AOX concentration of 140 – 860 µg/l would be indicated. This is corroborated by the studies by Josa et al which measured average AOX concentrations in cleaning solutions ranging from 600 µg/l to 1300 µg/l. Trihalomethane, and TCA and other haloacetic acids, according to Peters' estimates could thus together theoretically account for between 2% -50% and 1 – 18% respectively of total AOX. As with many ranges of scientific variables, the average is most likely to lie in the middle of this range i.e. THMs 5 – 25%, TCA 5 – 20% and other HAAs 3 – 8% respectively of the AOX produced during use, especially as these values are linked in that a greater proportion of one component limits the proportion of the other. The geometric mean of the range of possibilities, i.e. THMs comprising 12%, TCA 10% and other HAAs 5% of the AOX will thus be used as an assumption.

When used cleaning solutions are released into sewers, Cl:COD ratios will be low and the conditions will in many ways resemble those encountered during disinfection of sewage (practised extensively in the USA). In studies by WRc for the UK National Rivers Authority (Davis et al 1993) on an operating sewage disinfection plant with chlorine residuals maintained around 55 – 58 mg/l, average chloroform levels rose from 4 µg/l in the unchlorinated effluent to 71 µg/l following chlorination i.e. an increase of 67 µg/l (equivalent to 60 µg/l AOX). Other THM levels rose from 0.8 to 3.3 µg/l = 2.5 µg/l (equivalent to approx 2.4 µg/l AOX). The total AOX levels rose from an average of 91 µg/l in unchlorinated effluent to 801 µg/l following chlorination, an increase of 710 µg/l. In laboratory experiments using 40mg/l chlorine for 1 hour, carried out during the same series of studies, estimates of trichloroacetic acid formation (detected by GCMS as methyl ester) were 17 µg/l (equivalent to 10 µg/l AOX) and dichloroacetic acid 19 µg/l (equivalent to 10 µg/l AOX) whilst the average AOX level rose from 188 µg/l to 625 µg/l, an increase of 437 µg/l. On the basis of ratios seen in other scenarios other HAA concentrations are likely to be around 10% of the combined TCA + DCA concentration i.e. another 2 µg/l AOX.

The above data can be used to estimate the fraction of formed AOX that will be trihalomethanes (8.8%), TCA (2.3 %) and other HAAs including DCA (2.7%) in the domestic sewer reaction scenario. It is important to note, however, that sewage disinfection is likely to represent an extreme case since dosing of chlorine or hypochlorite is typically continuous, and sufficient to maintain significant chlorine residuals over a defined period (e.g 1 hour). In contrast, in the domestic scenario, the active chlorine from used solutions is likely to be rapidly consumed as the high levels of ammonia, nitrogen and sulfide groups reduce the hypochlorite to chloride ion. In both cases some chlorine will remain reactive in the form of inorganic chloramines. Thus by-product formation in the domestic scenario may not only be less extensive, but chlorination reactions may not proceed as far towards completion, such that trihalomethane and TCA levels would be substantially lower.

Calculation of specific by-product emissions

Assumptions:

Hypochlorite use in laundry = 15% total use. Other uses = 85% total. (from Table 2.6)

Table 3.2a

Phase	Total AOX formation as % active chlorine
Overall including use phase and sewer phase	1.5 %
Laundry - use phase	2.6 %
Hard surface and toilet cleaning – use phase	0.1 %

Assuming that by-product formation in sewer is the same after both types of use, the proportion of AOX formed in the sewer (AOX_{sewer} %) can be calculated by subtracting the estimated amounts formed during the use phase from the total known to be formed across all uses and phases from the field studies. Thus:

$$\begin{aligned} \text{AOX}_{\text{sewer}} \% &= 1.5 - (\text{AOX}_{\text{laundry}} * 0.15) - (\text{AOX}_{\text{cleaning}} * 0.85)\% \\ &= 1.5 - (2.6 * 0.15) - (0.1 * 0.85) = 1.025\% \end{aligned}$$

Table 3.2b

Individual OBP formation as % total AOX (from preceding section)			
	THMs	TCA	Other HAAs
OBP _{LU} = OBP%/AOX during laundry use	11.3	5.2	7.3
OBP _{OU} = OBP %/AOX during other uses	12	10	5
OBP _S = OBP %/AOX formed in sewers	8.8	2.3	2.7

For each of the above three phases, the amounts of the specific by-product that will arise expressed as a percentage of active chlorine applied is given by the formula:

$OBP/Cl \% = OBP/AOX \% * \text{proportion of total Cl usage passing through that phase} * AOX/Cl \%$

The total by-product formed across all phases expressed as a percentage of total AOX arising from household bleach use can be calculated by summing the individual contributions and dividing by the observed average rate of formation across all phases (1.5%).

Using the data and assumptions derived above, the amounts of each by-product arising can thus be calculated as a percentage of total AOX arising from household bleach use using the formula

$$OBP \% = \frac{(OBP_{LU} * 0.15 * 2.6) + (OBP_{OU} * 0.85 * 0.1) + (OBP_S * 1 * 1.025)}{1.5} \%$$

This can then be used to derive PECs for each specific by-product as follows.

i) THMs

$$CHCl_3 = \frac{(11.3 * 0.15 * 2.6) + (12 * 0.85 * 0.1) + (8.8 * 1 * 1.025)}{1.5} = 9.6\% \text{ of AOX}$$

Adjusting for 90% removal of volatile THMs in STPs vs 60% for total AOX:

$$PEC_{local\ THM} = PEC_{local\ AOX} * 9.6 \% * 0.1 / 0.4$$

For the realistic case scenario above ($PEC_{local\ AOX} = 0.8 \mu\text{g/l}$):

$$PEC_{local\ THM} = 0.8 * 9.6 \% * 0.1 / 0.4 = 0.019 \mu\text{g/l (as AOX)} = 0.022 \mu\text{g/l as } CHCl_3$$

For the worst case scenario ($PEC_{local\ AOX} = 3.9 \mu\text{g/l}$):

$$PEC_{local\ THM} = 3.9 * 9.6 \% * 0.1 / 0.4 = 0.094 \mu\text{g/l (as AOX)} = 0.11 \mu\text{g/l as } CHCl_3$$

ii) Trichloroacetic acid

$$TCA = \frac{(5.2 * 0.15 * 2.6) + (10 * 0.85 * 0.1) + (2.3 * 1 * 1.025)}{1.5} = 3.49\% \text{ of AOX}$$

Adjusting for 66% removal for TCA in STPs vs 60% for total AOX:

$$PEC_{local\ TCA} = PEC_{local\ AOX} * 3.49 \% * 0.34 / 0.4$$

For the realistic case scenario above ($PEC_{local\ AOX} = 0.8 \mu\text{g/l}$):

$$PEC_{local\ TCA} = 0.8 * 3.49 \% * 0.34 / 0.4 = 0.024 \mu\text{g/l (as AOX)} = 0.036 \mu\text{g/l as TCA}$$

For the worst case scenario ($PEC_{local\ AOX} = 3.9 \mu\text{g/l}$):

$$PEC_{local\ TCA} = 3.9 * 3.49 \% * 0.34 / 0.4 = 0.12 \mu\text{g/l (as AOX)} = 0.18 \mu\text{g/l as TCA}$$

iii) Other haloacetic acids

$$\text{HAA} = \frac{(7.3 * 0.15 * 2.6) + (5 * 0.85 * 0.1) + (2.7 * 1 * 1.025)}{1.5} = 4.0\% \text{ of AOX}$$

Adjusting for 87% removal for haloacetic acids other than TCA in STPs vs 60% for total AOX:

$$\text{PEC}_{\text{local HAA}} = \text{PEC}_{\text{local AOX}} * 3.49 \% * 0.13 / 0.4$$

For the realistic case scenario above ($\text{PEC}_{\text{local AOX}} = 0.8 \mu\text{g/l}$):

$$\text{PEC}_{\text{local HAA}} = 0.8 * 4.0 \% * (0.13/0.4) = 0.010 \mu\text{g/l (as AOX)} = 0.019 \mu\text{g/l expressed as DCA}$$

For the worst case scenario ($\text{PEC}_{\text{local AOX}} = 3.9 \mu\text{g/l}$):

$$\text{PEC}_{\text{local HAA}} = 3.9 * 4.0 \% * (0.13/0.4) = 0.051 \mu\text{g/l (as AOX)} = 0.092 \mu\text{g/l as DCA}$$

iv) Other identifiable molecules

All other identified molecules are expected to be present only in concentrations an order of magnitude lower than those of THMs and haloacetic acids.

3.1.2.3. Production of other Chemicals

Sodium hypochlorite reacts with organic intermediates in controlled closed systems. A solution of sodium hypochlorite is filled into the reaction vessels through closed systems. Emissions to the environment will not occur as NaClO either reacts or is reduced completely to sodium chloride during the process. The waste water is usually treated because of the organic compounds and at the same time any left available chlorine is destroyed.

Halogenated organic by-products

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

3.1.2.4. Swimming Pool

PEC hypochlorite

For the swimming pool scenario it is assumed that for each swimmer a certain quantity of water will be released into the environment via three different ways:

- 1 any difference between inputs and evaporation is assumed to be released continuously (20 -50 m³/d)
- 2 periodic washing of the filters releases water (20-50 m³/d every three days)
- 3 and complete emptying of the pool (1000 - 2000 m³)

This released waste water contains free available chlorine at a maximum of 1.4 mg/l which is immediately after discharge transformed into monochloramines.

Based on the three possibilities discussed above a realistic worst-case scenario assuming a discharge of 100 m³ per hour of wastewater (containing a maximum of 1.4 mg/l available chlorine to surface water is assumed. For this scenario the model as explained in appendix 2 can be used, predicting a hypochlorite concentration lower than 10-22 µg/l in a standard receiving river.

PEC halogenated organic by-products.

There are several studies which provide data on chlorinated by-products in swimming pool water, data which is summarised in Table 4.2 (Section 4.1.1.3.3). The variation in levels of individual by-products among the pools covered in these studies is very wide, some being only spot analyses which makes selecting suitable values for risk assessment more difficult. Not all studies provide information on all the major by-products. For these reasons, by-product concentrations have been taken from a single detailed study by the University of Barcelona which examined two large pools

morning and afternoon weekly over a period of 4 weeks, thus giving greater confidence that the data is representative. To make the scenario a realistic worst case, data have been used from an outdoor pool, where disinfectant dosing and haloacetic acid levels are normally significantly higher, the PNEC for haloacetic acids being much lower than for THMs.

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, The table 3.3 below summarises the calculations for the ‘chronic’ i.e. routine daily discharge scenario:

Table 3.3 Estimated routine emissions of halogenated by-products from a swimming pool

	TGD values	AOX	CHCl3	TTHMs	MCA	DCA	TCA	CAAs
Concentration of OBP in pool water		700	130	170	2	64	436	502
No. of visitors / day (per 10000 inh)	400							
Water discharged per visitor	0.05							
Volume replaced / day m3	20							
Emission to sewer / day g		14.0	2.6	3.4	0.0	1.3	8.7	10.0
STP influent / day (per 10000 inh)	2000000							
STP influent concn µg/l		7.0	1.3	1.7	0.0	0.6	4.4	5.0
Fraction not removed in STP		0.4	0.1	0.1	0.13	0.13	0.34	
STP effluent concn µg/l		2.8	0.1	0.2	0.0	0.1	1.5	1.6
Dilution factor	10							
PEC local water µg/l		0.28	0.01	0.02	0.00	0.01	0.15	0.16

Thus the PEC_{local water} for total THMs is 0.02 µg/l and for total chloroacetic acids 0.16 µg/l

Table 3.4 below shows the situation for the ‘acute’ situation i.e. when the pool is completely emptied:

Table 3.4 Estimated emissions of halogenated by-products from a swimming pool during complete emptying

	TGD values	AOX	CHCl3	TTHMs	MCA	DCA	TCA	CAAs
Concn of OBP in pool water µg/l		700	130	170	2	64	436	502
Area of pool m ²	440							
Depth of pool m	1.8							
Pool Vol m3	792							
Emission to sewer / day g		554.4	103.0	134.6	1.6	50.7	345.3	397.6
STP influent l/day (per 10000 inh)	2000000							
STP influent concn µg/l		277.2	51.5	67.3	0.8	25.3	172.7	198.8
Fraction not removed in STP		0.4	0.1	0.1	0.1	0.13	0.34	

STP effluent concn µg/l		110.9	5.1	6.7	0.1	3.3	58.7	62.2
Dilution factor	10							
PEC local water µg/l		11.09	0.51	0.67	0.01	0.33	5.87	6.22

Thus the PEC_{local water acute} for total THMs is 0.67 µg/l and for total chloroacetic acids 6.22 µg/l

The 'chronic' situation in Table 3.4 above will in fact also reflect the full year chronic effect of both routine releases and twice yearly emptying since the acute releases add about 20% to the total annual discharge, but the TGD default value for routine discharge is 300 days out of 365 which would reduce the annual load by about 20%.

In swimming pools, THMs and haloacetic acids make up the great majority of the chlorinated by-products measured as AOX. In the case of the Barcelona outdoor pool on which PEC calculations were based they accounted for 68% of the AOX. Chloral hydrate accounted for a further 12.6% of the AOX. In indoor pools, identified species account for a smaller percentage of the AOX: for the Barcelona indoor pool THMs and CAAs accounted for 29% of AOX and chloral hydrate for another 6.4%. This probably reflects the fact that reactions go more to completion in outdoor pools and a substantial proportion of the unidentified AOX in the indoor pools may well be chlorinated fragments of proteins, carbohydrates and fats for example. Dichloroacetonitrile is relatively volatile, and both it and chloral hydrate hydrolyse. The Barcelona study failed to detect any trichlorophenol above the 0.5 µg/l detection limit. Consequently, the PECs for these and other unidentified molecules will be much lower than for the THMs and HAAs.

3.1.2.5. Sewage Treatment

Release of treated sewage is always linked to a local permit and controlled by law.

The local measured environmental concentration of hypochlorite from use in waste water treatment in effluents under prechlorination is lower than the detection limit. Exposure calculations with the model described in Appendix 2 suggest that concentrations may be as low as 10⁻³² mg/l as FAC, so no FAC can be measured. Under postchlorination the total residual chlorine (measured as 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. When applied, this is usually required by local authorities, for example because of required recreational swimming water quality conditions in the vicinity.

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

In studies by WRc (Davis et al 1993), THM formed in the chlorinated effluent averaged 70 µg/l, almost all of which was chloroform (67 µg/l). Assuming no volatilization or degradation post-chlorination, and a dilution factor into the receiving water of 10, this would give a PEC for THMs of 7 µg/l.

The same studies identified DCA and TCA in effluents at 19 µg/l and 16 µg/l. Assuming no degradation post-chlorination and a dilution factor of 10, the PECs would be 1.9 µg/l and 1.6 µg/l respectively. The conditions used by Davis et al, 40 mg/l available chlorine for 1 hour, were quite severe in terms of normal sewage disinfection practice. Lower amounts may be produced at lower chlorine doses. Rebhun et al (1997) for example, using a dose of 10 mg/l, but with a contact time of 24 hours, found 7 µg/l DCA and 2 µg/l TCA in the chlorinated effluents. These figures would indicate PECs of 0.7 µg/l and 0.2 µg/l respectively.

3.1.2.6. Textiles:

PEC for NaClO in the effluent from wool shrinkproofing is expected to be negligible as the process involves a dechlorination stage using sulphite.

Halogenated organic by-Products

A PEC for AOX released to surface water can be calculated by the procedure described below. Section 3.1.1.6 describes the determination of the information in the first three rows of the table below. AOX typical removal rate is assumed to be in the order of about 50% (Wilson *et al.*, 1992). Using the TGD procedure for the PEC_{local} calculation for aquatic compartment for wool shrinkproofing we have:

Mass of goods processed per day	t d ⁻¹	1.5
AOX formation per mass of goods	kg t ⁻¹	0.27
AOX emission per day	kg d ⁻¹	0.4
Waste consumption from textile production	m ³ t ⁻¹	300
Waste water flow to wwtp	m ³ d ⁻¹	450
Total waste water flow of wwtp	m ³ d ⁻¹	2000
Fraction of emission directed to water		100%
Removal factor		50%
Dilution factor (TGD)		10
AOX influent concentration	mg l ⁻¹	0.20
AOX effluent concentration	mg l ⁻¹	0.10
AOX concentration in surface water (PEC_{local}_{Wool shrinkproofing})	mg l⁻¹	0.010

Given that volatiles in the chlorination line effluent accounted for less than 5% of AOX, the maximum concentration of trihalomethanes in wwtp influent would be 10 µg/l. Assuming 90% removal during wastewater treatment, and 10% dilution gives a maximum PEC_{local water} for THMs of 0.10 µg/l.

There is no specific information on haloacetic acids, but given the large amounts of amino nitrogen present, that chlorotyrosine accounted for almost 40% of AOX, and that chlorinated proteins account for a substantial proportion of the remainder, it is unlikely that haloacetic acids would account for more than 5% of the AOX. Assuming 30% of this was TCA, removed at 60% in wwtps, and the remainder 87% removed, PEC_{local water} for haloacetic acids would be:

$$\frac{0.20 \times 0.05 \times ((0.3 \times 0.4) + (0.7 \times 0.13))}{10} = 0.00021 \text{ mg/l} = 0.21 \text{ } \mu\text{g/l}$$

As regards dioxins, the line effluent concentration of 28.5 pg/l TEQ is of a similar order to domestic washing machine effluent (where the dioxins arise from various

sources via dirty clothing) and to that found in municipal treatment plant influent. The line effluent would, however, be further diluted by other processing operations on the site, and if the effluent were treated on site, this would partition almost entirely to the treatment sludge.

Applying the calculations above to the arising of 880ng TEQ per 12 hours (1.1 ng/l x 800l as per 3.1.1.6) or 1760 ng TEQ assuming 24 hr continuous operation, gives for discharge via a municipal STW:

Dioxins emission per day	ng TEQ d ⁻¹	1760
Waste water flow of wwtp	m ³ d ⁻¹	2000
Dioxins wwtp influent concentration	pg TEQ l ⁻¹	0.88

Note that it is not established whether the dioxins detected are formed in the process or from adventitious sources.

3.1.2.7. Drinking Water

Assuming a daily per capita consumption of 2 litres by a person weighting 60 kg, as reported by WHO 1993, the annual total intake of treated water is around $240 \times 10^6 \text{ m}^3$ versus to the $35,000 \times 10^6 \text{ m}^3$ of water overall treated. This means that the main part of water treated for human consumption is not drunk, but directly released in the municipal waste water network.

Considering that the water treated by sodium hypochlorite has a concentration of 0.5 mg/l of available chlorine as worst case, and assuming a water consumption in Europe around 200 l/capita/day (WSA - 1993), the quantity of available chlorine reaching a typical municipal WWTP (10,000 inhabitants equivalent) could be around 1000 g/day (TGD - 1996). This conservative calculation does not allow for sodium hypochlorite removal in the sewer. The more inclusive but still conservative model detailed in Appendix 2 based on above data predicts an environmental concentration of sodium hypochlorite in the receiving river of less than $10^{-23} \mu\text{g/l}$.

Halogenated organic by-Products

By-products in drinking water related to the use of chlorine/hypochlorite have been studied extensively. In practice measures are taken to reduce the amount of by-products as much as possible, without compromising microbiologically safe drinking water, the risks of which is generally accepted to be far more critical. The application of chlorine/hypochlorite in drinking water and the formation of by-products is regulated in the EU under Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

i. THMs

The concentrations of THMs in chlorinated drinking water vary very widely from supply to supply according to the raw water used and the connected issue of the treatment and chlorination conditions used to make it drinkable and microbiologically safe. Chloroform accounts for over 90% of THMs in most waters, the exceptions being where bromide levels are high [Le Bel et al 1997; Krasner 1989, Cancho et al 1999].

THMs were the first drinking water chlorination by-products to be controlled by legislation. In the EU, levels are controlled by Directive 98/83 EC which sets a maximum limit of 100 µg/l for total THMs measured at the customer's tap. This latter point is significant because the concentration of THMs often increases along the distribution system because of ongoing reactions with the chlorine residual that is maintained in the pipe to ensure microbiological safety. The increase in THMs is variable and is proportionately, though not numerically, greatest in waters with low initial concentrations. According to the report commissioned by the EU (Premazzi 1997a), a 2-fold increase from treatment works to tap may typically be expected. Many EU countries have national standards for THMs ranging from 10 µg/l measured at the works to 100 µg/l measured at the tap. The compliance date for the 100 µg/l THM limit under Directive 98/83 is end 2008 with an interim limit of 150 µg/l in force from end 2003.

There is no comprehensive data on THM levels in drinking water around Europe from which to derive a picture of environmental concentrations, but a number of attempts have been made to assess the position and to estimate compliance with Directive 98/83, the most recent being an exercise conducted for the EU Commission (DG SANCO 2002a,b). Despite the incomplete picture, there are enough pointers to make a broad assessment as follows:

- THM levels in chlorinated water produced from groundwater sources is normally very low, almost always <20 µg/l at the tap and often below 5 µg/l (Arora 1997, Techware 1997). It seems reasonable to take 5 µg/l as a typical case for chlorinated groundwater. Groundwater is the source for some 57% of the potable water supply in the EU (Premazzi et al (1997a)), the rest coming at least partly from surface water. The proportions vary for different countries from 99% groundwater in Austria and Denmark to 20% groundwater in Spain and 16% in Ireland, Most countries use both sources extensively.
- The levels of THMs in chlorinated surface water varies a lot depending on the raw water quality, treatment methods including prior dissolved organic carbon (DOC) reduction, disinfectants used (e.g. whether hypochlorite or chlorine is used for all steps or whether some are transformed into chloramination with co-use of ammonia, or substituted by ozone or ClO₂ for example) and disinfectant dose. Some of the highest levels of by-products generally occur not in waters from 'polluted sources' but from upland, acid waters draining from peat soils high in natural organic matter.
- The most recent study of THM levels in potable water for the EU Commission (DG SANCO 2002a,b) included 7 cities in 6 countries using surface water. The levels measured in surveys in each of the four quarters of the year were as follows:

City	Range over four quarters	Mean
------	--------------------------	------

	µg/l THM	µg/l THM
Florence, Italy	0.2 – 16	3.5
Athens, Greece	13 – 82	34
Dublin, Ireland	12.2 – 70	35
Antwerp, Belgium	17.2 – 95.7	68
Nancy, France	31 – 180	76
Sevilla, Spain	71.5 – 217	135
Huelva, Spain	115.6 – 232.7	170

The first four cities were already compliant with Directive 98/83 in that there were no samples in excess of the 100 µg/l limit. As the mean level for Antwerp, which came close to exceedance was 68 µg/l, perhaps 70µg/l could be taken as an annual mean for a supply which just remains compliant throughout the year with the Directive. By 2008 all EU potable water should comply with this, but the mean for much even derived from surface water will already be at much lower levels, as for Florence, Athens and Dublin above where the mean is <= 35 µg/l.

- One may thus consider four bands according to source water within which total THM levels may fall:

Water source	Water quality	TTHM µg/l
Groundwater		< 5
Surface Water:	Good quality	< 35
	DWD compliant	< 70
	Non-DWD compliant	~ 170

- Given that 57% of EU potable water comes from groundwater, and the broad findings of the 2002 survey, it seems likely that 80 – 90% of EU water already falls within the first 3 bands above.
- Assuming elimination in STPs of 90% as outlined in section 3.1.2, and a dilution factor from STP into receiving water of 10, the above figures would translate at their upper limits into PECs_{local water} for total THMs of 0.05 µg/l, 0.35 µg/l, 0.7 µg/l and 1.7 µg/l respectively.

ii. Haloacetic acids

Compared to THMs, data on haloacetic acid levels in potable water in the EU is relatively scarce, there being no regulatory limits for human health purposes, though there are WHO Guidelines of 200 µg/l, 40 µg/l and 20 µg/l respectively for TCA, DCA and MCA. Data published over the years shows that HAA levels are often low, as for THMs, but there will be sources for which levels are much higher. For example, Peters et al (1991) found that HAA levels in chlorinated Dutch surface waters ranged from 3.8 – 14.7 µg/l while Uden and Miller (1983) reported values up to 133 µg/l for DCA and 161 µg/l or TCA in a US study. Lahl et al (1984) reported levels up to 3 µg/l for several German waters. Krasner (1989) reported median levels in 35 US waters over four quarters between 13 and 21 µg/l.

The US regulates haloacetic acids: the stage 1 DBP regulations set a maximum contaminant level of 60 µg/l for HAAs (parameter HAA5 – the five most abundant acids) alongside 80 µg/l for THMs. In stage 2, these levels would reduce to 30 µg/l for HAAs and 40 µg/l for THMs. Arora *et al.* (1997) found that 16 % of supplies studied would fail the 60 µg/l HAA limit and 52% the 30 µg/l limit.

It is clear that HAA levels can be particularly high in chlorinated water derived from upland, acid sources partly because of the abundance of suitable precursors. For example, a survey by WRc plc for the UK Department of Environment (Hutchison *et al.* 1993) found levels ranged from 0.9 µg/l DCA and 0.3 µg/l TCA for groundwater from a chalk aquifer to 62.2 µg/l and 85.6 µg/l respectively for water from an upland lake. In a recent survey of Finnish potable water, Nissinen *et al.* (2002) found HAA levels ranged from 6 µg/l to 255 µg/l in 24 surface water derived samples whereas levels were undetectable in the four groundwater sources studied.

Total haloacetic acid concentrations are normally of the same order of magnitude as total THM concentrations, though most often HAAs are somewhat lower as is reflected in the US DBP limits. For example, Krasner (1989) and Nieminski (1989), for 35 US and Utah facilities respectively, found HAA levels to be approximately 50% of THM levels. Surveys in Spain (Villanueva *et al.* 2003, Cancho *et al.* 1999) and Canada (LeBel 1997) found ratios between 30% and 70%. This partly reflects the fact that whereas THM levels normally rise in distribution systems, HAA levels may rise but can also fall in mature water by hydrolysis and/or biodegradation within the pipes. Most often, TCA and DCA levels are similar and MCA levels are almost always low.

In contrast, in upland acid waters, HAA levels can exceed THM levels, often by large margins. In the Finnish waters surveyed by Nissinen (2002), HAA levels were uniformly higher than THM levels by a factor ranging from 1.5 fold to 67 fold. Here, TCA levels were somewhat higher than DCA levels.

The Nissinen study also highlights the effect of improved treatment techniques designed to control chlorinated by-products generally, but normally aimed at THMs. These techniques include physical organic matter removal, substitution of hypochlorite/chlorine in pre-treatment and use of chloramination to provide the residual, though pH adjustment can depress THMs but increase HAAs. In the Nissinen study 9 waters prepared using combinations of the above techniques showed HAA levels ranging from 6.4 to 36 µg/l whereas in the 14 samples prepared without them levels ranged from 39 to 255 µg/l.

Using these observed relationships, it is possible to make an assessment of the prevalence of different levels of haloacetic acids entering the aquatic environment from potable water as follows:

- Haloacetic acid levels in potable water made from groundwater are likely to be low and, given the absence of precursors, substantially lower than THMs. A level of 2 µg/l would be a conservative estimate.

- HAA levels in drinking water made from most surface waters will range between 30% and 70% of THM levels. Thus:
 - For a good quality surface water source with THM levels below 35 µg/l, which would equate to about 17.5 µg/l leaving the treatment works, and with HAA levels in mid-range at 50% of THM, HAA concentrations would be approximately 9 µg/l.
 - For a water just compliant with Directive 98/83 i.e. THM <70 µg/l, the most likely HAA concentration would be <24.5 µg/l
 - For waters as per those in Huelva with mean THM levels of 170 µg/l, HAA levels could typically be 38 µg/l
- Considering that the THM_{tap}:THM_{works} ratio could be between 1:1 and 1:2, and the HAA:THM ratio between 30% and 70% would give bands of values around these estimates.
- Upland, acid waters as per the Nissinen study constitute a fourth surface water category
- To derive a picture of most likely values and ranges for the PEC of haloacetic acids across the EU, an additional key factor is the proportion of HAA that is TCA, which is only 66% removed in an STP as opposed to other HAAs which are assumed to be 87% removed. For most waters, TCA typically accounts for 33% of total HAA. In the Nissinen study on upland acid water this proportion ranged from 40% to 60%.

Taking the above scenarios and respective removal rates for TCA and other HAAs, and a dilution factor of 10 into the receiving water, most likely PEC values and possible ranges for the various source water types would be as follows:

Table 3.5: Most likely PEC values for THMs and HAAs for different source waters and treatment levels

Water source	Water quality	THM µg/l	PEC HAA µg/l (Range) Most likely
Groundwater		5	0.04
Surface Water:	Good quality	35	(0.10 – 0.68) 0.17
	DWD compliant	70	(0.21 – 1.35) 0.34
	Non-DWD compliant	170	(0.51 – 3.30)
	Upland, acid		(1.08 – 7.80)

iii. Other identifiable molecules

THMs and HAAs account for most of the chlorinated by-products in potable water. Other identifiable substances types are formed at concentrations normally an order of magnitude lower, and of these the most common are relatively unstable and/or volatile such that the concentrations reaching the environment will be reduced even further. Because of the focus on identifiable substances from a human health perspective, AOX measurements have been relatively little used in this industry, but where raw waters have a significant natural organic matter content TOX or DOX values can be up to double the concentration of identifiable by-products. This material is believed

to be primarily sparsely chlorinated high molecular weight fragments of natural macromolecules.

3.1.2.8. Pulp and Paper

Hypochlorite

According to the information from CEPI (2003) the current specific uses of hypochlorite in the pulp and paper process as described in 3.1.1.8. are applied in the early phase of the process or during maintenance stops. There is a general drive to keep the concentrations low to prevent corrosion. Moreover, discharges are directed to sewage plants before reaching the environment, so it is assumed that no hypochlorite reaches the environment and consequently the PEC is null.

Halogenated organic by-products

According to CEPI (Sexton, pers. comm. October 2003) the machine cleaning use of hypochlorite in the P&P industry and any potential by-product formation and discharges is covered by the Industrial and Institutional Cleaning scenario described in this RAR.

Estimating effluent loads and PECs for chlorinated organics arising from the use of hypochlorite in repulping broke containing wet-strength resins is difficult: firstly, only part of the chlorine load arises from the hypochlorite, a second part coming from the wet-strength resin (WSR) itself; secondly the processing of broke will generally just be part of a larger mill operation such that the load from broke processing is mixed and treated with the rest of the factory effluent.

Data from laboratory experiments exploring factors influencing chloroform generation from WSR containing broke repulping (Chung 2003) suggest chloroform levels in the repulper liquor are of the order of up to 10 ppm. Use of hypochlorite for repulping WSR containing broke is covered in BAT descriptions under IPPC. The UK Technical Guidance document (UK Environment Agency 2000) indicates that UK paper mills, which with one exception do not produce chemical pulp, have benchmark emission values of 0.5 mg/l AOX (based on 10 m³/ADT water usage) whereas the value is double, i.e. 1.0 mg/l, for mills using wet-strength resins. This is reasonably consistent with the laboratory data allowing for extensive volatilisation of chloroform from the pulpers and or water treatment facility, and dilution with other factory effluents.

Assuming then as a worst case that:

- use of hypochlorite in broke repulping results in 0.5 mg/l AOX in final effluent
- 50% of the AOX is chloroform
- 50% of this was attributable to the hypochlorite as opposed to the WSR itself,
- A dilution factor of 10 into the receiving water

the PEC_{local water} for THMs from hypochlorite use would be:

$$0.5 \text{ mg/l} \times 0.5 \times 0.5 \times 0.1 = 0.0125 \text{ mg/l} = 12.5 \text{ } \mu\text{g/l as AOX} \\ = 14.0 \text{ } \mu\text{g/l as chloroform}$$

No data is available for haloacetic acids, but as noted previously formation, if any, is likely to be limited given the facile routes to chloroform and N-chloroamino compounds. A worst case estimate might be that total HAAs in effluents attributable to broke repulping would be 5% of AOX.

On this basis, using the same assumptions as for THMs above, the PEC_{local water} for haloacetics from hypochlorite use would be:

$$0.05 \text{ mg/l} \times 0.5 \times 0.5 \times 0.1 = 0.0125 \text{ mg/l} = 1.25 \text{ } \mu\text{g/l}$$

(NB. A PEC calculation for by-products arising from the discontinued use in pulp bleaching is given in Annex 5).

3.1.2.9. Cooling Water

PEC Hypochlorite

The graphs and model calculations presented in Appendix 2 for the sewage exposure scenario clearly show that concentrations of 0.5 mg/l TRO (maximum value at the condensers, worst-case regular scenario) as well as concentrations up to 8 mg/l (extreme worst-case shock dosing regime) will fall below the detection limit within seconds upon reaching the surface water.

Recently, some data on TRO concentrations in the discharge plumes in sea water of various power stations have been published (Jenner *et al*, 1997). These data vary from 0.02 mg/l TRO in the near vicinity of power stations to zero at further distances. Moreover it must be noted, that these data most likely do not represent hypochlorite but a variety of other oxidants. In general, observed concentrations will be variable and to a large extent influenced by local conditions. Local regulations generally are usually designed to prevent acute effects in the vicinity of the discharges.

Therefore a PEC value for hypochlorite in a worst-case regular cooling water scenario will rapidly drop to zero when reaching surface water. This can be expected based on the model calculations for the household/sewage scenario and is supported by measurements (Jenner *et al.*, 1997, 1998). It means that potential effects –if any - may only be expected in the near vicinity of the outlet.

PEC by-products

More important for the potential environmental impact of hypochlorite in cooling water is the formation of by-products, consisting of other oxidants (included in the TRO measurements) and other chemicals. Also in the cooling water application of hypochlorite the formation of by-products will vary strongly, both quantitatively and qualitatively, due to the fluctuations in surface water composition, temperature, residence time, etc. The impact of different environmental factors on the mechanism

of by-product formation has been studied extensively (e.g. American Water Works Association, 1982). A summary of the main by-products generated by hypochlorite use in seawater and in freshwater cooling systems is given in Tables 3.6a and 3.6b, respectively. The seawater data represent actual measurements, while the freshwater data are from simulation studies dosing chlorine to different surface waters. In all situations it is observed that elevated by-product concentrations only occur in the near vicinity of the discharges.

Table 3.6a Measurement of by-products of hypochlorite application in cooling water in sea water, summarizing data from Jenner et al. 1997.

Power stations	No. of samples	Bromoform ($\mu\text{g/l}$)		Dibromoacetonitrile($\mu\text{g/l}$)	
		Average	range	average	range
Several in UK, F and NL	90	16.32 \pm 2.1	0.72–29.2		
	29			1.48 \pm 0.56	<0.1-3.15

In Table 3.6a, the chlorine dosages are typically between 0.5 and 1.5 mg/l as Cl_2 .

Table 3.6b Measurements of chlorination by-products in cooling water applications in freshwater simulation studies (from Berbee, 1997)

Surface water (rivers)	Br^- $\mu\text{g/l}$	Cl_2 dose mg/l	CHCl_3 $\mu\text{g/l}$	$\Sigma \text{CHBr}_x\text{Cl}_y$ $\mu\text{g/l}$
Columbia	4	2.9	12.7	-
Ohio	?	4.6	6.5	4.1
L.Michigan	?	3.4	2.3	2.4
Missouri	75	4.2	11.5	16.1
Tennessee	?	4.5	22.9	7.8
L. Norman	?	4.1	3.6	1.7
Connecticut	?	4.6	21.6	2.9

For the marine cooling water scenario PEC values of TRO between 0 and 20 $\mu\text{g/l}$ were measured. Since hypochlorite is added at the beginning of the cooling system it is expected that the TRO measured after discharge will be mainly a mixture of oxidative compounds other than hypochlorite. Since the nature of TRO is not identified it is not useful nor possible to determine a PEC/PNEC ratio.

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, 2001). Another useful recent publication was published by Electricité de France (Khalanski, 2002) on organic by-products from cooling water chlorination from EDF marine power stations. Measurements of the main trihalomethane and haloacetic acid formed (bromoform and dibromoacetic acid) in cooling water samples from three power station showed bromoform levels up to 26.8 $\mu\text{g/l}$ and DBAA levels up to 10.19 $\mu\text{g/l}$. The report assesses the risks of the main organic CBP's, concluding that the margins between the most sensitive toxicity thresholds and the observed environmental concentrations

for these power stations have safety factors of 10^3 to 10^7 for the local scale and 10^4 to 10^9 for the regional scale.

In situ measurements (plume sampling in the field) for 10 coastal power stations in France, UK and The Netherlands were carried out for the following chemical class of compounds: haloforms, haloacetonitriles and halophenols. Five compounds were found at mean chlorine dosage levels of 0.5-1.5 mg/l (as Cl_2) of which 2 were consistently present above the detection limit. Bromoform was present in all effluents as well as dibromoacetonitrile. Dibromochloromethane, bromodichloromethane and 2,4,6-trichlorophenol were detected in a few cases at very low levels. Typical ranges are mentioned in Table 3.7.

For by-product risk assessment, the chlorination of seawater, where brominated species predominate, probably represents a worse case in terms of by-product loads in effluents than freshwater chlorination. As noted in section 3.2.1.6 the environmental properties and toxicity of brominated and chlorinated species are similar, but the brominated oxidants formed are more reactive and have been observed to yield somewhat elevated levels of by-products, notably THMs, and to a lesser extent HAAs (Pourmoghaddas and Stevens, 1995). This may to some extent be counteracted because by-product formation will be somewhat reduced at the higher pH that is typical of seawater. Secondly, seawater chlorination is usually associated with large facilities with very high throughputs of water (e.g. nuclear power stations), and are more likely to be operated continuously. Many freshwater cooling applications will be of smaller scale, and chlorination will be intermittent or restricted to occasional shock dosing.

Taking the by-product concentrations from the EDF study (Khalanski 2002) together with those in tables 3.3a and 3.3b would indicate conservative THM and HAA concentrations in the discharge during continuous dosing of approximately 30 $\mu\text{g/l}$ and 10 $\mu\text{g/l}$ respectively. Risk characterisation can then consider two cases:

a) Seawater case.

For marine discharges in coastal zones the TGD suggests a dilution factor of 100 can be considered as a worst case. This gives $\text{PEC}_{\text{localwater}}$ values of 0.3 $\mu\text{g/l}$ and 0.1 $\mu\text{g/l}$ for THMs and HAAs respectively.

b) Freshwater case

Where cooling water is abstracted from and discharged to inland freshwaters, a standard TGD dilution factor of 10 can be applied. This gives $\text{PEC}_{\text{localwater}}$ values of 3.0 $\mu\text{g/l}$ and 1.0 $\mu\text{g/l}$ for THMs and HAAs respectively.

3.1.2.10. Institutional and Food Industry

The use of hypochlorite in institutional and food industry cleaning can be broken down into different scenarios as shown in Table 3.7 below:

An approximate breakdown of the consumption would be:

A. Food Industry	50 – 60%
B. Institutional Housekeeping	10 – 20%
C. Hospital Disinfection	10 – 20%
D. Kitchen and catering	20 – 30%
E. Laboratory	<1%

Table 3.7 Parameters of main hypochlorite use scenarios in Institutional and Food Industry Cleaning

Reviewing the individual conditions of use, none of these processes is fundamentally different in terms of product concentrations used, temperatures, pH and contact times from the range of household uses. The most important processes in volume terms are the food industry uses, and factories using such equipment-based systems. The remaining uses are all very similar to household use and effluents will pass to the

Use	Use Concn ppm	COD	Use pH	Contact Time	Temperature	% Cl unreacted to drain	Effluent treatment
A Food Industry							
A1 – “Cleaning-In-Place”	400 – 800 low/no surfactant	Low (pre-cleaning)	12-13	20 -25 mins	Ambient	20 – 50 %	on site
A2 – Open spray plant cleaning	1000 – 4000 with surfactant	Medium (Pre-rinse with water)	12-13	10-15 mins	Ambient	20 %	on site
B Insitutional housekeeping							
B1 – Mop & bucket	500	As for household use					
B2 – Cloth & bucket	500	As for household use					
B3 – Trigger Spray	500	As for household use					
C Hospital Disinfection							
C – Hospital disinfection	500 – 10,000	As for household use NB The high levels are used for spills i.e. high COD					
D Kitchen and catering cleaning							
D1 – Kitchen cleaning	500	As for household use					
D2 – Machine Dishwashing	50	Medium	12	1-2 mins	45 -60 °C	50 - 80 %	As for household use
E Laboratory cleaning							
E1 – Bench cleaning	500	As for household use					
E2 – Lab equip. disinfection using MDW type mc ?	500	Medium	11-12	5 mins	45 – 60 °C	20 %	As for household use

municipal sewer system.

Overall, given that cleaning uses at ambient temperatures generate the lowest levels of by-products, it is probably a conservative estimate to assume that these uses will generate the same levels of by-products in relation to chlorine applied as in household use i.e. AOX = 1.5% of applied available chlorine.

Institutional and Food Industry use of Hypochlorite is estimated in Table 2.2 at 12 – 22.5 ktpa chlorine equivalent. Taking the higher figure as a conservative estimate, this equates to about 19% of the household use figure. Given that household use at European average levels generates a $PEC_{\text{local water}}$ for chlorinated by-products of 0.8 $\mu\text{g/l}$ as AOX, the average PEC for Institutional and Food Industry use would be $0.8 * 19\% = 0.15 \mu\text{g/l}$ AOX.

As regards individual substances, given that the parameters and conditions of Institutional and Food Industry use are not significantly different from household use, it is likely that the quantities of THMs and haloacetic acids formed would be similar. Thus, given the $PEC_{\text{local water}}$ derived for THMs and haloacetic acids from household use (section 3.1.2.2) of 0.022 $\mu\text{g/l}$ and 0.055 $\mu\text{g/l}$ respectively, the corresponding PECs for Institutional and Food Industry use would be:

THMs	$0.022 * 19\% = 0.004 \mu\text{g/l}$
Haloacetic acids	$0.055 * 19\% = 0.010 \mu\text{g/l}$

Alternatively, assuming in a local scenario one hospital with 400 bed places and a consumption of 30 l/day (corresponding, considering a density of 1.23 kg/l, to 36.9 kg/d (Qd)) of an NaClO 5% (P) solution and assuming a fraction consumed (not discharged) of 0.7 (Fc) and an AOX-NaClO conversion factor of 1.5% (T) the local emission value in water ($E_{\text{local water}}$) in kg/d for this scenario can be calculated as follow:

$$E_{\text{local water}} = P * Qd * (1 - Fc) * T = 0.025 \text{ kg/d}$$

This leads to an AOX $PEC_{\text{local water}}$ value of 1.25 $\mu\text{g/l}$. Assuming that THM, TCA and other haloacetic acids form the same proportions as in household use (9.6%, 3.49% and 4.0%, section 3.1.2.2), and adjusting for removal factors in STPs of 0.90, 0.66 and 0.87 respectively, the respective PECs would be:

$$\begin{aligned} \text{THMs} &= 1.25 * 9.6\% * 0.1 / 0.4 = 0.030 \mu\text{g/l as AOX} = 0.034 \mu\text{g/l as CHCl}_3 \\ \text{TCA} &= 1.25 * 3.49\% * 0.34 / 0.4 = 0.037 \mu\text{g/l as AOX} = 0.057 \mu\text{g/l as TCA} \\ \text{Other HAAs} &= 1.25 * 4.0\% * 0.13 / 0.4 = 0.016 \mu\text{g/l as AOX} = 0.030 \mu\text{g/l as DCA} \end{aligned}$$

Considering that in some situations I&I use of hypochlorite e.g. in a hospital may discharge into the same sewage treatment facility as household use, the PEC arising from the combined effluent can be derived by adding the component PECs. Thus:

THMs	PEC $\mu\text{g/l}$
Hospital scenario	0.034
Household scenario	0.022 – 0.11
Combined scenario	0.056 – 0.144
HAAs	PEC $\mu\text{g/l}$
Hospital scenario	0.086
Household scenario	0.055 - 0.27
Combined scenario	0.141 – 0.356

3.1.2.11. Summary of PEC values for Hypochlorite and halogenated by-Products.

PEC hypochlorite

Information presented in sections 3.1.1.1 to 3.1.2.10 shows that releases of hypochlorite to the aquatic compartment are generally low (below the detection limit of current analytical methodology), due to the rapid decay of hypochlorite as demonstrated in Appendix 2.

PEC by-products

The results of PEC calculations for chlorinated organic by-products are summarised below (Table 3.8).

Table 3.8: Calculated PEC_{localwater} for hypochlorite by-products

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

* Indicative figure assuming 2% Cl to AOX conversion (section 3.1.1.5) and 10-fold dilution into receiving water

** Based on UK benchmark emission value 500 µg/l (section 3.1.2.8); 50% from applied hypochlorite and 10-fold dilution into receiving water

The following table summarises other identified by-product types with a rough indication of relative prevalence of the type in terms of very approximate percentages of total halogenated by-products.

Table 3.8a: Summary of halogenated by-products other than HAAs and THMs

Scenario	Halogenated by-products					
	HAld	HKet	HAcn	HPhen	HAmA	Macro
Household	++	++	++	+	++	+++
Swimming Pools	+++	++	++	+	++	+++
Sewage Treatment	++	++	++	+	++	+++
Wool shrinkproofing	?	?	?	?	+++	+++
Drinking Water	++	++	++	+	+	+?
Pulp and paper						
Cooling Water	+?	+?	++	+	+?	+++?
Institutional and Food Industry (inc Hospitals)	++	++	++	+	++	+++

Key: HAld = Halo aldehydes, e.g. chloral hydrate
 HKet = Haloketones e.g. dichloroacetone
 HAcn = Haloacetonitriles e.g. dichloroacetonitrile
 HPhen = Halophenols e.g. 2,4-dichlorophenol
 HAmA = Haloaminoacids e.g. N-chloroglycine
 Macro = Halogenated macromolecules e.g. chlorinated protein fragments

+++ = major by-product (5-50%)
 ++ = minor by-product (0.5 – 5%)
 + = trace by-product (<0.5%)

3.1.3. Atmosphere

Because hypochlorite solutions are non volatile, no significant potential for dispersion in the air exists. However, hypochlorite may release chlorine when accidentally mixed with acids. The volatility of "chlorine" species has been described on a general basis under 2.7.

In the following scenarios it is possible to estimate the emission of the different "chlorine" species:

- Air concentrations in the local production environment are generally not measurable. In the process exhaust, concentrations from around 0.1 up to 2 mg/m³ have been measured.
- In household use the pH of the solution is generally higher than 8. Thus the main species present is ClO⁻, which is not volatile. At pH > 8 most of the emission to air will consist of NCl₃ produced with nitrogen compounds during the dilution of the product.
- In cooling circuits no volatile emission is expected as it is a closed system.
- Atmospheric exposure during formulation can be calculated as follows: formulated products use NaClO at high pH (>12). The finished products have an equally high pH (11.5-12). Therefore, the amount of undissociated HOCl is low (see figure 1). At pH12, the equilibrium OCl⁻/HOCl is 10^{19.53} (Ka=2.90.10⁻⁸ at 25 degrees). Only the HOCl fraction is volatile to a certain degree. As HOCl is virtually non-existent at these high pH values, exposure is equally low. These values indicate that emissions to air during formulation are extremely limited. In addition, the air above filling/formulation lines is very often evacuated by aspiration systems.
- In drinking water the content of total chlorine is under 2 mg/l and the pH between 6-8. Then, the emission is negligible. Also, the "smell of chlorine" will give an indirect measure of the emission of NCl₃.
- In swimming pools the content of NCl₃ in the atmosphere is easily detected by its smell and the mean content expressed in total chlorine is under 1 mg/m³ (*Massin et al.*, 1998).
For each swimmer in indoor swimming pools 20 to 50 m³ of air containing NCl₃ and CHCl₃ are rejected. In open swimming pools the concentration depends on the wind, but the total reject per swimmer is higher than for indoor ones.
- In the food industry aerosols are often used for disinfection. In this scenario, all chlorine species could potentially be found in the atmosphere although no quantitative data are available.

3.1.4. Terrestrial compartment

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

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

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

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

3.2. Effect assessment

3.2.1. Aquatic compartment (incl. sediment)

There is a large amount of documented data available on the aquatic toxicity of hypochlorite, from a number of sources, including general reviews (Brungs, 1973; Mattice and Zittel, 1976; Kalmaz and Kalmaz, 1981), peer-reviewed literature, personal communications and IUCLID (updated version 03/06/94). IUCLID data have been checked, and included alongside additional data from other references that were obtained from literature searches. For each study, experimental conditions and main results are summarised in Appendix 3. As the data available on the aquatic toxicity of hypochlorite have been generated over several decades using different testing methods, species and conditions they need to be carefully evaluated for validity.

The validity of the aquatic toxicity data was evaluated according to the criteria recommended by the European authorities and present in IUCLID. The evaluation criteria are defined as:

- Rated 1 = valid without restriction
- Rated 2 = valid with restriction
- Rated 3 = invalid (not reliable in the HH part)
- Rated 4 = not assignable

The main parameters that need to be documented when describing aquatic toxicity tests for sodium hypochlorite are:

(a) the pH and temperature

The experimental pH and temperature have an important role in the evaluation of aquatic toxicity data as they determine the chemical species present. In water, the hypochlorite ion is in equilibrium with hypochlorous acid, the ratio of each species being pH and temperature dependent. The amount of hypochlorous acid decreases as pH and temperature increase (Hellawell, 1986). At pH 7.0 70% is HOCl whereas at pH 8.0 80% is ClO⁻ when the temperature is 25°C (Taylor, 1993). Therefore in freshwater (characteristic pH range of 6.5-7.2) the dominant form is the more toxic HOCl while at estuarine pH's (7.5-8.2) the reverse is true (Gentile et al., 1976). At pH values above 4.0, Cl₂ does not exist - hence when authors have reported that they used chlorine in aquatic toxicity studies conducted at a pH of about pH 7.0, the chemical species present are a mixture of HOCl and ClO⁻. Temperature also affects the equilibrium between hypochlorous acid and hypochlorite, but to a much lesser extent than pH, with the ionization content (pKa) for hypochlorous acid decreasing from 7.75 at 5°C to 7.63 at 15°C and 7.54 at 25°C. Aquatic organisms are generally more sensitive to chlorine at higher temperature; an inverse relationship between LC50 and temperature was found in fish (Brooks and Seegert, 1977; Scott and Middaugh, 1977). It has been demonstrated that a thermal stress combined with exposure to chlorinated compounds produces a synergetic effect (Thatcher et al., 1976).

(b) the characteristics of the test media

Some characteristics of the test media may also affect the evaluation of aquatic toxicity data e.g. presence of ammonia and organic compounds, hardness and salinity. In clean aqueous test media the chlorine present is likely to exist as hypochlorous acid/hypochlorite ion (i.e. detectable as FAC) decaying rapidly due to reduction and photolysis, e.g. half-life < 2 hours for both hypochlorous acid and the hypochlorite ion (Taylor, 1993). In natural water there will be more interactions with nitrogen and organic compounds so that the hypochlorous acid/hypochlorite ion decays faster and the chlorine present is likely to be a mixture of FAC and chloramines (Ewell et al, 1986; Klerks and Fraleigh, 1991). The products formed from chlorination of natural water are also a function of salinity. Since sea water typically contains **60 mg/kg** bromide, bromination rather than chlorination may predominate as salinity increases (Scott *et al.*, 1980). In sewage the decay of hypochlorous acid is very rapid, with nearly all the chlorine present being as chloramines.

The effect of the hardness of the test media on the aquatic toxicity of sodium hypochlorite has not been systematically studied. However it is not considered to be substantial as the dissociation of calcium hypochlorite to the hypochlorite ion is reported as reversible suggesting that the availability of the hypochlorite ion in test media would not be reduced by the presence of calcium ions. Some authors report that variation caused by changes in hardness is less than a factor of 3 in some fish species.

(c) the measured test concentration

Sodium hypochlorite is rapidly hydrolysed in water and hypochlorous acid/hypochlorite ion concentrations can decay over the duration of the test, by mechanisms shown in sections 2.4 to 2.6. Therefore the initial dosed concentration is not representative of the concentration to which the test organisms have been exposed for the duration of the test. For example Taylor (1993) has shown that the aquatic toxicity of hypochlorite to *Ceriodaphnia dubia* in a flow-through test was 24h LC50 = 0.006 mg/l compared to 0.048 mg/l in a static test - in the latter case the concentration of hypochlorite was believed to be poorly maintained. In freshwater, measured concentrations are usually expressed as Free Available Chlorine (FAC) or Total Residual Chlorine (TRC), which encompass free plus combined chlorine; in saltwater, they are often expressed as Total Residual Oxidant (TRO) or Chlorine-Produced Oxidant (CPO), which encompass free and combined chlorine as well, but also include other oxidative products such as brominated species).

For data to be considered:

- * valid without restriction (i.e. rated 1) the test details should include the use of standard, or well-documented methodology, standard or known species, standard end-points for short and long-term toxicity, flow-through system, information on the pH, temperature, dissolved oxygen, number of concentrations, number of animals, duration of the test, measured concentrations of the test substance, performance of the control, clear concentration-effect relationship, statistical method used for calculating the endpoint.
- * valid with restriction (i.e. rated 2)

the test report should include a description of the methodology, information on the taxonomy of the species, number of concentrations, number of animals, pH, temperature, test duration, oxygen concentration (or the use of a flow-through method such to guarantee its adequate maintenance), measured test concentrations. A semi -static exposure regime can be considered satisfactory provided that the chemical concentration has been adequately maintained and its fluctuations have properly been monitored and taken into account in the calculation of the endpoint.

* invalid (i.e. rated 3)

the test methodology is poorly documented or does not include all the major information needed for ‘valid with restriction’ rating, or bad performance of the control(s).

* not assignable (i.e. rated 4)

the test details reported are insufficient to give the test any rate.

* supportive information. The reason for introducing this additional rating class stems from the complexity and diversity of the multitude of the studies which were not specifically designed for a Risk Assessment procedure as the present one, still they are *per se* good and reliable studies well conducted and described. We didn’t want to waste useful indication of toxicity from these studies which can support the discussion in the PNEC calculation. Examples are tests conducted under intermittent exposure, where effect are evaluated after a standard period (e.g. 96h) but refer to a much shorter and discontinuous exposure (in the order of minutes for few times a day), or cases when no clearly identified endpoint can be retrieved for short or long-term toxicity (e.g. LC50/NOEC can only be expressed as “smaller than” or “greater than”). These kind of data, although not adequate as such to derive a PNEC, can provide useful indication of toxicity and are retrieved as supportive information.

For this report the data have been assessed in three parts:

- Part 1 which covers only freshwater organisms (Section 3.2.1.1)
- Part 2 which covers marine organisms (Section 3.2.1.2)
- Part 3 which covers micro-organisms in sewage treatment plants (Section 3.2.1.4)

The valid data for freshwater and marine organisms have each been used to determine Predicted No Effect Concentrations (PNECs) for the aquatic compartment based on the Technical Guidance Document for New and Existing Substances - 1996 (Commission Regulation 1488/94/EC).

3.2.1.1. Freshwater

3.2.1.1.1. Fish

Short-term toxicity

Concerning the short-term toxicity to fish, the collected and evaluated literature refers only to exposures of very short duration, often on an intermittent regime. Hence a 96h LC50 adequate for the assessment cannot be retrieved but the LC50 values provided are useful as supportive information.

In the late 70's a number of studies in which fish were exposed to a variety of exposure regimes (one or more short pulse doses for 1 or more days), were carried out to simulate intermittent exposure occurring in natural waters receiving power plant cooling effluents. In two studies (Bass *et al.*, 1977 and Heath, 1978) six fish species (*Salmo gairdneri*, *Oncorhynchus kisutch*, *Ictalurus punctatus*, *Notemigonus crysoleucas*, *Lepomis macrochirus*, and *Cyprinus carpio*) were exposed for different time intervals (ranging from 24 to 168 hours) to 40' calcium hypochlorite pulses (3 per day) in flow through tap water at different temperatures. *S. gairdneri* and *I. punctatus* were the most sensitive species in both studies, showing, respectively, an 120h LC50=50 µgTRC/l (at 12 °C) and an 120h. LC50= 33 µgTRC/l (at 24°C). At 96h, the LC50 for the trout was 60 µgTRC/l (at 5°C) and 64 µgTRC /l for the channel catfish (at 24°C).

In the paper of Brooks and Seegert (1977) the effects of single (30 min) and multiple (5 min exposure at 3 hours interval) exposure to sodium hypochlorite in tap water with and without the addition of a thermal stress on two species of fish - *Perca flavescens* and *Salmo gairdneri* (juveniles) - have been described. A single 30' dose was more toxic than the triple exposure. Generally, *S. gairdneri* was more sensitive than *Perca flavescens*; after 24h recovery, the LC50 was 990 µg/l. With the addition of a thermal stress, the median lethal concentration lowered to 430 µg/l.

Seegert and Brooks (1978) exposed for 30 min. four fish species - *Oncorhynchus kisutch*, *Alosa pseudoharengus*, *Notropis hudsonius* and *Osmerus mordax* - to sodium hypochlorite to various temperatures. Coho salmon (*Oncorhynchus kisutch*) showed a sensitivity comparable with that of rainbow smelt (*Osmerus mordax*) and both were more sensitive than the other two species. As observed in other studies, the LC 50 values showed an inverse relationship with test temperature and a typical species-dependent variability; at 10°C the LC50s, measured after 48 hrs, were in the range of 1.26 - 2.41 mg/l.

The toxicity of hypochlorite following intermittent exposure was studied by Wilde *et al.* (1983a,b) in two studies conducted at two different temperatures (27.7 and 21.1 °C). Acute toxicity tests (96h) have been carried out on juvenile and adult fathead minnows (*Pimephales promelas*) and young-of-the-year bluegills (*Lepomis macrochirus*) in a mobile laboratory. For each test, sodium hypochlorite was dosed intermittently (for 1 hour at the beginning of each 24h interval) into a flow-through system using water from a reactor cooling reservoir as dilution water. The six test concentrations, as TRC and FAC, were measured at 10-minute intervals for the 2 hr per day that toxicant residuals were measurable. In the two studies, in the chamber receiving 100% biocide solution, FRC (the FAC measured after the reaction) contributed 50-70 and 83.2% to TRC during the 30 minute periods of maximum exposure. The lowest 96h LC50s, determined as intermittent exposure mean, was calculated as 0.08 mg/l for juvenile fathead minnow exposed to 27.7°C.

Tsai *et al.* (1990) exposed three species of fish (*Cyprinus carpio*, *Dorosoma petenense* and *Gambusia affinis*) of different age classes to sodium hypochlorite in a flow-through exposure system for one hour and evaluated the toxic effects 48h after exposure (fish) and 3 days after fertilization (eggs). *C. carpio* fertilized eggs were far less sensitive than later development stages (one-d-old eggs LC50 = 140 mg/l; 1 week-old prolarvae LC50 = 0.33 mg/l) but hardened fertilized eggs were much less sensitive than 1-h soft eggs (10-h-old eggs LC50 = 158 mg/l; 1-h-old (soft) eggs LC50 = 54). Sensitivity of *D. petenense* was slightly lower than that of *C. carpio*: LC50=0.260 mg/l for prolarvae. For *G. affinis* the sensitivity varied over the first year of life: the LC50 was 0.61 mg/l and 1.28 mg/l for 1 week-old postlarvae and 1 year-old young, respectively.

A toxicity testing system was developed by Mattice *et al.* (1981a) to test the effects of sodium hypochlorite, dosed for 30 and 60 minutes, to the fish *Gambusia affinis*. The LC50, determined after 48 hours, was 1.59 and 0.84 mg/l, respectively.

The reliability of the above mentioned studies is good because they are all well described, but they are judged not adequate to retrieve an LC50 useful for the assessment of short-term toxicity because they would underestimate the toxicity from a continuous exposure (e.g. 96h LC50). The effect of the exposure regime on toxicity has also been observed in invertebrates: oyster larvae survival under intermittent chlorination was much higher than continuous chlorination (Roberts *et al.* 1975). Nevertheless, these data are retrieved as useful supportive information because they mimic the short-term exposures expected in some scenarios and give an idea of the potential of sodium hypochlorite to produce acute effects in fish.

Long-term toxicity

The long-term toxicity to four standard fish species has been investigated by Hermanutz *et al.* (1990) in two field studies under flow-through conditions, lasting up to 134 days. In the first study, 3 chlorine concentrations were tested with one or two replicate fish pools; in the second study, only two concentrations with no replicates were tested. In all experiments, no effect on survival was observed in any species up to 183 µg/l TRC. In the first experiment, a concentration-effect relationship, although partial, was observed only for the growth endpoint in channel catfish. At the highest concentration tested (52 and 183 µg/l), the mean weight decreased by 25% and 34%, respectively, whereas at the immediately lower concentration (5 µg/l) it was equal to that of the control group. In the second experiment, growth reduction in the same species was observed only at 162 µg/l (37% reduction) but no effect at 53 µg/l. The experiment was not conducted under standard conditions, no statistical analysis of data was carried out by the authors to identify the NOEC or LOEC, and raw data do not allow the estimation of any endpoint useful for the assessment. Therefore we cannot derive any valid endpoint, but considering that 25% effect is biologically significant we can consider the NOEC for growth 5 µg/l and use it as an indication of the long term toxicity.

3.2.1.1.2. Invertebrates

Short-term toxicity

Several invertebrates belonging to different phyla (arthropods, mollusks, annelids) have been tested for sensitivity to sodium hypochlorite. Valid data were found only for crustaceans.

Taylor (1993) tested the acute toxicity of various forms of free and combined chlorine to *Ceriodaphnia dubia* in standard 24h toxicity tests, carried out under static and flow through conditions. Sodium hypochlorite was tested at pH 7 for HOCl (70% HOCl and 30% OCl⁻) and pH 8 for OCl⁻ (80% OCl⁻ and 20% HOCl). In static tests the decay of free chlorine was very rapid (1 minute and 7 hours in tests with or without food, respectively) and the results were not considered valid. Flow-through tests (without food) were carried out to maintain a constant concentration over the exposure time. The toxicity of free chlorine in these tests was much higher: 5 and 6 µg/l for HOCl and OCl⁻, respectively. These data were judged valid with restriction (rated 2) because the test concentrations were calculated from measured chlorine concentration of the stock solution and dilution ratios, the number of concentrations/replicates are not specified, the performance of the controls not mentioned, and the 24h LC50s determined by graphical interpolation.

Available data for other organisms were judged not valid, either because of lack of analytical measurements (associated with static/semi-static conditions) or the very short exposure regime (30-60 min.).

Long-term toxicity

The long-term toxicity of hypochlorite to invertebrates has been tested on bivalve mollusks. These organisms are selected as test species because they are biofouling organisms which need to be controlled. They also play an important ecological role in nutrient cycling and as a food source but are not among the most sensitive species.

Martin et al. (1993) measured mortality in *Dreissena polymorpha* exposed in a static test at 21 °C for 20 days in a darkened environment to minimize photolytic loss of sodium hypochlorite. The LC50 after 11 days was about 1 mg/l and remained practically unchanged at the end of the experiment. At 0.5 mg/l mortality was <10% after 20 d; this was the highest concentration with no significant effects, so that it can be considered as NOEC. The same authors (Martin et al., 1993) carried out a longer test at 12 °C, using the same experimental procedure. After 15d exposure at 1 mg/l 50% mortality occurred and at the end of the experiment (29d) it reached 70%. No NOEC has been calculated. In these studies the actual exposure chlorine concentrations are likely to be over-estimated: concentrations were measured and maintained by daily adjustments, but authors did not measure the decay curve and do not specify if initial or average concentrations were used in the endpoint calculation. We do not consider these data adequate for risk assessment because the toxicity is likely underestimated, also in consideration that the pulse dosing conditions allow a recovery of animals, in contrast to flow through conditions. The results of other tests with *Dreissena* (Klerks and Fraleigh, 1991, see below) support this reasoning.

Ramsay et al. (1988) carried out a field study to measure the time required for continuous chlorination (with sodium hypochlorite) to produce 100% mortality in adult *Corbicula fluminea* (asiatic clam). The TRC was continuously monitored during the flow-through test. At the lowest concentration (0.05 mg/l), 100% of the clams died after 36d exposure. From the effect-time curve we estimated that 50% clams were dead after 8d.

Klerk and Freileigh (1991) investigated the long-term toxicity of NaOCl to zebra mussel (*Dreissena polymorfa*) in a number of tests (28d, static renewal and intermittent exposure; 28 and 56 d flow-through), carried out using natural water at different temperatures. In the longer flow-through test, after 56d exposure to the lowest tested concentration (0.08 mg/l as free chlorine), the mortality reached 55%. At this concentration, 86% reduction in the filtering frequency was observed, but this effect was not concentration related. For the three treatments (0.08, 0.26, 1.35 mg/l of free Cl₂) the LT50 values ranged from 16 to 54 d.

The study by Kilgour and Baker (1994) was designed to evaluate the influence of many variables (season and place of animals' collection and experimental protocol) on the toxicity of sodium hypochlorite to *Dreissena polymorfa*. The test lasted 9 d, during which zebra mussels were exposed in a static system to 5 hypochlorite concentrations that were adjusted daily. The LC50 was calculated using average concentrations estimated on the basis of decay curves. The most sensitive mussels were those collected in late summer, whose 9d LC50 was about 0.5 mg/l (as TRO). It is worth noting that this concentration corresponds to the NOEC in the experiments of Martin et al (1993a). The study by Kilgour and Baker is reliable but no NOEC can be derived; it can only be retrieved the LC50 as an indication of long term toxicity (supportive information).

The studies by Ramsay et al. (1988), Klerks and Fraleigh (1991), and Kilgour and Baker (1994) are well conducted and described but no NOEC/LOEC is reported or can be derived. The end points provided cannot be used as such for risk assessment, the information gained only provides an indication of long term toxicity for an invertebrate species, which, it is important to consider, is neither a standard species nor one of the most sensitive. We used these results as supportive information (rated s).

3.2.1.1.3. Algae

Standard studies with algae have not been found in the literature searched.

Short-term toxicity

The short-term toxicity of hypochlorite to freshwater algae has not been widely studied. Data are only available on the aquatic toxicity of hypochlorite to *Chorella sorokiniana* specifically (Kott and Edlis, 1969) and phytoplankton generally (Brooks and Liptak, 1979).

Kott and Edlis (1969) ran a short-term test with *Chlorella* to determine the concentration needed to inhibit its growth. One litre *Chlorella* solutions (containing 225 cells/mm³) were maintained at 28-32°C for a 20 hour exposure (in the dark) to two concentrations of hypochlorite. The concentrations of chlorine were measured by amperometric titration and were initially 0.2 mg/l and 0.6 mg/l - these were checked and readjusted after 8 hours of contact (no information is given about the decay curve or concentration maintenance at the end of the test). The data were presented as % kill of algae after 20h: at 0.2 mg/l the % kill was 26.8%, whereas at 0.6 mg/l the % kill was 43.0%. The test report does not provide sufficient information and the test methodology does not meet the requirement for a valid test.

The study by Brooks and Liptak (1979) reports the results of a 30 minutes static test. The endpoint measured was chlorophyll *a* depletion. The experimental conditions are not sufficiently described (not valid).

Long-term toxicity

Data on the long-term effect of sodium hypochlorite to algae can be drawn from laboratory microcosm and field mesocosm studies (see below). The study of Cairns et al. (1990) on the periphytic community indicated a 7d NOEC=3 µgTRC/l for the measure of algal biomass; the 28d laboratory microbial microcosm test (Pratt et al., 1988) produced supportive information of significant reduction of chlorophyll *a* (about 50%) at 2.1 µgTRC/l of; from the field mesocosm test (Pratt et al., 1988) a 24dNOEC= 79 µgTRC/l for chlorophyll and number of algal genera was obtained.

3.2.1.1.4 Laboratory Microcosm Study

Cairns et al. (1990) used a laboratory multispecies microcosm to study the chronic effects of chlorine (alone or together with ammonia) to naturally derived periphytic communities exposed for 7 days to sodium hypochlorite in a flow-through system. Sodium hypochlorite concentration was expressed as TRC; FAC accounted for 73 ± 19.9%. Chlorine was tested at nominal concentration of 6 and 60 µgTRC/l. Mean measure TRC were 6.3 ± 3.9 µg/l and 56.6 ± 24.5 µg/l in the low and high treatment respectively. The reduction in protozoa species richness was statistically significant (LOEC) at 6 µgTRC/l, while for a reduction of 20%, considered biologically significant, a concentration of 2.7 µgTRC/l was calculated. At 6 µg/l the composition of protozoa communities (number of taxa) changed significantly; since the effect was about 10% we can calculate for this endpoint a NOEC (LOEC/2) = 3 µgTRC/l. The results from this study are interesting because protozoa represent a group with a great diversity in physiology and function; data were judged reliable and relevant but rated 2 because a non-standard test system was used. Non-taxonomic responses were also measured. In vivo fluorescence, used as an index of algal biomass, was significantly reduced (22%) at 6 µgTRC/l (the lowest tested concentration). This data can be used to calculate a NOEC = 3 µgTRC/l as an indication of long-term toxicity to algae.

Pratt et al. (1988) carried out a 28 day laboratory microcosm study in freshwater with the purpose of investigating the effects of chlorine on the structure and function of a microbial community developed on artificial substrates and derived from naturally

colonized substrates. Six test solutions were delivered continuously to polyethylene test chambers, where the TRC was determined by titration three times a week (virtually all chlorine was present in its free form i.e. FAC = 100%). Nominal chlorine concentrations were 3, 10, 30, 100, 300 $\mu\text{gTRC/l}$; the corresponding analytical measurements were 2.1, 6.1, 25, 100, 308 $\mu\text{gTRC/l}$. The measured taxonomic parameter was the number of protozoan species and the non-taxonomic responses included chlorophyll *a* (expression of algal biomass), ATP, total protein, extracellular alkaline phosphatase activity, and potassium. The results from both types of parameter were analysed using standard statistics.

The lowest NOEC was calculated for the number of protozoan species and for depression of alkaline phosphatase activity (28d NOEC = 2.1 $\mu\text{g TRC/l}$). The latter response likely reflects the toxicity to bacteria. This study is rated 2 because the test is non-standard.

As far as chlorophyll *a* is concerned, a reliable NOEC cannot be derived because a clear concentration-effect relationship is lacking. However, this appeared to be the most sensitive endpoint, as a significant reduction of chlorophyll *a* (about 50%) was recorded at 2.1 $\mu\text{g/l}$ of TRC (the lowest tested concentration). We can keep this data as supportive information.

3.2.1.1.5 Field Mesocosm Study

Another study on the microbial community was carried out in outdoor enclosures by the same researchers (Pratt et al., 1988). Each enclosure consisted of a 130L polyethylene bag containing lake water and littoral sediment, which provided immigrating pelagic and benthic microorganisms for the colonization of the artificial substrates added. In the enclosures chlorine was introduced as a daily pulse, and decay curves were used to estimate the average chlorine concentration over a 24 h period. The substrates were examined once a week for protozoan species and algal genera. At the end of the exposure period (day 24) the water was sampled for zooplankton enumeration (filtered with a Wisconsin plankton net n. 10) and substrates were sampled for non-taxonomic measures (chlorophyll *a*, total protein, alkaline phosphatase activity) and microscopic examination.

In the 24 d field test, both taxonomic and non-taxonomic parameters showed lower sensitivity than in the laboratory test, likely due to differences in test design (water, source of species and, most important, method or chlorine application). The authors comment that "Possibly the timing of dosing could have maintained communities in a constant state of recovery and therefore made them appear less sensitive to chlorine stress". At 79 $\mu\text{g TRC/l}$, neither chlorophyll *a* nor the number of algal genera was reduced (NOEC). Protozoan species number was not significantly reduced at the lower test concentration, i.e. NOEC = 24 $\mu\text{gTRC/l}$. The most sensitive endpoint was the zooplankton density (24d NOEC = 1.5 $\mu\text{gTRC/l}$). Anyhow, the authors report only the number of zooplankton/ml of water without providing any other information about the effects on taxonomic composition of zooplankton community, so that it is not possible to draw any conclusion about the eventual elimination of taxa from the system. Also the potential for system recovery was not evaluated. In this study FAC

concentration accounted for 100% of the measured TRC so that the above endpoint can be expressed also as µgFAC/l.

Because of the uncertainty associated to the most sensitive endpoint and likely underestimation of toxicity due to the pulse dosing system, the results of this test should be interpreted with caution. This conclusion is supported by the comparison of the long term zooplankton NOEC from this test (24d NOEC = 1.5 µgFAC(or TRC)/l) with the laboratory short-term toxicity to daphnia (24h LC50 = 5 µgFAC/l) which suggests that a continuous long term exposure of 1.5 µgFAC/l might dramatically affect daphnia populations. For these reasons data from this study are not considered valid for the assessment, but have been used in the final discussion as supportive information (rated s).

3.2.1.1.6. Summary of data used

The data selected for the determination of the PNEC for freshwater organisms is shown in Table 3.9.

Table. 3.9 Summary of ecotoxicity data selected for the determination of the PNEC for freshwater organisms

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

			(rated 2) 1.5 µg FAC/l (FAC 100%)	
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FAC (free available chlorine); TRC= total residual chlorine; *FAC as HOCl
rates: 1= valid; 2= valid with restriction; s= supportive information

3.2.1.2. Brackish and sea water

3.2.1.2.1. Fish

Short-term toxicity

The short-term toxicity of chlorinated salt water has been tested on many estuarine and marine fish species in bioassays conducted at different exposure regimes, from a single pulse dose of few minutes to a continuous 96 hours standard exposure. Data valid for the assessment were retrieved from the papers by Bellanca and Bailey (1977), Thatcher (1978) and Roberts et al. (1975).

Bellanca and Bailey (1977) evaluated the short-term toxicity of chlorine to the estuarine fish *Leiostomus xanthurus* (ocean spot) in a flow through laboratory experiment, using a continuous flow serial diluter fed with river water. The authors calculated a **96h-TLm** (equivalent to an LC50)= **0.090 mg/l** of TRC, which consisted principally of free chlorine. This data is rated 1.

Thatcher (1978) conducted many laboratory flow-through bioassays on 8 species of estuarine and marine fish, belonging to different families including salmonidae, clupeidae and percidae. Since the main purpose of the study was to investigate the impact of chlorinated effluents from power plants, fish were simultaneously exposed to sodium hypochlorite and to a 5°C thermal stress. The 96h LC50 ranged from 0.032 mg/l (as TRO), for the most sensitive species (*Oncorhynchus kisutch*), to 0.167 mg/l (*Gasterosteus aculeatus*). These data were considered relevant for the assessment because heat is usually associated to chlorine in power plants effluents, but they were rated 2 because the authors report that in a previous study the addition of thermal stress resulted in a toxicity higher than chlorine alone and, moreover, LC50 was calculated pooling data from different tests.

Roberts et al. (1975) tested the toxicity of continuous exposure of chlorinated river water (salinity 20‰) to three estuarine fish species. The lowest LC50 was calculated for *Menidia menidia*: **96h LC50= 37 µg/l** (as TRC). This data was judged valid with restriction because Ca(OCl₂) was applied as chlorine source and some information on the experimental procedure is lacking.

Middaugh et al. (1977) tested the toxicity of chlorinated brackish pond water to early-life stages of *Morone saxatilis* in a flow-through test. Only data relative to eggs hatchability could be retrieved. A rough estimate of the 48h LC50 = 8 µg/l TRC was calculated by us using the authors' raw data relative to percentages of hatched eggs per test concentration. This data can be used as indicative information of eggs sensitivity.

Long- term toxicity

For the evaluation of long-term toxicity to estuarine fish, the searched literature provided one fully valid data. Goodman et al. (1983) developed a method for testing the early-life stages of *Menidia peninsulae*, an estuarine fish of the Atherinidae family. They carried out a 28d test starting with 36h old eggs, under flow through conditions using natural seawater diluted with freshwater to a 20‰ salinity, and measured the effects of sodium hypochlorite on eggs survival and fry survival and growth. Fry were the most sensitive stage. The authors calculated a **NOEC (fry survival)= 0.04 mg CPO/l** (CPO is to be considered analogous to TRC measured by other authors in saline waters), concentration at which only 5% of fish died. At this concentration no sublethal effects were evident. The results of this test are considered fully valid (rated 1).

One prolonged field study has been carried out by Liden et al. (1980) on two different estuarine fish species *Brevoortia tyrannus* and *Leiostomus xanthurus* exposed to chlorinated condenser cooling effluents for 19 and 20 days, respectively. All experiments were carried out in long troughs system where discharge waters, at three levels of chlorination, were continuously pumped, with inflow rates maintained at 0.038 l/s to simulate cooling water retention times observed in the plant's discharge canal. Up to the highest concentration (62 µg/l as TRO) a negligible mortality occurred among *B. tyrannus*, whereas at all TRO concentrations, the survival of *L. xanthurus* was significantly lower than that of control fish. At the lowest concentration (14 µg/l) mortality occurred in 26% of animals but, because of the lack of a clear concentration-effect relationship, no NOEC or EC10 can be calculated or extrapolated. These data are therefore not usable for assessment.

3.2.1.2.2. Invertebrate

The acute toxicity of sodium hypochlorite to saltwater invertebrates has been widely studied with many organisms, including rotifers, mollusks, crustaceans and worms, but data adequate for the assessment are available only for a few classes.

Thatcher (1978) tested seven species, including shrimps, mysids, amphipods and crabs, in flow through apparatus where animals were simultaneously exposed to chlorinated unfiltered seawater and 5°C thermal stress to mimic a common scenario in the real environment. The most sensitive species was the shrimp *Pandalus goniurus* for which a **96h LC50= 90 µg/l** was calculated pooling data from different tests. These data have been rated 2 because of data pooling and, above all, because the additional thermal shock might have influenced the sensitivity to sodium hypochlorite.

Very short-term exposure to pulse chlorination, with and without thermal stress, has been evaluated by Capuzzo and coworkers (1976, 1979a,b), who conducted flow-through bioassays with *Brachionus plicatilis*, *Acartia tonsa*, and larvae of *Crassostrea virginica* with exposure periods of 30-60 minutes at various temperatures. In bioassays performed at acclimation temperatures, lethality (measured after 48 h after exposure) was LC50= 820, 180 and **120 µg/l**, respectively. For all species tested,

except the copepods, the thermal stress showed a synergistic effect with residual chlorine concentration, lowering LC50 values down to **10 µg/l** ($\Delta T=7.5^{\circ}\text{C}$) for *B. plicatilis* and **80µg/l** ($\Delta T=5^{\circ}\text{C}$) for *C. virginica*.

Four invertebrate species were tested by Roberts et al. (1975) using estuarine river water, chlorinated by addition of $\text{Ca}(\text{OCl})_2$ in flow through or static systems. When static systems were used the TRC concentrations were kept as stable as possible by constant addition of the chemical and average values were used to calculate the endpoints. The lowest lethal concentrations to be used as supportive information are extrapolated values for *Mercenaria mercenaria* larvae (**48h TL50=1 µg/l TRC**, in the static test) and *Crassostrea virginica* juveniles (**96hEC50(shell deposition)=23 µg/l TRC**, in the flow through test). The authors report that when oyster larvae were exposed intermittently (manual additions at 6-8h intervals) the 48h LT50 was 0.11 mg/l, i.e. two orders of magnitude higher.

In later experiments Roberts and Gleeson (1978) observed a similar toxicity in oyster and copepods continuously exposed for 48 hours to $\text{Ca}(\text{OCl})_2$ in flowing estuarine river water. For *Crassostrea virginica* larvae the **48EC50** was **26 µg/l** and for adults of *Acartia tonsa* the lowest **48hLC50** was **29 µg/l** as residual chlorine measured amperometrically. In the absence of other, more reliable studies with the relevant chemical species (sodium hypochlorite) it was decided to use these data, because they provide valuable information for the toxicity assessment of chlorinated natural water, and assigned these data the rate 'valid with restriction' because of the different parent compound.

The range of acute toxicity of chlorinated seawater to invertebrates appears therefore to span almost two orders of magnitude.

Long-term toxicity

In the scientific literature, three studies investigating the long-term toxicity of sodium hypochlorite have been found. In a field study on chlorinated condenser cooling effluents using mollusk bivalves (Liden et al., 1980), the survival of oysters (*Crassostrea virginica*) and clams (*Rangia cuneata*) maintained at three TRO concentrations for 15 days was not affected at concentration as high as 62 µg/l, while oyster mean shell deposition was significantly reduced in the treated animals. At the lowest test concentration (14 µg/l) a 14% reduction in shell deposition was observed, so that **following TGD the NOEC can be estimated as LOEC/2**, i.e. **7 µg/l**. This data is rated 2 because it was obtained from a non-standard test.

Scott and Middaugh (1977) examined the lethal and sublethal effects of chlorine to adult oyster (*Crassostrea virginica*) during seasonal chronic exposures (45-75 days) to incoming estuarine sea water, whose temperature, pH and salinity was naturally fluctuating. Survival was reduced at relatively high concentrations of Chlorine-Produced Oxidants (CPO); a rough estimate is $\text{LC}_{10}\cong 160$ µg/l CPO on the basis of the concentration-effect curves. On the other hand, severe sublethal effects (mean condition index and gonadal index) were observed also at the lowest tested concentration (140 µg/l CPO), so that the NOEC for these effects would be expected

to be $\ll 140 \mu\text{g/l}$ CPO. Because of the lack of a clear endpoint, these data cannot be used in risk assessment.

In another experiment conducted in summer Scott. *et al.* (1979) found that mortality of *C. virginica* was not significantly reduced at $110 \mu\text{g/l}$ but the high mortality observed in the control make this result unreliable. At the same concentration marked sublethal effects were observed, but no direct concentration-effects relationship was found (not valid data).

3.2.1.2.3. Algae

Phytoplankton

Short-term toxicity

Data on short-term toxicity to algae were retrieved from the literature but they were not considered adequate for the effects assessment of sodium hypochlorite.

The effects of chlorine to three phytoplanktonic algae species were tested by Videau *et al.* (1979) in static tests with filtered sea water, aimed to evaluate a number of variables. The most sensitive species was *Dunaliella primolecta*, for which a initial dose of $400 \mu\text{g/l}$ TRO caused 50% mortality in 24 hours. After 3 hours from dosing, free chlorine had disappeared in chlorinated water below $500 \mu\text{g/l}$. Based on their experimental results, the authors extrapolated that in a natural medium, having a population of 1 cell/ml, mortality would reach 65% after 24 h exposure at $200 \mu\text{g/l}$.

Gentile *et al.* (1976) report the Cl_2 concentrations causing 50% growth reduction in a series of 24 h static tests on 11 phytoplanktonic species; the LC50 ranged from 75 to $330 \mu\text{g/l}$. Only the highly concentrated stock solution was measured. Other tests performed on the diatom *Thalassiosira pseudonana*, using different exposure times up to 20 minutes showed that, 48h after exposure to $200 \mu\text{g/l}$ chlorine, growth was reduced by about 60%.

These effect concentrations very likely underestimate the toxicity following a continuous exposure.

Long- term toxicity

Long-term toxicity data for algae were not found.

Sanders *et al.* (1981) studied the effects of prolonged chlorination on natural marine phytoplankton communities cultivated in large tanks under flow through conditions (semi-field test). To achieve measurable concentration in the exposure tanks, HOCl was added by single daily additions directly to the tanks, where it degraded within 2 hours (an intermittent exposure was therefore resulting). A 50% reduction in cell density (the most sensitive endpoint) was observed in the 21 day test at concentrations as low as **1-10 $\mu\text{g/l}$ TRC**. These data provide evidence of the severe impact of free

chlorine on phytoplankton at very low concentrations, even at intermittent exposure (data used as supportive information).

Microcosms

Long- term toxicity

Erickson and Foulk (1980) used outdoor and indoor flow-through systems to evaluate the effects of continuous chlorination (1 year) on entrained estuarine plankton communities consisting of eggs, larvae, algae and juveniles (not better specified). NaOCl was continuously applied at dose levels of 125 to 1441 µg/l, which resulted in concentrations of residual chlorine in the systems below the detection limits of the amperometric analyzer used (**10 µg/l**). In all treatments a reduction of ATP, measured as indication of biomass, was observed (from 13% to 58%). This result is used as supportive information.

3.2.1.3 Summary of Ecotoxicity Data Selected for the Determination of the PNEC for Brackish and Sea Water Organisms.

The valid and supporting data discussed in sections 3.2.1.2.1 to 3.2.1.2.3, which are acceptable for use in the determination of the PNEC for brackish and sea water organisms are collected in Table 3.10.

TABLE 3.10 SUMMARY OF ECOTOXICITY DATA SELECTED FOR THE DETERMINATION OF THE PNEC FOR BRACKISH AND SEA WATER ORGANISMS

SHORT-TERM TOXICITY				
	Valid data		Supportive information	
	Endpoint	Study Details/Reference	Endpoint	Study Details/Reference
Fish	96hLC50 = 32µg TRO/l (rated 2)	Thatcher, 1978	48hEC50 = 8µg TRC/l	(eggs) Middaugh et al., 1977
Fish	96hLC50 = 90µg TRC/l (rated 1)	Bellanca and Bailey, 1977		
Crustaceans	-	-	-	-
Mollusks	48h EC50 = 26µg TRC/l (rated 2)	Roberts and Gleeson, 1978		
Algae	-	-	-	-
LONG TERM TOXICITY				
	Endpoint	Study Details/Reference	Endpoint	Study Details/Reference
Fish	28d NOEC =	(fry survival)		

	40 µg CPO /l (rated 1)	Goodman et al., 1983		
Crustaceans	-	-	-	-
Mollusks	15d NOEC = 7 µg TRO/l (rated 2)	(shell deposit) Liden et al., 1980		
Algae	-		21d EC50 = 1-10 µg TRC/l	(periphytic community, intermittent exposure) Sanders et al., 1981
Phyto and Zoo- plankton	-		1y EC50 < 10 µg TRC/l	(biomass reduction) (microcosm study) Erickson and Foulk, 1980

TRO =Total residual oxidant

TRC= total residual chlorine

CPO = Chlorine-produced oxidants

rates: 1= valid; 2= valid with restriction; s= supportive information

3.2.1.4. Micro organisms used in Sewage Treatment

Despite the strong antimicrobial potential of hypochlorite, concern for inhibition effects on biological sewage treatment at the current hypochlorite utilization pattern is undue. Activated sludge flocs are not very sensitive to NaClO, probably due to protection by their glycocalix made out of polysaccharides.

The EC50 for the inhibition of activated sludge respiration is situated around 3000 µg/l for a continuous hypochlorite dosage, with a LOEC of ca. 375 µg/l (Raff et al., 1987). The sludge concentration used and the pH were not mentioned in the paper. The result obtained is very much dependent on the sludge concentration used (i.e. the organic content in the test vessel). Therefore the figure mentioned is just a figure and different data will be obtained using different sludge concentrations. Also different pH values will probably generate different data. The tentative LOEC of 375µg/l derived by the authors should only be used as an indication for potential effects on a sewage treatment plant with the limitations mentioned before (Raff *et al.*, 1987).

Nitrifying bacteria were found to be somewhat more sensitive to hypochlorite than the average sludge organism. Marstaller et al. (1992) reported a decrease of nitrifying activity as of batch doses of 1500 µg NaClO/mg sludge suspended solids.

3.2.1.5. Conclusion and PNEC Determination

In the scientific literature of the last 30 years, a great number of short and long term aquatic toxicity studies on sodium hypochlorite, conducted with fresh and saltwater organisms belonging to all trophic levels, have been found. In Appendix 3, for each study, details on experimental conditions and test results are reported for fish, invertebrates, algae and microorganisms. Nevertheless, after their evaluation following the criteria indicated in the European Commission TGD, the number of valid data judged adequate for risk assessment were drastically reduced because many of them did not meet the validity criteria specified at the beginning of this chapter. In spite of the high number of studies conducted, only a few provide reliable information useful for the assessment. This because most of the studies were carried out in the 70's and 80's and were tailored to answer specific questions such as, for example the efficacy of sodium hypochlorite as biofouling agent, the effect of temperature stress and/or of intermittent exposure of very short pulse additions of hypochlorite. Hence, their evaluation is not straightforward. From many of these studies, although good and reliable, we were not able to retrieve the proper end-point requested for derivation of PNEC (e.g. the NOEC for long-term studies), so that, following the TGD indications, they were used as additional information in support of valid toxicity data (rated 1 or 2) used in the PNEC calculation. In addition, it should be noted that none of the evaluated experiments were conducted according to GLP, due to the fact that most of them were carried out long before the requirements of the Directive 87/18/EEC. The ecotoxicity data considered adequate for the effects assessment of sodium hypochlorite in fresh water and salt water have been summarised in Tables 3.6 and 3.7, respectively. Short and long term toxicity data are available for microorganisms, algae, invertebrates and fish but not equally distributed between fresh and saltwater environments. The evaluation and comparison of toxicity data are made difficult by the complexity of sodium hypochlorite chemistry in water and by the different analytical methods used to measure its concentration. As reported in previous chapters, TRC is a measure of both free and combined chlorine (such as chloramines). It is difficult to separate the contribution to toxicity of the free available chlorine such as HOCl/OCl from that of the combined chlorine species. Also, the relative amounts of the different chlorine species will be different for each test, due to pH and other medium related effects, test duration and ammonium level effects, etc. For those studies where the percentage of FAC out of the TRC had been measured and reported the toxicity endpoints have also been expressed as concentration of FAC/l (table 3.6). In chlorinated salt water, toxicant concentration is often expressed as Total Residual Oxidant (TRO) or Chlorine Produced Oxidants (CPO), which include, in addition to free end combined chlorine, also other oxidative products. This makes the assessment task and the comparability of fresh and salt water toxicity data even harder.

In the following we summarise the results for the two aquatic habitats and attempt to derive the respective PNECs.

3.2.1.5.1 Freshwater

Available freshwater toxicity data, considered for PNEC calculation are summarized in table 3.6. For short term toxicity valid acute data are available only for invertebrates (daphnia 24 h LC50 = 5 µgFAC/l). In the searched literature, adequate standard acute tests with fish are surprisingly lacking, as in preference many reliable studies have been performed under intermittent exposure. From these latter studies, the trout was shown to be the most sensitive

species; three 40 minutes pulses per day produced an LC50 = 60 µgTRC/l after 96h and an LC50 µg/l = 33 µgTRC/l after 168h. As the intermittent exposure regime is known to have a lower impact on animals, permitting a certain degree of recovery, than continuous exposure, we can expect that the 96h LC50 for fish, exposed in a standard test, would be << 60 µgTRC/l. For algae the very few data examined were judged not valid.

For long-term toxicity, no valid NOEC values from standard long-term tests on freshwater species are available. Anyhow, results from a microcosm study on periphytic community provide a NOEC for algae which can be used for the assessment: 7d NOEC = 3 µgTRC/l, corresponding to 2.1 µgFAC/l. There are supportive data from another microcosm study showing that a 28d exposure to the same hypochlorite concentration causes 50% reduction in algal biomass (28d EC50 = 2.1 µgFAC/l). For fish there are supportive information from a field study indicating a 134d NOEC ≥ 5 µgTRC/l, i.e. fish appear less sensitive than algae after long term exposure. Proper data on crustaceans (*Daphnia*) are lacking. The results of a mesocosm study, although for the reasons discussed above (par. 3.2.1.1.5) do very likely underestimate the long-term toxicity of sodium hypochlorite, they do provide indication that zooplankton density (24d NOEC = 1.5 µgTRC (or FAC)/l) is an endpoint much more sensitive than algal or chlorophyll *a* reduction (24d NOEC = 79 µgTRC (or FAC)/l). Supportive information on bivalves only suggest for this group a NOEC <<50 µgTRC/l.

The TGD gives guidance on which assessment factors should be applied to derive a PNEC when different kinds and types of data are available. From table 3.6 it can be seen that the minimum data set required (at least one short-term L(E)C50 from each of three trophic levels) is not met so that it is not possible to determine which trophic level is the most sensitive. Long-term valid (with restriction) data are available for one trophic level, i.e. primary producers (algae). Indications of long-term toxicity to fish and molluscs suggest that these groups are less sensitive than algae.

3.2.1.5.2 Saltwater

In table 3.7 toxicity data adequate for risk assessment have been listed together with supportive data. Valid short-term toxicity data have been collected for molluscs and fish, which show a similar sensitivity: 48h EC50 = 26 µgTRC/l and 96h LC50 = 32 µg TRO/l, respectively. Supportive information indicate that acute toxicity is higher for fish eggs: 48h EC50 = 8 µg TRC/l. No data for crustaceans or algae are available, so that it is not possible to determine which trophic level is the most sensitive in short-term tests.

For the same groups, molluscs and fish, long-term toxicity data have also been found. Molluscs (15d NOEC = 7 µgTRO/l) are more sensitive than fish fry (28d NOEC (fry survival) = 40 µgCPO/l) For crustaceans and algae, adequate data for risk assessment are again not available. Anyhow a study conducted on periphytic community under intermittent exposure provides a 21d EC50 laying between 1 and 10 µgTRC/l, suggesting that following continuous exposure the NOEC for algae is likely to be lower than that.

3.2.1.5.3 PNEC derivation

Considering the aspecific mode of action of sodium hypochlorite, which is a strong oxidizer, and the recommendations given in the TGD (final version May 2002), short- and long-term toxicity data for fresh and saltwater organisms have been pooled. In this way a set of three valid NOEC values is obtained, one for each trophic level: fish, molluscs and algae.

Freshwater

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

Based on these considerations a factor of 10 for the derivation of the PNEC is judged not sufficiently protective and we suggest to apply a factor of 50 to the lowest NOEC: $PNEC = 3 \mu\text{gTRC/l}/50 = 0.06 \mu\text{gTRC/l}$ corresponding to $2.1 \mu\text{gFAC/l}/50 = 0.04 \mu\text{gFAC/l}$.

Saltwater

When, after pooling the data from fresh and salt water the dataset consists of two long-term NOECs representing two trophic levels (e.g. algae and fish) plus a NOEC from an additional marine taxonomic group (e.g. molluscs), as it is the case in the present assessment, the TGD recommends that a factor of 50 is applied to the lowest figure. Hence, $PNEC_{\text{saltwater}} = 3 \mu\text{gTRC/l}/50 = 0.06 \mu\text{gTRC/l}$ corresponding to $2.1 \mu\text{gFAC/l}/50 = 0.04 \mu\text{gFAC/l}$.

Conclusive remarks

In those scenarios (e.g. discharge of power plant cooling effluents), where the release of chlorinated effluents is often associated with an increased temperature, the assessment of potential impact of NaOCl should take into account the synergistic effect that a thermal stress may have with residual chlorine as demonstrated in many studies specifically designed to simulate real environment scenarios.

3.2.1.6 Halogenated organic by-products

3.2.1.6.1 *Identifiable reaction products*

i) Trihalomethanes

The draft Risk Assessment for chloroform (Chloroform Risk Assessment, 2007) estimates a PEC regional_{water} = 0.268 µg/l in surface water (see section 3.1.2.2) and a PNEC_{aquatic} of 146 µg/l (see section 3.2.1.4).

In most situations the dominant trihalomethane produced during hypochlorite use is chloroform: only in high bromide situations, such as chlorination of sea-water used for cooling, do the brominated trihalomethanes become major components.

It is beyond the scope of this risk assessment to derive PNECs for the brominated trihalomethanes. However, ecotoxicological data gathered by Khalanski et al (2000) in connection with assessment of seawater chlorination suggest that the ecotoxicities of the brominated THMs are not markedly different from chloroform. The table below highlights some published studies with useful comparative data:

Species, biological stage	Compound	Toxicity mg/l	Reference
Daphnia magna (Freshwater)	Chloroform Bromoform	48 hr LC50 = 29 48 hr LC50 = 46	Le Blanc 1980
Lepomis macrochirus (Freshwater)	Chloroform Bromoform	96 hr LC50 = 13 – 22 96 hr LC50 = 29	Anderson and Lusty, 1980 Buccafusco et al., 1981
Cyprinus carpio (Carp embryos)	Chloroform BDCM DBCM Bromoform	96 hr LC50 = 161 96 hr LC50 = 119 96 hr LC50 = 53 96 hr LC50 = 76	Trabalka et al 1981
Cyprinus carpio (Carp embryos)	Chloroform BDCM DBCM Bromoform	96 hr LC50 = 97 96 hr LC50 = 67 96 hr LC50 = 34 96 hr LC50 = 52	Mattice et al 1981b

In view of the above, it seems reasonable for the purposes of a broad assessment to regard the trihalomethanes as of similar aquatic toxicity and to use the chloroform PNEC for total trihalomethanes.

ii) Haloacetic acids

The OECD SIDS risk assessment arrived at an aquatic PNEC for TCA of 0.17 µg/l based on algal toxicity and a PEC_{regional} of 0.12 µg/l. It has since been accepted by the TM, and by Germany who were the Rapporteurs for the SIDS assessment, that the data is such that an assessment factor of 10 can be used rather than 50 which give rise to a PNEC for TCA of 0.85 µg/l, and this is used here.

For DCA, a PNEC of 0.72 µg/l was already set against based on algal toxicity and using the risk assessment factor of 10 on data for TCA and MCA in the EU Risk Assessment for trichloroethylene. The comparable data for MCA would indicate a PNEC of 0.58 µg/l.

While it is similarly beyond the scope of this risk assessment to derive formal PNECs for other haloacetic acids, a broad assessment can be made, bearing in mind that in all but high bromide situations the TCA and DCA are formed in at least an order of magnitude higher concentrations than MCA or the brominated acids.

Kuhn and Pattard (1990) found the algal toxicity of monobromo- and monochloroacetic acids against *Scenedesmus subspicatus* compared as follows:

Substance	End point	Toxicity µg/l
Monochloroacetic acid	EC50 biomass	28
Monobromoacetic acid		200
Monochloroacetic acid	EC10 biomass	7
Monobromoacetic acid		20
Monochloroacetic acid	EC50 growth	70
Monobromoacetic acid		1400
Monochloroacetic acid	EC10 growth	14
Monobromoacetic acid		100

On this basis, MBA is less toxic than MCA against the most sensitive species for the chlorinated haloacetic acids generally. While the MCA is slightly more toxic than TCA in terms of the PNEC, and DCA has been considered to be intermediate between these, mono and dichloroacetic acids are readily biodegradable and have short half lives in the environment such that there would effectively be no PEC regional. Since the PEC regional for TCA is 0.12 µg/l, it would thus be conservative to treat all haloacetic acids simplistically as being TCA as regards PNEC and PEC regional. Where necessary, all haloacetic acids could thus be considered to have a PNEC of 0.85 µg/l and a PEC regional of 0.12 µg/l.

It is also relevant to calculate a $PNEC_{\text{water intermittent}}$ for the acute swimming pool discharge scenario. Taking the lowest EC_{50} (from the same algal study used to derive the PNEC) of 264 µg/l, and applying an assessment factor of 100 gives a $PNEC_{\text{water intermittent}}$ of 2.64µg/l. As outlined above, it seems reasonable to use this also as a value for total haloacetic acids.

In the risk characterisation, it becomes apparent that there are some specific cases where the PECs exceed the above PNECs by a factor of between 1 and 10, indicating a need for further information. The PNEC for TCA, which is used as an approximation for haloacetics in general, does, however, have some uncertainties:

- The lowest NOEC from which the PNEC is derived is from a single study with a non-standard species of algae *Chlorella pyrenoidosa* (now almost unavailable) using non-standard conditions
- The NOEC (~8 µg/l) is about 30 times lower than the EC_{50} (264 µg/l), possibly due to wide test intervals in this non-standard study. This raises the possibility that a true NOEC could be up to an order of magnitude higher.
- The NOEC and EC_{50} appear out of line compared to that published for other species of algae (Lewis et al 2004), generally being about 2 or more orders of magnitude lower
- The product tested in the study on which the PNEC is based may well have been a commercial pesticide grade product rather than pure TCA. The study was titled “The

effect of pesticides on the growth of green and blue-green algae cultures". No data on source or purity of the test substance are given in the study.

To try to shed additional light on the toxicity of haloacetic acids, a further series of algal toxicity tests have been conducted to current standards under GLP using high-purity TCA (>99.5) and some other haloacetic acids. The tests were conducted on a range of species i.e. two standard species; the now obsolete strain of *Chlorella pyrenoidosa*, obtained from the Institute which conducted the original test; and two other current *Chlorella* species. This additional test data is summarised below:

Table 3.11 Results of algal tests conducted to EU/OECD Guidelines under GLP at Unilever Research Laboratory, Colworth, UK 2005

	Species	72hr EC50 (mg/L)		72hr NOEC (mg/L)		Comments
		Growth	Biomass	Growth	Biomass	
Trichloroacetic acid						
	<i>Pseudokirchneriella subcapitata</i>	16.2	4.9	3.0	3.0	
	<i>Scenedesmus subspicatus</i>	67.9	4.66	3.0	3.0	
	<i>Chlorella vulgaris</i>	>100	>100	100	100	Rangefinder result Concentration range : 0, 0.1, 1.0, 10 and 100 mg/L
	<i>Chlorella pyrenoidosa</i> Str 366	>100	>100	100	100	
	<i>Chlorella kessleri</i>	>100	>100	100	100	
Dibromoacetic acid						
	<i>Pseudokirchneriella subcapitata</i>	5.96	9.8	3.0	3.0	
Sodium dichloroacetate						
	<i>Pseudokirchneriella subcapitata</i>	28.1	1.2	<1	<1	
Monochloroacetic Acid						
	<i>Chlorella pyrenoidosa</i> Str 366	10-100	16.4	10	10	Rangefinder result Concn range: 0, 0.01, 0.1, 1.0, 10 and 100 mg/L 100 mg/L = 63% inhibition of growth rate
	<i>Chlorella kessleri</i>	10-100	13.1	10	10	Rangefinder result Concn range: 0, 0.01, 0.1, 1.0, 10 and 100 mg/L 100 mg/L = 63% inhibition of growth rate

The following comments can be made on this data:

- The data for TCA against *Chlorella pyrenoidosa* conflict with the test on the same strain on which the PNEC is based. The NOEC found in this new standard test is 5 orders of magnitude higher, and the data on the other two *Chlorella* species are similar.
- MCA is more toxic than TCA to these species of chlorella, as would be expected.
- *P. subspicatus*, the standard species we used in the Whole Effluent Test, was 30 times more sensitive to TCA than the *Chlorella* species

- Against *P. subspicatus*, sodium dichloroacetate was more toxic than TCA, and more toxic than dibromoacetic acid, which is the expected ranking of toxicity discussed above.
- Apart from the single study on which the TCA PNEC is based, these data fit well with other published data [Lewis et al 2004, OECD TCA SIDS)

The above findings suggest that the current TCA PNEC may be considerably too low. Since the PNEC value used for DCA is interpolated between TCA and MCA, this may also be too low, and thus the PNEC in this risk assessment for haloacetics too low. The risk assessment could thus be further refined by revision of the TCA PNEC, and reassessment of the interpolated DCA PNEC. It would not be appropriate for this risk assessment to undertake this task but, given that TCA and DCA dominate the haloacetic acids found in effluents from hypochlorite use, there is a limit to the weight that can be given in risk characterisation to the PNEC for haloacetic acids derived above.

iii) N-chloroamino compounds

N-chloramines and amides are likely to be formed in most scenarios as hypochlorite reacts with organic matter that contains amino acids and proteins (see table 3.8a. section 3.1.2.11) Though little eco-toxicity data for these compounds has been discovered, an indication can be obtained using QSARs

The table below shows data obtained using the US EPA EPIWIN prediction software

Predicted properties of aminoacids and their N-chlorinated derivatives as estimated by EPIWIN (v3.11)

Amino acid / N-chloro derivative	SMILES	Log Kow		Measured water solubility mg/L	Predicted toxicity mg/L	
		Predicted	Measured		<i>Daphnia</i> 48h EC50	Algal 96h EC50
L-Alanine	CC(N)C(=O)O	-2.99	-2.96	164000	14860*	5006*
N-chloro-alanine	CC(NCl)C(=O)O	-1.05	N/A	N/A	585000**	307000**
Phenylalanine	NC(Cc1ccccc1)C(=O)O	-1.28	-1.44	26900	2764*	1681*
N-chloro-phenylalanine	O=C(O)C(Cc1ccccc1)NCl	0.66	N/A	N/A	26281**	15211**
Tryptophan	NC(Cc2cc1cccc1[nH]2)C(=O)O	-1.22	-1.44	13400	3152*	1957*
N-chloro-tryptophan	O=C(O)C(Cc1cnc2ccccc12)NCl	0.72	N/A	N/A	27708**	16092**
N-chloro-tryptophan	NC(Cc1cn(Cl)c2ccccc12)C(=O)O	-1.22	N/A	N/A	3684*	2287*

* Aliphatic amines QSAR (acid moiety predictions multiplied by 10) **Neutral Organics QSAR (acid moiety predictions multiplied by 10)

The following comments can be made:

- The small precursor molecules such as amino-acids that are likely to react with hypochlorite in use scenarios tend to be highly water soluble;
- N-chlorinated analogues of these amino acids are predicted to be more hydrophobic, but are unlikely to present a toxicological concern as they have predicted log Kow values that are < 1;
- The QSAR predictions using EPIWIN v3.11 (US-EPA prediction software) show that a selection of N-chlorinated aminoacids have estimated toxicities to *Daphnia* and algae which are much greater than 100 mg/L;

3.2.1.6.2 Whole effluents and unidentified by-products

The range of halogenated organic substances created as minor by-products during reactions of hypochlorite in various use scenarios is inevitably complex and the individual substances are in the main as unidentifiable as the unchlorinated reaction substrates would be, as these are commonly mixtures of proteins, carbohydrates, fats and their metabolic fragments.

Consequently, ecotoxicity studies of these by-product mixtures have often been conducted on whole effluents. Some studies, described above, have examined effluents containing residual chlorine which is rapidly destroyed on entering the aquatic environment, which obscures the potential longer-term toxic effects of more stable halogenated organic by-products.

Some studies have, however, examined effluents where any residual chlorine has been eliminated. For example, tests on fish and invertebrates of domestic laundry bleaching waste waters that had been biologically treated to simulate sewage treatment, leaving maximum AOX concentrations of 250 and 143 µg/l respectively, showed that the residual compounds present gave no observed adverse effects.

A study was undertaken to provide additional information for this risk assessment. The full study report is presented as document Test_045_Env_I5 which forms Annex 7 of this document. In this “WET testing” study, samples of raw settled sewage (RSS) which had not been treated and RSS that had been chlorinated and subsequently dechlorinated (i.e. residual chlorine was removed)(C/D-RSS) were prepared. These samples were then compared to assess whether chlorinated organic by-products formed in the chlorination process were toxic, or potentially bioaccumulable and persistent. Although the primary purpose of the testing was to cover the many minor chlorinated by-products (i.e. other than THMs and haloacetic acids, for which conventional PEC/PNEC calculations have been performed) the effluents also *de facto* contained these principal by-products and provide an additional perspective on their effects.

Chlorination of raw sewage was chosen to be the test conducted first because as outlined in the test protocol agreed with the TM it is considered to represent a ‘worst case’ that would cover several other use scenarios where the substrates (i.e. natural organic matter including proteins, carbohydrates and fats) and reaction conditions (i.e. pH > 6 with excess available chlorine) are similar or less severe, viz:

- Wastes from household bleach use discharged to a sewage treatment works (STW);
- Wastes from Industrial and Institutional cleaning (IIP) discharged to an STW;
- Water from swimming pools discharged to an STW;
- Wastes from drinking water treatment facilities discharged to a STW;
- Treated cooling waters discharged directly to a receiving water;
- Treated swimming pool water discharged directly to a receiving water;
- Sewage disinfected prior to discharge to a receiving water.

Raw sewage chlorination represents a ‘worst case’ 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. In the first four of the above scenarios, effluent toxicity would also be reduced by biodegradation during sewage treatment.

The relative toxicity of the samples was assessed using a series of tests with representatives of different taxonomic groups (namely bacteria, algae and invertebrates). It is important to note that these whole effluent tests are not intended to determine toxicity in absolute terms. Undiluted raw settled sewage, which was the control for these tests, is toxic to aquatic organisms, but following dilution after discharge into receiving waters this toxicity is not manifest in either acute or chronic effects on aquatic organisms. The tests on chlorinated effluent were designed to show whether the by-products present in this 'worst case' were sufficiently toxic and present in sufficient concentration to increase the toxicity of the raw settled sewage at various dilutions.

For the sewage treatment scenario itself, the whole effluent test would thus demonstrate firstly whether chlorination is likely to increase toxicity of the sewage effluent, and if so at what dilutions, and secondly whether additional toxic effects would be likely at normal operational dilutions such that there could be additional risks to aquatic organisms which would need to be further assessed.

The potential for bioaccumulation of chlorinated organic by-products was assessed using Solid Phase Micro-Extraction (SPME) fibres which are 1cm lengths of polyacrylate coated with polydimethylsiloxane. The SPME fibres have the advantage of being 'biomimetic' in that, when exposed to samples, they absorb highly lipophilic substances more than less lipophilic substances, simulating the way that mixtures of lipophilic substances will be taken up by aquatic organisms. Note that uptake is not limited to potentially bioaccumulating 'high log K_{ow} substances: the fibres also absorb some quantities of substances of modest lipophilicity.

The formation of substances which may be persistent and have the potential to bioaccumulate was thus examined by exposing SPME fibres to samples of RSS and C/D-RSS before and after degradation in a Zahn-Wellens test. The quantities of chlorinated organics collected on the fibres were measured using two different methods: a total organo-halide (TOX) technique and by measuring the area under the curve produced by injection into a GC-MS operating in ECD mode.

The table below summarises the results of studies assessing the toxicity, biodegradation and bioaccumulation of RSS and C/D-RSS samples. The latter contained chlorinated by-products (measured as AOX) at around 1000 µg/l.

Table 3.12. Summary of the results of the toxicity, biodegradation and bioaccumulation studies

Type of measurement	Description	Findings
---------------------	-------------	----------

Toxicity	Bacterial (<i>V. fischeri</i>) bioluminescence test	Replicate tests showed that the RSS sample exhibited greater toxicity (15 minute EC ₅₀ values of 4.2 – 7.4 %v/v) compared to the C/D-RSS sample (15 minute EC ₅₀ values of 27.2 – 33.0 %v/v).
	Algal (<i>P.subcapitata</i>) growth inhibition test	Both the RSS and C/D-RSS samples showed similar responses with a reduction in algal growth being evident at concentrations exceeding 3.2% v/v and greater than 50% reduction in algal growth being evident in both samples at concentrations of 32% v/v. Resulting EC ₅₀ values were 19.5 %v/v for the RSS sample and 25.7% v/v for the C/D-RSS sample.
	<i>D.magna</i> reproduction and survival test	Both the RSS and C/D-RSS samples showed similar responses with mortality of daphnids at 100% v/v. The numbers of juveniles per surviving adult showed a similar pattern for both samples; namely increasing numbers from 1.0 to 10% v/v sample with a reduction at 32% v/v back to the numbers found at 1.0% v/v sample.
Biodegradation	Zahn-Wellens test	Although the DOC level in the C/D-RSS sample was higher at the start of the test than in the RSS sample, levels in the two samples were the similar after 28 days degradation
Bioaccumulation	SPME fibres	Although the TOX level on the fibre exposed to the C/D-RSS sample was higher at the start of the test than in the RSS sample fibre, levels in the fibres from the two samples were the same after 28 days degradation. A similar pattern was observed for the total extractable chlorinated organics as measured by GC-MS in ECD mode

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.

3.2.2 Atmosphere

There are no data on effects of hypochlorite (ClO^-) in the atmospheric compartment but as mentioned previously (3.1.3) it is only present at very low levels in the atmosphere. So effect assessment is not applicable.

3.2.3 Terrestrial compartment

There are no data on effects of hypochlorite in the terrestrial compartment but as mentioned previously (3.1.4), it is normally not present in soil. So effect assessment is not applicable.

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

No data on hypochlorite effects relevant to the food chain are available but as mentioned previously (3.1.5) no hypochlorite residue is thought to be present or to accumulate in the food chain. So an effect assessment is not applicable.

3.3 Risk characterisation

3.3.1 Aquatic compartment (incl. sediment)

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

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

3.3.1.1. Sodium Hypochlorite

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

Conclusion (ii)

- Household, Swimming Pool, Drinking Water: Calculated PEC are between 10^{-22} and 10^{-32} $\mu\text{g/l}$ of FAC based on modelling of the decay of hypochlorite in the sewer. In

conclusion, these scenarios lead to a risk estimation of no concern and no risk reduction measures are applicable.

Conclusion (ii)

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

Conclusion (ii)

- Cooling Water: Hypochlorite concentrations in cooling water effluents are expected to be extremely low due to its reactivity and the composition of surface water, both freshwater and saline water. For saline water TRO values, probably representing a mixture of oxidative substances have been measured of 20 $\mu\text{g/l}$ nearby the discharge point, decreasing to zero after mixing with the receiving water. The amount and nature of oxidative by-products will depend mainly on dosing regime and specific local conditions, which are normally controlled by local permits in compliance with the reference document on BAT (best available techniques) to industrial cooling systems (European Commission 2001).

Conclusion (ii)

- Textile Bleaching, Pulp and Paper, Institutional and Food Industry: Hypochlorite is shown to disappear rapidly from these use scenarios, either being rapidly reduced in factory effluent or in the sewer, where the sewer scenario in Appendix 2, giving calculated PEC values of 10^{-22} $\mu\text{g/l}$ to 10^{-32} $\mu\text{g/l}$ applies.

Conclusion (ii)

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

3.3.1.2. By-Products of sodium hypochlorite applications

For most use scenarios where by-product assessment is appropriate, the risk characterisation for halogenated by-products is based on several complementary sets of information:

1. The risk from the two major by-product types, THMs and haloacetic acids, are assessed by conventional PEC/PNEC calculations.
2. This is supplemented for several scenarios where reaction conditions and substrates are similar or less severe, and the range of by-products are known to be similar, by the results of the whole effluent testing carried out on chlorinated raw settled sewage as a 'worst case' model. The chlorinated sewage test effluents contained chlorinated by-products at a concentration of around 1000 $\mu\text{g/l}$ measured as AOX. No increased toxicity was observed compared to the unchlorinated effluent, and the toxic effects of both effluents disappeared in parallel upon progressive dilution. While comparative whole effluent tests do not provide an absolute assessment, and have various uncertainties, it is reasonable to

conclude, for sewage chlorination itself and for other use scenarios likely to contain lower concentrations of a similar range of by-products, that significant additional toxic effects are unlikely to arise as a result of the chlorinated by-products when effluents are diluted into receiving waters.

The reaction of hypochlorite with organic matter can lead to some level of chlorination, although the effects of this can to some extent be offset by oxidation reactions. Chlorination generally leads to an increase in the lipophilicity of a substance. It often also reduces aerobic biodegradability though anaerobic biodegradability may increase (Field et al., 2007). The whole effluent test, however, also found no indication that substantial quantities of persistent, bioaccumulative by-products were created in the test effluent, and similar results could be expected in those other scenarios for which this represents a worst case. The sensitivity of this test was not sufficient that it alone could rule out formation of trace quantities of halogenated persistent and bioaccumulative substances. However, the formation of highly-chlorinated, particularly aromatic, substances that might be PBTs through successive chlorination is unlikely. The neutral or alkaline conditions and the presence of substrates for the preferred oxidation and N-chlorination reactions such as apply for the scenarios covered by the WET test, would mitigate against successive chlorination above one or two substitutions (de Sinnighe Damstè et al., 1985, Jolley 1975, Reinhard 1976). This is illustrated for example by the previous WRc studies on chlorinating sewage (Davis et al 1993) which found minimal formation of chlorophenols even though phenol, in contrast to most aromatics, is readily chlorinated in isolation in aqueous solution at these pHs (Carlson et al 1975, Patnaik et al 2000). The overall load of any PBT substances may also be reduced during hypochlorite treatment through oxidation reactions leading, for example, to ring opening (Sinninghe Damstè et al., 1985, Gallard and von Gunten 2002).

These previous WRc studies (Davis et al 1993), which have been used as the basis for calculating the PEC for sewage chlorination (Section 3.1.2.5), also indicate that the chlorinated test effluent would have contained approximately 40 µg/l of haloacetic acids. For scenarios covered by this 'worst case', the absence of increased toxic effects and progressive disappearance on dilution provides 'higher tier' information from a real effluent situation for certain cases where a PEC/PNEC ratio greater than 1 indicates a need for additional information. This data is consistent with standard tests newly conducted under GLP of TCA, sodium dichloroacetate and dibromoacetic acid against the standard species of algae *P. subspicatus* as used in the Whole Effluent Test.

3. For each scenario, there is an additional assessment of the likelihood of formation of significant quantities of polychlorinated dioxins and furans which are high hazard substances. For some scenarios this is based on direct studies; in others there is indirect evidence that dioxin studies on closely related topics have failed to report any significant contribution from hypochlorite use. In addition, as explained in section 3.1.1, dioxin formation is not expected in circumneutral or alkaline pH (i.e. pH > 6) where hypochlorite ion and/or hypochlorous acid are the only species of free available chlorine present (i.e. there is no chlorine gas see

2.4.1). In several scenarios pH is known to be consistently maintained above this level for various reasons, especially to avoid chlorine gas formation, such that the formation of significant quantities of dioxins is inherently unlikely.

3.3.1.2.1 Production

No organic by-product arise during the production process

Conclusion (ii)

3.3.1.2.2 Household

i) Trihalomethanes

The PEC/PNEC ratio for trihalomethanes, treating them all as chloroform, by-product from household hypochlorite use in the realistic case (section 3.1.2.2) is:

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.022 + 0.268) / 146 = 0.0020$$

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

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

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = 0.11 + 0.268 / 146 = 0.0026$$

Conclusion (ii)

ii) Haloacetic acids

The PEC/PNEC ratio for TCA for the realistic case can be calculated against the PNEC of 0.85 µg/l as follows:

$$\text{PEC}_{\text{local}} + \text{PEC}_{\text{regional}} / \text{PNEC} = (0.036 + 0.12) / 0.85 = 0.184.$$

The worst case PEC/PNEC ratio would be:

$$(0.18 + 0.12) / 0.85 = 0.353$$

For other haloacetic acids , treating them all as DCA,

$$PEC_{\text{local}}/ PNEC = 0.019 / 0.72 = 0.026 \text{ (realistic case)}$$

$$PEC_{\text{local}}/ PNEC = 0.092 / 0.72 = 0.128 \text{ (worst case)}$$

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

$$0.184 + 0.026 = 0.21 \text{ (realistic case)}$$

$$0.353 + 0.128 = 0.48 \text{ (worst case)}$$

Conclusion (ii)

iii) Other identifiable molecules

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

Conclusion (ii)

b) Non-identified reaction products

The environmental hazards of the unidentified species which make up the bulk of the chlorinated reaction products can be assessed by considering the following parameters:

i) biodegradability

The AOX content of household or model effluents is extensively biodegradable – typically 60 to 90% (see 3.1.1.2). The production of persistent by-products is thus unlikely to be significant.

ii) bioaccumulation potential

Studies on laundry bleaching effluents after simulated sewage treatment, using HPLC and GC-MS, failed to identify any chlorinated, potentially bioaccumulative species (see 3.1.1.2).

iii) degree of chlorination

Generally speaking, the environmental hazards of chlorinated species increase, with increasing chlorination for a given parent molecule. With the exception of the small molecular weight molecules, such as chloroform and trichloroacetic acid, the degree of chlorination of the by-products is believed to be low, generally mono- or di-substituted with little if any formation of polychlorinated species. Chlorinated phenols are only detected in trace quantities and are generally mono-chlorinated.

iv) molecular weight

A significant proportion, of the order of 25 – 50% according to use, of the total chlorinated species measured as AOX is expected to be high molecular weight material (> 600 – 1000 Dalton) and thus of low bioavailability with limited potential to exert toxic effects on aquatic organisms.

v) presence of high-hazard species

All household cleaning with hypochlorite is carried out at neutral or alkaline pH, especially to avoid chlorine formation, so dioxin formation would not be expected. Studies on household bleaching effluents have indicated that there is no formation of dioxins, nor are other highly-chlorinated ‘chemicals of highest concern’ detected.

vi) toxicity of whole effluents

Studies on household effluents following simulated biological sewage treatment show that there is no elevation of aquatic toxicity of bleached effluents compared with unbleached controls. Effluents with AOX concentrations up to 150 – 300 times the PEC showed no adverse effects in chronic tests with *Ceriodaphnia dubia* and Fathead minnows.

In summary:

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

Conclusion (ii)

3.3.1.2.3 Production of Other Chemicals

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

3.3.1.2.4 Swimming Pools

i) Trihalomethanes

The PEC/PNEC ratio for trihalomethane by-products from hypochlorite use in swimming pools (section 3.1.2.4) is thus:

Routine discharge:

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.02 + 0.268) / 146 = 0.0020$$

Complete emptying (twice per year)

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.67 + 0.268) / 146 = 0.0064$$

Conclusion (ii)

ii) Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by-products from hypochlorite use in swimming pools (section 3.1.2.4) is thus:

Routine discharge:

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.16 + 0.12) / 0.85 = 0.33$$

Complete emptying (twice per year)

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (6.22 + 0.12) / 0.85 = 7.46$$

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

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC}_{\text{intermittent}} = (6.22 + 0.12) / 2.58 = 2.46$$

For complete emptying, the PEC/PNEC ratio would point to a possible concern and need for further information. In this regard, the whole effluent tests conducted on chlorinated raw sewage which would be expected to contain around 40µg/l of haloacetic acids show no elevated toxicity versus unchlorinated effluents. This is consistent with standard algal toxicity tests newly conducted against standard species of algae. It should be noted that the complete emptying scenario is highly conservative. The pool volume used is higher than average for public pools, more towards olympic size. The contents are assumed to be discharged into a standard 10,000 population equivalent STW but there may be few cases where such large pools discharge into such STWs. In larger centres of population, where STWs are often larger and the largest pools are more likely to be located, the PEC/PNEC would only be exceeded if two or more pools were emptied into the same STW on the same day, which is unlikely, since a pool is normally completely emptied only once or twice a year.

Taking the uncertainty about the TCA, and thus DCA, PNECs, and the lack of increased toxicity in the whole effluent test together with the highly conservative scenario for pool emptying, the overall weight of evidence thus indicates no concern for the PEC_{local} of 6.22 µg/l.

Conclusion (ii)

iii) Other halogenated organic by-products

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

Conclusion (ii)

3.3.1.2.5 Sewage Treatment

i) Trihalomethanes

The PEC/PNEC ratio for trihalomethane by-products from hypochlorite use in sewage treatment (section 3.1.2.5) is thus:

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

Conclusion (ii)

ii) Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by-products from hypochlorite use in sewage treatment (section 3.1.2.5) is thus:

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

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

Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence thus indicates no concern for the PEC_{local} of 3.5 µg/l.

Conclusion (ii)

iii) Other halogenated organic by-products

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

Conclusion (ii)

3.3.1.2.6 Textiles

i) Trihalomethanes

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

$$(PEC\ local + PEC\ regional) / PNEC = (0.10 + 0.268) / 146 = 0.0025$$

Conclusion (ii)

ii) Haloacetic acids

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

$$(PEC\ local + PEC\ regional) / PNEC = (0.21 + 0.12) / 0.85 = 0.39$$

Conclusion (ii)

iii) Other halogenated organic by-products

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

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

Conclusion (ii)

3.3.1.2.7 Drinking Water

i) Trihalomethanes

The PEC/PNEC ratio for trihalomethane by-products from hypochlorite use in drinking water chlorination for the worst case concentrations for various raw water quality scenarios (section 3.1.2.7) is thus:

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

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

Conclusion (ii)

ii) Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by-products from hypochlorite use in drinking water chlorination for the worst case concentrations for various raw water quality scenarios (section 3.1.2.7) is thus:

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

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

For poorer quality surface water sources, the PEC/PNEC ratio would point to a possible concern and need for further information. Considering the cases further, the high levels of HAAs potentially arise in ordinary surface waters when several worst case assumptions are combined (see 3.1.2.7 ii). For DWD compliant water, the most likely case shows a PEC/PNEC well below 1. The non-DWD compliant case should disappear as the Directive becomes fully implemented. The case of upland acid waters is less directly controlled by the DWD which focuses on THMs, but as noted in the discussion the data show that where improved treatment processes have been implemented, implicitly focused on THMs, the levels of HAAs have fallen dramatically, enough to bring HAA levels in many cases low enough not to exceed the PNEC. Since 57% of water used in the EU in 2002 came from groundwater, and upland acid waters are normally drawn upon by small populations, it seems likely that when the DWD is fully implemented only a few per cent of EU drinking water would be likely to exceed the HAA PNEC.

Another perspective is provided by the whole effluent tests conducted on chlorinated raw sewage. Effluents which would be expected to contain around 40µg/l of haloacetic acids, showed no elevated toxicity versus unchlorinated effluents. In comparison, PEC_{local} values up to 7.80 µg/l have been calculated for an extreme worst case for drinking water. The hypochlorite doses and ranges and concentrations of substrates available in raw sewage are much greater than would apply in drinking water production. The possibility that exceptionally high HAA levels in potable water might constitute an environmental risk should be noted though the risk assessment for this scenario could be refined by reassessment of the TCA and interpolated DCA PNECs.

Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence indicates no concern.

Conclusion (ii)

iii) Other halogenated organic by-products

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

Conclusion (ii)

3.3.1.2.8 Pulp & Paper

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

Conclusion (ii)

i) Trihalomethanes

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

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

Conclusion (ii)

ii) Haloacetic acids

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

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

Such a PEC/PNEC ratio would point to a possible concern and need for further information. In this regard, the whole effluent tests conducted on chlorinated raw sewage which would be expected to contain around 40µg/l of haloacetic acids shows no elevated toxicity versus unchlorinated effluents.

The risk assessment for this scenario could be refined by reassessment of the TCA and interpolated DCA PNECs.

Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence thus indicates no concern for the PEC_{local} of 1.25 µg/l.

Conclusion (ii)

iii) Other halogenated organic by-products

N-chloroamino compounds, which are expected to be the other dominant halogenated species would be expected to be biodegradable, not liable to bioaccumulation, and of low toxicity.

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

Conclusion (ii)

3.3.1.2.9 Cooling Water

i) Trihalomethanes

The PEC/PNEC ratio for trihalomethane by-products from hypochlorite use in cooling water treatment (section 3.1.2.9) is thus:

Seawater case

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.3 + 0.268) / 146 = 0.004$$

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

Conclusion (ii)

ii) Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by-products from hypochlorite use in cooling water treatment (section 3.1.2.9) is thus:

Seawater case

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.1 + 0.12) / 0.85 = 0.26$$

Conclusion (ii)

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

This PEC/PNEC ratio would point to a possible concern and need for further information. Though detailed data on by-products sufficient to refine the PEC have not become available, it is clear that the hypochlorite dosage regime, and thus the chronic loads of by-product discharged, will normally be much less than for the large coastal plants. Continuous dosing, where practised at all, is likely to run for only a few weeks a year, and often will be for only part of each day.

Another perspective is provided by the whole effluent tests conducted on chlorinated raw sewage, which act as a worst case for this scenario. The effluents tested, which would be expected to contain around 40 µg/l of haloacetic acids, showed no elevated toxicity versus unchlorinated effluents.

The risk assessment for this scenario could be refined by reassessment of the TCA and interpolated DCA PNECs.

Taking the uncertainty about the TCA, and thus DCA, PNECs, together with the lack of increased toxicity in the whole effluent test, the overall weight of evidence thus indicates no concern for the $\text{PEC}_{\text{local}}$ of 1.0 µg/l.

Conclusion (ii)

iii) Other halogenated organic by-products

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

effluent. Because current hypochlorite use is at pH close to neutral, formation of dioxins or similar high-hazard molecules is not expected,

Conclusion (ii)

3.3.1.2.10 Institutional and Food Industry Cleaning

i) Trihalomethanes

The PEC/PNEC ratio for trihalomethane by-products from hypochlorite use in Institutional and Food Industry Cleaning (section 3.1.2.10) is thus:

$$(PEC\ local + PEC\ regional) / PNEC = (0.004 + 0.268) / 146 = 0.0019$$

For the local hospital scenario, the ratio would be:

$$(PEC\ local + PEC\ regional) / PNEC = (0.034 + 0.268) / 146 = 0.0021$$

Conclusion (ii)

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

$$0.056 - 0.144$$

Household: realistic case:

$$(PEC\ local + PEC\ regional) / PNEC = (0.056 + 0.268) / 146 = 0.0022$$

Household: worst case:

$$(PEC\ local + PEC\ regional) / PNEC = (0.144 + 0.268) / 146 = 0.0028$$

Conclusion (ii)

ii) Haloacetic acids

The PEC/PNEC ratio for haloacetic acid by-products from hypochlorite use in Institutional and Food Industry Cleaning (section 3.1.2.10) is thus:

$$(PEC\ local + PEC\ regional) / PNEC = (0.010 + 0.12) / 0.85 = 0.15$$

For the local hospital scenario, the ratio would be:

$$(PEC\ local + PEC\ regional) / PNEC = (0.086 + 0.12) / 0.85 = 0.24$$

Conclusion (ii)

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

Household: realistic case:

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.141 + 0.12) / 0.85 = 0.31$$

Household: worst case:

$$(\text{PEC local} + \text{PEC regional}) / \text{PNEC} = (0.356 + 0.12) / 0.85 = 0.56$$

Conclusion (ii)

iii) Other halogenated organic by-products

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

Conclusion (ii)

3.3.2 Atmosphere

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

3.3.3 Terrestrial compartment

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

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

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

4. HUMAN HEALTH

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

4.1.1. Exposure assessment

4.1.1.1 General aspects

Sodium hypochlorite solutions contain three species of chlorine in equilibrium: gaseous chlorine, hypochlorous acid (HOCl) and ClO⁻. Their concentration is a function of the pH of the solution (see paragraph 2.4). The pH of commercial solutions of sodium hypochlorite can range from pH 9 (diluted) to 13 (concentrated) and as such the dominant species are the hypochlorite anion and hypochlorous acid, with the former predominating.

Sodium hypochlorite solutions are currently classified as irritant for concentrations from 5% to 10% available chlorine (risk phrases: R31, R36/38) and as corrosive for concentrations above 10% (risk phrases: R31, R34).

Inhalation exposure

Being an anion, ClO⁻ will not volatilise from aqueous solutions. The minute fraction of HOCl present in commercial solutions has a very low volatility (see paragraph 2.7). Gaseous chlorine can be released from a sodium hypochlorite solution only in accidental case by mixing with strong acids.

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

Some scenarios can result in inhalation exposure to chlorination by-products, formed when sodium hypochlorite solution reacts with organic matter (i.e. swimming pool scenario).

Dermal exposure

Consumer exposure to sodium hypochlorite generally occurs via dermal contact with diluted solutions. This contact is only occasional (household, swimming pool).

Under occupational conditions, generally only accidental dermal exposure to concentrated solutions may occur. Some scenarios can result in dermal exposure to solutions with lower concentration of sodium hypochlorite and chlorination by-products (i.e. swimming pool scenario, I&I, etc.).

Oral exposure

Oral exposure to sodium hypochlorite and to chlorination by-products is possible for consumer via drinking water and by accidental ingestion in the swimming pool scenario. Chapter 4.1.1.4.1 presents data from Poison Control Centre (table 4.12).

4.1.1.2 Potential for dermal uptake

There is no data from experimental studies describing the rate of absorption of hypochlorite ions through the skin. However, the potential for hypochlorite ions to be absorbed through the skin is low, given their reactivity towards proteinaceous material.

Estimate of a fixed fraction of hypochlorite for absorption

A fixed amount of sodium hypochlorite actually penetrating the skin can be estimated, it is suggested here to assume the amount to 10%. Given the reactivity and polarity of the chemical as well as the known barrier functions of skin, this is likely a conservative factor (in order to err rather on the conservative side). However, this approach has been used further to estimate the dermal exposure to hypochlorite.

4.1.1.3. Occupational exposure

For each scenario, occupational exposure to sodium hypochlorite is described in as much detail as possible.

Where no measured data are available, the EASE model is applied.

4.1.1.3.1. Production

Data available for occupational exposure assessment

Sodium hypochlorite production is in most cases integrated in a Chlor-Alkali plant, where chlorine and other chlorinated substances are produced. Measured data are available on chlorine atmospheric concentration in the workplace in different parts of the Chlor-Alkali plant and for different tasks.

As explained in paragraph 2.4, no sodium hypochlorite as such can be present in the atmosphere and the formation of aerosols is excluded during production. Workers involved in sodium hypochlorite production can be exposed to chlorine in the atmosphere, which could be emitted during chlorine production or during its use for the synthesis of hypochlorite and other chlorinated chemicals. Chlorine emissions can take place when the closed system is breached, for maintenance purposes or during coupling and decoupling of pipelines, both during hypochlorite and chlorine production.

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, 2000). Chlorine concentration measured in the atmosphere of a Chlor-Alkali plant takes into account the exposure coming from the production of various substances (chlorine and, in most cases, other chlorinated chemicals). Available monitoring data will be presented.

OELs

There is no specific European regulation for safety procedures during the production of hypochlorite. Since available data on exposure to chlorine will be used for the evaluation, current national occupational exposure levels for chlorine are applicable.

Table 4.1 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 ppmV or 1.5 mg/m³, with the only exception of The Netherlands, where limits are higher. In some cases, a short term exposure limit (15 minutes STEL - Short-Term Exposure Limit) of 1 ppmV is applied. A draft proposal of European Directive on occupational exposure limits establishes as indicative limit for short term exposure (15 minutes) to chlorine a value of 0.5 ppmV.

Table 4.1. OEL for chlorine in European countries

Country	Limit	Reference
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	Long term exposure	Short term exposure	
Austria	MAK: 0.5 ppmV; 1.5 mg/m ³	Peak limit value is maximum 2x MAK, for up to 5 min.; permitted 8x per shift.	MAK Liste. 1994 Amtliche Nachrichten Arbeit-Gesundheit-Soziales, 48. Jahrgang, Sondernummer 2/1993
Belgium	8-hour TWA: 0.5 ppmV; 1.5 mg/m ³	15-minute STEL: 1 ppmV, 2.9 mg/m ³	Moniteur Belge/Belgisch Staatsblad 14.06.1995
Denmark	TWA: 0.5 ppmV, 1.5 mg/m ³		National Labour Inspectorate. Exposure Limit Values For Substances and Materials. Instruction No. 3.1.0.2. Dec 1996
Finland	8-hour limit: 0.5 ppmV, 1.5 mg/m ³	15-minute limit: 1 ppmV, 2.9 mg/m ³	HTP-Arvot 1996, Turvallisuustiedote 25, Työministeriö, Kemia Työsuojeluneuvottelukunta, Tampere 1996, as amended
France		VLE (valeur limite d'exposition): 1 ppmV, 3 mg/m ³	INRS, Valeurs limites d'exposition professionnelle aux agents chimiques en France 1996 - Cahiers de Notes Documentaires ND 1945-153-93
Germany	TRGS 900 limit value: 0.5 ppmV, 1.5 mg/m ³	MAK value should never be exceeded. AGS (Commission on Hazardous Substances) can establish other peak limitations for individual substances.	TRGS 900, Limit Values in the Ambient Air at the Workplace -- MAK and TRK values (Bundesarbeitsblatt 10/1996 as last amended in 5/1998)
Ireland	8-hour OEL (TWA): 0.5 ppmV, 1.5 mg/m ³	15-minute OEL (STEL): 1 ppmV, 3 mg/m ³	Code of Practice for the Safety, Health and Welfare at Work [Chemical Agents] Regulations, 1997
The Netherlands	MAC TWA (TGG): 1 ppmV, 3 mg/m ³		National MAC List 1997-98
Norway	threshold limit value: 0.5 ppmV, 1.5 mg/m ³	ceiling value: 1 ppmV, 3 mg/m ³	Administrative Norms for Contaminants in the Workplace 1996 (Arbeidstilsynet best. nr. 361)
Spain	VLA-ED: 0.5 ppmV, 3 mg/m ³	VLA-EL: 1 ppmV, 3 mg/m ³	Instituto nacional de seguridad e de higiene en el trabajo
Sweden	Level Limit Value (NGV) 0.5 ppmV, 1.5 mg/m ³	Ceiling Limit Value (TGV) 1 ppmV, 3 mg/m ³	National Board of Occupational Safety and Health. Occupational Exposure Limit Values. 1996 (AFS 1996:2)
Switzerland	TWA 0.5 ppmV, 1.5 mg/m ³	STEL 1 ppmV, 3 mg/m ³	SUVA. Grenzwerte am Arbeitsplatz 1997 (Limit Values at the Workplace 1997)) SUVA-Publikation 1903.d, Jan 1997
United Kingdom	TWA 0.5 ppmV, 1.5 mg/m ³	STEL 1 ppmV, 2.9 mg/m ³	Health and Safety Executive. EH40/98; Occupational Exposure Limits 1998

Note: Italy, Greece 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/m³ (for long term exposure) and TLV-STEL of 1 ppmV or 3 mg/m³ (for short term exposure).

Description of workers' tasks and safety procedures

Sodium hypochlorite production is integrated in Chlor-Alkali electrolysis. In a Chlor-alkali plant, workers can generally perform one of the following tasks: production work, maintenance, sampling, and packaging of the end product. Details concerning the hypochlorite unit are presented below.

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.

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 hypochlorite system takes place only after its emptying, purging and shut-off via blind flange, disconnection. In case of chlorine leaks, detection and monitoring are performed. Self-contained breathing apparatus are used for emergency operation.

Sampling generally consists in the analysis of hypochlorite (OCl^-), free caustic (OH^-), and carbonate (CO_3^{2-}) by titration. The sample is taken from the tank of road or rail tankers, and from sampling stations in plant.

The end product generally leaves the plant via rail or road tankers (bulk transport up to 57 tones) and, in some cases, via small packages. Main elements of hypochlorite loading station for road trucks are articulated arms or flexible hoses. When the tank is in right position, workers achieve the connection between the fixed and the mobile storage. The loading can start.

The process for the production of hypochlorite is closed and during normal work exposure to chlorine or to hypochlorite is possible only in case of accident.

Inhalation exposure to chlorine and dermal exposure to sodium hypochlorite could be possible during some specific maintenance activities. In most plants maintenance personnel has 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 protective equipment to be used to prevent dermal and inhalation exposure are dictated by the plant supervisor and documented in the work permit.

Protective equipment used is the following:

- Always used: safety glasses, safety shoes, long sleeved shirt, long pants, mask.
- Used in case of handling of the product: goggles, face shield, gloves, mask.
- Used in case of opening of the system: goggles, face shield, gloves, rubber overall, rubber boots, gas mask or self-contained breathing apparatus.

The efficacy of protective clothing is defined by the breakthrough time. For sodium hypochlorite, all the materials used (PVC, nitrile rubber, neoprene rubber, PE, natural rubber) have a breakthrough time of more than 8 hours during performance test (Forsberg/Mansdorf). This means that workers are fully protected from dermal exposure during 8 hours.

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 can inhale no 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

Safety procedure and the use of appropriate protective equipment limit the dermal exposure to hypochlorite and the inhalation exposure to chlorine to hypochlorite or chlorine to accidental events.

Potential for exposure to chlorine exists as a result of leaks. Unexpected leaks are readily detected by smell. The threshold of smell is in the range of STEL (0.5-1 ppmV). Plants are equipped with chlorine detectors in different locations. They can generally detect 0.1 ppmV and have a pre-alarm level of 0.25 ppmV and an alarm level of 0.5 ppmV. In case of leak, the presence of chlorine in the atmosphere is detected and workers shall wear the appropriate PPE. All personnel normally carry a mask.

Most of the plants perform TWA analysis and some of them STEL analysis on a regular basis. Data are provided in the following paragraph.

Inhalation exposure

Available data on inhalation exposure to chlorine during production are presented in chapter 4.1.1.2.1 of Chlorine Risk Assessment (2006).

Dermal exposure

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

The hypochlorite solution in the concentrations of production scenario is corrosive. Therefore, we can assume that PPE are always used in case of breaching of the closed system and no dermal exposure is possible, except in case of accident.

4.1.1.3.2. Production of other chemicals

Sodium hypochlorite is used as a chlorinating and oxidizing agent of organic intermediates. This use of hypochlorite usually takes place in the production plant and the solution is transferred via pipelines to on-site users. Sodium hypochlorite solution is filled into the reaction vessel through closed systems, while off-gases from the reactor are treated before release in the atmosphere. The concentration of sodium hypochlorite normally used in chemical synthesis is 10%.

When handling the product, or during maintenance or sampling operations, workers have to wear goggles and PVC rubber gloves. In case of opening of the system, approved gas masks have to be used. Maintenance and repairs of pumps, dosing

systems and automatic control systems is only carried out by specialised companies or trained workers. For information on the efficacy of PPE, see paragraph 4.1.1.3.1.

One of the processes which accounts for a great fraction of hypochlorite use as intermediate is the production of hydrazine hydrate (see paragraph 3.1.1.3). The production takes place in a closed system and the process is continuous. Workers' tasks include production work (rounds, process monitoring) and maintenance. Maintenance is subjected to conditions defined in the "work permit". In case of shut down of the system, a flushing of pipelines and apparatus is carried out before any maintenance and repair activities can take place. Procedures stated in the work permit have to be followed and prescribed protective equipment has to be used (protecting clothing, gloves, goggles, self contained breathing apparatus).

The hypochlorite solution in the concentrations of use as a chemical intermediate scenario is corrosive. Therefore, we can assume that PPE are always used in case of breaching of the closed system and no dermal exposure is possible, except in case of accident.

As explained in 4.1.1.3.1, no inhalation exposure to sodium hypochlorite is possible in this scenario.

4.1.1.3.3. Swimming pools

Exposure to sodium hypochlorite

Two groups of workers can be exposed to sodium hypochlorite in swimming pools: workers handling the product to disinfect the pool and swimming instructors. When no data are available, the EASE model will be used to estimate the exposure

Occupational exposure to sodium hypochlorite for workers handling the product in swimming pools does not normally occur, as the product is added via closed circuits.

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

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

Safety procedures to be followed when sodium hypochlorite is used in swimming pools are described in the Euro Chlor document "Safe use of sodium hypochlorite at swimming pools" (1999).

Under these conditions no worker exposure is expected, while existing and evolved safety procedures will restrict any accidental exposure to a minimum. However an

estimate of dermal exposure for operators handling solutions with a concentration of sodium hypochlorite lower than 5% is made with EASE 2.0 (see below).

Calculation of chronic and acute exposure

Dermal exposure for swimming pool instructors/competition swimmers

A calculation for swimming pool instructors/competition swimmers exposure to sodium hypochlorite in water was performed, assuming an exposure of 6 hours per day (6 events of 1 hour) for 5 days per week of the whole body surface, an average concentration of substance (C_{derm}) of 3.0 mg/l and a thickness of layer of product on skin of 0.01 cm. A fixed amount of sodium hypochlorite actually penetrating the skin can be estimated. Given the reactivity and polarity of the chemical as well as the known barrier functions of skin, this amount can be estimated to lie between 1 - 10 %, and the upper estimate 10 % is used here. Thus, a conservative approach has been used to estimate the dermal exposure to hypochlorite. The potential dermal uptake (U_{derm}) calculated according to TGD default values under the assumption that 10% is absorbed is **1.66×10^{-3} mg/kg/day (1.66 $\mu\text{g/kg/day}$)** (see calculation below). This value will be used in the risk characterization.

Model Parameters:

(HYPOCHLORITE) in the product [mg.cm ⁻³]	C_{der}	= 3.0×10^{-3}
External exposure to skin [mg/d]	A_{der}	= 2.49
Potential dermal uptake rate [mg.kg BW ⁻¹ day ⁻¹]	$U_{\text{der pot}}$	
Thickness of the film layer on skin [default = 0.01cm]	T_{der}	= 0.01
Surface area of skin exposed [cm ²]	$AREA_{\text{der}}$	= 19400
Bioavailability for dermal exposure (default = 1)	BIO_{derm}	= 1
Number of events per period (usually, events.day ⁻¹)	N_{events}	= 6
Number of events per week		= (5/7)
Average male bodyweight [default = 70kg]	BW	= 70
Default factor to quantify absorption [10%]	F_{absorp}	= 10%

$$A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} \times N_{\text{events}} \times 5/7 = 2.49 \text{ mg/d}$$

$$U_{\text{derm pot}} = A_{\text{der}} / BW \times F_{\text{absorp}} = 2.49/70 \times 0.1 \times 1000 = 3.56 \mu\text{g/kg/d}$$

Oral exposure for swimming pool instructors/competition swimmers

Assuming an ingestion of 0.1 l of water per event as a reasonable worst case for normal-skill swimmers, an additional oral exposure of 18.4 $\mu\text{g/kg/d}$ is calculated ($3.0 \text{ mg/l} \times 0.1 \text{ l} / 70 \text{ kg} \times 6 \times 5/7$).

Total systemic exposure for swimming pool instructors/competition swimmers

The above calculations lead to a total systemic chronic exposure of **21.93 $\mu\text{g/kg/d}$** ($18.4 + 3.56$).

This latter value will be taken forward for Risk Characterisation.

The acute systemic exposure (ASE) can be calculated from a single event:

ASE = Uderm pot + Uoral

where:

Uderm pot is the potential dermal uptake from a single event = $A_{\text{der}} / \text{BW} \times F_{\text{absorp}}$
 $A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} = 0.58 \text{ mg/d}$; hence Uderm pot = 0.83 $\mu\text{g/kg}$.

Uoral is the oral uptake and is given by the following: Uoral = 3 mg/l x 0.1 l/70 kg = 4.3 $\mu\text{g/kg}$

ASE = 4.3 + 0.83 = 5.13 $\mu\text{g/kg}$

Estimate of the chronic occupational dermal exposure for operators handling solutions in swimming pool scenario (Conservative estimate in case of solutions with a sodium hypochlorite concentration lower than 5%)

The exposure to solutions with a concentration lower than 5% during coupling decoupling operations, can be estimated using EASE 2.0:

EASE 2.0 session log:

The physical-state is **liquid**

The exposure-type is **dermal**

The use-pattern is **Non-dispersive use**

The pattern-of-control is **Direct handling**

The contact-level is **Incidental** (1 event per day)

CONCLUSION: The predicted dermal exposure to Sodium Hypochlorite 5% solution is **0-0.1 mg/square cm/day**

This corresponds to 0-0.005 mg Sodium Hypochlorite/cm²/day. Considering the two hands (front and back) with a surface area of 840 cm² the maximum dermal exposure corresponds to 4.2 mg/day (Ader).

$U_{\text{derm pot}} = A_{\text{der}}/\text{BW} \times F_{\text{absorp}} = 4.2 \text{ mg/day} / 70 \text{ kg} \times 0.1 = \mathbf{0.006 \text{ mg/kg BW/d}}$

Exposure to chlorination by-products

People working as instructors or supervisors in the swimming halls may be exposed to irritating by-products originated by the reaction of disinfecting agents with organic substances in the water.

When swimmers enter the pool, they transfer into the water soluble chemical products (soap residues, cosmetics, oils) and a large number of microorganisms 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 or calcium hypochlorite,
- chloroisocyanuric salts (used mainly in small swimming pools),
- 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, H₂SO₄ or CO₂) to decrease the pH, and flocculants (Al³⁺, Fe³⁺ or polyelectrolytes), to help clarify the water. The presence of filters is absolutely necessary to stop the suspended matters circulating in the water circuit.

For spot oxidization and disinfection outside the pool, ozone can be used, but it has to be destroyed before entering the pool, because of its high toxicity.

The consumption of hypochlorite and chlorine in European swimming pools in 1994 amounted to 16.22 kt/y and 10.95 kt/y respectively (see tables 2.2 and 2.3). The presence of chlorinated compounds other than HOCl in the water is in constant dynamic equilibrium, principally linked to the pH, contents of urea and FAC (free available chlorine). The increases of pH and of urea content are linked to the number of swimmers.

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 Cl₂ equivalent per m³ of water per day in indoor pools, between 7 and 16 g of Cl₂ equivalent per m³ of water per day in outdoor pools.

The main regulations on swimming pool water quality relates to the minimum content of FAC (free available chlorine), which is always around 0.4 mg/l, and to the pH, which has to be in a range of 6.5 to 8.5 (Legube et al., 1996). There is also a limit concerning chlorine linked with nitrogen as chloramines, which has to be under 0.6 g/m³. Some countries give a maximum of FAC (for example, 1.4 mg/l in France), some others a maximum of urea content (in Belgium and the Netherlands). Other regulations restrict the number of swimmers per m² or prescribe the quantities of air and water replaced per swimmer or per year.

The formation of chlorinated by-products associated with disinfection of pool water varies with the chemical used. Input of reactive organic precursors is continuous and a function of the number of swimmers. According to studies in various swimming pools, organic by-products (OBPs) compounds represent virtually all the AOX values measured. The unidentified proportion in swimming pools seems to be low. Virtually all AOX measured in the water can be attributed to the amount of the following substances (OSPAR, 1999):

- Trihalomethanes: 90% is represented by chloroform (CHCl₃).
- Chloral hydrate
- Dichloroacetone
- Chloroacetic acid: mainly trichloroacetic (TCA), dichloroacetic (DCA), and monochloroacetic (MCA) acid.

Chloramines can be present, but the knowledge about their occurrence in swimming pool water is very limited. Currently, there are no suitable analytical methods for their

determination and study in swimming pool water (WHO, 2000). Nitrogen trichloride (NCl₃) has been measured in pools atmosphere.

Trihalomethanes are the by-products most frequently studied and measured in swimming pool water. They have also been measured in air of indoor pools because they are volatile and evaporate from the pool water.

The following table presents concentrations of main disinfection by-products measured in air and water of European swimming pools in most recent studies. Data show that by-products concentration is highly variable, depending on operational practices (chlorine dose, pool occupancy, swimmers' hygiene and water and air renewal).

Table 4.6 Disinfection by-products concentrations in swimming pools in water and air

By product	Concentration		Pool type	Reference
	Mean	Range		
Concentration in pool water (µg/l)				
Chloroform		19-94	indoor	Aggazzotti et al., 1993
	93.7	9-179	indoor	Aggazzotti et al., 1995
	33.7	25-43	indoor	Aggazzotti et al., 1998
	80.7		indoor	Purchert, 1994
	74.9		outdoor	
		3-27.8	indoor	Cammann and Hübner, 1995
		1.8-28	indoor	Jovanovic t al., 1995
	14	0.51-69	indoor	Stottmeiser, 1998,1999
	30	0.69-114	outdoor	
	83	70-95 (90 P = 92)	indoor	Universidad de Barcelona, 1996
128	99-178 (90 P = 163)	outdoor		
MCA	26	2.6-81	indoor	Stottmeister and Naglitsch, 1996
	26	2.5-112	outdoor	
	8	6-12 (90 P = 10)	indoor	Universidad de Barcelona, 1996
	2	1-3 (90 P = 2)	outdoor	
DCA	23	1.5-192	indoor	Stottmeister and Naglitsch, 1996
	132	6.2-562	outdoor	
	70	58-82 (90 P = 81)	indoor	Universidad de Barcelona, 1996
	64	50-95 (90 P = 84)	outdoor	
TCA	42	3.5-199	indoor	Stottmeister and Naglitsch, 1996
	249	8.2-887	outdoor	
		2.3-100	indoor	Mannschott et al., 1995
	119	112-126 (90 P = 124)	indoor	Universidad de Barcelona, 1996

	436	263-533 (90 P 518)	outdoor	
Chloral hydrate		0.5-104	indoor	Mannschott et al., 1995
	69	38-97 (90 P = 95)	indoor	Universidad de Barcelona, 1996
	137	84-209 (90 P = 190)	outdoor	
Dichloroacetonitrile	13	0.13-148	indoor	Stottmeister, 1998, 1999
	24		indoor	Baudisch et al., 1997
Concentration in the air above the pool water surface ($\mu\text{g}/\text{m}^3$)				
Chloroform	214	66-650	indoor (1)	Aggazzotti et al., 1995
	140	49-280	indoor (1)	Aggazzotti et al., 1993
	169	35-195	indoor (1)	Aggazzotti et al., 1998
	65		indoor (1)	Jovanovic t al., 1995
	36		indoor (2)	
	5.6		outdoor (1)	
	2.3		outdoor (2)	
	3.3	0.33-9.7	outdoor (1)	Stottmeister, 1998, 1999
	1.2	0.36-2.2	outdoor (2)	
	39	5.6-206	indoor (1)	
	30	1.7-136	indoor (2)	
	100-1500	indoor (2)	Héry et al., 1995	
Nitrogen trichloride		100-1500	indoor (2)	Héry et al., 1995
	240 (\pm 170)		indoor	Massin et al., 1998
	670 (\pm 370)		indoor	

All data are presented in WHO "Guidelines for safe recreational-water environments", 2006, with the exception of NCl_3 concentration in air and data from an unpublished Spanish study.

1: measured 20 cm above the water surface; 2: measured 150 cm above the water surface

There are three main routes of exposure to chlorination by-products in swimming pools:

- inhalation of volatile or aerosolized solutes,
- dermal contact,
- direct ingestion of the water.

In indoor pools, inhalation is an important pathway for uptake of trihalomethanes and nitrogen trichloride. Swimming instructors or supervisors can be exposed to NCl_3 and CHCl_3 in the atmosphere. In outdoor pools, the atmospheric concentration of trihalomethanes above the water surface is very low, even when their concentration in water is high. Inhalation is likely to be less important than dermal or oral intake.

Dermal exposure will be a function of body surface area, time in water, by-products water concentration and skin permeability, which is a function of the octanol/water partition coefficient of the chemical and other factors.

Direct ingestion is probably the least of exposure sources, since it is limited to the probably low amount of water that would be swallowed, but it can be more important for children swimmers.

Conclusion

An estimation of exposure of swimming pool workers to water chlorination by-products is difficult, because of the high variability of available data, which depends on operational practices.

4.1.1.3.4. Textile

The use of NaClO in textile industry is mainly related to the cotton and linen processing sector. Its use accounts for only the 1% of the total bleaching agents used, being H₂O₂ used for about 85%.

Linen is treated with sodium hypochlorite before dyeing also to eliminate the lignine residues. The use for cotton is limited to some finished products such as to bleach jeans.

Another important use of sodium hypochlorite is the wash machinery previously used with dark colours, before starting a new dyeing cycle with light colours.

In all cases a 13% NaClO solution is the starting one. For bleaching purposes it is diluted to about 0.05 – 0.07%, while to wash machinery the starting solution is used.

Sodium hypochlorite is filled into the machinery and then processing is carried out in closed system, including the final step with NaHSO₃ to remove sodium hypochlorite residues.

The only stage where workers could be exposed to NaClO is during its transfer from the reservoir tank to the machinery.

Indeed, in some cases the substance could be filled into buckets and then manually filled into the machinery. In such cases workers are committed to use adequate PPE, as the solution used is corrosive.

It should be also taken into account that the use in textile is not continuous and the frequency of machinery loading is once per week.

In a typical textile plant where sodium hypochlorite is used only as washing agent machinery, the consumption is 1300 kg/year (about 100 kg/month)

Estimate of the occupational dermal exposure during coupling-decoupling operations in Textile scenario

As reported above, for bleaching purposes the solutions of sodium hypochlorite are diluted to about 0.05-0.07%

The exposure to those solutions during coupling decoupling operations, can be estimated using EASE 2.0:

EASE 2.0 session log:

The physical-state is **liquid**

The exposure-type is **dermal**

The use-pattern is **Non-dispersive use**

The pattern-of-control is **Direct handling**

The contact-level is **Incidental** (1 event per day)

CONCLUSION: The predicted dermal exposure to Sodium Hypochlorite 0.07 % solution is **0-0.1 mg/square cm/day**

This corresponds to a maximum of 0.00007 mg Sodium Hypochlorite/cm²/day. Considering the two hands (front and back) with a surface area of 840 cm² the maximum dermal exposure corresponds to 0.06 mg/day (Ader).

Uderm pot = Ader/BW x Fabsorp = 0.06 mg/day / 70 kg x 0.1 = **0.00009 mg/kg BW/d**

4.1.1.3.5. Sewage Treatment, Drinking Water Treatment and Cooling Water Treatment

The exposure to sodium hypochlorite for the workers of cooling plants and waste water and drinking water treatment plants is generally accidental, in occasion of filling or displacement of the storage tanks. The closed disinfection system can be opened especially in occasion of filling of the disinfection product or extraordinary maintenance.

The lines of delivery of the product are normally protected for corrosive liquids.

The time of exposure during the phases of spilling is limited to the operations of coupling and decoupling and a conservative value can be of 5 minutes.

For drinking water treatment, in the the small aqueducts solutions with lower concentration can be used (6%) and containers of 50 liters can be employed. The time of displacement could be also higher, according to the circumstances.

For sewage treatment, sodium hypochlorite is used for the disinfection before the discharge. The filling operations are similar to those already described for the drinking water and for the cooling water scenarios.

Estimate of the occupational dermal exposure during coupling-decoupling operations in Sewage Treatment, Drinking Water Treatment and Cooling Water Treatment scenarios (Conservative estimate in case of solutions with a sodium hypochlorite concentration lower than 5%)

The exposure to solutions with a concentration lower than 5% during coupling decoupling operations, can be estimated using EASE 2.0:

EASE 2.0 session log:

The physical-state is **liquid**

The exposure-type is **dermal**

The use-pattern is **Non-dispersive use**

The pattern-of-control is **Direct handling**

The contact-level is **Incidental** (1 event per day)

CONCLUSION: The predicted dermal exposure to Sodium Hypochlorite 5% solution is **0-0.1 mg/square cm/day**

This corresponds to 0-0.005 mg Sodium Hypochlorite/cm²/day. Considering the two hands (front and back) with a surface area of 840 cm² the maximum dermal exposure corresponds to 4.2 mg/day (Ader).

Uderm pot = Ader/BW x Fabsorp = 4.2 mg/day / 70 kg x 0.1 = **0.006 mg/kg BW/d**

4.1.1.3.6. Institutional and Food industry (I&I)

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

- a) Industrial Premises Cleaning/Disinfection in Food & Beverage industries
 - a.1) cleaning-in-place (CIP) application
 - a.2) open plant spray cleaning application
- b) Professional general hard surface cleaning
 - b.1) mop & bucket
 - b.2) cloth & bucket
 - b.3) trigger spray with ready-to-use solution
- c) Hospital Disinfection
 - c.1) general disinfection
 - c.2) instrument disinfection
- d) Cleaning/Disinfection in food preparation establishments (kitchens / restaurants)
 - d.1) kitchen disinfection (mop & bucket)
 - d.2) mechanical ware washing
- e) Cleaning/Disinfection in Microbiological laboratories
 - e.1) cleaning of bench tops
 - e.2) cleaning and disinfection of laboratory tools (bottles, tubes, etc.).

4.1.1.3.6.1. Scenarios (for technical details see table 4.8)

a) Industrial Premises Cleaning/Disinfection in Food & Beverage industries (incl Dairy)

- a.1) Cleaning-in-place (CIP) application

Concentrated, neat products are delivered at the customer premises in 200 l drums, 500 – 1000 l semi-bulk or in bulk. The products are highly alkaline and contain 4 – 8 % hypochlorite expressed as available chlorine and generally do not contain surfactants.

From the units delivered a pipeline-connection is made to a stock tank for making the in-use solution. The product is dosed automatically into the stock tank using a transfer pump and dosing control unit.

The strength of the in-use solution is 0.04 – 0.08 % hypochlorite expressed as available chlorine.

The stock tank is connected to the processing circuit to be cleaned/disinfected and the solution is circulated in the closed system for a given time. The system is pre-rinsed with water before cleaning starts and, depending on soil level, also pre-cleaned before the disinfection stage. The coupling/decoupling operation from the pipeline to the tank and from the tank to the processing circuit to be cleaned/disinfected is designed to avoid any contact with product. Indeed though systems may vary, the opening of the two sides to be connected only takes place when they have been fixed together (see CIP coupling scheme in Figure 4.1 provided by Ecolab).

Coupling in CIP application

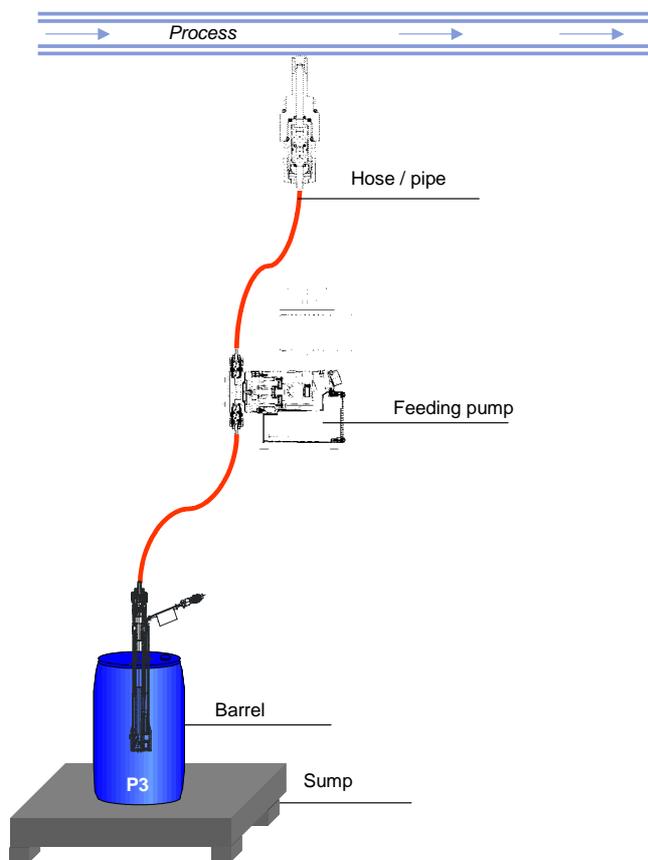


Figure 4.1. CIP Application Coupling Scheme

a.2) Open plant spray cleaning application

This application is typically used in slaughter houses, meat processing, processed food in general, etc..

Concentrated, neat products are delivered at the customer premises in 20 l containers, 200 l drums and semi-bulk. The products are highly alkaline and contain 4 - 8 % hypochlorite expressed as available chlorine. In this instance the hypochlorite is formulated with surfactant. More than 90% of these spray cleaners is estimated to consist of foam/gel cleaners (foam/gel stick better to the surface which is not flat for improved efficacy and also acts as an indicator for the operator to check what has already been cleaned).

The in-use solution is made in various ways depending on the spraying:

- automatic dosing (e.g. via a venturi system) in case of a pressure ringmain or a decentralized pressure pump. No exposure is to be expected at this stage.
- decanting or dosing into a pressure vessel: such a preparation may take place 1-2 times per day.

The strength of the in-use solution is 0.1 – 0.2 % hypochlorite expressed as available chlorine.

The products are sprayed in the form of foam or sticky gel onto walls, floors, belts, etc. using a pressure between 3 – 8 bars depending on the spraylances/spraynozzles. Before the product is applied the surface has been pre-rinsed with water (up to 20 bars) to removed the loose soil. The product is left some time onto the surfaces before removing it with a water spray. The total cleaning operation is a wet exercise and operators are therefore dressed up with watertight clotng, boots and facial masks. The application of the cleaning product takes ca. 1 hour per day. Exposure is low based on industry study data for this specific scenario. See details in section 4.1.1.3.6.2.2.

b) Professional general hard surface cleaning

b.1) Mop & bucket (typically for floor applications)

Concentrated, neat products are delivered at the customer premises in 1 – 5 l bottles/canisters. The products are mildly alkaline and contain 4 – 5 % hypochlorite expressed as available chlorine.

The in-use solution is prepared into a bucket by either decanting, dosing cap or dosing station, its strength is typically 0.05 % hypochlorite expressed as available chlorine. This preparation of in-use solutions may happen 2-3 times per day.

The product is applied onto the floor through a mop and let dry. Such an application may last max. 3 hours per person per day.

b.2) Cloth & bucket (for other surfaces than floors)

Concentrated, neat products are delivered at the customer premises in 1 – 5 l bottles/cannisters. The products are mildly alkaline and contain 4 – 5 % hypochlorite expressed as available chlorine.

The in-use solution is prepared into a bucket by either decanting, dosing cap or dosing station, its strength is typically 0.05 % hypochlorite expressed as available chlorine. This preparation of in-use solutions may happen 2-3 times per day.

The product is manually applied on the surface via a wet or damp cloth, for prolonged contact gloves are recommended. The surface is left to dry or wiped with a cloth form from a fresh water bucket depending on the circumstances. Such an application may last max. 3 hours per person per day.

b.3) Trigger spray with ready-to-use solution

Trigger sprays are becoming more and more popular in replacing the cloth & bucket approach. Trigger can be filled with the in-use solution at the customer premises, see procedure under 2.2.2.

For convenience reasons the trigger spray can also be delivered to the customer with the in-use solution already in it so-called ready-to-use concept. The strength of the ready-to-use solution is typically 0.05 % hypochlorite expressed as available chlorine.

The product is sprayed either directly onto the surface or onto a cloth and then applied to the surface.

The surface is normally left to dry. Such an application may last max. 2 hours per person per day.

This scenario is similar to the one on consumer use.

c) Hospital Disinfection

This use seemed to have decreased. It could still exist in some countries but albeit was not possible to collect data.

In hospitals, hypochlorite seems now in many countries to be used for disinfection mainly on specific occasions where it is specified in official guidelines, such as for terminal disinfection after patient isolation, or after known contamination events or spills. The concentrations used are matched to the organisms suspected to be involved. Most use is likely to be at concentrations of 0.05 - 0.1%, with specific viruses requiring e.g. 0.5 - 1%. We have as yet no detailed information on usage patterns but concentrations used are similar to other hard surface disinfection and consumer uses and because use is occasional the frequency of use will probably be similar. We consider that the kitchen disinfection scenario (d1) is the most similar to the hospital disinfection scenario and exposure can be assumed to be the same.

- c.1) General disinfection
- c.2) Instrument disinfection

d) Cleaning/Disinfection in food preparation establishments (kitchens / restaurants)

- d.1) Kitchen disinfection (mop & bucket)

Concentrated, neat products are delivered at the customer premises in 2 – 10 l bottles/canisters. The products are alkaline and contain 2 – 3 % hypochlorite expressed as available chlorine.

The in-use solution is prepared into a bucket by either decanting, dosing cap or dosing station, its strength is typically 0.05 % hypochlorite expressed as available chlorine. This preparation of in-use solutions may happen 2-3 times per day.

The product is manually applied on the surface via a wet cloth and left for some time in line with the disinfection instructions. After that the surface is wiped with a cloth from a fresh water bucket.

Gloves are recommended. The duration of this application is 1-2 hours.

- d.2) Mechanical ware washing

Concentrated, neat products are delivered at the customer premises in 10-20 l canisters and 200 l drums. The products are highly alkaline and contain 1 – 2 % hypochlorite expressed as available chlorine. The function of hypochlorite is to bleach away difficult stains like tea stains

The packaging units are connected to a dosing pump, whereby exposure hardly can occur, yet the gloves and goggles are recommended at this stage, which may happen up to 3 times a week.

The dosing pump will dose the product into the machine and a sensor steers the pump to achieve and maintain the right in-use solution, ca. 0.003 % hypochlorite expressed as available chlorine. This is a closed system and no exposure is to be expected.

Sometimes the machine has to be opened e.g. to take away a blockage; typically 3 times per day for 2 minutes. In this case accidental exposure can occur, hence gloves and goggles are recommended when opening the machine.

e) *Cleaning/Disinfection in Microbiological laboratories*

e.1) Cleaning of bench tops

A standard product will contain ca. 3-4 % hypochlorite expressed as available chlorine. Often, this stock solution is further diluted before application down to 0.05%. The stock is stored in plastic canisters and decanted for use into polyethylene laboratory wash/squeeze bottles provided with a spout. These standard bottles are designed so that the angled spout directs the fluid away (and downwards) from the one doing the squeezing.

The hypochlorite solution is splattered (not sprayed) onto the surface. The user while wearing gloves will then wipe off the bench top with a pulp sheet that is then thrown away into the special waste bin. Such a procedure will typically last maximum 5 min and be applied not more often than once per day (e.g. at the end of the working day). When no gloves are used contact with the skin must be considered.

e.2) Cleaning and disinfection of laboratory tools (bottles, centrifuge tubes, etc.)

A standard product will contain ca. 3.1 % hypochlorite expressed as available chlorine. Often, this stock solution is further diluted before application down to 0.05%. The stock is stored in plastic canisters and decanted for use into polyethylene laboratory wash/squeeze bottles provided with a spout. These standard bottles are designed so that the angled spout directs the fluid away (and downwards) from the one doing the squeezing.

The hypochlorite solution is splattered with wash bottles into vessel which are to be cleaned/disinfected or which contain equipment to be cleaned/disinfected. The closed vessels are then incubated for a period ranging from several hours to days. The used solution is then emptied into the sink. The vessels are then rinsed. Such a procedure will typically last not longer than 15 min and be applied not more often than once per day. No skin contact should occur.

Table 4.7 Summary of human exposure scenarios for Sodium Hypochlorite in I&I (Professional) Cleaning and Disinfection products/applications

Product /Application	% of sodium hypochlorite in undiluted product as available Cl₂	Handling of undiluted product		% of sodium hypochlorite in use-solution as available Cl₂	Handling of use-solution	
		Exposure route:	Frequency		Exposure route:	Frequency
Industrial Premises Cleaning / Disinfection in Food & Beverage Industries						
-cleaning-in-place circulation of use –solution through the already (pre-) cleaned equipment e.g. pipelines	4 – 8 % pH ⁶ : 14	<ul style="list-style-type: none"> • Skin: nihil (automatic dosing) • Eye: nihil (automatic dosing) • Ingestion: not applicable • Inhalation: negligible 	N.A.	0.04 – 0.08 % pH: 12 -13	None: closed system, circulation of use-solution through equipment	N.A.
- open plant cleaning low pressure spraying of foam or gel onto walls, floors of eg. slaughter houses Pressure: 3 – 8 bar	4 – 8 % pH: 14	<ul style="list-style-type: none"> • Skin: minimal manual (gloves) or automatic dosing • Eye: minimal (goggles) • Ingestion: not applicable • Inhalation: negligible 	1-2 x day	0.1 – 0.2 % pH: 12 - 13	Skin and eye: Operators are dressed up with watertight clothing, boots and facial mask because of wet environment Ingestion: not applicable Inhalation: Exposure is low based on industry study data for this specific scenario. See details in section 4.1.1.3.6.2.2.	ca. 1 hour per day
Professional general hard surface cleaners						

⁶ pH values provided in the table 4.7 are indicative and refer to the formulations.

Product /Application	% of sodium hypochlorite in undiluted product as available Cl₂	Handling of undiluted product		% of sodium hypochlorite in use-solution as available Cl₂	Handling of use-solution	
		Exposure route:	Frequency		Exposure route:	Frequency
- mop & bucket - cloth & bucket	4 - 5 %; pH: 12 4 -5 %; pH: 12	<ul style="list-style-type: none"> • Skin: minimal manual (gloves) or automatic dosing • Eye: minimal • Ingestion: negligible • Inhalation: negligible 	2-3 x day	0.05%; pH 10-11 0.05%; pH 10-11	<ul style="list-style-type: none"> • Skin: yes, in case of prolonged contact gloves are recommended • Eye: negligible • Ingestion: negligible • Inhalation: negligible 	max. 3 hours per day max. 3 hours per day
- trigger spray (ready to use solution)	not applicable, see use-solution	<ul style="list-style-type: none"> • Skin: not applicable • Eye: not applicable • Ingestion: not applicable • Inhalation: not applicable 		0.05%; pH 10-11	<ul style="list-style-type: none"> • Skin: yes, in case of prolonged contact gloves are recommended. • Eye: minimal, when used as recommended • Ingestion: not expected • Inhalation: minimal, this scenario is similar to the consumer one 	max. 2 hours per day
Hospital Disinfection						

Product /Application	% of sodium hypochlorite in undiluted product as available Cl₂	Handling of undiluted product		% of sodium hypochlorite in use-solution as available Cl₂	Handling of use-solution	
		Exposure route:	Frequency		Exposure route:	Frequency
In hospitals, hypochlorite seems now in many countries to be used for disinfection mainly on specific occasions (see 4.1.1.3.6.1 c)	Most use is likely to be at concentrations of 0.05 - 0.1%, with specific viruses requiring e.g. 0.5 - 1%.	See kitchen disinfection scenario d1	See kitchen disinfection scenario	See kitchen disinfection scenario	See kitchen disinfection scenario	
Restaurants, Food preparation establishments						
- kitchen disinfection (cloth & bucket)	2 – 3 % pH: 12 - 13	<ul style="list-style-type: none"> • Skin, Eye, Ingestion, Inhalation: see cloth & bucket application under “Professional general hard surface cleaners” 	2-3 x day	ca. 0.05 % pH: 10 - 11	<ul style="list-style-type: none"> • Skin: yes, in case of prolonged contact gloves are recommended. • Eye: negligible • Ingestion: negligible • Inhalation: negligible 	max. 1 hour per day

Product /Application	% of sodium hypochlorite in undiluted product as available Cl₂	Handling of undiluted product		% of sodium hypochlorite in use-solution as available Cl₂	Handling of use-solution	
		Exposure route:	Frequency		Exposure route:	Frequency
- mechanical ware washing	1 - 2 % pH: 14	<ul style="list-style-type: none"> • Skin: negligible (automatic dosing, gloves during connection) • Eye: negligible (automatic dosing, goggles during connection) • Ingestion: not expected • Inhalation: negligible 	1 x week	ca. 0.003 % pH: 12	<ul style="list-style-type: none"> • Skin and Eye: minimal, accidental exposure possible when opening ware washing machine, for opening machine goggles and gloves are recommended • Ingestion: not expected • Inhalation: not expected 	3 x day for 2 minutes
Use of Hypochlorite in Microbiological Laboratories						
- cleaning of bench tops as surface	3– 4 % pH: 12 –13	<ul style="list-style-type: none"> • Skin: yes, gloves are recommended • Eye, Ingestion, Inhalation: negligible, only decanting from cannister into lab squeeze bottle 	3 x week	% 0.05 pH: 10-11	<ul style="list-style-type: none"> • Skin: yes, gloves are recommended • Eye, Ingestion, Inhalation: negligible • 	5 min/day
- disinfection and cleaning of laboratory tools (bottles, tubes, etc.) as kitchen	3- 4 % pH: 12 –13	<ul style="list-style-type: none"> • Skin: yes gloves are recommended • Eye, Ingestion, Inhalation: negligible, only decanting from canister into lab squeeze bottle 	1 x day	0.05 % pH: 10-11	<ul style="list-style-type: none"> • Skin: yes gloves are recommended • Eye, Ingestion, Inhalation: negligible 	15 min/day

4.1.1.3.6.2 Exposure in I&I
4.1.1.3.6.2.1 Dermal Exposure in I&I

The use of hypochlorite in I&I (professional) cleaning and disinfection applications could lead to some dermal exposure if the standard recommendation to wear personal protection (gloves) is not followed.

Typical diluted concentrations include 0.5 g/l or 0.05% in professional general hard surface cleaning and 0.003 – 0.05 % (0.03 – 0.5 g / l) used for disinfection purposes in restaurants and also in laboratories. No routine use of undiluted bleach products was reported (Information from AISE I&I companies).

In line with the approach followed to estimate dermal exposure to hypo for consumers, the dermal exposure in I&I applications is predicted below.

The following "worst case" assumptions have been made for the I&I exposure scenario in analogy to the consumer scenario:

- No gloves are worn.
- A fixed amount of sodium hypochlorite actually penetrating the skin is estimated and assumed as 10%.
- The Exposure model considers a 0.01 cm film of substance solution is left to dry on skin, meaning all substance in it would be available for absorption.
- The surface area of the entire hand is assumed to be wetted with cleaning solution in a household scenario, whereas realistically, often only the palm might be exposed.
- The concentrations (mg/cm³) of hypochlorite in the end volume of the general cleaning / disinfection solutions are:

Cder = 0.5 mg /cm ³ (0.05% hypochlorite)	General hard surface cleaning
Cder = 0.03 mg /cm ³ (0.003% hypochlorite)	Mechanical ware washing
Cder = 0.5 mg /cm ³ (0.05% hypochlorite)	Restaurant / Kitchen disinfection

Model Parameters:

(HYPOCHLORITE) in the product [mg.cm-3]	Cder
External exposure to skin	Ader
Potential dermal uptake rate [mg.kg BW-1 day -1]	Uderm pot
Thickness of the film layer on skin [default = 0.01cm]	Tderm
Surface area of skin exposed [cm2]	AREAderm
Bioavailability for dermal exposure (default = 1)	BIOderm
Number of events per period (usually, events.day ⁻¹)	Nevents
Average female bodyweight [default = 60kg]	BW
Default factor to quantify absorption [10%]	F _{absorp}

Additional data:

- ✓ surface area of exposed skin (one hand) = 420 cm² (hard surface cleaning)
- ✓ number of cleaning jobs per day:
Nevents = 3 for general hard surface cleaning & restaurant / kitchen disinfection and
Nevents = 1/7 (equals 1 x a week) for mechanical ware washing.

General hard surface cleaning (b1 and b2)

$$A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{derm}} \times \text{Nevents} = 0.5 \text{ mg/cm}^3 \times 0.01 \text{ cm} \times 420 \text{ cm}^2 \times 3 = 6.3 \text{ mg/d.}$$

$$U_{\text{derm pot}} = A_{\text{derm}} / \text{BW} \times F_{\text{absorp}} = 6.3 \text{ mg} / 60\text{kg} \times 0.1 = 0.0105 \text{ mg/kg BW/d.}$$

Restaurant / Kitchen disinfection (d1)

$$A_{\text{derm}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{derm}} \times \text{Nevents} = 0.5 \text{ mg/cm}^3 \times 0.01 \text{ cm} \times 420 \text{ cm}^2 \times 3 = 6.3 \text{ mg/d.}$$

Mechanical ware washing (d2)

$$A_{\text{derm}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{derm}} \times \text{Nevents} = 0.03 \text{ mg/cm}^3 \times 0.01 \text{ cm} \times 420 \text{ cm}^2 \times 1/7 = 0.02 \text{ mg/d.}$$

$$U_{\text{derm pot}} = A_{\text{derm}} / \text{BW} \times F_{\text{absorp}} = 6.32 \text{ mg} / 60\text{kg} \times 0.1 = 0.0105 \text{ mg/kg BW/d.}$$

The total dermal exposure in the I&I scenarios is therefore

In General hard surface cleaning: **0.0105 mg Hypochlorite/kg BW/day**

In restaurant/kitchen disinfection and mechanical ware washing: **0.0105 mg Hypochlorite/ kg BW/day**

Based on the above outlined conservative assumptions, this value is described as a conservative I&I exposure estimate.

As the use concentration for laboratory disinfection is the same as for restaurant/kitchen disinfection (0.05%), but the frequency is lower (3 x per week vs 3 x per day), exposure in laboratories will be lower and therefore not calculated separately here.

Dermal exposure during dilution phase

Solutions are usually diluted before use. Two main cases have been foreseen where some dermal exposure might occur though accidentally. For these two cases, dermal exposure estimates based on EASE 2.0 have been calculated:

1. **Estimate of the occupational dermal exposure through EASE2.0 when diluting solutions lower than 5% in several I&I scenarios** [a.2) Open plant spray cleaning application; b.1) Mop & bucket, b.2) Cloth & bucket]

The exposure to solutions with a concentration lower than 5% when handling starting solutions, can be estimated using EASE 2.0:

EASE 2.0 session log:

The physical-state is **liquid**

The exposure-type is **dermal**

The use-pattern is **Non-dispersive use**

The pattern-of-control is **Direct handling**

The contact-level is **Incidental** (1 event per day)

CONCLUSION: The predicted dermal exposure to Sodium Hypochlorite 5% solution is **0-0.1 mg/square cm/day**

This corresponds to 0-0.005 mg Sodium Hypochlorite/cm²/day. Considering the two hands (front and back) with a surface area of 840 cm² the maximum dermal exposure corresponds to 4.2 mg/day (Ader).

$$U_{\text{derm pot}} = A_{\text{der}}/\text{BW} \times F_{\text{absorp}} = 4.2 \text{ mg/day} / 70 \text{ kg} \times 0.1 = \mathbf{0.006 \text{ mg/kg BW/d}}$$

2. **Estimate of the occupational dermal exposure through EASE 2.0 when diluting solutions lower than 3% in several I&I scenarios** [d.1) Kitchen disinfection (mop & bucket), d.2) Mechanical ware washing, e.1) Cleaning of bench tops, e.2) Cleaning and disinfection of laboratory tools (bottles, centrifuge tubes, etc.)]

The exposure to solutions with a concentration of 3% when handling starting solutions, can be estimated using EASE 2.0:

EASE 2.0 session log:

The physical-state is **liquid**

The exposure-type is **dermal**

The use-pattern is **Non-dispersive use**

The pattern-of-control is **Direct handling**

The contact-level is **Incidental** (1 event per day)

CONCLUSION: The predicted dermal exposure to Sodium Hypochlorite 5% solution is **0-0.1 mg/square cm/day**

This corresponds to 0-0.003 mg Sodium Hypochlorite/cm²/day. Considering the two hands (front and back) with a surface area of 840 cm² the maximum dermal exposure corresponds to 2.5 mg/day (Ader).

$$U_{\text{derm pot}} = A_{\text{der}}/\text{BW} \times F_{\text{absorp}} = 2.5 \text{ mg/day} / 70 \text{ kg} \times 0.1 = \mathbf{0.004 \text{ mg/kg BW/d}}$$

4.1.1.3.6.2.2 Inhalation Exposure in I&I

Some inhalation exposure to hypochlorite can occur under the above mentioned scenarios

a.2) open plant spray cleaning and b.3) use of trigger spray products for hard surface cleaning. For scenario a.2), some exposure measurement data have been obtained from I&I product manufacturers (Diversey-Lever 1997). The main contents is detailed here⁷.

The aim of the work undertaken was to establish the potential for operator exposure to airborne aerosols, and their constituent chemical components, whilst applying a range of foam based cleaners and sanitising agents using a method generally termed as “open plant spraying”.

The spraying equipment was operated at a pressure of 20 bar, although different application rates were used for application, and rinsing down. The latter task utilising clean water at higher rates.

“Real time” monitoring instruments (Miniram’s) were employed. These instruments are capable of measuring the airborne concentration of aerosol in the respirable size range (0.1 – 10 µm) over 10 second intervals, allowing a detailed pattern of exposure to be established over a consecutive series of 10 second intervals.

Using the assumption that the compounds in the airborne aerosol remained in the same concentration as the formulation of the material under test, the exposure to the individual components could be estimated.

The study was not aimed specifically at hypochlorite containing materials, and only two out of the 15 formulations used during the study contained this compound. These products did not however demonstrate any significant differences in behaviour with respect to aerosol formation.

A combination of static sampling and personal dosimetry was undertaken utilising the Miniram instruments. Spraying of each material was undertaken for a period of approximately 15 minutes, to achieve a stable condition.

Table 4.9 – Measured exposure to Product Aerosols

All aerosol concentrations are expressed as mg/m³ and relate to exposure measured over a time period of 15 minutes (approx.).

	Product Application		Rinsing	
	Personal Dosimetry	Static Samples	Personal Dosimetry	Static Samples
Mean Exposure	0.52	0.34	0.49	0.51
Range	0.19 – 0.97	0.06 – 0.72	0.30 – 0.80	0.11 – 0.69
No Studies	12	12	12	12

Conclusion of the Internal Report (Diversey-Lever 1997):

Based on the measurements of exposure to respirable aerosol the report concluded that exposure to the components of the cleaning and sanitising products under test by inhalation or airborne aerosol was negligible. In addition, where occupational exposure limits existed for some of the components, exposure was estimated to be several orders of magnitude below the legal limits.

⁷ The complete summary has been made available to the rapporteur.

Discussion: Estimated exposure to Hypochlorite (as available chlorine)
Using the above measurements it is possible to estimate the potential exposure to hypochlorite (expressed as available chlorine) assuming that the aerosol composition is identical to that of the formulation as discussed in the introduction.

Starting from a typical formulation concentration range of 4 - 8 % hypochlorite (as available chlorine) which is diluted by the spray equipment to a cleaning foam or sanitising product containing approximately 0.2% hypochlorite (independent from the original concentration, the final concentration is maintained at 0.2% available chlorine), then exposure can be estimated as follows:

Table 4.10 – Theoretical Exposure to Hypochlorite (as available chlorine)

Note: Results are expressed as micrograms per cubic meter (µg/m³)

	Product Application		Rinsing	
	Personal Dosimetry	Static Samples	Personal Dosimetry	Static Samples
Mean Exposure	1.04 (ie: 520 µg/m ³ X 0.002 (ie 0.2%)) ⁸	0.68	0.98	1.02
Range	0.4 – 1.9	0.1 – 1.4	0.6 – 1.6	0.2 – 1.4

¹ One illustrative calculation to show the link between table 4.9 and 4.10

Conclusion

Based on the data generated by the study, for the equipment used, the process of open plant spraying is unlikely to result in significant exposure to hypochlorite (as available chlorine).

There is no Occupational Exposure Limit [OEL] or Threshold Limit Value [TLV] set for hypochlorite [available chlorine], the nearest comparison would be for chlorine gas which is set in the UK at 1.5 mg/m³ TWA and 2.9 mg/m³ STEL. Alternatively comparison with other respiratory irritants such as sodium hydroxide (2 mg/m³ STEL), potassium hydroxide (2 mg/m³ STEL), or hydrogen peroxide (1.4 mg/m³ TWA, 2.8 mg/m³ STEL) may be relevant. Clearly the estimated exposures to hypochlorite from the above table are well below any of these exposure limits.

Therefore it can be concluded from the data generated for exposure to airborne aerosol during “open plant spraying”, and under the conditions of the trial, inhalation exposure to hypochlorite is likely to be very small and is well below occupational exposure limits set for other similar respiratory irritants.

Based on the above estimated concentration in the air I&I workers are typically exposed to the systemic uptake of hypochlorite via inhalatory route from scenario a.2) can be derived as follows:

$$f_{\text{resp}} \times C_{\text{air}} \times Q_{\text{inh}} \times t \times N_{\text{events}}$$

⁸ One illustrative calculation to show the link between table 4.9 and 4.10

$$I_{inh} = \frac{\quad}{BW} \quad [g / kg BW / day]$$

$$I_{inh} = \frac{1 \times 1.9 \mu g \times 1.25 m^3 \times 1 \times 2}{70 kg \times m^3} = 0.068 \mu g / kg BW / day = \mathbf{70 ng / kg BW / day}$$

Model Parameters:

Inhalatory Intake

Average conc. of hypochlorite in air
(highest concentration from table 4.10 was used: 1.9 $\mu g/m^3$)
Respirable or inhalable fraction of product (default = 1)
Ventilation rate of an adult (default workers = 1.25 m^3 /hour)

I_{inh}
 C_{air}
 f_{resp}
 Q_{inh}

Duration of exposure (hour)

t

Number of events per period (usually, events.day⁻¹)
Average human bodyweight [default = 70kg]

N_{events}
BW

The systemic uptake of hypochlorite via the inhalatory route from scenario b.3) trigger spray use is derived as follows (in analogy to household scenario, see 4.1.1.4.1):

$$I_{inh} = \frac{q \times w_f \times f_{resp} \times C_{air} \times Q_{inh} \times t \times N_{events}}{BW} \quad [g / kg BW / day]$$

$C_{air\ inhaled}$ was determined in section 4.1.1.4.1 to be 1.68 $\mu g / m^3$ of sprayed product (for high end hypochlorite concentration for household spray products of 3 %, the inhalable hypochlorite concentration from this measured mean mass concentration is:

$$C_{air\ inhaled} = \mathbf{56 \times 0.03 = 1.68 [\mu g / m^3]}$$

The product used in I&I scenario b.3) contains 0.05% hypochlorite (see summary table 4.8). Therefore, $C_{air\ inhaled}$ for this scenario is:

$$= \mathbf{56 \times 0.0005 = 0.028 \mu g / m^3 \text{ hypochlorite}}$$

$$= \mathbf{0.000028 mg/m^3}$$

$$I_{inh} = \frac{20 g \times 1 \times 0.028 \mu g \times 1.25 m^3 \times 2 h \times 0.75}{m^3 \times 11.8 g \times h \times 70 kg} \quad [\mu g / kg BW / day]$$

$$I_{inh} = 0.00127 \mu g / kg BW / day$$

Model Parameters:

Inhalatory Intake	I_{inh}
Amount of undiluted product used	q
Weight fraction of hypochlorite in product (1, as already considered in $C_{air\ inhalable}$)	w_f
Average conc. of inhalable aerosol in air ($0.028\ \mu\text{g} / \text{m}^3$ hypochlorite, see above)	C_{air}
Respirable or inhalable fraction of product (default = 1)	f_{resp}
Ventilation rate of an adult (default = $1.25\ \text{m}^3/\text{hour}$)	Q_{inh}
Duration of exposure	t
Number of events per period (usually, $\text{events}\cdot\text{day}^{-1}$)	N_{events}
Average human bodyweight [default = 70kg]	
Weight fraction (percentage) absorbed or bioavailable: = 75 % (TGD, 1996).	f_{bio} BW

The inhalation exposure values from scenario a.2) and b.3) are not added up as a.2) open plant spraying happens mostly in industrial settings while scenario b.3) applies to professional cleaning personnel for example in restaurants or public buildings.

Exposure concentration used to evaluate local irritation effects in the respiratory system for scenario b.3) (in analogy to household scenario, see 4.1.1.4.1):

The exposure concentration considered for local irritation effects is assumed to be **$56\ \mu\text{g} / \text{m}^3$ of spray product**, as explained in detail in section 4.1.1.4.1. Based on a hypochlorite concentration of **0,05 %** for the I&I trigger spray products this equals **$0.000028\ \text{mg} / \text{m}^3$ hypochlorite**.

4.1.1.3.7. Pulp and Paper

It should 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 led to the current situation in Europe, where the use of chlorine-based bleaching processes is minimal.

A 1998 review from CEPI (Confederation of European Paper Industries), though not complete, suggests that chlorine and sodium hypochlorite are no longer used for bleaching purposes in Western Europe (see paragraph 3.1.1.8). In some cases, sodium hypochlorite can be used for disinfection and cleaning purposes. These uses are part of the general I&I scenario.

In the past, bleaching operations with sodium hypochlorite were performed in bleaching reactors. Afterwards the pulp was washed in a vacuum filter. Sodium hypochlorite solution was filled into the reactor through closed systems.

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. No health problems related to the use of hypochlorite were mentioned.

Therefore we can conclude that human exposure to hypochlorite in the pulp and paper industry in Western Europe is insignificant.

Table 4.11 Conclusions of the occupational exposure assessment for sodium hypochlorite

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

Swimming pools instructors/competition swimmers								Cl ₂			
	Short term							0.00513 ³ (0.0049 as av. Cl ₂)	EASE/ Calculated		
Textile bleaching	Full shift/ Short term							0.00009 (0.000085 as av. Cl ₂)	EASE/ Calculated		
STP, DW and CW	Full shift/ Short term							0.006 (0.0057 as av. Cl ₂)	EASE/ Calculated		
I&I (b1,b2)	Full shift							0.0105 (0.01 as av. Cl ₂)	EASE/ Calculated		
I&I (d1+d2)	Full shift							0.0105 (0.01as av. Cl ₂)	EASE/ Calculated		
I&I (a2)	Full shift				6.8E-05 (6.48E-05 as av. Cl ₂)	Calculated					
I&I (b3)	Full shift				6.0E-07 (5.7E-07 as av. Cl ₂)	Calculated					

1: Full shift, short term, etc.

2: Measured, EASE, Expert judgment, Calculated, etc.

3: Dermal + oral

4.1.1.4. Consumer exposure

For each scenario the general public exposure is described. Exposure for general public is relevant in household, swimming pool and drinking water scenarios, and only those will be dealt with in detail.

4.1.1.4.1. Household

There are three typical usage conditions of bleach products:

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

In each of these conditions exposure is likely to be less than 30 minutes. The characteristic odour of “bleach” arises from the volatility of the hypochlorous acid which is present in solutions at very low concentrations given the pHs applying during both neat and diluted usage ($\text{pH} \geq 9.0$).

Household hypochlorite preparations are sold in Europe at concentrations which vary between 0.5-12.5% available chlorine levels, with a prevalence of concentrations ranging from 3-5%.

Accurate Market Research Data are available which record penetration of household bleaches together with consumption of product per household. The volumes allocated to laundry and hard surface cleaning usage are also known (OSPARCOM, September 1996). Table 2.6 summarizes household usage of hypochlorite bleach products in countries of significant penetration ($>10\%$ households). In some countries, depending on the end usage (e.g. laundry, hard surface cleaning), a dosage recommendation is made. If the product is used for disinfection purposes then a dosage recommendation is made which is designed to guarantee the level of microbial life remaining after cleaning is below that which is believed to be dangerous to health. The dosage recommendation will depend on the level of bleach in the product and the end usage.

Under the Dangerous Substances Directive (67/548/CEE) and the dangerous Preparations Directive (88/379/CEE) hypochlorite solutions are classified as “Corrosive” above 10% and “Irritant” between 5-10%. The final classification of the product will also depend on the levels of other materials present such as caustic soda and surfactants.

Dermal Exposure

Hypochlorite can be considered as a substance in a non-volatile medium (household bleach), which is diluted for normal use.

Under normal use conditions, the key route of exposure to hypochlorite is via dermal contact when hands may be dipped into a diluted hypochlorite solution in a laundry bleaching or household cleaning task. Typical diluted concentrations range from 0.1-0.5 g/l (or 0.01-0.05%) (AISE, March 1997). Exposure to concentrated solutions (25-50 g/l, or 2.5 – 5.0 %) is less frequent and is due to undiluted use in toilet bowl cleaning for example (AISE, March 1997). The concentrated solutions will rarely be in direct contact

with skin for any appreciable time period, as a cleaning implement will be used and the skin will be wiped or rinsed after contact with the concentrated bleach product.

The potential dermal exposure was calculated considering the two typical usages of NaClO which could lead to exposure to the substance: hand washing/laundry pre-treatment and hard surface cleaning. To this end, the habits and practice data collected by industry (AISE companies of HERA, <http://www.heraproject.com/Index.cfm>) and included in the updated version of the TGD (Appendix submitted to ECB in 2002) have been used.

The total dermal exposure was estimated assuming 2 laundry bleaching tasks/ week plus 1 hard surface cleaning task / day (both are maximum use data).

The total amount of hypochlorite to which the skin may be exposed externally as well as the potential uptake via skin has been determined.

In the absence of experimental data on skin penetration of hypochlorite, two routes could be followed to estimate the amount absorbed through the skin:

Estimate a fixed fraction of hypochlorite for absorption

A fixed amount of sodium hypochlorite actually penetrating the skin can be estimated. Given the reactivity and polarity of the chemical as well as the known barrier functions of skin, this amount can be estimated to lie between 1 - 10 %, and the upper estimate 10 % is used here. Thus, a conservative approach has been used to estimate the dermal exposure to hypochlorite.

Assuming a "worst case" scenario using upper levels of ranges, the concentration (mg/cm³) of hypochlorite in the end volume of the bleaching / cleaning solution is:

For laundry bleaching / pre-treatment:

$C_{der} = 0.5 \text{ mg /cm}^3$ (0.05% hypochlorite)

(Data from AISE, 1997 cite 500 ppm which equals 0.05% hypochlorite as maximum concentration for laundry bleaching.)

Habits & Practices data in the updated TGD consumer exposure section, 2002 report 1% bleach solution as the high-end concentration used in laundry bleaching. Using a hypochlorite bleach product with 5% hypochlorite content, this equals a 0.05% hypochlorite concentration in the laundry bleaching solution).

For household cleaning:

$C_{der} = 5.0 \text{ mg /cm}^3$ (0.5% hypochlorite)

(Data from AISE, 1997 0.5% hypochlorite reported as upper level of range in use for kitchen surface cleaning).

Model Parameters:

(HYPOCHLORITE) in the product [mg.cm ⁻³]	C_{der}
External exposure to skin [mg/day]	A_{der}
Potential dermal uptake rate [mg.kg BW ⁻¹ day ⁻¹]	$U_{derm \text{ pot}}$
Thickness of the film layer on skin [default = 0.01cm]	T_{derm}
Surface area of skin exposed [cm ²]	$AREA_{derm}$
Bioavailability for dermal exposure (default = 1)	BIO_{derm}
Number of events per period (usually, events.day ⁻¹)	$Nevents$

Average female bodyweight [default = 60kg]
Default factor to quantify absorption [10%]

BW
 F_{absorp}

Additional data:

- ✓ typical level of HYPOCHLORITE in household bleach products = 3 – 5%
- ✓ upper hypochlorite concentration in laundry use = 0.05%
- ✓ upper hypochlorite concentration in household applications = 0.5%
- ✓ surface area of exposed skin (both hands) = 840 cm² (laundry pre-treatment)
- ✓ surface area of exposed skin (one hand) = 420 cm² (hard surface cleaning)
- ✓ number of laundry bleaching jobs per week = 2
- ✓ number of cleaning jobs per day = 1

1. Laundry Bleaching/Pre-treatment:

$$A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} \times \text{Nevents} = 0.5 \text{ mg/cm}^3 \times 0.01 \text{ cm} \times 840 \text{ cm}^2 \times 2/7 \text{ days} = 1.2 \text{ mg/d.}$$

$$U_{\text{derm pot}} = A_{\text{der}} / \text{BW} \times F_{\text{absorp}} = 1.2 \text{ mg} / 60 \text{ kg} \times 0.1 = 0.002 \text{ mg} / \text{kg BW/d.}$$

2. Hard surface cleaning

$$A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} = 5.0 \text{ mg/cm}^3 \times 0.01 \text{ cm} \times 420 \text{ cm}^2 \times 7/7 = 21 \text{ mg} / \text{d.}$$

$$U_{\text{derm pot}} = A_{\text{der}} / \text{BW} = 21 \text{ mg} / 60 \text{ kg} \times 0.1 = 0.035 \text{ mg} / \text{kg BW} / \text{d.}$$

The total dermal exposure in the household using the conservative dermal uptake assumption of 10% is therefore

0.002 + 0.035 = 0.037 mg Hypochlorite/kg BW/day corresponding to 0.035 mg/kg BW day as av. Cl₂.

This value described is conservative based on the fact that high end use concentration data were used and multiplied in the calculation with the following conservative assumptions:

- TGD exposure model considers a 0.01 cm film of substance solution is left to dry on skin, whereas in practice this film is likely to be wiped off at least or rinsed.
- A 10 % absorption value from this amount is very likely a conservative assumption for this polar, reactive chemical.
- 2 laundry bleaching tasks per week plus 1 household cleaning task per day were assumed
- The surface area of the entire hand was assumed to be wetted with cleaning solution in a household scenario, whereas realistically, often only the palm might be exposed.

Inhalation Exposure

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

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

Trigger spray bottles for household cleaners are designed to deliver essentially all their contents to the surface to be cleaned. Unlike spray containers that are under pressure, trigger sprayers do not have sophisticated delivery systems to deliver a fine, mist-like spray. They are designed to mostly deliver product in large particles (average > 75 µm) or as a foam to the surfaces to be cleaned. Small amounts of product will become temporarily suspended in air, but only particles smaller than 30 µm will remain in the air for any appreciable time. The standard trigger spray apparatus is designed to minimize the numbers of particles ejected that may become airborne.

Industry has some knowledge about the amount of airborne particles discharged from trigger spray bottles of different manufacturers (data from repeated internal control measurements as well as product & packaging development). Based on that data, the consumer exposure to this airborne fraction of hypochlorite-containing spray products is calculated below.

A) Exposure concentration used for systemic uptake of hypochlorite through inhalation:

Derivation of average concentration of inhalable hypochlorite in air C_{air} :
Aerosol measurements were done on hypochlorite-based trigger spray cleaners typical of the EU market (see Annex 8 for details). Two test samples were tested in triplicates. The sprays were pumped, using 10 successive squeezes of the trigger, against the back wall of a 512 litre chamber (= 0.512 m³, dimensions 0.8m x 0.8m x 0.8m) to simulate its use in a confined environment. The number and mass of airborne particles in the “breathing zone” (the chamber) were determined by sampling the atmosphere from the chamber at a rate of five litres a minute via a short tube connected to a TSI Model 3320 Aerodynamic Particle Sizer (APS) which samples particles in the size range 0.5 to 20 µm.

Data from the breathing zone measurements relating to particle number and particle mass were automatically calculated by the APS and associated software. Also the mean respirable and inhalable mass concentrations were determined this way and the output obtained in µg/m³ of product sprayed.

The mean mass concentration determined was **56 µg/m³** (range 26 – 92 µg/m³). This concentration was measured in the chamber upon 10 trigger spray squeezes which released on average 1.18 g of product each. This experimental set-up conservatively mimics typical consumer product use in confined spaces.

Based on the high end hypochlorite concentration for household spray products of 3 %, the inhalable hypochlorite concentration from this measured mean mass concentration is:

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

$C_{\text{air inhalable}}$ is determined via this experiment based on the entire aerosol fraction measured in the size range 0.5 – 20 µm. As typically only aerosols in the size range < 10 µm can actually reach the deep lung and be available for systemic uptake, the concentration used in the subsequent equation could be considered a conservative value.

Systemic exposure derived from this $C_{\text{air inhalable}}$:

$$I_{\text{Inh}} = \frac{5 \text{ g} \times 1 \times 1.68 \text{ } \mu\text{g} \times 0.8 \text{ m}^3 \times 0.125\text{h} \times 4 \times 0.75}{\text{m}^3 \times 11.8 \text{ g} \times \text{h} \times 70 \text{ kg} \times 1000} \text{ [mg/kg BW/day]}$$

$$I_{\text{Inh}} = 0.00305 \text{ } \mu\text{g} / \text{kg BW} / \text{day}$$

Model:

$$I_{\text{inh}} = \frac{q \times w_f \times f_{\text{resp}} \times C_{\text{air}} \times Q_{\text{inh}} \times t \times N_{\text{events}} \times f_{\text{bio}}}{\text{BW}} \text{ [g/kg BW/day]}$$

Model Parameters:

Inhalatory Intake	I_{inh}
Amount of undiluted product used per task	q
Weight fraction of hypochlorite in product	w_f
Average conc. of hypochlorite in air, derived from experimental set-up and corrected per g product	C_{air}
Respirable or inhalable fraction of product: = 100%, given that the experimentally determined value of C_{air} refers to the fraction of likely respirable particles	f_{resp}
Ventilation rate of an adult (default = 0.8 m ³ /hour)	Q_{inh}
Duration of exposure	t
Number of events per period (usually, events.day-1)	N_{events}
Average human bodyweight [default = 70kg]	BW
Weight fraction (percentage) absorbed or bioavailable: = 75 % (TGD, 1996).	f_{bio}

Other data used:

- ✓ 1) typical level of hypochlorite in household bleach sprays= 1 – 3%
(3 % is used in calculation)
- ✓ 2) assume the number of events or jobs per day = 4
- ✓ 3) assume the duration of a spray cleaning event to 7.5 minutes (0.125 h)
- ✓ 4) assume amount of bleach spray product used per event to 5 g
(based on industry data / HERA)

B) Exposure concentration used to evaluate local irritation effects in the respiratory system:

Data obtained with the TSI Model 3320 Aerodynamic Particle Sizer from the same breathing zone measurement of aerosols generated by spraying hypochlorite-based spray products are used for this exposure assessment as well.

As above, $C_{\text{air inhalable}}$ based on particles collected in the 0.5 – 20 μm size range is determined to:

$$\begin{aligned} C_{\text{air inhalable}} &= \mathbf{1.68 \text{ } [\mu\text{g} / \text{m}^3]} \\ &= \mathbf{0.00168 \text{ } [\text{mg} / \text{m}^3]} \end{aligned}$$

In addition, an attempt was also made using an Andersen Cascade Impactor to determine whether any particles greater than 20 μm would remain airborne long enough so that they could be inhaled and potentially cause effects in the upper respiratory tract. The amounts of material collected using the ACI was too small for analysis indicating that no significant amounts of material remain suspended in the air, and thus inhalable, in particles greater than 20 μm . This confirms what would be expected because particles of 20 μm and above rapidly fall out of the air and are not available for breathing.

Hence, the concentration of inhalable hypochlorite determined to 1.68 $\mu\text{g} / \text{m}^3$ is a realistic estimate of a concentration which needs to be evaluated for local irritation effects in the respiratory system.

Accidents

An overview of reported accidents linked to the household use of hypochlorite is given here for information. The data show that incidence and severity are limited. This paragraph is based on a four-year survey (from 1989 to 1992) by Poison Control Centers across Europe (Racioppi et al., 1994). As data were available for all Poison Control Centers for 1992 and no significant effect variation was observed over years, only data from 1992 have been reported in the table 4.12. On average, the products involved in these accidental exposures contained 6% sodium hypochlorite, except for France where products containing 12.5% were marketed. From the survey, it appears

that the numbers of calls related to exposure to sodium hypochlorite is limited and vary from 1.7 to 5.4% of the total number of calls and from 5 to 20% of the calls related to domestic products. The data show that the main exposure route is oral ingestion, followed by inhalation. The authors noted that “exposure of humans to bleaches results in no or minor transient adverse health effects with no permanent sequelae”.

Table 4.12. 1992 Data from Poison Control Centers (Racioppi et al., 1994) ⁹

	France				Italy				Belgium		Greece		Turkey		Spain	
	Lyon ¹⁰		Paris		Milan		Rome		Brussels		Athens		Ankara		Madrid	
	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%
Ingestion	514	74,7	1323	77,1 ¹¹	617	88,5	160	62,5	413	38,3	934	49,2	92	82,1	754	61,7
Inhalation ¹²	134	19,5	285	16,6	55	7,9	90	35,2	570	52,8	950	50,1	18	16,1	322	26,4
Skin irritation	16	2,3	33	1,9	8	1,1	3	1,2	31	2,9	4	0,2	2	1,8	21	1,7
Eye irritation	24	3,5	76	4,4	17	2,4	3	1,2	65	6,0	9	0,5	0	0,0	125	10,2
total	688		1717		697		256		1079		1897		112		1222	
total calls	20350		52260		28442		4710		48713		33263		6677		41781	
total domestic	3908		11261		7435		1272		14270		7838		na		6670	
total hypochlorite	623		1673		759		255		1082		1897		112		1240	
ratio hypochlorite/total calls	3,1		3,2		2,7		5,4		2,2		5,7		1,7		3,0	
ratio hypochlorite/domestic	15,9		14,9		10,2		20,0		7,6		24,2		na		18,6	

Potential exposure to by-products and contaminants from hypochlorite used in household applications

Contaminants and by-products can be present in hypochlorite solutions. These can be introduced during the preparation stage (e.g. mercury), or can be formed during the storage of the product (e.g. chlorate).

In the household scenario mercury doesn't represent a problem as only a minimal percentage deposits as residues on washed surfaces, from which it cannot evaporate as it is the form of ionised inorganic soluble mercury. After use, when sodium hypochlorite solution discharged to sewers reaches the depuration plant, mercury is adsorbed on biological sludge producing contamination. Information about mercury species will be detailed in Appendix 1.

⁹ Data from Paris Poison Control Center (1994) have been received separately and have also been added.

¹⁰ One third of the products refer to concentrated bleach (12.5% sodium hypochlorite)

¹¹ 15% of accidental ingestion refer to concentrated bleach (12.5% sodium hypochlorite)

¹² Moreover, it has been reported that in 80% of the accidents, where hypochlorite was mixed with another product causing release of dangerous gases, the human effect it was mild; i.e. more than 75% were free of symptoms after 6 hours (RPA, 1997).

4.1.1.4.2. Swimming Pool

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

For data on disinfecting agents used in swimming pools, see paragraph 4.1.1.3.3. The average contact time of the general public with the atmosphere of the closed swimming pool is generally around one hour. Long time swimmers or sportsmen stay for a much longer time, breathing the atmosphere just at the surface of the pool, which contains a higher content of volatile by-products.

Exposure to sodium hypochlorite

A. Calculation of chronic and acute exposure for swimming pool users (adult)

Dermal exposure for swimming pool users (adult)

A calculation of sodium hypochlorite uptake for **swimming pool users** was performed assuming an exposure of 1 hour per day (3 events of 1 hour per week) of the whole body surface, an average concentration of substance of 3.0 mg/l and a thickness of layer of product on skin of 0.01 cm

A fixed amount of sodium hypochlorite actually penetrating the skin can be estimated. Given the reactivity and polarity of the chemical as well as the known barrier functions of skin, this amount can be estimated to lie between 1 - 10 %, and the upper estimate 10 % is used here. Thus, a conservative approach has been used to estimate the dermal exposure to hypochlorite.

Model Parameters:

(HYPOCHLORITE) in the product [mg.cm ⁻³]	C _{der}	= 3.0 x 10 ⁻³
External exposure to skin [mg/d]	A _{der}	= 0.249
Potential dermal uptake rate [mg.kg BW ⁻¹ day ⁻¹]	U _{derm pot}	
Thickness of the film layer on skin [default = 0.01cm]	T _{derm}	= 0.01
Surface area of skin exposed [cm ²]	ARE _{derm}	=19400
Bioavailability for dermal exposure (default = 1)	BI _{Oderm}	= 1
Number of events per period (usually, events.day ⁻¹)	Ne _{vents}	= 1
Number of events per week		= (3/7)
Average male bodyweight [default = 70kg]	BW	= 70
Default factor to quantify absorption [10%]	F _{absorp}	=10%

$$A_{der} = C_{der} \times T_{der} \times Area_{der} \times Nevents \times 3/7 = 0.249\text{mg/d}$$

$$U_{\text{derm pot}} = A_{\text{der}} / \text{BW} \times F_{\text{absorp}} = 0.249/70 \times 0.1 \times 1000 = 0.356 \mu\text{g/kg/d}$$

Oral exposure for swimming pool users (adult)

Assuming an ingestion of 0.1 l of water per event as a reasonable worst case for normal-low-skill swimmers, an additional oral exposure of 1.84 $\mu\text{g/kg/d}$ is calculated ($3.0 \text{ mg/l} \times 0.1 \text{ l} / 70 \text{ kg} \times 1 \times 3/7$).

Total systemic exposure for swimming pool users (adult)

The above calculations lead to a total systemic chronic exposure of **2.19 $\mu\text{g/kg/d}$** ($2.1 \times 10^{-3} \text{ mg/kg/d}$ as av Cl_2). This latter value will be taken forward for Risk Characterisation.

The acute systemic exposure (ASE) can be calculated from a single event:

ASE = U_{derm pot} + U_{oral}

where:

U_{derm pot} is the potential dermal uptake from a single event = $A_{\text{der}} / \text{BW} \times F_{\text{absorp}}$
 $A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} = 0.58 \text{ mg/d}$; hence U_{derm pot} = 0.83 $\mu\text{g/kg}$.

U_{oral} is the oral uptake and is given by the following: U_{oral} = 3 mg/l x 0.1 l/70 = 4.3 $\mu\text{g/kg}$

ASE = 4.3 + 0.83 = 5.13 $\mu\text{g/kg}$ corresponding to 0.0049 mg/kg BW as av. Cl_2 .

B. Calculation of chronic and acute exposure for swimming pool users (children 1 year)

Dermal exposure for swimming pool users (children 1 year)

A calculation of sodium hypochlorite uptake for **swimming pool users (children 1 year)** was performed assuming an exposure of 1 hour per day (1 event of 1 hour per 2 weeks) of the whole body surface, an average concentration of substance of 3.0 mg/l and a thickness of layer of product on skin of 0.01 cm

A fixed amount of sodium hypochlorite actually penetrating the skin can be estimated. Given the reactivity and polarity of the chemical as well as the known barrier functions of skin, this amount can be estimated to lie between 1 - 10 %, and the upper estimate 10 % is used here. Thus, a conservative approach has been used to estimate the dermal exposure to hypochlorite.

Model Parameters:

(HYPOCHLORITE) in the product [mg.cm ⁻³]	C _{der}	= 3.0 x 10 ⁻³
External exposure to skin [mg/d]	A _{der}	= 0.021
Potential dermal uptake rate [mg.kg BW ⁻¹ day ⁻¹]	U _{derm pot}	

Thickness of the film layer on skin [default = 0.01cm]	T _{derm}	= 0.01
Surface area of skin exposed [cm ²]	AREAd _{derm}	= 10000
Bioavailability for dermal exposure (default = 1)	BIO _{derm}	= 1
Number of events per period (usually, events.day-1)	Nevents	= 1
Number of events per week		= (0.5/7)
Average male bodyweight [default = 10kg]	BW	= 10
Default factor to quantify absorption [10%]	F _{absorp}	=10%

$$A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} \times \text{Nevents} \times 0.5/7 = 0.021 \text{ mg/d}$$

$$U_{\text{derm pot}} = A_{\text{der}} / \text{BW} \times F_{\text{absorp}} = 0.021/10 \times 0.1 \times 1000 = 0.21 \text{ } \mu\text{g/kg/d}$$

Oral exposure for swimming pool users (children 1 year)

Assuming an ingestion of 0.1 l of water per event as a reasonable worst case for a 1 year children in the swimming pool, an additional oral exposure of 2.14 $\mu\text{g/kg/d}$ is calculated (3.0 mg/l x 0.1 l/10 kg x 1 x 0.5/7).

Total systemic exposure for swimming pool users (children 1 year)

The above calculations lead to a total systemic chronic exposure of **2.35 $\mu\text{g/kg/d}$** ($2.24 \times 10^{-3} \text{ mg/kg/d}$ as av Cl₂). This latter value will be taken forward for Risk Characterisation.

The acute systemic exposure (ASE) for children of 1 year can be calculated from a single event:

$$\text{ASE} = U_{\text{derm pot}} + U_{\text{oral}}$$

where:

$$U_{\text{derm pot}} \text{ is the potential dermal uptake from a single event} = A_{\text{der}} / \text{BW} \times F_{\text{absorp}}$$

$$A_{\text{der}} = C_{\text{der}} \times T_{\text{der}} \times \text{Area}_{\text{der}} = 0.3 \text{ mg/d; hence } U_{\text{derm pot}} = 3 \text{ } \mu\text{g/kg.}$$

U_{oral} is the oral uptake and is given by the following: U_{oral} = 3 mg/l x 0.1 l/10 = 30 $\mu\text{g/kg}$

$$\text{ASE} = 30 + 3 = 33 \text{ } \mu\text{g/kg corresponding to } 0.031 \text{ mg/kg BW as av. Cl}_2.$$

C. Calculation of chronic and acute exposure for swimming pool users (children 10 year)

Dermal exposure for swimming pool users (children 10 year)

A calculation of sodium hypochlorite uptake for **swimming pool users (children 10 year)** was performed assuming an exposure of 1 hour per day (1 events of 1 hour per week) of the whole body surface, an average concentration of substance of 3.0 mg/l and a thickness of layer of product on skin of 0.01 cm

A fixed amount of sodium hypochlorite actually penetrating the skin can be estimated. Given the reactivity and polarity of the chemical as well as the known barrier functions of skin, this amount can be estimated to lie between 1 - 10 %, and the upper estimate 10 % is used here. Thus, a conservative approach has been used to estimate the dermal exposure to hypochlorite.

Model Parameters:

(HYPOCHLORITE) in the product [mg.cm ⁻³]	C _{der}	= 3.0 x 10 ⁻³
External exposure to skin [mg/d]	A _{der}	= 0.051
Potential dermal uptake rate [mg.kg BW ⁻¹ day ⁻¹]	U _{derm pot}	
Thickness of the film layer on skin [default = 0.01cm]	T _{derm}	= 0.01
Surface area of skin exposed [cm ²]	AREA _{derm}	= 12000
Bioavailability for dermal exposure (default = 1)	BIO _{derm}	= 1
Number of events per period (usually, events.day ⁻¹)	Nevents	= 1
Number of events per week		= (1/7)
Average male bodyweight [default = 30kg]	BW	= 30
Default factor to quantify absorption [10%]	F _{absorp}	=10%

$$A_{der} = C_{der} \times T_{der} \times Area_{der} \times Nevents \times 1/7 = 0.051 \text{ mg/d}$$

$$U_{derm \text{ pot}} = A_{der} / BW \times F_{absorp} = 0.051/30 \times 0.1 \times 1000 = 0.17 \text{ } \mu\text{g/kg/d}$$

Oral exposure for swimming pool users (children 10 year)

Assuming an ingestion of 0.1 l of water per event as a reasonable worst case for a 10 year children in the swimming pool, an additional oral exposure of 1.43 $\mu\text{g/kg/d}$ is calculated (3.0 mg/l x 0.1 l /30 kg x 1 x 1/7).

Total systemic exposure for swimming pool users (children 10 year)

The above calculations lead to a total systemic chronic exposure of **1.6 $\mu\text{g/kg/d}$** (1.52x 10⁻³ mg/kg/d as av Cl₂). This latter value will be taken forward for Risk Characterisation.

The acute systemic exposure (ASE) for children of 10 year can be calculated from a single event:

ASE = U_{derm pot} + U_{oral}

where:

U_{derm pot} is the potential dermal uptake from a single event = A_{der} / BW x F_{absorp}
A_{der} = C_{der} x T_{der} x Area_{der} = 0.36 mg/d; hence U_{derm pot} = 1.2 $\mu\text{g/kg}$.

U_{oral} is the oral uptake and is given by the following: U_{oral} = 3 mg/l x 0.1 l/30 = 10 $\mu\text{g/kg}$

ASE = 10 + 1.2 = 11.2 $\mu\text{g/kg}$ corresponding to 0.011 mg/kg BW as av. Cl₂.

NOTE:

The exposure estimates for competition swimmers have been considered to be similar as for the swimming pool instructors/competition swimmers (see section 4.1.1.3.3).

Exposure to chlorinated by-products

Data and information presented under workers' exposure scenario are valid also for consumers. The main chlorinated by-products measured in swimming pools water and air are presented in paragraph 4.1.1.3.3. Typical ranges are mentioned in table 4.6.

A study regarding public open swimming pool was carried out in the town of Modena (Italy) (Aggazzotti et al., 1995). The results of this study showed concentration levels of CHCl_3 between 20-40 and 90-140 $\mu\text{g}/\text{m}^3$ in the atmosphere near the pool. In the stands and in the changing rooms the levels ranged between 10 and 30 $\mu\text{g}/\text{m}^3$. This variation is related to physico-chemical properties of the water and to microclimatic environmental parameters. CHCl_3 concentration values in alveolar air and in blood are related to the activity of the people present in the swimming pool. Visitors in the stands showed an average value of 48 $\mu\text{g}/\text{m}^3$ while the swimmers values ranged between 60-85 $\mu\text{g}/\text{m}^3$ depending on physical effort.

Conclusion

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

4.1.1.4.3. Drinking water

Exposure to sodium hypochlorite

It is possible to define the exposure of the general population to free available chlorine (the sum of molecular chlorine, hypochlorous acid and hypochlorite ion expressed in mass equivalent of chlorine) derived from the use of sodium hypochlorite in drinking water treatment.

The European population served by water distribution network is around 325 - 335 million of inhabitants (90% of total population) and generally this water is treated with different disinfectants.

The fraction of inhabitants served by aqueducts supplied by water treated with NaClO is different in each country: the available data shows a range from 3% in Spain to 68% in Portugal (Table 4.15).

Table 4.14: European use of treated drinking water (Techware - 1996)

MEMBER STATE	population served by water distribution network (%)	population served by water distribution network (x 10⁶)	drinking water average production (mio m³/yr)
Austria	56	4.125	450
Belgium	98	9.868	735
Germany	98	77.420	5,800
Denmark	92	4.784	480
Spain	91	35.035	1479
Finland	80	4.000	412
France	76	43.852	7000
Great Britain	98	56.840	6890
Greece	n.a.	n.a	n.a.
Ireland	98	3.500	511
Italy	90	55.860	7940
Luxembourg	100	0.400	15
The Netherlands	100	15.400	1231
Portugal	86	8.480	525
Sweden	86	7.396	

In many cases the water disinfection is obtained with the combination of chlorine and sodium hypochlorite and in this case the sum of two fractions is from 23% in Spain to 100% in France (see table 4.15).

Table 4.15: Use of hypochlorite or chlorine in drinking water treatment (Techware - 1996)

MEMBER STATE	% of inhabitant served by water disinfected with NaClO	% of distributed water disinfected with NaClO	% of inhabitant served by water disinfected with NaClO /Cl₂	% of distributed water disinfected with NaClO/Cl₂
Austria				
Belgium	59.9	73.8	40.1	26.2
Germany		52.6		
Denmark				
Spain	3	3.7	20	3.6
Finland				
France	43.3	51.4	56.7	48.6
Great Britain				
Greece				
Ireland				
Italy	47.7	60.6	23.9	16.3
Luxembourg				
The Netherlands		18		(18) tot. combination
Portugal	68	62		
Sweden				

Assuming almost 50% of European population served by water treated by NaClO, the number of inhabitants “exposed” to NaClO is around 185 million.

The admissible concentration of available chlorine in drinking water varies from country to country from 0.1 to 0.5 mg/l (Techware, 1996).

Assuming that a daily per capita consumption of 2 litres by a person weighing 60 kg (the more conservative TGD default - for a female) and that the concentration of admissible available chlorine admissible in the water is 0.1 mg/l in many European countries, the uptake per person of available chlorine derived from water treated with NaClO is **0.003 mg/kg/day**.

For a 10 year children weighing 30 kg the uptake of av. Chlorine per day is calculated as 0.0033

The acute exposure can be estimated considering the consumption of a glass of water (0.2 l) and the value is: $0.1 \text{ mg/l} \times 0.2 \text{ l} / 70 \text{ kg} = 0.0003 \text{ mg/kg BW}$ for an adult and 0.0007 for a 10 year children weighing 30 kg.

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

As stated in section 1.2, the 15% NaClO solution used to disinfect drinking water contains some contaminants such as NaOH (1-10 g/kg), Fe (4mg/kg max), NaClO₃ (5 mg/kg max), Hg (10-100 x10⁻³ mg/kg), formed or used during the production process, and some decay species forming during storage as chlorate ion (ClO₃⁻), chlorite (ClO₂⁻) and chloride (Cl⁻).

Exposure to by-products

The use of NaClO in water disinfection is generally associated with the formation of trihalomethanes, chloroacetic acids and other compounds due to the reaction between chlorine species and organic matter, especially when surface waters are treated. Typical ranges of most common disinfection by-products are found in Table 4.16. The table presents also WHO guidelines values (WHO-2006), defined taking into consideration available toxicity data. The Directive 98/83/EC on the quality of water intended for human consumption regulates only the concentration of trihalomethanes.

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

Although the link between water disinfection treatment and by-products occurrence is evident, the high variability of concentration data shows a dependency on the way the disinfection treatment is carried out. The quantity of these substances is related, among others, to the quality of the treated waters and the good maintenance and cleanliness of

the water distribution networks. The optimisation of the treatment process (reduction of organic matter before the treatment, control of operative conditions, etc.) seems to be the solution to reduce by-products concentration in drinking water. For example, a cut-off value in terms of organic type and concentration in the original water should be defined, above which the use of NaClO must be discouraged due to the high production of by-products.

Table 4.16. Occurrence of most common disinfection by-products and guidelines values.

By-product	Measured concentration (µg/l)	WHO guidelines (µg/l)	Directive 98/83/EC (µg/l)
Chloroform	Around 50 (1) 11.73-13.38 (2)	300	THM: 100
Bromodi-chloromethane	Up to 25 (UK), up to 50 (US); higher concentration in case of ozonation followed by chlorination of water rich in bromide (1)	60	
Chlorodi-bromomethane	Below 20, up to 100 in case of ozone treatment of water rich in bromide (1)	100	
Tribromo-methane (bromoform)	Up to 4.4 (US), around 10 in case of ozone treatment of water rich in bromide (1) 6.26-26.72 (2)	100	
Monochloro-acetic acid	Around 5 (1)	20	Not regulated
Dichloroacetic acid	0.9-62, the highest concentrations in water rich in humic and fulvic acids (1) 0.83-1.07 (2)	50	Not regulated
Trichloroacetic acid	0.3-86 (1) 0.1-86 (2)	200	Not regulated
Dichloroaceto-nitrile	Around 2, some samples up to 24 (1)	20	Not regulated
Bromochloro-acetonitrile	Up to 10 (1)	Not established	Not regulated
Dibromoaceto-nitrile	Up to 2.5 (1)	70	Not regulated
Chloral hydrate	Up to 2.6 (UK) or 19 (US); unstable, it decomposes to give trichloromethane (1)		Not regulated
Halogenated phenols	2-chlorophenol+2,4-dichlorophenol+2,4,6-trichlorophenol: less than 1; median concentration: 0.01-0.1 (1)	Not established	Not regulated
Nitrotrichloro-methane (chloropicrin)	Up to 5.6; higher concentrations with pre-ozonation (1)	200 for 2,4,6 trichlorophenol	Not regulated

References:

- 1) FWR (Foundation for Water Research), 1994¹³
- 2) Techware report for EU, 1996

¹³ Foundation for Water Research "Disinfection by-products: occurrence and significance to health", November 1994

4.1.1.5. Indirect exposure via the environment

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

By-products have been measured under sewage treatment conditions. The main species identified was chloride. Additionally chlorate, monochloramine and to a less extent trihalomethanes and chloroacetic acids have been measured. Typical ranges are mentioned in Table 3.4 (see environment).

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

4.1.1.6. Combined exposure

Although combined exposure is occurring, routes of exposure may differ or levels would not be too different compared to the ones described under 4.1.1.3. and 4.1.1.4. **Since levels in 4.1.1.3 and 4.1.1.4 are small, combined exposure is not thought of concern.**

4.1.2. Effect assessments

Hazard identification and Dose (concentration) - response (effect) assessment

A sodium hypochlorite solution contains three chemical species, in equilibrium with each other: chlorine (Cl_2), hypochlorous acid (HOCl), hypochlorite ion (OCl^-). Their concentration depends on the pH of the solution (see paragraph 2.4). As a consequence, different concentration units are found in literature to measure the species present in a hypochlorite solution (see appendix 4 for more information). The studies on the effects of a sodium hypochlorite solutions found in literature use different units to define the concentrations tested:

- Available chlorine: it measures the concentration of the three species (in practice, only HOCl and OCl^- can be present, because chlorine is formed only at very low pH values)
- Active chlorine: it measures the concentration of Cl_2 and HOCl (in practice, only HOCl)
- HOCl or OCl^- (mostly used in cases in which, because of the pH value of the tested solution, one of the two species was predominant).
- Sodium hypochlorite (NaClO): the “theoretical” concentration of sodium hypochlorite in the solution, calculated on the basis of the available chlorine concentration (see appendix 4 for more information).

In this RAR, the units used in the original studies will be reported in the description of the studies. For the purpose of Risk Characterisation, available chlorine unit will be used, since it covers all the different pH situations of the hypochlorite solution. If the unit used in the original studies is different, the use of available chlorine unit will be evaluated on a case by case basis

Validity of available data as well as their relevance for the risk assessment have been assessed as described below:

Category 1 – Reliable without restriction

For study reports or literature data

- which were carried out or generated according to generally valid and/or internationally accepted testing guidelines (preferably according to GLP) or
- in which the test parameters documented are based on a specific (national) testing guideline (preferably according to GLP) or
- in which all parameters are described closely related/comparable to a guideline method.

General interpretation/conclusion on a TOX chapter (NOAEL, etc.) may be based on such data, if relevant for the RA in consideration.

Category 2 – Reliable with restrictions

For study reports or literature data

- in which the tests parameters documented do not totally comply with the specific testing guideline, but are sufficient to accept the data or
- in which investigations are described which cannot be subsumed under a testing guideline, but which are nevertheless well documented and scientifically acceptable.

General interpretation/conclusion (NOAEL, etc.) may be based on such data if relevant for the RA in consideration, but with a lower weight compared to category 1.

Category 3 – Not reliable

For study reports or literature data

- in which there are interferences between the measuring system and the test system or
- in which organisms/test system were used which are not relevant in relation to the exposure, (e.g. justification by expert judgement) or
- which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for an assessment and which are not convincing for an expert judgement.

These studies may be helpful for RA but not sufficient in itself to conclusion (so giving qualitative rather than quantitative information).

Category 4 – Not assignable

- Which are only listed in short abstracts or secondary literature (books, reviews, etc.)

These studies are not useful for RA because it is impossible to judge their quality.

Relevance of data for the current use has also to be considered. Data classified in validity category 1 or 2 may be judged as not relevant for the Risk Assessment

considered, e.g. the route of exposure in the animal study is not relevant for human exposure.

Results obtained by Biotest Laboratories have been reported as supportive information but they are not used for Risk Characterisation.

4.1.2.1. Toxicokinetics, metabolism and distribution

Sodium hypochlorite dissolved in water exists as a mixture of different chlorine species, whose relative amounts depends mainly on the pH. In the biological systems, characterised by pH values in the range 6-8, the most abundant active chemical species are HOCl and ClO⁻, in equilibrium. The latter is predominant at alkaline pH values, while Cl₂ is mainly present at pH below 4 (see paragraph 2.4). Sodium hypochlorite readily interacts with organic molecules and cellular components, leading to the formation of chlorinated organic compounds possessing their own inherent toxicity (BIBRA, 1990).

Very few data have been produced on ADME for HOCl and are limited to the oral route. No information is available on dermal exposure or inhalation.

4.1.2.1.1. Endogenous occurrence

Hypochlorous ions are physiologically present in the human body, being formed by white blood cells (neutrophils and monocytes) as a powerful antimicrobial agent during inflammation processes. When the recognition of “non-self” proteins in an invading micro-organism triggers the immune response, the enzyme myeloperoxidase located in mammalian neutrophils catalysed hypochlorous acid formation through the oxidation of chloride ion in combination with hydrogen peroxide (Weiss, 1989; Babior, 1984; IARC, 1991). The endogenously formed hypochlorous acid plays a key role in the process of phagocytosis through which bacteria are killed. Due to its potent cytotoxic action, hypochlorite is also responsible for neutrophil-mediated tissue damage associated with the inflammatory response. Its high efficiency as antimicrobial agent is associated with the lack of a catalytically active detoxifying mechanism for HOCl in both bacteria and mammalian cells. Although it has been suggested that HOCl-induced cytotoxicity can be associated to the degradation of a number of functionally important molecules (Weiss, 1989; Bernofsky, 1991) the primary mechanism of action is still not fully elucidated.

Besides being an oxidant itself, HOCl can react with H₂O₂ and superoxide anion to generate other highly reactive oxidizing molecules (singlet oxygen and hydroxyl radical), which very likely contribute to the onset of toxicity. In addition, hypochlorite can react with a number of cellular components, such as amino-acids, thiolic compounds, nucleotides and lipoproteins, forming organochloride species (Weiss, 1989; Bernofsky, 1991; Fleming, 1991), some of which endowed with their own toxicity. As well as many N-chloramines, derived from reaction with both nucleotides and amino acids, chlorohydrins of unsaturated fatty acids (Winterbourn, 1992) and chlorinated sterols (Hazen *et al.*, 1996 a ,b) have been identified as by-products of in vitro reactions of the myeloperoxidase/peroxidase/chloride system.

Based on a mean HOCl production rate of 3.15×10^{-8} μM/cell-h for the myeloperoxidase-catalysed reaction and assuming that about 0.1% of total neutrophils are triggered at any one time, Haas (1994) estimated a production ratio of 16 μM/day HOCl from the human immune

system. Considering a possible 1-5% yield, the total amount of hypochlorite corresponds to a total generation of organochlorine compounds in the human body in the range of 5.7 to 28 µg/day (equal to 0.16 - 0.8 µM/day).

4.1.2.1.2. Animal data

Absorption, distribution and excretion

Abdel-Rahman *et al.* (1983) studied the toxicokinetics of hypochlorous acid (HOCl). Three groups of 4 Sprague-Dawley rats were orally administered with different quantities of HO³⁶Cl solution (range of specific radioactivity 1340-2190 dpm/µg ³⁶Cl): the first group of 4 non-fasted rats received 3 ml of 250 mg/l HO³⁶Cl aqueous solution (0.75 mg per animal); the second group of 4 fasted rats received 200 mg/l HO³⁶Cl aqueous solution (0.60 mg per animal). Blood samples were taken from animals of these two groups at different times (0-96hr) and tissue specimen were prepared at sacrifice for ³⁶Cl content assessment. The third group of fasted rats receiving 200 mg/l HO³⁶Cl aqueous solution (0.60 mg per animal) were housed in metabolic cages in order to collect urine, faeces and expired air at different times for ³⁶Cl radioactivity measurement.

³⁶Cl is readily absorbed and found into the bloodstream: a peak of radioactivity in rat plasma occurred 2 hours after HO³⁶Cl administration in group I (fasted rats) (7.9 µg/ml) and 4 hr after administration in group II (non-fasted rats) (10.7 µg/ml). The half-life of ³⁶Cl in group II resulted 2-fold higher (88.5 h) than the one measured in group I (44.1 h), very likely due to the different fasting conditions of animals (Abdel-Rahman *et al.*, 1983).

Indirect indication of rapid absorption through the GI tract was given by the occurrence of blood GSH depletion evidenced soon after (15-120 min) the acute treatment of Sprague Dawley male rats with 3 ml aqueous solution containing 10, 20, 40 mg/l HOCl by gavage (Abdel-Rahman and Suh, 1984).

³⁶Cl radioactivity was distributed throughout the major tissues, 96 hr after HO³⁶Cl administration. The higher levels were found in plasma (1.92 µg/g), whole blood (1.59 µg/g), bone marrow (1.55 µg/g), testis (1.26 µg/g), skin (1.20 µg/g), kidney (1.13 µg/g) and lung (1.04 µg/g). The lowest levels were found in the liver (0.51 µg/g), carcass (0.40 µg/g), and fat tissue (0.09µg/g) (Abdel-Rahman *et al.*, 1983).

The distribution of ³⁶Cl in plasma and whole blood studied 24 hr after treatment showed that plasma ³⁶Cl content was 4-fold higher than radioactivity measured in packed cells. In plasma about 20% of total ³⁶Cl was bound to protein, while in red cells a high percentage of ³⁶Cl was loosely bound to the erythrocyte membrane or exchangeable with chloride in saline. The subcellular distribution of ³⁶Cl in the liver, showed that the main fraction of the radioactivity recovered in hepatic homogenate was localised in the cytosol, and only 4% was bound to proteins (as measured in the TCA precipitate) (Abdel-Rahman *et al.*, 1983).

HO³⁶Cl-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).

Metabolism

As previously indicated, HOCl is not enzymatically metabolised and its (bio)transformation readily occurs through direct reactions with organic compounds or with other chemicals present in the cellular environment, including hydrogen peroxide.

Results from the toxicokinetic study carried out by Abdel-Rahman *et al.* (1983), showed that the chloride ion accounted for >80% ³⁶Cl radioactivity present in rat plasma.

When Sprague-Dawley rats were administered HClO at 0, 1, 10 or 100 mg/l daily in drinking water for one year, no significant chloroform concentrations, were observed in rat blood at any time (4, 6, 9, 12 months) during the treatment (Abdel-Rahman and Suh, 1984).

The formation of organochlorinated compounds was tested in the stomach content and in the blood samples of four groups of three Sprague-Dawley rats each: fasted/non-fasted control group, fasted / non-fasted dosed group. The dosed groups were administered by gavage with 7 ml of a 8 mg/l solution of sodium hypochlorite at pH 7.9 (about 140 mg/kg bw) and sacrificed after one hour: the results were expressed as detectable or not-detectable for the very low levels of reaction products (detection limit range: 0.06-1.3 µg/ml plasma). Qualitatively it resulted that acetic acid was found in all the blood and stomach content samples from all the 4 groups, including controls. Trichloroacetic acid, dichloroacetic acid and chloroform were detected only in the stomach content of dosed animals (fasted and not fasted), suggesting its formation independently from the presence of food content in the gut. On the contrary, dichloroacetonitrile detection was limited to gut samples from non-fasted rats. Some plasma samples of dosed animals resulted positive to the presence of trichloroacetic acid (Mink 1983).

In the same laboratory, a multiple dose study was also carried out dosing rats for 8 days orally with 8 and 16 mg/kg bw/day NaOCl, a much lower concentration with respect to the acute study by Mink *et al.* (1983) and more consistent with drinking water intake. Following the final dose rats were placed in metabolism cages, and urine was collected in water-cooled vials. No organo-chlorinated compounds were detected in urine extract by means of GC/MS analyses (Kopfler *et al.*, 1985). The presence of Cl⁻ was not assessed.

4.1.2.1.3. Human data

No specific studies on humans have been conducted so far. Nevertheless, it is possible to obtain some information from some reported cases of accidental ingestion. Reported effects included some systemic symptoms, such as laboured breathing, decreased blood pressure, increased sodium levels in the blood and acidosis, probably due to the formation of hypochlorous acid and Cl₂ gas at the low pH typical of the gastric environment (Done, 1961; Ward and Routledge, 1988). The systemic effects could suggest the absorption and distribution of NaOCl, although it is not possible to exclude they are secondary to its local irritating and/or corrosive action producing tissue damage.

Intoxications caused by the direct inhalation of hypochlorite vapours have never been reported; it is generally due to misuse of bleaching solutions, when mixed with ammonia or acids, responsible for dramatic pH changes.

Conclusions

Animal data suggest that after exposure via oral route, HOCl is absorbed and excreted mainly through urine as chloride (36.43% + 5.67 of the administered dose after 96h); a lesser extent of HO³⁶Cl-derived radioactivity not necessarily associated with absorption was detectable in the faeces 96h after exposure (14.8% + 3.7). Once in the body, it reacts directly with organic molecules to form some organochlorinated compounds, characterised by their own toxicity. No data are available for other routes of exposure, including dermal and inhalation.

Human data are very scant and indirect. Absorption is suggested by some transient and not severe systemic symptoms following ingestion, although the possibility they are secondary to a local effect could not be ruled out with certainty.

4.1.2.2. Acute toxicity

The effect values reported below are referred to sodium hypochlorite expressed as available chlorine and are reported in Table 4.17.

4.1.2.2.1. Studies in animals

Oral route

Several acute toxicity studies, the majority in rats, have been reported and are summarised in Table 4.17. The LD₀ value for a 3.6 % solution (as available chlorine) was reported to be greater than 10.5 g/kg (corresponding to 0.378 g/kg as available chlorine). No deaths and no alteration of the gastric mucosae of the exposed animals were reported (CERB 1985). Similarly, the LD₀ of 3.6% solution of sodium hypochlorite was reported to be > 11.8 g/kg (>0.425 g/kg as available chlorine) (AISE, 1997). The LD₅₀ of a solution of 5.25 % sodium hypochlorite was reported to be approximately 13.0 g/kg, corresponding to 0.682 g/kg as available chlorine (Chlorine Institute 1982).

A solution of sodium hypochlorite at a concentration of 12.5% (available chlorine) caused no mortality up to the level of 5.8 g/kg. Gastric lesions were found in all animals exposed and sacrificed after 14 days of observation (CERB, 1985).

An oral LD₅₀ of 8.8 g/kg in rats was quoted for a 12.5% bleach solution (based on available chlorine). Five groups of 10 male Wistar rats each were given 20 ml/kg bw of a dilution of chlorine bleach containing 12.5% available chlorine. During the observation period of 14 days, the following symptoms of toxicity were recorded: ungroomed fur, light to moderate sedation, diarrhea, ataxia, and increased breathing of differing severity. The deaths observed occurred in most cases within 24 hours after application. Pathology upon dissection showed strong gas accumulation in the stomach and intestines, swelling of the liver, bleeding gastritis and enteritis. There were no symptoms noted in the animals that survived. The LD₅₀ was determined to be 8.83 (8.2 – 9.51) g/kg bw, and the NOAEL was found to be 5.01 g/kg bw, all based on the 12.5% available chlorine solution (or 626 mg/kg bw of sodium hypochlorite expressed as available chlorine) (Kaestner, 1981 in BIBRA, 1990).

Osterberg (1977) reported an LD₅₀ > 5.0 g/kg for commercial bleach containing 4.74% of available chlorine, corresponding to a value > 0.237g/kg available chlorine.

Using an unspecified commercial solution of sodium hypochlorite an LD₅₀ value of 8.91 g/kg (6.83-11.68g/kg) was reported for the the Male Albino rat. Signs of intoxication reported were hypoactivity, muscular weakness, hemorrhagic rhinitis, emaciation and death. No significant findings were observed following examination of both survivors and decedents (Industrial Bio-Test Laboratories Inc., 1970).

In the mouse the LD₅₀ was reported as 5.8 ml/kg and 6.8 ml/kg for females and males respectively for a commercial solution of sodium hypochlorite of 10% as available chlorine diluted 50% v/v with water, leading to 0.36 and 0.42 g/kg available chlorine respectively. Signs of toxicity consisted of depression of spontaneous activity and irritation of the gastrointestinal tract (Momma, 1986).

A LD₅₀ of 0.88 g/kg sodium hypochlorite solution in the mouse is also reported in the literature (Klimm, 1989). The concentration of sodium hypochlorite was not reported and the methodology used was not fully explained. Therefore the value was not considered to be relevant for the risk assessment.

Dermal route

An LD₀ value > 10.0 g/kg in rabbits was reported for a sodium hypochlorite solution of unspecified concentration. The animals showed no signs of intoxication, however moderate to severe erythema was observed at the site of the application. No adverse effects were found at necropsy at the end of the observation period (Industrial Bio-Test Laboratories Inc., 1970).

Acute dermal toxicity is reported to be > 2.0g/kg body weight for a 5.25% available chlorine solution, corresponding to a value greater than 0.105 g/kg available chlorine (Chlorox unpublished data, in AISE, 1997).

Inhalation route

The LC₀ value by inhalation in rat was found to be greater than 10.5 mg/l for 1 hour exposure, using an unspecified commercial solution. The test was carried out at room temperature with a total air flow of 10 litres per minute. No death occurred and there was no sign of inactivity or lacrimation and no significant gross pathological changes reported (Industrial Bio-Test Laboratories Inc., 1970). This study is considered of limited interest since inhalation exposure of sodium hypochlorite is only possible if aerosols are formed.

Other routes

The only information available is a very old study (Taylor *et al* 1918), where sodium hypochlorite was administrated subcutaneously and intraperitoneally in mice and guinea pigs. The results demonstrated the low toxicity of sodium hypochlorite. However, these routes of administration are not relevant for the direct human exposure and therefore the studies are not considered for the risk assessment.

Table 4.17: Acute Toxicity (LD₀ - LD₅₀) for sodium hypochlorite as av Cl₂ (oral)

% AVAIL.	SPECIES	LD ₀	LD ₅₀	LD ₀ g/kg	LD ₅₀ g/kg	REFERENCES	VAL
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CHLORINE (or comp.)		g/kg (of the solution)	g/kg (of the solution)	as av Cl ₂	as av Cl ₂		
ORAL							
10	mouse				0.36 females 0.42 males	Momma, 1986	
3.6	rat	> 10.5 (a)		> 0.378		CERBa, 1985	1
12.5	rat	> 5.8 (a)		> 0.725		CERBb, 1985	1
12.5	rat	5.01	8.83	0.626	1.1	Kaestner, 1981	2
3.6	rat	> 11.8 (a)		> 0.425		AISE, 1997	3
5.25	rat		ca.13		0.682	Chlorine Inst., 1982	3
4.74%	rat		> 5		> 0.237	Osterberg, 1977	3

(a) no death in the study

4.1.2.2.2. Human data

Some information is available from accidental exposure due to ingestion of commercial products or in patients undergoing hemodialysis where massive hemolysis, hyperkalemia, cyanosis and cardiopulmonary arrest were observed (Hoy, 1981, Dedhia, 1989).

Oral routes

The lethal dose of sodium hypochlorite in humans (adult) has been reported to be about 200 ml of a solution containing 3-6% of available chlorine (Bozza Marrubini *et al.*, 1989, reported in Racioppi *et al.*, 1994). But the survival of patients who swallowed up to 1 l of a 5.25 % NaClO solution (Strange *et al.*, 1951) and about 500 ml of a 10% NaClO solution has also been reported (Ward and Routledge, 1988).

The distinctive smell/taste makes unintentional ingestion of large volumes of hypochlorite bleaches virtually impossible.

Suicides attempts by adults can lead to death after ingestion of at least 250-500 ml of fairly concentrated (12.5%) NaClO solutions (Racioppi *et al.*, 1994).

Clorox (US commercial bleach preparation containing 5.25% sodium hypochlorite) is frequently listed among the corrosive substances commonly ingested. However, there have been no specific reports of tissue injury apart from one case of a 49 year old man who attempted suicide by drinking approximately 1000 ml of Clorox. He sustained a severe corrosive injury to the stomach with subsequent scarring that necessitated a total gastrectomy (Strange *et al.*, 1951).

129 cases of sodium hypochlorite solution (5.25%) ingestion seen at the Children's Hospital of the District of Columbia have been reviewed and no severe complications have been encountered: 65 of these cases were examined by oesophagoscopy within

96 h after ingestion and only two cases exhibited any evidence of oesophageal injury (Pike *et al.*, 1963).

Hook and Lowry (1974, cited in Racioppi *et al.*, 1994) reported on 26 children admitted to the Children's Memorial Hospital of Chicago since 1969 with bleach ingestion as the reason for admission. Severe irritation of the oesophageal mucosa was observed in only one case, which evolved positively without symptoms of stricture. Only minor transient irritation effects were observed in some of the other 25 patients.

Yarrington (1965) reported on injury from ingestion of Clorox (5.25% sodium hypochlorite) in his experience: in the 31 cases observed, 11 patients showed mouth burns, 17 oesophageal burns and 9 severe oesophageal burns.

Muehlendahl *et al.* (1978) investigated the consequences of household products ingested by children: 90% of the children involved were from 1 to 3 years old. On a total base of 1157 cases, only 23 involved NaClO solutions. One of these 23 cases showed signs of superficial burns in the oesophagus that had disappeared 2 weeks later when examined by oesophagoscopy.

These data are comparable to the previous observations made by French *et al.* (1970): on 160 patients admitted to the Tulane Services (New Orleans) because of the ingestion of household bleach, 5 showed oesophageal burns but only 2 developed oesophageal stricture.

The clinical effects of accidental chlorine bleach ingestion in 80 children, admitted to hospital in Turkey between 1976-1986, have been evaluated. It has been reported that bleaches manufactured in Turkey can cause significant oesophageal injury due to their high content of sodium hydroxide which increases the corrosive effect (Tanyel *et al.*, 1988).

Metabolic consequences of bleach ingestion which are less investigated are hypernatraemia and hyperchloraemic acidosis: the first one due to the large sodium hydroxide load contained in household bleaches, the second one due to the reaction, in the stomach, with hydrochloric acid to form hypochlorous acid and chlorine (Ward and Routledge., 1988).

Table 4.18: Human acute cases

REFERENCE	PRODUCT	NOTE
ORAL		
Strange - 1951	1 liter of 5.25% sol.	suicide attempt- total gastrectomy for severe corrosion
Pike - 1963	5.25% sol.	children accidental ingestion - 129 cases with 2 cases of oesophageal injury
Hook and Lowry - 1974	nd	children accidental ingestion -26 cases: one irritation
Yarrington - 1965	5.25% sol.	31 cases observed with different type of burns
Muehlendahl-1978	nd	children accidental ingestion - 23 cases: one with superficial oesophagus burn
French - 1970	nd	accidental ingestion in 160 cases with 2 severe oesophageal effects
Tanyel - 1988	10-200 ml of 5-6% sol.	children accidental ingestion - 80 cases: three with

		oesophageal effects
Ward – 1988	1 l of 5.25% solution	2 cases: hypernatraemia and hyperchloraemic acidosis due to ingestion
PARENTERAL		
Froner - 1987	0.3 ml of 5.25% sol.	suicide attempt - no death
Becker - 1974	0.5 ml of 5.25% sol. injected in periapical tissue	strong inflammation, hematoma - 1 month for normal status
Hermann - 1979	1.8 ml of 5.25% sol. injected in facial nerve	pain, edema – two weeks to resolve
Hoy – 1981	30 ml of 5.25% sol. intravenous infusion	cardio-respiratory arrest - resolved after recovery

nd: not determined

Parenteral exposure

Sodium hypochlorite is a standard disinfectant for various applications and an accidental exposure by parenteral route can happen.

Four cases have been reported:

- The first is referred to a suicide attempt by a 27-year-old man, who had ingested 60 ml and injected 0.3 ml of a 5.25% solution of sodium hypochlorite; he experienced no local pain during or following the injection, nor loss of consciousness; on physical examination he was lethargic but awake and he had normal vital signs (Froner *et al.*; 1987).
- The second involved an injection of 0.5 ml sodium hypochlorite solution (5.25%), commonly used as a disinfectant during root canal surgery, accidentally into periapical tissue, resulting in an acute reaction. The patient experienced extreme pain, inflammation of the mouth and face and hematoma formation. The patient's face returned to normal one month after the accident (Becker *et al.*, 1974).
- The third involved injection of 1.8 ml of sodium hypochlorite solution (5.25%), which had been stored in an anesthetic bottle, into the mandibular branch of the facial nerve, resulting in pain, edema and trismus that resolved within two weeks (Hermann *et al.*; 1979).
- The final case involved intravenous infusion during hemodialysis of approximately 30 ml of sodium hypochlorite (5.25%), which had been inadvertently added to the dialysate, leading to a cardiorespiratory arrest but with eventual recovery (Hoy *et al.*; 1981)

4.1.2.2.3. Summary of acute toxicity

The acute toxicity of marketed hypochlorite solutions by the oral route is low. The LD₅₀ values for solutions containing active chlorine concentrations up to 12.5 % are greater than 5.8 g/kg. The data for dermal acute toxicity as well as inhalation toxicity indicate a low level of toxicity even for these routes of administration.

Accidental human data are reported for ingestion and parenteral route: it can be concluded that the effects of accidental ingestion of domestic sodium hypochlorite bleaches are not expected to lead to severe or permanent damage of the gastro-

intestinal tract as recovery is rapid and without any permanent health consequences. This is also expected for small quantities of solutions accidentally injected in blood system or in the tissues.

Although the overall lowest LD₅₀ available is from the Momma study (see table 4.17), it is preferred to use the value of the Kaestner study as the key reference study. The Osterberg study is poorly reported and the LD₅₀ value is not exactly defined but indicated just as higher than 5000 mg/kg. The Momma study (see table 4.17) is poorly reported as well. Therefore the Kaestner data is considered of higher reliability, and it is based on the rat, the standard animal, contrary to the Momma study which used mice. The LD₅₀ and LD₀ values were calculated as follows:

$$\text{LD}_{50} = 12.5\% (\% \text{ of available Cl}_2 \text{ in sol.}) \times 8.83 \text{ (g/kg BW LD}_{50} \text{ of the sol. to female rat)} = 1.1 \text{ g/kg BW (LD}_{50} \text{ as available Cl}_2) = 1100 \text{ mg/kg BW NaClO as av. Cl}_2$$
$$\text{LD}_0 = 12.5\% (\% \text{ of available Cl}_2 \text{ in sol.}) \times 5.01 \text{ (g/kg LD}_{50} \text{ of the sol. to female rat)} = 0.626 \text{ g/kg BW (LD}_{50} \text{ as available Cl}_2) = 626 \text{ mg/kg BW NaClO as av. Cl}_2$$

Because the acute toxicity of corrosive substances is more related to concentration than to dose, extrapolation from data obtained from using a hypochlorite solution to a fictive 100% sodium hypochlorite is not possible. As the highest concentrations of hypochlorite solutions as industrially produced and marketed are about 15%, and solutions marketed for consumer use are typically 5% or less, it can be concluded from the data presented that hypochlorite solutions are of low acute oral toxicity. This is confirmed by the available data from human accidents, where the few deaths that have occurred after hypochlorite ingestion are mostly attributable to aspiration pneumonia.

The information available shows that sodium hypochlorite has a very low dermal acute toxicity.

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

4.1.2.3 Irritation/corrosivity

4.1.2.3.1 Studies in animals

Skin

A solution of sodium hypochlorite (4.74% available chlorine) in a mixture with other ingredients used as control bleach in a patch study was applied (0.5 ml) under a semi-occlusive patch on the dorsal skin of the rabbits for a 24-hour period. The skin was examined for erythema and edema directly after patch removal and 48 hours later. The evaluation of the lesions was carried out according to the FHSA Regulation (1973). A primary irritation index (PII) of 5 or higher indicates a primary irritation response in accordance with FHSA Regulations. The compound was considered to be non irritant to the rabbit skin based on the PII reported as < 5. (Osterberg et al., 1977).

Sodium hypochlorite 5.25 % solution (pH 10.7, 0.5 ml) was applied on rabbit and guinea pig abraded and non-abraded skin in a 4-hour patch test as outlined in the revised FHSA procedure that had been proposed by FDA (Edwards, 1972). The skin was examined at 4, 24 and 48 hours after patch removal. Results showed the compound to be slightly irritant to both rabbits (PII = 1.2) and guinea pigs (PII = 0.8) (Nixon *et al.*, 1975).

0.5 ml of sodium hypochlorite 12.5 % available chlorine was applied to the intact and abraded rabbit skin for 24 h. The skin was examined for effects up to 72 hours. The scoring of the irritation response was carried out according to the Draize classification. Initial solution (12.5 %) and dilution of ½ (6.25 %) were considered as severe irritant (with PII = 5.6 for both concentrations); a dilution of ¼ (3.12 %) was considered to be moderately irritant (PII = 4.0) and a dilution of 1/8 (1.56 %) as slightly irritant (PII = 1.9) (Duprat et al., 1974). It is pointed out that Duprat used a much longer exposure time (24 hours) compared to the standard classification patch test, which recommends patching for 4 hours. This can also explain the higher scores in comparison to the Nixon study, which did use the standard 4 hours exposure time.

0.5 ml of sodium hypochlorite 12.7 % active chlorine was applied to intact and abraded rabbit skin for 24 h. The skin was examined for effects up to 72 h. Scores from intact skin and abraded skin were added and a mean was calculated. Hypochlorite at 12.7 % was considered to be moderately irritant (PII = 4.04) (Colgate-Palmolive, unpublished data-1985).

In a dermal irritancy/corrosion test on 20 compounds in aqueous solution, sodium hypochlorite solution 8-12% available chlorine applied to the dorsal skin of the rabbit, was tested at different concentrations (2, 20, 35, 50% w/v, i.e. 0.24, 2.4, 4.2 and 6 % available chlorine): The study showed slight irritation effects at the lowest concentration, moderate irritation at the other concentrations and corrosive effects at the highest concentration tested probably according to the Draize scale) (Loden et al., 1985). Based on poor reporting, the study protocol followed could not be verified, although the Draize scale appears to have been used.

The primary skin irritation score in the rabbit was found to be 5.08 using 0.5 ml of undiluted liquid. This score was an average of mean scores on intact and abraded skin. Contact time is not specified. The compound was considered as “corrosive” (Industrial Bio-Test Laboratories Inc., 1970). However, this study is considered of very limited value to assess the irritation properties of hypochlorite, as neither the test substance concentration in this study nor the exact protocol used are described.

The studies from Loden and Biotest had been given a validity 4 based on too little study details reported.

Eye

An eye irritation test was carried out in rabbits by Momma *et al.*, using the Draize method (1986). The ocular irritation score was calculated from examinations up to 21 days post exposure of 5% solution. The eyes were either left unrinsed or rinsed with water after the application of sodium hypochlorite. Scoring at 24, 48 and 72 hours revealed slight – moderate eye irritation potential in both groups. In the group where rinsing was applied, eyes had returned to normal by day 14. More persistent and more pronounced injury to the cornea and the conjunctiva was observed in the group without washing. Day 21 was the end of observation time in this study at which some effects were still noted. The study indicates that rinsing of the eyes either 4 or 30 seconds after instillation significantly reduced the degree of ocular irritation.

Osterberg also performed an eye irritation test using an unofficial ocular irritation classification method (with similarities to the FHSA and Draize methodology). A dose of 0.1ml of an otherwise unspecified mixture containing hypochlorite at a conc. of 4.74 % available chlorine, was placed into the rabbit eyes and the score for alteration was followed up to 7 days post exposure. The compound was found to be severely irritant to the rabbit eye according to the specific grading scale used. Detailed scores observed however are not reported in the study. Recovery was not complete at day 7 (Osterberg *et al.*, 1977). It has to be noted that mixture was specified as laundry bleach by the author and contained other ingredients, which would have contributed to irritancy.

The standard Draize method was applied for the evaluation of eye irritation in the rabbit. In addition to the Draize mean average scores, a non-standard microscopic evaluation was used in the grading. Commercial sodium hypochlorite (12.5% available chlorine) and a ½ dilution (6.87%) were considered severe irritants with a Draize MAS score of 60 and 49, respectively. Complete recovery was observed in week 10 for the 12.5% solution and in week 4 for the 6.25% solution. ¼ Dilution (3.6%) of the solution was found to be moderately irritant with a Draize MAS of 11 and complete recovery at day 15 while a 1/8 dilution (1.85%) was found to be slightly irritant (Draize MAS 1) with complete recovery at day 4. Rinsing with 20 ml physiological saline was done at 10 sec, 1 min and 5 min after application of the test substance. Washing was also done using higher volumes of physiological saline (300 ml or 600 ml). The immediate rinse (at 10 sec with 20 ml physiological saline) was the most effective in reducing the irritant effect significantly (Duprat *et al.*, 1974).

According to the Draize method, a quantity of 0.1 ml of sodium hypochlorite 12.7 % active chlorine was applied in rabbit eyes. At day 7, Hypochlorite 12.7% was considered to be severely irritant (MAS of 64.75). Most effects had not cleared by the end of the observation period, day 14 (Colgate-Palmolive, unpublished data-1985).

Undiluted solutions at 5.25% or 8% were found to be low to moderate eye irritants in rabbits. Specifically, a 8% concentrated solution resulted in moderate irritant effects in a Draize test, with recovery being completed within 7 days. Low irritant effects were observed when the 8% solution was tested in an LVET study (Low Volume Eye Test, applied dose = 0.01 ml), with recovery being completed in 3 days. 5.25% sodium hypochlorite was tested according to the LVET protocol only and led to low irritant effects. Exact scores are not reported in the study. The authors emphasize that the LVET provides a better correlation with human eye irritancy experience than the Draize test. Dilutions of 1:10 of the described bleaches (0.55% and 0.8 % sodium hypochlorite) also had only a low eye irritant potential in an LVET study. It was observed that a rinse with water following the eye contact reduced the degree of irritation. (Racioppi et al., 1994).

The instillation of 0.1 ml of undiluted sodium hypochlorite (unspecified concentration) into the rabbit eye gives a MAS score for irritation of 61.3 according to the Draize methodology. The compound was considered as “severe irritant“ (Industrial Bio-Test Laboratories Inc., 1970). However, this study is considered of very limited value to assess the irritation properties of hypochlorite, as the test substance concentration in this study was not described.

Griffith et al. (1980), studied hypochlorite amongst other chemicals using the Draize scale for grading of the effects. Different dose volumes were applied (0.01, 0.03 and 0.1 ml) with the purpose of comparing the observed effects to data from human experience (literature, occupational incidents and consumer accidental exposures). 0.01 ml was considered the volume leading to effects most consistent with human eye reactions. Therefore, application of 0.01 ml (as used in the LVET protocol) was proposed to be a much more realistic test of eye hazard than the Draize test. A 5 % solution of sodium hypochlorite (pH 11.1-11.6) produced only mild transient effects in a Draize test (MAS of 11 after 1 day) when rinsed out with water in the first 30 seconds. When the LVET protocol was used (0.01 ml), similar mild and transient effects were noted. Effects had cleared completely by day 7. If 0.1 ml was applied and the eyes were not rinsed, moderate irritation effects involving the cornea and the conjunctiva occurred (MAS of 31 after 1 day). Recovery was not entirely complete at the end of the observation period (day 21). At the intermediate dosing volume of 0.03 ml applied, also moderate effects were observed (MAS of 28 at day 1) which had cleared completely by day 18 (Griffith *et al.*, 1980).

A 15% solution of sodium hypochlorite caused severe pain and damage and there were indications that healing was not complete 2-3 weeks after exposure (Grant, 1962).

Carter and Griffith (1965) summarized effects that Buehler and Newsman (1964) observed when comparing the eye irritation potential of a sodium hypochlorite aqueous solution 5.5 % in rabbits and monkeys. The eyes were not rinsed. The Draize methodology appears to have been used. No detailed scores apart from the recovery times are reported. The irritant response was much greater in rabbits (recovery between day 7 and day 35) than in monkeys (recovery at day 2). Data were also compared to recovery dates from human exposure in factory eye accidents. The author noted that the irritation response observed in the monkey

seemed to be a better indicator of eye irritation following accidental exposure in workers than the response observed in the rabbit.

Pashley et al. (1985) reported rabbit eye experiments following a Draize-related methodology. Detailed scores are not reported. Sodium hypochlorite, applied to rabbit eyes at concentration of 5.25 % NaClO produced moderate to severe conjunctival palpebral edema and hyperemia within 30 minutes of exposure with the maximum severity observed at 2 h. The eyes exposed to 5.25 % revealed corneal pitting but no ulceration. Some conjunctival edema was observed, which had not fully cleared up at day 7 (and of observation period). With a 0.52 % NaClO solution, only moderate effects were observed and the reaction was gone within 24 hours. The author pointed out that “the rabbit eye model tends to exaggerate the toxicity of agents since rabbits blink their eyes at a much lower frequency than humans” (Pashley, 1985).

Other Data (in-vitro)

Solutions of sodium hypochlorite were also tested “in vitro“ using different cell systems. The principal aim of the studies was to compare the results obtained “in vitro“ with the “in vivo“ Draize score methods. The results obtained “in vitro“ basically confirmed the irritation properties on the sodium hypochlorite solution obtained with the standard methodology (Chan, 1985; Borenfreund and Borrero, 1984, Borenfreund and Shopsis 1985; Shopsis and Sate, 1984). However, the use of in-vitro methods for eye irritancy assessment of hypochlorite containing products at this point in time is questionable, as current in-vitro methods are known not to realistically predict the irritant properties of oxidizing substances like hypochlorite.

Respiratory Tract

The respiratory (sensory) irritation potential of sodium hypochlorite has been assessed in the mouse and has been compared to that of chlorine. An aerosol of sodium hypochlorite was generated from a 10% v/v solution in distilled water using a glass concentric jet atomiser with cyclone. Three groups of mice (gender and age not defined) were exposed to sodium hypochlorite aerosols at atmospheric concentrations of 9.2, 5.7 or 2.6 ppm, expressed as chlorine. The particulate concentrations of each atmosphere were 24, 11 and 9 mg/m³, respectively, and the mass median aerodynamic diameter of the three aerosol atmospheres ranged from 2.3 to 4.3 µm. The RD50 value, the exposure concentration causing a 50% reduction in the respiratory rate due to respiratory irritation, for sodium hypochlorite aerosol was estimated to be 4.11 ppm, expressed as chlorine. A similar test was conducted concurrently with chlorine for which an RD50 value of 5.7 ppm was estimated.

It was concluded that the similarity of the results showed that the degree of respiratory irritation seen after exposure to an aerosol of sodium hypochlorite is most likely related to its content of chlorine (Lewis, 1990).”

Table 4.19: Skin and Eye Irritation Data (Validity 1 - 3)

AUTHOR	YEAR	TEST	RESULT	NOTES	VAL
Skin Irritation					
Nixon	1975	FHSA method (equal to Draize) (semioccl. for 4 h on abraded and non abraded skin) – guinea pig and rabbit	slightly irritant	Sol. 5-5.25% FAC	2
Duprat	1974	irritation test (abraded and non abraded skin for 24 h.) – rabbit	severly irritant at 6.25%. moderat – slight effects at lower concentration.	Sol. 12.5% and 6.25% FAC	2
Colgate-Palmolive	1985	Rabbit	moderately irritant	Sol. 12.7% FAC	2
Osterberg	1977	FHSA method (equal to Draize). (semioccl. for 24 h.) - rabbit	not irritant (mixture containing other ingredients)	Sol. 4.74% FAC	3
Eye Irritation					
Carter	1965	Rabbit	irritant	Sol. 5.25% FAC	2
Carter	1965	Monkey	irritant	Sol. 5.25% FAC	2
Momma	1986	Rabbit	moderately irritant	Sol. 4.76% FAC	2
Pashley	1985	Rabbit	irritant	Sol. 5.25 % FAC	2
Duprat	1974	Rabbit	severly irritant slightly irritant	Sol. 12.5% FAC Sol. 1.6% FAC	2
Colgate-Palmolive	1985	Rabbit	severly irritant	Sol. 12.7% FAC	2
Osterberg	1977	FHSA m. rabbit	severly irritant, effect observed in mixture containing other ingredients	Sol. 4.74% FAC	3
Griffith	1980	Rabbit	mild –moderately irritant severe irritant	Sol. 4.76% FAC Sol. 15% FAC	3
Racioppi	1994	Rabbit Rabbit Rabbit (Draize)	low irritant potential low irritant potential moderately irritant	Sol. 0.52% FAC Sol. 5.25% FAC Sol. 8% FAC	3
Grant	1962	Rabbit	slightly irritant severly irritant	Sol. 4.76% FAC Sol. 14.25% FAC	3

4.1.2.3.2. *Human data*

Skin

The human skin irritation potential of hypochlorite bleaches has been investigated under occluded patch test conditions and /or prolonged contact times.

Nixon et al. (1975) reported that a hypochlorite solution at 5-5.25% available chlorine (pH 10.7) was found to be severely irritating to intact human skin after 4 h exposure under occluded patch conditions. In this study a clear evidence of irritating effects above 5% is identified.

Weak to moderate irritation was observed in 15 of 69 dermatitis patients patch tested (48 h, patch conditions not specified, reported as “covered contact”) with 2% NaClO. No irritation was observed in 20 persons from the same group after additional patch testing (48 h “covered contact”) with 1% NaClO (Habets *et al.*, 1986).

A recent survey of accidental exposure to hypochlorite containing products during the years 2000 and 2001 is available from the Spanish Poison Control Center. Only 1.3% of all contacts on bleach products (total of 2924 contacts) are about skin contacts. Of these, 52.6% of persons remain asymptomatic and 47.4% (18 cases) of all skin contacts lead to some skin effects. Slight skin irritation or local burns are the prevailing symptoms (Instituto Nacional de Toxicologia, 2002).

Eye

In two cases where Clorox (containing 5.25% sodium hypochlorite) was accidentally splashed into the eyes, a burning sensation and slight damage to the cornea was reported: prompt rinsing of the eyes with water led to complete recovery within 48 h (Grant *et al.*, 1974 cited in BIBRA, 1990).

With 5% NaClO solutions only very few human eye injuries have been reported. Apparently it causes burning discomfort, but only superficial disturbance of the corneal epithelium, which recovers completely in one or two days.

Poison Control Centres record relatively few cases of ocular exposure to bleach (in Italy e.g. this represents about 4% of the total number of bleach contacts), and return to normality is rapid (Racioppi et al., 1994).

The above mentioned survey of accidental exposures to hypochlorite containing products in 2000 and 2001 from the Spanish PCC cites 18% of all contacts on bleach products (total of 2924 contacts) being about eye contacts. 41.5% of all eye contacts lead to some symptoms (218 cases). Most of them report eye mucous membrane irritation and all were reversible within two to maximum three days (Instituto Nacional de Toxicologia, report Nr. 07168/02).

In conclusion, under typical use conditions, accidental spillage of hypochlorite bleach into the eyes is expected to cause slight, temporary discomfort, which subsides within a short period of time or after rinsing with water (BIBRA, 1990).

Other data

Usually sodium hypochlorite at low concentrations comes in contact with the eye in swimming pools where it is the most widely employed disinfectant. If the pH is kept at approximately 7-9, levels of up to 1.5 ppm of available chlorine in water are usually not irritating to the eyes. In susceptible individuals, slight irritant effects may occur. However, this effect is always transient. At lower pH there may be smarting and redness of the conjunctiva, but no significant injury occurs. It is thought that products formed by the reaction of chlorine with nitrogenous compounds (such as urea and ammonia) and by the formation of chlorinated and non-chlorinated aldehydes in the water are responsible for the eye irritation; maintaining the pH above 7 reduces the formation of these products.

Erdiger et al. (1998) examined the mucous membrane irritating potential for compounds which can occur as disinfection-by-products in swimming pool water. The study report that halogenated carboxyl compounds, which act as precursor during the formation of chloroform may be responsible for eye irritation. These compounds were found to have a significantly increased irritating effect when compared to a chlorine/chloramines mixture of the same concentration, and significantly enhanced effects when combined with aqueous chlorine. The result of this study suggests that the mucous membrane irritating potential is a consequence of the effects and synergistic action of a number of disinfection-by-products in the presence of chlorine.

A study by Héry et al. (1994) describes that swimming pool instructors exposed to the same agents reported irritation phenomena (acute ocular and upper respiratory irritation) at chloramines values of around 0.5 mg/m^3 in the atmosphere.

Massin et al. (1998) measured trichloramine levels in the atmosphere of indoor swimming pools and examined their relationship to irritant and chronic respiratory symptoms. They concluded that lifeguards working in indoor swimming pools can develop irritant eye, nose and throat symptoms.

Various authors have suggested that a number of changes and symptoms may be associated with exposure to the atmosphere in swimming pools, in particular with nitrogen trichloride (Carbonelle et al., 2002; Thickett et al., 2002; Bernard et al., 2003), although the studies were unable to confirm the specific chemicals that were cause of the symptoms experienced. Symptoms are likely to be particularly pronounced in those suffering from asthma (WHO, 2006).

Hecht et al. (1998) carried out a study on worker exposure to levels of chloramines when washing vegetables in 6 industrial facilities using chlorinated water. In all cases but one the levels in the atmosphere are below the comfort level advised by French INRS of 0.5 mg/m^3 . Another study was published by the same authors the same year (Hery et al., 1998), that reported cases of acute eye and upper respiratory irritation in one industrial facility processing green salads in water containing hypochlorite. These effects were related to chloramines resulting from reaction of hypochlorite and nitrogen compounds coming from the sap proteins released when the vegetables were cut. The exposure of workers determined by personal sampling ranged from 0.2 to 5 mg/m^3 . The authors conclude that increased level of chloramines occur when the industrial facility uses recycled water.

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

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

Concerning eye irritation, some irritant responses have been recorded below 5% available chlorine on rabbits. However, the study results cannot be compared on a common basis, because different protocol variations were used and the original data on which the scores were determined are not retrievable from the study reports. All data obtained using the LVET method or another method (e.g. monkey) that resulted in similar effects as seen from human experience, showed reversibility of effects within short time periods. The available data from human exposure (Poison Control Centers) support Pashley's observation (1985), according to which irritant effects in the human eye are less severe than in rabbits. Rinsing with water shows a reduction in the irritant effects both in animals and humans.

As regards the studies by Héry et al. and Erdiger et al., these clearly report that the observed eye effects can be linked to the reaction products (found in swimming pools, e.g. chlorinated carboxyl compounds) and not to hypochlorite, therefore they are not considered in the hypochlorite assessment.

With respect to corrosivity, animal data show that a 12.7% hypochlorite solution produced severely irritant or corrosive effects to the eye. However, the same concentration applied to rabbit skin does not show corrosive effects there, as only moderate irritation was observed. For these concentrated products, data from accidents are also available (mostly from the French market). No serious or long-term consequences were associated with accidental skin and eye contact.

Sodium hypochlorite aerosols may be irritant to the respiratory tract.

Despite some difficulties in interpreting the older animal data, the overall evaluation of both animal and human data supports the current EU classification as irritant above 5% and as corrosive above 10%.

4.1.2.4. Skin Sensitization

4.1.2.4.1. Studies in animals

A sample containing 8.0 % of sodium hypochlorite was tested for delayed contact hypersensitivity in guinea pigs. The test material was administered undiluted at induction and as a 3.2 % solution in distilled water at challenge. The test was preceded by an irritation test

carried out at concentration up to 100 % v/v (= 8 % NaClO) in distilled water. Occluded application of the undiluted test material during the irritation screen resulted in increased incidence and severity of irritation (erythema) observed. Applications of test material at 40% (= 3.2% NaClO) were well tolerated. There were no erythematous responses to challenge with 40 % v/v (= 3.2% NaOCl) in either the test group or the control group, hence the test material did not show any potential to cause delayed contact hypersensitivity (P&G unpublished data, 1982).

Mixtures of sodium hypochlorite and different surfactants were tested for skin sensitization potential in two guinea pig sensitization studies. A 50:50 (v/v) mixture of a sodium hypochlorite solution and surfactant was tested in one study and a mixture (50:50 v/v) of sodium hypochlorite and another surfactant was tested in the other study. The concentration of sodium hypochlorite in the test substance was in both cases 4.5 %. During induction, 4.5%, 3.35%, 2.25%, and 1.1% hypochlorite were patched. Only the two higher concentrations resulted in slight patchy erythema. During challenge, 2.25% hypochlorite was used. The tests were carried out according to the guinea pig sensitization test modified by Ritz H.L. and Buehler E.V. There were no differences in skin alteration between test and control groups upon challenge, therefore both studies did not show any potential to cause delayed contact hypersensitivity for hypochlorite (P&G unpublished data, 1985).

Table 4.20: Sensitization studies and Case Reports with sodium hypochlorite

AUTHOR	YEAR	TEST	RESULT	NOTES	VAL.
Sensitization		Animal Data			
P&G	1982	g.pig test	Negative	Sodium Hypochlorite	1
P&G	1985	g.pig test	Negative	Sodium Hypochlorite + surfactant A	1
P&G	1985	g.pig test	Negative	Sodium Hypochlorite + surfactant B	1
		Human Data			
P&G	1987	Hum.Patch test	Negative	well conducted study – 86 subjects	2
P&G	1989	Hum.Patch test	Negative	well conducted study – 90 subjects	2
		Human Case Reports from Dermatologist practices			
Osmundsen	1978	Diagnostic Hum.Patch test	1/225 alleged positive	225 control (CD) patients, 3 of which showed a reaction to hypochlorite, but only 1 was accepted as true reaction to hypochlorite	4
Habets	1986	Diagnostic Hum.Patch test, including a larger control group	Positive Negative	case report No sensitization potential unidentified in a control group of 69 contact dermatitis patients	4
Eun	1984	Diagnostic Hum.Patch test Including a small control group	Positive negative	case report (1 patient, hypochlorite accepted as cause of contact dermatitis) no reactions to hypochlorite were seen in 3 control patients.	4
Ng	1989	Diagnostic Hum.Patch test Small negative control group	Equivocal negative	case report (1 patient) Reaction could be due to crossreactivity with iodide or flavine. Negative patch test result in 20 volunteers	4
Hostynek	1989	Diagnostic Patch test	Equivocal	case report (1 patient, no controls)	4
van Joost	1987	Diagnostic Hum.Patch test	Positive	case report (2 patients) (doubtful positive, as 1 patient suffered from nickel allergy and the other from kathon allergy)	4

4.1.2.4.2. Human data including Case Reports

Sensitization tests conducted on human volunteers (H.R.I.P.T.: human repeated insult patch test) with hypochlorite bleach formulations have shown no evidence of potential allergic contact dermatitis.

A first test had been performed on 86 volunteers. The solutions (containing 0.034% solution hypochlorite) caused an acceptable level of irritation during both preliminary

and main tests. There was no evidence of sensitization observed on eighty-six subjects upon challenge.

The second test involved 90 volunteers. The material (sodium hypochlorite solution at a concentration of 0.076%) caused an acceptable level of irritation through both the preliminary irritation screen and main test. At challenge, one subject gave some evidence of skin sensitization. This subject also reacted to another product patched in an adjacent site and a rechallenge on the same above mentioned other test article would be necessary to confirm the nature of this reaction. There was no evidence of skin sensitization on the other eighty-nine subjects and the one positive reaction could not be clearly attributed to the test substance hypochlorite (unpublished data from Procter & Gamble 1987 and 1989).

Habets *et al.* (1986) reported that two housewives with diagnosed dermatitis showed a positive reaction to sodium hypochlorite patched in different dilutions. In both patients, additional reactions to other standard allergens were found together with a positive reaction to sodium hypochlorite solutions of 2%, 1%, 0.5%, 0.1%. The specific test allergens showed a positive reaction. In a control study, 69 control patients (randomly selected with suspect allergic contact dermatitis) were patched with NaClO 2% in water; 15 of them showed a weak or moderate irritant reaction; 20 of the control were further tested with concentrations of 1% and 0.5%, but no reaction indicating an allergic response was seen.

Inclusion of sodium hypochlorite at about 0.5% in water in a series of routine patch tests involving 225 patients in total showed three positive reactions (at gradings 48h and 96h after patch removal). From these 3 out of 225 patients who tested positively, one positive response was be directly attributed to sodium hypochlorite by the author (Osmundsen *et al.*, 1978).

A case of occupational allergic contact dermatitis to NaClO has been seen in a veterinary surgeon, who during his work has occasionally washed his hands and forearms with undiluted Halasol (containing 4-6% sodium hypochlorite and Betadine as antiseptic). As the patch test results suggested sodium hypochlorite allergy, the same concentration of Halasol and sodium hypochlorite have been tested on three normal healthy controls: all were negative except the undiluted Halasol closed patch test. (Eun *et al.*, 1984). It should be noted that the short test report does not allow a conclusion whether the reactions of the 3 control subjects were of an irritant or contact dermatitis type.

Isolated cases of hypochlorite sensitivity of the delayed type (allergic contact dermatitis), as well as immediate-type reactions from inhalation or topical challenge of sensitized individuals have been observed according to Hostynek *et al* (1990).. Only one case where an immunologic component to the patient's reaction could not be ruled out is reported. The author also concludes that such rare hypersensitivity is usually preceded by either long-term or exaggerated skin exposure to hypochlorite (Hostynek *et al.*, 1989).

A very short report is available on the case of a patient who had a history of allergic contact dermatitis from flavine. The patient had developed symptoms upon wound treatment with a hypochlorite-containing wound disinfectant. In a patch test, he

reacted positive to flavine, potassium iodide as well as the hypochlorite containing disinfectant. Crossreactivity cannot be excluded. 20 volunteers also patched with the disinfectant did not show any reaction (Ng and Goh, 1989).

In a group of 40 housewives selected for suspected allergic hand dermatitis, sensitization by patch test was established. Thirty-eight housewives gave a negative response to sodium hypochlorite, although several had apparently used bleaching agents for longer periods. For two of them a sodium hypochlorite sensitization was concluded but concomitantly with a nickel allergy in the first case and with Kathon allergy in the second case (van Joost *et al.*, 1987). Therefore the two cases cannot be clearly interpreted as positive sensitization reaction to hypochlorite.

Sodium hypochlorite does not induce contact sensitization when tested according to standard skin sensitization test protocols; however, there have been rare reports of alleged allergic contact sensitization. Literature reports place NaClO in the category of non-sensitizing chemicals that can, on rare occasions, be implicated in sensitization reactions. It is important to underline that in the past hypochlorite solutions were associated with skin sensitization owing to the presence of chromium salts added to the product as staining agent. However the voluntary decision taken by industry to remove chromium from the hypochlorite solutions more than 15 years ago was a major contribution to the solution of the problem (Raccioppi *et al.*, 1994).

In conclusion, given the widespread use of sodium hypochlorite, the likelihood of allergic contact sensitization due to NaClO in practice is negligible.

4.1.2.4.3. Summary of sensitization.

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

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

4.1.2.5. Repeated Dose Toxicity

4.1.2.5.1. Studies in animals

The toxicity of sodium hypochlorite has been studied in a number of species following repeated or continuous administration (by the oral route by adding it to drinking water

or to milk) and by the dermal route. There are no studies available in which exposure has been by inhalation.

For the evaluation of repeated dose drinking water toxicity studies, the quantity of available chlorine as total concentration of hypochlorous acid and hypochlorite ions is described.

Oral

Rat

Subchronic studies

Groups of 5 male weanling Wistar rats were given sodium hypochlorite administered in their milk ad-libitum at concentrations of 0, 40, 200 and 1000 mg/l as av. Cl₂ for 9 days (only whole cow's milk, mixed daily with sodium hypochlorite, was available – no water). In addition, groups of 10 female Wistar rats were given either 0, 8, 40 or 200 mg available chlorine/kg bw/day by gavage, for 14 days. Finally, groups of 10 male rats were given either 0, 20, 40 or 80 mg/l available chlorine in their drinking water ad-libitum for 6 weeks. Observations were confined to the measurement of body weight and to the weights of the liver, kidneys, heart and brain. Weanling rats given sodium hypochlorite showed a non-statistically significant increase in body weight gain. There were no effects on organ-to-body weight ratios. Female rats receiving 8.0 mg/l sodium hypochlorite (as av. Cl₂) by gavage showed an increase in body weight gain when compared to controls. Those receiving 200 mg available chlorine/kg bw/day showed an increase in kidney weight compared to controls. No other effects were noted in treated female rats. Male rats receiving sodium hypochlorite in their drinking water at all dose levels showed an increase in body weight gain. No effects on organ weights were reported. The NOEL for sodium hypochlorite in the study was 1000 mg/l for weanling rats (9 days), 40 mg available chlorine/kg bw/day for females (14 days) and 80 mg/l available chlorine in drinking water for males (6 weeks). The NOEL for sodium hypochlorite was reported to be 15.7 mg/kg/day as av. Cl₂ (Cunningham, 1980).

Four groups of 10 male albino rats were given 0, 30, 2500 or 7500 mg/l available chlorine for 28 days by mixing a sodium hypochlorite solution in corn oil with the normal laboratory diet (equivalent to 2.7, 221 and 683 mg available chlorine per day). No deaths occurred during the study and no significant gross lesions were noted among treated rats when compared to controls. No differences in liver, kidney or testes weight were observed between the four groups. Adrenal weights in rats given 7500 mg/l available chlorine were statistically significantly increased (P>0.01) when compared to controls. The NOEL for sodium hypochlorite in this study was 2500 mg/l available chlorine (Industrial Bio-testlaboratories, 1970).

Groups of male and female F344 rats were given sodium hypochlorite dissolved in their drinking water at concentrations of 0, 0.05, 0.1, 0.2 or 0.4 % for 92 days (corresponding 0, 475, 950, 1900, 3800 mg/l available chlorine). Toxicity was assessed in terms of effects on body weight, organ weight, serum biochemistry and pathology. Both male and female rats given 4000 mg/l sodium hypochlorite showed a

significant decrease in body weight gain (47% and 31% reduction in males and females respectively compared to controls). Significant reductions in the absolute weights of certain organs in both males and females given 0.4% sodium hypochlorite were reported. However, the organ weight to body weight ratios were not reported and so the true significance of these findings could not be established. No remarkable pathological changes were observed among the treated rats. In this study the daily intakes of NaClO in $\mu\text{l/day}$ as av. Cl_2 are reported. The NOEL for sodium hypochlorite in the study was 0.2 % for both males and females (44.4 and 97.1 mg/kg/d available chlorine, respectively considering the drinking water intakes reported in the study) (Furukawa et al., 1980).

Groups of 10 male and 10 female F344 rats were given sodium hypochlorite dissolved in their drinking water (distilled water) at concentrations of 0, 0.025, 0.05, 0.1, 0.2 or 0.4% (from a solution of 14% available chlorine, purity not specified) for 13 weeks to determine maximum tolerated doses for further long-term carcinogenicity studies. These concentrations correspond to 120, 240, 480, 950, 1900 and 3800 mg/l available chlorine respectively. Toxicity was assessed in terms of daily clinical observations, mortality, and changes in body and organ weights, haematology and blood biochemistry and histopathology of all major organs. The maximum tolerated dose of sodium hypochlorite given in the drinking water to F-344 rats was estimated to be between 0.1 and 0.2% for males and 0.2 and 0.4% for females. No mortality occurred in any group. A dose-related decrease in body weight gain was observed in both sexes with a marked effect in both male and female rats given 0.4% sodium hypochlorite. Differences were statistically significant only for male rats given 0.2% and 0.4% sodium hypochlorite and female rats given 0.4% sodium hypochlorite. No histological changes attributable to treatment were reported. Biochemical examination of the blood sera was reported to show signs of slight liver damage in both male and female rats given 0.2% and 0.4% sodium hypochlorite (details not given). Absolute weights of the lung, liver and spleen of males and the salivary gland, lung, heart and brain of females were significantly lower in those given 0.4% sodium hypochlorite than in the controls. The NOEL for sodium hypochlorite in the study was 0.1% for both males and females (47.5 and 54 mg/kg/d available chlorine, respectively) (Hasegawa, 1986).

Chronic studies

Groups of 50 male and 50 female F344 rats (7 weeks old) were given sodium hypochlorite dissolved in their drinking water (distilled water) at concentrations of 0, 500 or 1000 ppm (0, 29.3 or 58.7 mg/kg/day as available chlorine) for males and 0, 1000 or 2000 ppm (0, 67.0, 133.9 mg/kg/day as available chlorine) for females (14% available chlorine, purity not specified) for 104 weeks. All surviving rats were sacrificed at week 112. At week 112, the incidences of surviving rats were: control 30/50, low dose 26/50, high dose 31/50 for males and control 31/50, low dose 36/50, high dose 35/50 for females. A dose-related decrease in body weight gain was seen after 16 weeks treatment in all treated groups of rats. This effect was accompanied by decreases in absolute organ weight that, in some cases, were reflected in decreases in relative organ weight (eg salivary glands in both groups of treated females; heart in males given 58.7 mg/kg/day NaClO expressed as available chlorine). The magnitude of the changes in both body and organ weights were small. Drinking water intake and food consumption were comparable among treated and control groups. Haematology

and serum biochemical analysis did not show significant treatment-related changes for any parameter in either sex. No treatment-related non-neoplastic lesions were reported. The NOELs for sodium hypochlorite in the study were 0.1 % (1000 ppm) corresponding to 58.7 mg/kg/day as available chlorine for males and 67.0 mg/kg/day as av. Cl₂ for females (Hasegawa, 1986; Kurokawa, 1986).

Groups of 70 male and 70 female F344 rats were given sodium hypochlorite dissolved in their drinking water at concentrations corresponding to 0 mg/l av. Cl₂, 70 mg/l av. Cl₂ (3.5 mg/kg/d for male rats), 140 mg/l av. Cl₂ (7 mg/kg/d for male rats) and 275 mg/l av. Cl₂ (13.75 mg/kg/d for male rats) for two years. Groups of 10 rats of each sex were pre-selected for evaluation at weeks 14 and 66. Mean body weights for males and females were similar among treated and control groups at both the 14-week and 66-week interim evaluations. A dose-related decrease in water consumption was observed throughout the study in the treated groups from both sexes. Food consumption was comparable among treated and control groups. There were no clinical findings attributable to the treatment at 14-week and 66-week interim evaluations. There were no alterations in haematological parameters and no biologically significant differences in relative organ weights between treated and control groups at the interim evaluations. The NOEL for sodium hypochlorite in the study was 275 mg/l available chlorine in the drinking water for both males and females (corresponding to a NOEL of 13.75 for males and 15.7 for females) (NTP, 1992).

Mouse

Chronic studies

Groups of 50 male and 50 female B6C3F1 mice, 4 to 6 weeks old, were given sodium hypochlorite (14% available chlorine, purity not specified) dissolved in their drinking water at concentrations of 0, 500 or 1000 mg/l (0, 477 or 954 mg/l as available chlorine) for 103 weeks. Groups of 73 male and 72 female mice were used as controls. All surviving mice were sacrificed at week 106. At that time, the survival rates were for males: controls 48/73, low dose 39/50, high dose 37/50 and for females: controls 56/72, low dose 40/50, high dose 39/50. A dose-related reduction in body weight gain occurred in treated groups from both sexes. Water consumption, haematology, blood chemistry and histopathology were apparently recorded but no information is given about these parameters apart from carcinogenicity data discussed later. The NOEL for sodium hypochlorite in the study was 477 mg/l available chlorine in the drinking water for both males and females (Kurokawa et al, 1986).

Groups of 70 male and 70 female B6C3F1 mice were given sodium hypochlorite dissolved in their drinking water at concentrations corresponding to 0, 70, 140 or 275 mg/l available chlorine for two years. Groups of 10 mice of each sex were pre-selected for evaluation at weeks 15 and week 66. Mean body weights were similar among treated and control groups after 15 weeks. After 66 weeks, the body weight of males given 275 mg/l available chlorine was significantly lower than that of the controls. A dose-related decrease in water consumption was observed throughout the study in treated groups from both sexes. Mean food consumption of treated males was slightly higher than for the controls for the first 52 weeks. During the same

period, mean food consumption of the treated females was slightly lower than for the controls. The mean food consumption for the remainder of the study was similar for both sexes and all groups. There were no clinical findings, no haematological changes and no changes in relative organ weights attributable to the consumption of chlorinated water at either the interim evaluations or the end of the experiment. No treatment-related non-neoplastic findings were reported in either sex. The NOEL for sodium hypochlorite in the study was 140 mg/l available chlorine in the drinking water for both males and females (NTP, 1992).

Other species

Groups of 20 male guinea pigs were given sodium hypochlorite dissolved in their drinking water at concentrations of either 0 or 50 mg available chlorine/l for 5 weeks. No adverse effects were observed (Cunningham, 1980).

Dermal

Mouse

The effect of sodium hypochlorite on epidermal hyperplasia was studied in female SENCAR mice exposed cutaneously to sodium hypochlorite at concentrations of 1000 mg/l for 10 minutes/day for four days. Whole body exposure, except the head, was performed using specially designed Plexiglass chambers to prevent inhalation of any vapours or aerosols. Concentrations of 1000 mg/l sodium hypochlorite caused increases in epidermal thickness when exposed for four days. In a similar preliminary study using 1000 mg/l HClO with 10 minutes exposure for 8 consecutive days, the maximal response was observed after four daily 10 minute exposures. No effects were observed following treatment with concentrations of 1, 10 or 100 mg/l hypochlorous acid for four days. Significantly increased numbers of both total and basal epithelial cells in the skin were observed following four daily 10-minute exposures to 300 mg/l hypochlorous acid and above (Robinson, 1986).

The results of this study suggest that the threshold concentration for the local skin irritant effects of sodium hypochlorite (as hypochlorous acid) is 300 mg/l, and that the effects were seen following repeated exposure to 0.1% sodium hypochlorite solution. Such local effects are dependant on the concentration of the applied irritant and not on the total dose. The study only reported the effects of a single concentration of sodium hypochlorite solution, there were inconsistencies on the reported effects of different concentrations of hypochlorous acid, suggesting that the findings of the study may be unreliable. It is noted that the non-treated control mice showed an unexplained reduction in skin thickness that will also have impacted on the outcome of the study.

Sodium hypochlorite was tested for promoting and complete carcinogenic activities in a skin carcinogenesis model using groups of 20 female SENCAR mice. A sodium hypochlorite solution (1% conc.) was applied twice a week for 51 weeks with or without initiation with dimethylbenzanthracene. Analysis of the number of skin tumours, squamous cell carcinoma and epidermal hyperplasia was performed. No animal died and no epidermal hyperplasia was observed in the group treated with sodium hypochlorite alone (Kurokawa, 1984).

Guinea Pigs

The effects of the repeated administration of sodium hypochlorite solutions on the skin has been studied in the guinea-pig. 0.1% and 0.5% solutions of sodium hypochlorite (950 and 4765 mg/l as available chlorine - prepared daily by diluting a proprietary household bleach (Clorox), which was a 5.25% solution of sodium hypochlorite) were applied to female guinea pig skin for up to 14 days, using gauze bandages soaked at 8 hour intervals with the solutions. The pH of the freshly prepared solutions were 7.4 and 9.65 for the 0.1% and 0.5% solutions respectively. Toxicity was assessed in terms of basal epidermal cell viability (trypan blue exclusion), the growth of single-cell cultures of epidermal cells to confluence *in-vitro*, and by histopathological examination. Tissue taken from areas of treated skin was compared to control adjacent tissue taken from the same animals. Basal epidermal cell viability was reduced from 85% to 65% in skin treated with the 0.5% solution for 14 days, but not for 1, 4 or 7 days and was not affected by treatment with the 0.1% solution. Similarly, the growth of epidermal cells *in-vitro* was affected only after treatment for 14 days with the 0.5% solution. Marked epidermal hyperplasia with an influx of inflammatory cells into the papillary dermis was observed in guinea-pigs treated with the 0.1% solution for 14 days, but not 1, 4 or 7 days and with the 0.5% solution for either 7 or 14 days, but not 1 or 4 days (Cotter et al., 1985). These results suggest that the LOAEC (expressed as a concentration) for the local irritant effects following repeated administration of this proprietary bleach solution for 14 days is 0.1%. It is noted that the test solutions were dilutions of proprietary bleach, which may have contained components in addition to sodium hypochlorite and that no adequate control was used (eg. a solution of equal osmolarity and/or pH).

A 0.1 ml solution of 0.125% (1190 mg/l av. chlorine) sodium hypochlorite was applied daily to guinea pig skin of the dorsal site of the ear for 1, 2, 4 and 8 weeks using 10 animals per group. No effect on epidermal proliferation, development and differentiation was observed. In the same study, sodium hypochlorite solution was blended with milk to assess the effects due to the formation of chloramines: no adverse effects were reported (Wohlab and Wozniak, 1982)

Other studies

The immunotoxic potential of sodium hypochlorite was assessed in male Sprague-Dawley rats from weaning to 12 weeks of age given drinking water containing 0, 5, 15 or 30 mg/l sodium hypochlorite for 9 weeks. No significant effects were observed on body weights, thymus weight, antibody response, natural killer cell cytotoxicity, interleukin production and phagocytic activity. Reductions in spleen weight and delayed-type hypersensitivity reactions were observed in the rats given 30 mg/l sodium hypochlorite (about 1.5 mg/kg bw/day), while in those given 15 and 30 mg/l, a reduction in macrophage oxidative metabolism and a statistically significant increase in prostaglandin E2 production were observed. No information on the reversibility of the effects was provided (Exon, 1987).

Effects on delayed-type hypersensitivity, hemagglutination titres and reticulo-endothelial clearance were studied in two groups of 30 CR1: CD-1 mice each given sodium hypochlorite in their drinking water at concentrations of 15 and 30 mg/l as available chlorine for 120 days. Other groups of mice were exposed to distilled water, tap water or other water treatment chemicals. No significant differences in antibody titres, reticulo-endothelial clearance or spleen weight were observed in the treated groups compared with the control group, suggesting that sodium hypochlorite does not significantly affect the immune function of mice (Hermann et al., 1982).

In a pharmacodynamics and toxicity study, groups of 4 Sprague-Dawley rats each were exposed to HClO as a single dose of 10, 20 and 40 mg/l (30, 60 and 120 µg, respectively) to control the rat blood glutathione after 15, 30, 60 and 120 minutes after the treatment. Other groups of 4 Sprague-Dawley rats, including a control group, were each treated daily for a period of 1 year by drinking water with 1, 10 and 100 mg/l of hypochlorous acid. Data collected were: the heparinized blood, collected at 3 and 6 months after HClO administration to control hematological parameters, chloroform content (at month 4, 6, 9 and 12), blood glutathione, and ³H-thymidine incorporation (both at month 2, 3, 4, 6, 8, 10 and 12). For the acute exposure a maximum decrease in blood GSH was observed 60 min after dosing. In the long term study a decrease of blood glutathione and increase of osmotic fragility after 6 months were observed. In animals exposed for 3 months, the ³H-thymidine incorporation into nuclei of rat kidney and testis in the 100mg/l group was increased. There was no dose-related effect and no information on the reversibility after treatment, no significant changes were observed relating the hematological parameters. Blood chloroform levels were without change during 1 year of treatment with hypochlorous acid (Abdel-Rahman and Suh, 1984).

A group of five C57BL/6N mice were given sodium hypochlorite in their drinking water at a concentration of 25-30 mg/l available chlorine for 4 weeks. A second group of mice served as controls. A decrease in the number of peritoneal exudate cells (suggestive of an effect on macrophage function) along with an overall depression of macrophage function was observed (Fidler, 1977).

Table 4.21: Repeated dose toxicity test with sodium hypochlorite

Author	Year	Animal/ route	Dura tion	Result (as av. Cl ₂)	Result (as av. Cl ₂ in mg/kg/day)	Note	Val
ORAL – in diet / by gavage							
Ind.Bio-Test	1970	rats m/in diet	28 d	NOEL 2500 ppm	NOEL 221	limited data	3
Cunningham	1980	rats f/gavage	14 d	NOEL 40 mg/kg /d	NOEL 40	non standard test	3
ORAL via drinking water (dw)				(as av. Cl₂ in mg/l)			
Cunningham	1980	Weanling rats/ in milk	9 d	NOEL 1000	NOEL 200*	non standard test	3
Cunningham	1980	Rats m/d.w.	6 wk	NOEL 80	NOEL 15.7**	non standard test	3
Hasegawa	1986	F344 rats/d.w.	13 wk	NOEL (males) -950 NOEL (females) - 950	NOEL (males) 47.5 NOEL (females) 54	MTD study	2

Furukawa	1980	rats/d.w.	92 d	NOEL 1900	NOEL 44.4 (males) and 97.1 (females)	subchronic test	2
Hasegawa Kurokawa	1986	rats/d.w.	104 wk	NOEL 0.1% (1000 ppm)	NOEL 58.7 (males) and 67.0 (females)	chronic/carcinogenicity study	2
NTP	1992	rat/d.w.	2 y	NOEL 275 ppm	NOEL 13.75 (males) and 15.7 (females)	carcinogenicity study	2
Kurokawa	1986	mice/d.w.	103 wk	NOEL 477	LOEL 78.3 (males) and 95.4 (females)	carcinogenicity study	2
NTP	1992	mouse/d.w.	2 y	NOEL 140 ppm	NOEL 23.3 (males) and 28.0 (females)	carcinogenicity study	2
Cunningham	1980	g.pigs/d.w.	5 wk	NOEL 50		non standard test	3
DERMAL							
Cotter	1985	g pigs/dermal	14 d	NOEL 950 (0.1% sodium hypochlorite)		non standard test; continuous, 14 d	3
Kurokawa	1984	mice female	51 wk	NOEL 9500 (1% sodium hypochlorite)		0.2 ml, 2x/wk, 51 wk	3
Robinson	1986	mice female	4 d	LOEL 950 (0.1% sodium hypochlorite)		whole body 10 min/d, 8 d; skin thickness	3
Wohlrab	1982	g.pigs	8 wk	NOEL 1190 (0.125% sodium hypochlorite)		0.1 ml, daily, 8 wk; only dose tested.	3
OTHER ORAL							
Abdel-Rahman	1984	rats/oral	12 m			solution of HClO	3
Exon	1987	rat/d.w.	9 wk			immune system endpoint	3
Fidler	1977	mice/d.w.	4 wk			specific end point	3
Hermann	1982	mice/d.w.	120 d			immune system no standard test	3

* NOEL in mg/kg/day derived using the assumption that weanling rats weigh 50 g and consume 10 ml milk/day (conversion factor of 5)

**NOEL in mg/kg/day taken from original paper.

The values expressed as av. Cl₂ expressed in mg/kg bw/day, reported in the table above, are calculated using values of body weight and water consumption for rats and mice reported in the document NO_NL/01/99_Rev.1 (table below) and based on Gold *et al.*, 1984 and Wilschut *et al.*, 1998. The use of this values reported below is considered to be a conservative approach.

Experimental animal	Standard lifespan (years)	Sex	Body weight (kg)	Water per day (ml)
Mouse	2	Male	0.03	5
	2	Female	0.025	5
Rat	2	Male	0.5	25
	2	Female	0.35	20
Hamster	2	Male	0.125	15
	2	Female	0.110	15

4.1.2.5.2 Human data

No indications of chronic toxicity in humans following exposure to sodium hypochlorite are reported in the literature: some case studies refer to specific effects and epidemiological studies designed for the evaluation of the potential carcinogenicity of chlorinated drinking-water have been evaluated (see more details in section 4.1.2.7.).

Inhalation

Although indirect exposure to sodium hypochlorite solution by aerosol or mist is possible, no cases on human exposure have been reported.

Oral

One case is reported about a child who sucked clothing that had been heavily bleached with NaClO solutions, although there was no information about the residual amount of sodium hypochlorite in the bleached cloth. Intermittent vomiting, stomach pains and inflammation of the lungs were reported, the effects disappearing after some time (Loeb and King, 1974).

A further case reported the continued use of 500 ml aqueous sodium hypochlorite solution (ca. 1%) as a wound dressing, 2-3 times a day for 1-2 weeks. Hypernatraemia due to poor kidney function was reported, along with the patient's inability to complain of thirst or to drink (Thorp et al., 1987).

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).

Dermal

Available studies on repeated dose toxicity after dermal exposure in humans are focused on evaluation of local dermal effects. No signs of irritation were observed after patch testing 69 patients with suspect allergic contact dermatitis (48 h “covered contact”) with 1% NaClO (Habets et al., 1986).

Studies involving HRIPT (human repeat insult patch test) with repeated 24-hour dermal application and epidemiological studies to the occurrence of dermatitis are described in chapter 4.1.2.4.2. Despite the widespread use of sodium hypochlorite, the occurrence of dermatitis through repeated dermal exposure is very rare. In the studies mentioned in chapter 4.1.2.4.2, 0.5 ml of 0.034% sodium hypochlorite induced an ‘acceptable level of irritation’ (unpublished data from Procter and Gamble, 1987 and 1989). No control group was present, and therefore it cannot be excluded that the reaction was caused by the application of an occlusive plaster and was not related to exposure to sodium hypochlorite.

Inhalation

No repeat dose inhalation studies are available on sodium hypochlorite aerosol, either in animals or humans. It might be possible to use data that is available on chlorine gas

as a surrogate, although it is recognised that this data will be derived following exposure to the gas and not to an aerosol. This difference may affect both the qualitative and quantitative aspects of the findings, although it is anticipated that the use of data on chlorine gas is likely to be a conservative assessment of the potential effects of sodium hypochlorite aerosol. The relevant data on chlorine is as follows:

Animal studies.

Groups of approximately 70 male and 70 female F344/N rats and B6C3F₁ mice were exposed to either 0, 0.4, 1.0 or 2.5 ppm (0, 1.2, 3.0 or 7.4 mg/m³) chlorine gas for 6 h/d, either for 5 d/week (male and female mice and male rats) or for 3 alternate days/wk (female rats), for 2 years. An interim post-mortem of 10 rats/sex was performed at 12 months. Exposure-related lesions were confined to the nasal passage in all exposed groups. They were 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 (Wolf et al, 1995). The LOAEL for respiratory irritation was 0.4 ppm. A NOAEL was not established in the study.

Groups of 4 male and 4 female rhesus monkeys were exposed to either 0, 0.1, 0.5 or 2.3 ppm (0, 0.3, 1.5 or 6.8 mg/m³) chlorine gas for 6 h/d, 5 d/week for 12 months. Eye irritation, mild focal hyperplasia and cilia loss in the nasal passages and trachea occurred in those exposed to 2.3 ppm. Only very mild hyperplasia of the nasal epithelium, a lesion also seen in some of the control animals, was observed in those exposed to lower concentrations. 0.5 ppm was considered to be a NOAEL in this study (Klonne et al, 1987).

An independent examination of these lesions confirmed that the responses were less severe in the monkey than in rodents and that the pathological effects in the rhesus monkey extended further into the respiratory tract than in the rodent species, in which the pathology was confined to the nasal passages. It was concluded that the rhesus monkey was a more appropriate model for the inhalation of chlorine gas in humans than rodents (Ibanes et al, 1996).

Human volunteer studies.

There are three relevant studies reported in which human volunteers have been exposed to chlorine. A group of 8 volunteers were exposed on a single occasion to either 0.5 or 1.0 ppm (1.5 or 3.0 mg/m³) chlorine gas for either 4 or 8 hours. Sensory irritation and a transient impairment in lung function were seen in those exposed to 1.0 ppm chlorine gas. No effects were reported in those exposed to 0.5 ppm. (Rotman et al, 1983).

A group of 8 male volunteers were exposed to either 0, 0.1, 0.3 or 0.5 ppm (0, 0.3, 0.9 or 1.5 mg/m³) chlorine gas for 6 h/d on 3 consecutive days. Each individual was exposed to each of the four exposure scenarios in a double-blind fashion. A range of respiratory function parameters was measured and, in addition, nasal lavage fluid was analysed for a number of indicators of inflammatory cell damage. No significant

effects were seen in parameters measured. 0.5 ppm was a NOAEL in the study (Schins et al, 2000).

The studies in rhesus monkeys are consistent with those in human volunteers and confirm that 0.5 ppm is a NOAEL for the effects of chlorine gas on the respiratory tract. This level of exposure could thus be used as an indicator of the NOAEL for sodium hypochlorite aerosol.

4.1.2.5.3 Summary of effects for repeated exposure

Oral

No standard 28-day or 90-day repeated dose toxicity studies on sodium hypochlorite in animals by the oral route have been reported. However, the data available from non-standard studies are sufficient to derive a NOAEL for sodium hypochlorite by this route of exposure. The dermal exposure studies reflect the reversible irritant effects of sodium hypochlorite at the doses tested.

No systemic effects have been observed in any of the studies reported. A general decrease of body weight or body weight gain was usually observed following treatment with the highest doses used, most probably due to a secondary effect linked to low water consumption.

In male and female rats treated with 0.2% and 0.4% of sodium hypochlorite in drinking water, a decrease in body weight and in specific organ weights, associated with some biochemical changes, were reported. A NOEL of 0.1% of sodium hypochlorite (950 mg/l available chlorine or 24 mg/kg bw/d) can be derived from this study (Hasegawa, 1986).

Some slight effects on body weight or specific organ weights were shown in male mice treated with 275 mg/l available chlorine in drinking water for two years. The NOEL in this study was 140 ppm available chlorine or 23.3 mg/kg bw/d (NTP, 1992).

Some incidental effects related to the immune system were reported in rats and mice administered with low doses of NaClO in chlorinated water for 12 or 17 weeks). These effects were observed in rats receiving chlorinated water containing 15-30 mg/l available chlorine (about 0.75-1.5 mg/kg bw/day) (Exon, 1987). However, in long term studies, no differences were reported between treated and controls for haematological analysis or thymus weight in rats given higher doses of NaClO in water (275 mg/l available chlorine or 13.75 mg/kg bw/d) (NTP, 1992). It is not possible to derive a no effect level for this specific end-point.

Dermal

Four experimental studies are available to evaluate the dermal toxicity of sodium hypochlorite following repeated exposure, in which damage of viable basal skin cells has been evaluated.

Daily exposure of mice to 1% sodium hypochlorite solution for 10 minutes on four consecutive days caused an increase in epidermal thickness (Robinson, 1986).

No effects were observed in the dermal studies except for specific skin toxicity in guinea pigs (marginally lowered *in vitro* basal cell viability) of uncertain toxicological relevance at 0.5% sodium hypochlorite solution which is related to the acute irritant effects of the substance (Cotter, 1985). In the same study, epidermal hyperplasia was observed following 14 days exposure (8 hours/day) to 0.1% sodium hypochlorite solution, but not following one, four or seven days exposure.

In a dermal two-stage carcinogenicity study, a clear no effect level was observed in female mice treated twice weekly for 51 weeks with 1% sodium hypochlorite solution. No animals died and no epidermal hyperplasia was observed in the treated group (Kurokawa, 1984). No effects were observed after exposure of guinea pigs to 0.125% sodium hypochlorite solution for up to 8 weeks (Wohlab, 1982).

The NOAEL for repeated dermal exposure to sodium hypochlorite solution is related to its cytotoxicity/ irritating properties and is dependant on the concentration of the applied solution. Therefore, irritation can be seen as a threshold for dermal toxicity. No dermal toxicity will occur at concentrations of sodium hypochlorite solution that do not cause irritation, either after single or repeated exposure.

A study in guinea pigs suggests that exposure to a formulated bleach solution containing 0.5% sodium hypochlorite for 8 hours/day for seven days caused significant epidermal hyperplasia. These effects were only seen following 14 days exposure to a 0.1% solution of sodium hypochlorite. A study in mice suggests that ten minutes exposure to 0.1% sodium hypochlorite solution for four days causes an increase in epidermal thickness. However, inconsistencies in the reporting of the study suggest that the finding might be unreliable.

Taking all of these comments into account, it is concluded from the available animal data (which is unreliable and might not adequately reflect human experience) that a very conservative NOAEL for repeated effects following dermal exposure to sodium hypochlorite solution is 0.1%.

There is no information on systemic toxicity following dermal application route. Fully dissociated in water, and immediate oxidising organic molecules, sodium hypochlorite is not expected to pass the skin to become systemic available. The amount of chlorinated substances passing the skin depends on the amount of mobile organochlorine substances being formed on and in the skin.

Conclusion

The NTP (1992) study is used as the key study for deriving a NOEL for risk characterisation for the **oral route**.

From this study a NOEL of **13.75 mg/kg bw/d** (or **275 mg/l available chlorine**) administered in drinking water can be identified for repeated oral exposure in the rat following exposure to sodium hypochlorite. This was the highest level tested and it is the lowest NOEL that can be calculated among all studies. Additionally, the selection

of this NOEL seems to be more reliable than the one from the same study on mouse which is 23.3 mg/kg bw/day (or 140 mg/l available chlorine). Indeed the rat looks somewhat more sensitive than the mouse as a study identified 24 mg/kg bw/d (450 mg/l available chlorine) as a LOEL in rat.

Slight local irritant effects have been observed following **dermal exposure** to a 1000 mg/l sodium hypochlorite solution. No systemic effects were seen following dermal exposure to 10000 mg/l sodium hypochlorite. A NOEL of **1%** from the study of Kurokawa (1984) is chosen to evaluate the local dermal effects from repeated exposure to sodium hypochlorite solutions.

For the evaluation of the effects of repeated **inhalation exposure** to hypochlorite aerosols, it is proposed to use data from chlorine. The NOAL for repeated exposure to chlorine gas is **0.5 ppm**, as confirmed by studies in rhesus monkeys and human volunteers.

4.1.2.6 Mutagenicity

4.1.2.6.1 *In-Vitro Bacterial Systems*

Sodium hypochlorite has been examined for its potential mutagenicity in a number of in-vitro studies using bacterial systems. In many cases the methodology is not fully valuable with only limited data presented.

Sodium hypochlorite was tested in a standard assay on mutagenicity in *Salmonella typhimurium* strain TA 1530, TA 1535 and TA 1538 at concentrations ranging from $1.4 \cdot 10^{-1}$ to $1.4 \cdot 10^{-4}$ $\mu\text{mole/plate}$ without metabolic activation. Only a weak, not dose-related, effect was reported in TA 1530 strain. The high toxicity displayed by the agent was claimed for the negative result and a modified procedure was applied in the attempt to overcome this problem. Bacteria were treated in liquid medium and before plating, sodium hypochlorite was decomposed by addition of ascorbic acid. Data presented only in graphic form indicated a clear effect in TA 1530 strain but not in TA1538 (Wlodkowski and Rosenkranz, 1975). These results are consistent with a presumable oxidative activity of the agent.

In a Japanese study sodium hypochlorite was mutagenic in TA 100 strain in the presence of S9 mix but negative in TA 98 strain. No further information on doses and test procedures were provided (Kawachi *et al.*, 1980).

In a study conducted under a project operated by Japanese Institution on chemical additives, sodium hypochlorite was tested in *Salmonella typhimurium* strain TA 92, TA 94, TA 98, TA 100, TA 1535 and TA 1537 with or without metabolic activation (S9 mix from the rat liver treated with polychlorinated biphenyls). In the presence of S9 mix, a 3.4 fold increase over the control was observed in TA 100 strain at 5 mg/plate (Ishidate *et al.*, 1981) (Ishidate *et al.*, 1984).

A negative result, based on the limited data presented, was reported for sodium hypochlorite in the Ames test using two *S. typhimurium* tester strains TA97 and TA102, with and without S9-mix, at concentrations 0.01, 0.05, 0.1, 0.5 and 1 $\mu\text{l/plate}$, (Fujita and Sasaki, 1987).

A negative result in *S. typhimurium* by fluctuation test, a modified Ames test, was reported for sodium hypochlorite in strains TA 100, TA 98 and TA102 tested without metabolic activation at concentrations ranging from 0.1 to 100 µg/ml (Le Curieux *et al.*, 1993). In the same studies a negative results for sodium hypochlorite was reported in the SOS chromotest in *E. Coli* (Le Curieux *et al.*, 1993).

It has been reported that the activity of some known mutagens in the Ames test was reduced in the presence of sodium hypochlorite (Tsuda *et al.*, 1983).

In a non-standard assay, sodium hypochlorite inhibited the growth of a DNA repair deficient strain of *Escherichia coli*, indicating DNA damage (Rosenkranz, 1973). Little methodology or data is provided and the presence or absence of metabolic activation is not specified. The significance of the positive response reported is questionable and is deemed to be of limited value. In two further studies, negative responses were obtained in the *Bacillus subtilis* rec assay with and without metabolic activation (Kawachi *et al.*, 1980), and in the SOS chromotest (Klimm *et al.*, 1980). However, in both these studies, only limited data has been reported and the protocols are insufficient to enable full assessment.

4.1.2.6.2 In-Vitro Mammalian Cells

Data on cytogenetic effects of sodium hypochlorite in mammalian cells are reported in a series of studies from Japanese groups.

Chromosome aberrations were analyzed in Chinese hamster cells treated for 24 or 48 hours with three different doses, in the absence of metabolic activation. A positive increase of chromosome aberrations (including gaps) was observed only in culture treated with 0.5 µg/ml for 48 hours. All the other experimental points reported were negative (Kawachi *et al.*, 1980; Ishidate *et al.*, 1981 and 1984).

Chinese hamster cells were treated for three hours with 0.5 µg/ml (6.7 mM) of the agent in the presence of metabolic activation with S9 mix from liver of PCB treated Wistar rats. A slight increase of chromosome aberration (including gaps) was observed (Matsuoka *et al.*, 1979).

Because gaps were included in the evaluations and no other data are provided the results of both studies cannot be interpreted satisfactorily.

In human cells, a non-standard embryo fibroblast line (HE2144) was used for the analysis of chromosome aberrations and SCE. In these cells no increase of chromosome aberrations was reported at both 0.0744 (10^{-3} M) and 0.1488 µg/ml (2×10^{-3} M). No other information was provided. In the same cell line the agent was tested for the induction of SCE after 40-48 hours treatment. A doubling and a 50% increase of the background level of SCE was produced by the highest (0.1488 µg/ml) and the lowest tested doses (0.0744 µg/ml), respectively (Sasaki *et al.* 1980).

No mammalian cell gene mutation studies have been conducted.

4.1.2.6.3 *In-Vivo Studies*

In a series of assays, sodium hypochlorite has been tested for its ability to induce genetic damage in-vivo. Chlorine gas bubbled in water (leading to hypochlorite and hypochlorous acid solution) has been evaluated for induction of chromosomal aberrations and micronuclei in bone marrow of CD-1 mice (Meier *et al.*, 1985). In these assays, chlorine at pH 8.5, where hypochlorite predominates, was administered orally at dose levels equivalent to 1.6, 4 and 8 mg/kg/day for 5 days. In the mouse micronucleus assay, a small but statistically significant increase in the percentage of micronucleated polychromatic erythrocytes were observed in the combined male and female data but not separately. However the micronucleus frequency in the hypochlorite treated animals was in the range of other control groups present in the same study. The statistic significance of the increase is considered to be due to the low value recorded in the concurrent vehicle control rather than to any clastogenic effects of sodium hypochlorite (Meier *et al.*, 1985). No statistically or biologically significant increase in the frequency of either structural or numerical chromosome aberrations was observed in the mouse chromosomal aberration assay (Meier *et al.*, 1985). The methodology used in these studies is well described, however no rationale for dose level selection is reported and it cannot be ascertained whether a maximum tolerated dose (MTD) has been achieved because no information on bone marrow toxicity were reported.

In a well conducted mouse micronucleous assay, no statistically or biologically significant increase in micronucleated polychromatic erythrocytes was observed in the bone marrow following a single intraperitoneal injection of sodium hypochlorite (6.6% Cl active) at dose levels from 312.5 to 2500 mg/kg. A reduction of polychromatic erythrocytes was observed at 1250 mg/kg and all animals died at 2500 mg/kg. An additional study involving the use of 4 repeated doses of 300 mg/kg, 24 hours apart, with a single sampling time at 24 hours following the final dose, was also clearly negative (Hayashi *et al.*, 1988).

A negative result in the induction of chromosome aberrations in rat bone marrow has been reported by Kawachi *et al.*, 1980. No other information was provided.

In a non-standard assay, rats given 900 mg/kg orally showed no evidence of DNA damage, detected as 8-hydroxyguanosine adducts, in the kidney (Kasai *et al.*, 1987).

Meier *et al.*, 1985 have tested chlorine, as hypochlorite and hypochlorous acid, in a sperm head abnormality test in B6C3F1 mice. Sperm head abnormality tests are also indicative for germ-line genotoxicity (although of limited validity, if any) (see 4.1.2.8)

Table 4.22: Mutagenicity tests with sodium hypochlorite

AUTHOR	YEAR	TYPE	RESULT	NOTES	VAL.
Genetic toxicity in vitro: bacteria					
Wlodkowski and Rosenkranz	1975	Ames / S.typh.	Positive TA1530 Negative TA 1535 TA1538	Positive only with modification of standard procedure	3
Kawachi	1980	Ames / S.typh.	Positive TA100 (+S9) Negative TA98	limited data presented	2
Ishidate	1981/ 1984	Ames / S.typh.	Positive TA100 (+S9)	limited data presented	2
Fujita	1987	Ames / S.typh.	Negative TA97 TA102 (±S9)	limited data presented	2
Le Curieux	1993	Ames / S.typh SOS Chromotest	Negative TA 100 TA 98 TA 102 (-S9) Negative	not standard assay	2
Tsuda	1983	Ames / S.typh.	Not applicable	supplemental information	2
Rosenkranz	1973	Pol. A / E.Coli	Positive	supplemental information	3
Kawachi	1980	Rec A / B. Subt.	Negative (±S9)	supplemental information	3
Klimm	1989	SOS chromotest	Negative	supplemental information	3
Genetic toxicity in vitro: mammalian cells					
Ishidate	1984	CA / CHL cells	Positive (-S9)	limited data presented	2
Matsouka	1979	CA / CHL Cells	Positive (+S9)	limited data presented	2
Sasaki	1980	CA / HEF Cells	Negative	limited data presented	2
Sasaki	1980	SCE / HEF Cells	Positive	limited data presented	2
Shaw	1970	CAA HL	negative	no data presented	3
Genetic toxicity in Vivo					
Meier	1985	MN / Mouse BM	negative	data on bone marrow toxicity is missing	2
Meier	1985	CA / Mouse BM	negative	data on bone marrow toxicity is missing	2
Hayashi	1988	MN / Mouse BM	negative	data well presented	1
Kawachi	1980	CA / Rat BM	negative	no data presented	3
Kasai	1987	DNA adduct / Rat kidney	negative	supplemental information	2

4.1.2.6.4 Human Data: Genetic and Related Effects

No data available.

4.1.2.6.5 Conclusions

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 positive results produced in bacteria assays and the induction of chromosome aberrations (including gaps) and SCE in mammalian cells suggest, even if mammalian

cell gene mutation studies are lacking, that sodium hypochlorite may exert an in vitro mutagenic activity.

Sodium hypochlorite was without effect in a well-conducted mouse micronucleus assay suggesting that sodium hypochlorite is not mutagenic in vivo.

The available data are not conclusive with respect to genotoxicity. Although, since sodium hypochlorite has shown lack of carcinogenicity effects (see paragraph 4.1.2.7), no additional testing is required.

4.1.2.7 Carcinogenicity

4.1.2.7.1 *Animal data*

The potential carcinogenicity of sodium hypochlorite has been examined in different strains of rats and in B6C3F1 mice (Kurokawa *et al.*, 1986, Hasegawa *et al.*, 1986, NTP, 1992; Soffritti *et al.*, 1997) by long term oral administration in drinking water and, in female Sencar mice, NMRI mice and in female ddN mice by skin application (Hayatsu *et al.*, 1971, Pfeiffer, 1978, Kurokawa *et al.*, 1984). Its potential carcinogenicity has also been studied in a multigeneration study by the oral administration of chlorinated drinking water to BDII (cPah albino) rats (Druckrey, 1968).

There are no reports of carcinogenicity studies by the inhalation route, although two-year inhalation toxicity/carcinogenicity study on chlorine is available (Wolf, 1995)

Sodium hypochlorite has also been tested for tumour promoting effects in female Sencar mice following initiation with dimethylbenzanthracene (Kurokawa *et al.*, 1984), in NMRI mice with benzo-pyrene (Pfeiffer, 1978) and in female ddN mice following initiation with 4-nitroquinoline 1-oxide (Hayatsu *et al.*, 1971).

Oral administration

Groups of 50 male and 50 female B6C3F1 mice, 4-6 weeks old, were given 500 or 1000 mg/l (0.05 or 0.1%) sodium hypochlorite prepared from commercial product (14% available chlorine) in drinking water for 103 weeks. Groups of 73 male mice and 72 female mice were used as controls using distilled water. All surviving mice were sacrificed at week 106 at which time the survival rates were; control males, 48/73; low-dose, 39/50; high dose 37/50; control females, 56/72; low-dose 40/50; high-dose, 39/50. Dose related reductions in body weight occurred in both sexes. Combined tumour incidences of leukemias and malignant lymphomas and of adenomas and adenocarcinomas of the lung were very high in all groups (control and all treated) for both sexes. Also, a high incidence of hyperplastic nodules and hepatocellular carcinomas of the liver in males of all groups was noted. However, no statistically significant differences in tumour incidences were observed for any organ in treated animals. It was concluded that there was no effect upon tumour incidence in either male or female mice (Kurokawa *et al.*, 1986)

Groups of 50 male and 50 female F344 rats, 7 weeks old, were given 0, 500 or 1000 mg/l (0, 0.05 or 0.1% - males) and 0, 1000 or 2000 mg/l (0, 0.1 or 0.2% - females) sodium hypochlorite prepared from a commercial product (14% as available chlorine), in drinking water for 104 weeks. The control groups were given distilled water. Survival rates at 112 weeks were high; control males, 30/50; low-dose, 26/50; high-dose, 31/50; control females, 31/50; low-dose, 36/50; high dose, 35/50. Dose-dependent inhibition of body weight increase was observed in both male and female rats. Drinking water intakes were comparable among treated and control groups. All three treated groups demonstrated relatively high incidences of tumours of the testis, pituitary, thyroid, lung, pancreas, uterus, mammary gland, spleen and subcutaneous tissue. Histologically, chromophobic adenomas of the pituitary, adenomas and adenocarcinomas of c-cells of the thyroid, adenomas of the lung, insulomas of the pancreas, fibroadenomas of the mammary gland and mononuclear cell leukemias were identified in both males and females. Also, a high incidence of interstitial cell tumours of the testis and fibromas in subcutaneous tissues in males and endometrial polyps of the uterus in females were observed. However, the occurrence of tumours at any site was not significantly greater in rats receiving sodium hypochlorite than in the controls. The proportions of low-dose and high-dose female rats with fibroadenomas of the mammary gland were significantly lower than that of controls. Similarly, the proportion of high-dose male rats with nodular hyperplasia of the liver was decreased. Haematological and serum biochemical analyses did not show significant dose-related changes of any parameters in either sex treated with sodium hypochlorite (Hasegawa *et al.*, 1986, Kurokawa *et al.*, 1986).

Groups of 70 male and 70 female F344 rats were given drinking water containing 0, 70, 140 or 275 ppm available chlorine for up to 2 years. Groups of 10 rats of each sex were pre-selected for evaluation at 14 or 15 and 66 weeks. Survival at 2 years of rats receiving chlorinated water was similar to that of the controls. After 2 years of exposure, the mean body weights of dosed male rats and high-dose female rats were slightly lower than those of their respective control groups. There was a dose related decrease in water consumption by rats. Water consumption by high-dose rats during the second year of these studies was 21% lower than that of control males and 23% lower than that of control females. The incidence of mononuclear cell leukemia in mid-dose, but not high-dose, female rats was significantly higher than that in controls (control, 8/50; low-dose, 7/50; mid-dose 19/50; high-dose 16/50). The proportion of female rats that died of leukemia before the end of the study and the mean time for observation of animals dying with leukemia were similar among all treated groups and controls. Although the marginal increase in leukemia incidence in the mid- and high-dose female rats suggested a possible association with the administration of chlorinated water, the incidence of leukemia was not clearly dose related. There was no indication of reduced latency of leukemia and the incidence of leukemia in concurrent controls was less than the mean for historical controls. Furthermore, there was no supporting evidence of an effect in male rats. Thus the marginal increase in leukemia incidence in female rats was considered equivocal evidence of carcinogenic activity. There were no neoplasms or non-neoplastic lesions in male rats that were clearly associated with the consumption of chlorinated water (NTP, 1992).

In the same study, water containing 0, 70, 140 or 275 ppm available chlorine was also given to groups of 70 B6C3F1 mice of each sex for up to 2 years. Groups of 10 mice

of each sex were pre-selected for evaluation at 14 or 15 and 66 weeks. Survival at 2 years of mice receiving chlorinated water was similar to that of the controls. Mean body weights oftreated mice were slightly lower than those of their respective control groups. There was a dose related decrease in water consumption by mice: water consumption by high-dose mice was 31% lower than that of controls for males and 26% lower for females. There were no neoplasms or non-neoplastic lesions in male or female mice that were clearly associated with the consumption of chlorinated water (NTP, 1992).

Four groups of 50 male and 50 female Sprague-Dawley rats each, 12 weeks old at the start of the study, received drinking water with added sodium hypochlorite, with concentrations of active chlorine of 750, 500 or 100 mg/l (treated groups) or tap water (active chlorine <0.2 mg/l) (control group), respectively, for 104 weeks. No group was treated with non-chlorinated water. In the male rats, a slight increase of total tumours was seen in all treated groups, compared to controls, but the effect was not dose-related. Among the treated female rats, an increased incidence of lymphomas-leukemias (not specified) was observed, but the effect was not clearly dose-dependant. The control group (at <2mg/l of active chlorine) showed an unusually low incidence of leukemia (0 cases against 4 cases in male control group). Some unusual tumours in Sprague-Dawley rats were observed randomly but were not treatment related. Considering the conclusions not definitive, the authors suggested further studies for a quantitative assessment of cancer risk (Soffritti *et al.*, 1997).

Chlorinated water, containing available chlorine at a periodically controlled level of 100 mg/l was well tolerated when given daily as drinking water over the whole lifespan (maximum of 2 years) to 236 BDII (cPah albino) rats for five generations (excluding F3 and F4). Following haematological tests and final necropsy of all animals, the results indicated that there was no difference in survival and in malignant tumour incidence in any generation group when compared to the untreated controls (Druckrey, 1968).

Summary of oral administration

The available animal studies are not sufficient to indicate a clear relationship between the oral administration of sodium hypochlorite in drinking water and cancer. Slight and equivocal evidence is reported in two studies (NTP, 1992, and Soffritti *et al.*, 1997) for leukaemia in female rats. No other evidence is reported in other tests.

Inhalation exposure

No chronic or carcinogenicity study is available for inhalation exposure of sodium hypochlorite and the only information available concerns chlorine inhalation.

A 2-year inhalation study in male and female F344 rats exposed to 0, 0.4, 1.0 and 2.5 ppm (v/v) chlorine gas for 6 hrs/day, 5 days/week (female rats only exposed for 3 days/week), showed that exposures did not affect survival and did not cause tumours. Various non-neoplastic lesions were observed in the nasal passages of both species at all exposure levels (Wolf *et al.*, 1995).

In the same test male and female B6C3F1 mice exposed to 0, 0.4, 1.0 and 2.5 ppm (v/v) chlorine gas for 6 hrs/day, 5 days/week showed that exposures did not affect

survival and did not cause tumours. Various non-neoplastic lesions were observed in the nasal passages of both species at all exposure levels (Wolf *et al.*, 1995).

Skin application

There is no dermal carcinogenicity study on sodium hypochlorite available.

In a mouse skin two-stage carcinogenesis model study, a control group of 40 ddN female mice, 5 weeks old, were given 60 topical applications of sodium hypochlorite (10% effective chlorine solution) (purity, vehicle and frequency of application unspecified). Another group of 40 female mice (group 2) were given 20 applications of 4-nitroquinoline 1-oxide, a potent carcinogen, (purity, vehicle and frequency of application unspecified); and a third group of 40 mice (group 1) were first given the carcinogen, painted on in 20 applications of 0.05 mg in 0.25% (w/v) benzene solution over the course of 50 days (1mg/mouse total), followed, six days later, by 45 applications of approx. 0.05 ml sodium hypochlorite solution (10% available chlorine), during a period of 245 days (frequency of application unspecified). No skin tumours occurred in the mice given sodium hypochlorite alone. However, skin tumours were seen in 9/32 mice given applications of sodium hypochlorite following initiating doses of 4-nitroquinolene 1-oxide and included one fibrosarcoma, three squamous cell carcinomas and five papillomas. No skin tumours occurred in mice given applications of 4-nitroquinolene 1-oxide only. The results of this study suggest that sodium hypochlorite might have the potential for co-carcinogenicity or tumourpromoting (Hayatsu *et al.*, 1971).

A 1% solution of sodium hypochlorite applied to the skin twice weekly for 10 weeks prior to, or after treatment with 750 and 1500 µg of 3,4-benzopyrene, a potent carcinogen, reduced the number of NMRI mice developing skin tumours when compared with those receiving dermal applications of two doses of the carcinogen alone (Pfeiffer, 1978).

In another mouse skin two-stage carcinogenesis model study, a group of 20 female Sencar mice, 6 weeks old, were given a single topical application of 20 nmol (5µg) dimethylbenzanthracene (DMBA) in acetone, followed by applications of 0.2 ml of 1% sodium hypochlorite solution in acetone twice weekly for 51 weeks. A group of 15 female mice given a single application of DMBA followed by applications of acetone served as controls. The effective number of mice was 20; the number of survivors was not reported. A squamous cell carcinoma of the skin occurred in 1/20 mice treated with DMBA and sodium hypochlorite, whereas none occurred in the initiated controls. In the same test to verify the complete carcinogenic activity, another group of 20 female Sencar mice, 6 weeks old were given topical applications of 0.2 ml of a solution of 1% (10 g/l) sodium hypochlorite in acetone twice weekly for 51 weeks at which time the study was terminated. A group of 15 female mice given applications of acetone were used as controls. All animals survived to the end of the study. No skin tumours were observed in the treated or control groups (Kurokawa *et al.*, 1984).

Summary of skin application

The available data show no carcinogenic effect due to topical application of sodium hypochlorite solution at different concentrations. There is an indication, supported by a poorly described study, of co-carcinogenicity using NaClO as a promoting agent. In the same study, 4-nitroquinolene 1-oxide alone did not show carcinogenicity, suggestive of methodological problems or unusual responses of the mouse strain used. Two other studies using different initiators did not show promoting effects of NaClO, although the doses employed were lower.

4.1.2.7.2 Human Data

There are no case reports or epidemiological studies of human carcinogenicity directly linked to administration of sodium hypochlorite. The only human data relating with sodium hypochlorite are in connection with its use to disinfect drinking water.

Drinking water epidemiological studies

The addition of sodium hypochlorite and chlorine gas gives the same chlorine species in solution - i.e., an equilibrium mixture of mainly hypochlorous acid and hypochlorite anion. In this way much of the general population is exposed to hypochlorite via drinking water.

Several epidemiology studies are available to evaluate the carcinogenicity of chlorinated drinking water, but their use in sodium hypochlorite risk assessment is questionable considering the great differences in water quality in diverse geographical areas and the contribution of the chemical species present in water supplies and the derived reaction products. For an overall assessment of the effect of chlorinated drinking water on the general population, including sodium hypochlorite as the active chlorine source, specific activity should be assessed while the following text is only an initial contribution.

IARC reviewed in 1991 the available studies and gave prominence to the difficulties in the interpretation of the data for an evaluation of the carcinogenicity of chlorinated drinking water. In the studies performed there are several methodological inadequacies, many confounding variables, and no causal link between increased cancer risk and consumption of chlorinated drinking water. Some studies have reported a correlation between the higher risk of cancer of the urinary bladder and the long-term consumption of chlorinated drinking water. Evidence from other studies, although showing some degree of consistency, is severely compromised by the weaknesses outlined above.

IARC overall evaluation was that chlorinated drinking water and hypochlorite salts are not classifiable as to their carcinogenicity to humans and that there is inadequate evidence for the carcinogenicity of chlorinated drinking water and hypochlorite salts in humans (IARC, 1991).

Recent ecological studies reported a weak association between consumption of chlorinated drinking water and cancer of the colon and rectum in men and women (Flaten, 1992 in IPCS EHC 2000); no associations between chlorinated surface water

supplies and bladder or stomach cancer were found in the Valencia Province, Spain (Suarez-Varela *et al.*, 1994 in IPCS EHC 2000).

A study in Taiwan reported associations between use of chlorinated drinking water and cancer of the rectum, lung, bladder and kidney (Yang *et al.*, 1998 in IPCS EHC 2000).

Some population-based case-control studies were conducted for bladder, colon, pancreatic, brain and cancer risk by different authors: King and Marrett (1996 cited in IPCS EHC 2000) conducted in residents between 25 and 74 years of age with a histologically confirmed primary cancer or carcinoma in situ of the bladder; they found higher relative risk estimates for a group of nonsmokers associated with many years of exposure to chlorinated surface water.

In a Colorado residents case-control study, McGeehin *et al.* (1993, cited in IPCS EHC 2000) suggested the hypothesis that prolonged (+30 years) exposure to chlorinated surface water is associated with an increased risk of bladder cancer, while Freedman *et al.* (1997, cited in IPCS EHC 2000) found a weak association between bladder cancer risk and the use of municipal chlorinated water, limited to cigarette smokers, in a population based case-control study in Maryland.

In a population-based case-control study for bladder, colon and rectal cancer, conducted by Cantor *et al.* (1998) in Iowa, an increased risk of bladder cancer in current and past male smokers and an association between brain cancer among men and increased duration of exposure to chlorinated surface water was found.

Hildesheim *et al.* (1998, cited in IPCS EHC 2000) suggested in another, similar study in Iowa, the same association with bladder cancer and found a larger relative risk for rectal cancer among persons with low dietary fiber intake and longer duration exposure to chlorinated surface water sources compared to persons with high fiber diets and no exposure to chlorinated surface water.

In a population-based case-control for pancreatic cancer conducted by Ijsselmuiden *et al.* (1992, cited in IPCS EHC 2000) in Maryland, no increased risk of pancreatic cancer was associated with the consumption of chlorinated drinking water.

Summary of epidemiological studies

Although some studies reported small relative risks for colon and bladder cancer incidence for population consuming chlorinated drinking water for long periods of time, they are equivocal or insufficient to establish a causal relationship, considering the quality and the completeness of the studies and the interpretation of the available data and of the confounding factors.

4.1.2.7.3 Conclusions

In long term carcinogenicity studies, sodium hypochlorite administered in the drinking water did not increase the proportion of F344 rats and B6C3F1 mice with tumours. Under the conditions of the 2 year NTP drinking water study there was no evidence of carcinogenic activity of chlorinated water in male rats or in male and female mice. However, the study concluded that there was equivocal evidence of carcinogenic

activity of chlorinated water in female rats based on a marginal statistical increase in the incidence of mononuclear cell leukemia. Similarly non-dose dependant increases in lymphoma/leukemia were found in female Sprague-Dawley rats in another long term rodent bio-assay with chlorinated drinking water. This study was deemed suggestive but inconclusive by its authors. Drinking water containing 100mg/l chlorine was tested for carcinogenicity in a multigeneration study in male and female BDII rats. No increase in the incidence of tumours was seen in the treated animals relative to controls through six generations. **Taking into account all the available information, it can be concluded that carcinogenicity is not a relevant endpoint for the oral route.**

In dermal carcinogenic studies sodium hypochlorite applied to the skin did not produce skin tumors in Sencar mice and ddN mice. No skin promoting effect was observed in the study with DMBA, whereas some effect was seen in the study with 4-nitroquinoline 1-oxide. This study suggests that sodium hypochlorite might have tumor-promoting effects, although it raises methodological questions and its quality cannot be fully evaluated because of the lack of details.

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.

Table 4.23: Carcinogenicity studies with sodium hypochlorite

AUTHOR	YEAR	TYPE	DOSES (expressed as active chlorine)	RESULT	NOTES	VAL.
Oral						
Soffritti	1997	drinking water, Sprague-Dawley rats (m/f), 104 weeks	Control (tap water), 100, 500, 750 mg/l	Not dose-related increase in leukemia-lymphomas in female group	well conducted study	1
Druckrey	1968	drinking water, BDII rats, 2 yrs, 5 generations	100 mg/l	negative	sample analysis, necropsy	3
Hasegawa/ Kurokawa	1986	drink.water F344 rats, 104 wks	0, 475, 950 mg/l in male - 0, 950, 1900 mg/l in female	negative	well conducted study	1
Kurokawa	1986	drink.water, B6C3F1 mice, 103 wks	0, 475, 950 mg/l	negative	well conducted study	1
NTP	1992	drink.water, F344/N rats, 2 yrs	0, 70, 140, 275 mg/l	equiv. evidence in females	well conducted study	1
NTP	1992	drink. water B6C3F1 mice, 2 yrs	0, 70, 140, 275 mg/l	negative	well conducted study	1
Inhalation						
Wolf	1995	chlorine gas, B6C3F1 mice 2 ys	0, 0.4, 1.0, 2.5 ppm Cl	negative	supplemental information	3
Wolf	1995	chlorine gas, F344 rats, 2 ys	0, 0.4, 1.0, 2.5 ppm Cl	negative	supplemental information	3
Dermal						
Hayatsu	1971	female ddN mouse skin two-stage model, 450 days	NaClO 10000 mg/l; NQ-oxide 0.25% - combined	skin cancers in combined group	promoting test ; the strain mouse is unusual,	3
Kurokawa	1984	female Sencar mouse skin two-stage model for 51 weeks	NaClO 1000 mg/l-DMBA (initiator) 20nM - combined	negative	promoting test	2
Pfeiffer	1978	NMRI mouse tumour promotion, 104 weeks	NaClO 10000 mg/l - BP (initiator) 750, 1500 µg - combined	cancer decrease in combined group	promoting test, lack of data	3

4.1.2.8. Reproductive toxicity

4.1.2.8.1 Animal data

The data discussed in this section are summarized in Table 4.24.

There are no specific data on sodium hypochlorite itself. However, according to section 2.4.1 sodium hypochlorite exists as a solution in which the composition of ions depends on the pH. Considering the biological systems, the active chemical

species available are HOCl and ClO⁻ in equilibrium in the pH range 6-8, and Cl₂ at pH below 4. As a consequence, when sodium hypochlorite is administered orally, it is transformed to chlorine in the stomach and can be transformed back to hypochlorous acid and hypochlorite depending on the pH of the substrate. For this reason, the toxicological profile of sodium hypochlorite is linked to that of chlorine and hypochlorous acid. Available data on these species are therefore relevant for the toxicological assessment of sodium hypochlorite.

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

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

Reproductive effects

Meier *et al.*, 1985 have tested chlorine, as hypochlorite and hypochlorous acid, in a sperm head abnormality test in B6C3F1 mice. In this assay, a chlorine solution at pH 8.5, where hypochlorite anion predominates, was administered orally at dose levels equivalent to 1.6, 4 and 8 mg/kg/day as hypochlorite anion for 5 days. No abnormalities were detected for sampling times of 1 and 5 weeks. However, statistically significant increases in the frequency of sperm head abnormalities, at 3 weeks post-treatment, were observed at the two highest dose levels without dose-related increase. The mean percentage of abnormalities was 2.12, 4.07 and 3.68 for the negative control, the 4 mg/kg and the 8 mg/kg dose levels respectively. This effect was reproduced in an independent repeated experiment and, in addition, a small statistically significant increase was observed at 1.6 mg/kg/day (1.41% compared to 0.91% for the negative control).

Although this study is validated as category 2 because it is well documented and meets generally accepted scientific principles, the toxicological significance of the findings is doubtful for several reasons:

- Concerning the assay itself, the authors pointed out that the major drawback of this assay was a low specificity with high number of false positives.
- Moreover, in the two experiments, the increases were small, (less than or about 2 fold) and without dose-dependency (the highest dose of 8 mg/kg had a lower rate of abnormality than the 4 mg/kg dose).
- Furthermore, this report showed that the background incidence of sperm abnormalities was very variable ranging from 0.91 to 3.3%. In the light of this observation, all of the statistically significant increases described by the authors in the treated groups fall in the background incidence of sperm abnormalities except for the 4 mg/kg dose which was slightly outside of this range in the first experiment only (4.07%).
- In the same study, at the same doses and under the same conditions, administration of chlorine solution at pH 6.5 did not cause any increase in the number of sperm

abnormalities. Taking into account the acid pH of the stomach and the reaction with hypochlorite, there is no plausible mechanism which can explain the difference in terms of effect between a solution administered orally at pH 8.5 and pH 6.5. It is also expected that sodium hypochlorite will never reach the testes due to rapid decomposition (see section 4.1.2.1)

- In a rat reproductive toxicity study performed by Carlton *et al* (1986; see below), no sperm head abnormalities were found at similar doses and with treatment duration of 56 days against 5 days in this study. Under chronic exposure conditions the rat has been proven to be more sensitive to toxic effects of sodium hypochlorite with a NOAEL of 14 mg/kg and LOAEL of 24 mg/kg than the mouse (NOAEL of 23 mg/kg; see section 4.1.2.5.3).

In conclusion, the Meier *et al.* study, although well reported, cannot be considered for the risk characterisation of hypochlorite. The findings are of statistical significance but they are not supported by a biological and mechanistic point of view.

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 (when all pups of a same litter had open eyes, this day was considered as day of eye opening 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 *et al.*, 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 a study by Abdel-Rahman and Suh (1984), a statistically significant increase of incorporation of ³H-Thymidine was observed in testes of rats receiving 100 mg/l

HClO in drinking water for three consecutive months. Concentrations of 1 and 10 mg/l were also tested and the small number of animals included in the assay (only four animals per group) lead to consider this finding as not valid for the Risk Assessment procedure.

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.

Two other studies were performed on CD1 mice given municipal tap water (Durham, North Carolina) and compared with mice given the same but purified tap water (disinfectant was removed via organic removal cartridge, demineralizer and still). No indication about the dose of chlorine or HClO in tap water was provided:

- In a study by Chernoff et al. (1979) several groups of mice (unspecified number per group) were bred, successively over a period of 8 consecutive months, observed until gestational day 18 for body weight gain, and then sacrificed for pregnancy data and litter examination (external, visceral and skeletal examination). Finally, 236 pregnant female mice (in tap water group) and 257 (in control purified water group) were examined. There were no significant water-related effects on maternal data (% pregnant females, body weight gain and % implants) or any foetal parameter (% live/dead foetuses, body weight, external, visceral or skeletal anomalies).
- In a study by Staples (1979), a similar protocol was used for a 11 months period. An overall amount of 247 (tap water) and 217 (control) pregnant females were involved. No significant differences were noted between the 2 groups in the reproductive status and in the foetal parameters including malformations.

Developmental effects

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 fetuses 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 sternbrae 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 fetuses 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 foetus as the unit for the statistical analysis. The choice of the foetus 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, see below).

Table 4.24: Summary: Animal Reproduction studies with sodium hypochlorite

AUTHOR	YEAR	TYPE	RESULT	NOTES	VAL.
Toxicity to reproduction					
Carlton	1986	gavage, rat 1 generation	no effects obs.	TS: Aq chlorine, well conducted study NOAEL determined	2
Druckrey	1968	drinking water, rats, 2 yrs, 7 generations	no effects obs.	German paper, only limited data available	3
Meier	1985	sperm head assay, mutagenicity mice	doubtful positive	data well presented	2
Developmental toxicity developmental					

effects					
Abdel-Rahman	1982	drinking water development effects, rat foetus	minor effects at 100 mg/l	study well conducted	2
Chernoff	1979	tap water foetal devel. mice	no evidence	limited available data	3
Kavlock	1979	concentrated organic material from tap water, foetal devel. mice	no evidence	limited available data not relevant	3
Staples	1979	tap water, foetal devel. mice	no evidence	limited available data	3
Abdel-Rahman	1984	3H-thymidine incorporation in tests	equivocal result	limited protocol and data	4

4.1.2.8.2 Human data

Several exploratory epidemiological studies assessing possible adverse developmental outcomes associated with chlorinated water are available. However, the results of these studies should be cautiously interpreted because of limitations of study design and likely bias.

Aschengrau *et al.*, 1993, conducted a case-control study in Massachusetts to determine the possible relationship between community drinking water quality and adverse pregnancy outcomes. This study included infants from mothers delivering at Brigham and Women's Hospital between 1977 and 1980. There was no statistically significant increased risk of neonatal death or total congenital anomalies in women exposed to chlorinated drinking water. The stillbirth risk was no longer significantly increased after adjustment for appropriate confounding factors.

In a case-control study (Savitz *et al.*, 1995), assessment of miscarriage, pre-term delivery and low birth weight in central North Carolina did not show any association between these parameters and chlorinated drinking water.

A cross-sectional study (Kanitz *et al.*, 1996) was conducted in Italy comparing two groups of pregnant women/newborns during 1988-89. Assignment to a group (water source and type of disinfectant) was based on the mother's address. The treated group included 548 births at Galliera Hospital (Genoa) from mothers living in an area where drinking water was disinfected either by chlorine (108), chlorine dioxide (277) or both (163). Control group included 128 births at Chiavari Hospital from mothers living in Chiavari where well water was untreated.

Information was collected about mother's age, smoking and alcohol habits, education level and also about family income. Assessment of birth outcomes included birth weight (<2500 g or > 2500 g), pregnancy duration (< 37 weeks or > 37 weeks), body length (< 49.5 cm or > 49.5 cm), cranial circumference (< 35 cm or > 35 cm) and neonatal jaundice.

Statistically significant increased risks of smaller cranial circumference and smaller body length were associated with drinking water disinfected with chlorine. The adjusted odd ratios and 95 % confidence intervals were: 2.3 (1.3 - 4.2) for body length and 3.5 (2.1 - 8.5) for cranial circumference respectively.

The results of this study should be interpreted very cautiously (as rightly pointed out by the authors themselves), because of lack of information about real exposure, and likely bias in assessment of pregnancy outcomes. No information was collected to assess the mothers' tap water consumption (or bottled water consumption). Exposures to surface and ground water sources are being compared, and no information is presented about other possible water quality differences. There is also concern about whether the population may be different in respects other than the water system differences studied. Concerning pregnancy outcomes, parity was astonishingly not taken into account by the authors. Moreover, body length and cranial circumference measurements are subject to possible differences between hospitals. It is noteworthy that only two hospitals were involved in that study, one for the control group (Chiavari hospital) and the other one for the treated groups (Galliera hospital in Genoa). So, the reported differences in body length and cranial circumference might be due to differences in measurement methodology between hospitals, irrespective to the exposure.

Swan, S.H. *et al.* (1992) presented an overview of 5 retrospective studies, reported in the same issue of "Epidemiology", in which the risk of spontaneous abortion was examined in relation to the source and amount of drinking water consumed during the early pregnancy (period 1982-1987). At first, in December 1981, a drinking water well in Santa Clara County, California, was found to be contaminated by organic solvents. Although two epidemiology studies conducted by the California Department of Health Services found associations between location of residence and spontaneous abortion, uncertainties about the exposure characterisation precluded any firm inferences. A subsequent study, including a hydrogeologic model of the water distribution system, showed clearly that the solvent leak was not causally related to the observed cluster of spontaneous abortions. Unexpectedly, women who reported drinking tap water appeared at extra risk of spontaneous abortion, regardless of location residence. Consequently, the California Dept of Health Services included questions on prenatal water consumption in all reproductive studies conducted between 1982 and 1988 (about 5000 cases). Results from four of the five studies suggest that women drinking tap (or mostly tap) water compared with those drinking no tap water were at extra risk of spontaneous abortion. However, even with the large body of available data, it was not possible to decide whether the apparent differences in risk of spontaneous abortion can be accounted for by artifacts of the study design (especially reporting bias).

Next, a prospective study was conducted to extend the previous investigation in Santa Clara County to three different water systems (about 1600 cases per region), to later time period, as well as to eliminate recall bias by a prospective design. Regions I (mixed ground and surface water) and II (surface water) are in northern California, the region III (ground water) is in southern California. Region I is located within the Santa Clara County previously studied (see above). The results of the prospective study, reported by Swan, S.H., *et al.* 1998 showed that neither tap or bottled water

consumption altered the risk of spontaneous abortion in regions II and III. However, the study confirmed the association between cold tap water consumption (but only for high consumption) and risk of spontaneous abortion previously seen in region I. Adjusted odds ratios comparing high (≥ 6 glasses /day) consumption of cold tap water with none was 2.17 (with a 95% confidence interval of 1.22 - 3.87). The adjusted odd ratio for 0.5 to 5.5 glasses cold tap water per day was 1.10 (95% confidence interval 0.76-1.59). Taking into account total tap water consumption (cold and heated tap water), a very marginal increase of risk (if any) was observed for a high tap water consumption. The adjusted odds ratios were respectively: 1.66 (95% confidence interval 0.99-2.78) for ≥ 6 glasses and 1.03 (95% confidence interval 0.7-1.52) for consumption of 0.5 to 5.5 glasses per day.

These findings, indicating an apparent decrease in risk of spontaneous abortion when tap water is heated, could evoke a possible link with volatile by-products. This hypothesis was studied (by Waller, K. *et al.* 1998) taking into account the estimated total trihalomethanes (THMs) levels in tap water in the three regions considered in the prospective study cited above. The additional analysis of the data indicates a slight increase of risk of spontaneous abortions for a high consumption of cold tap water (≥ 5 glasses per day) containing ≥ 75 $\mu\text{g/l}$ of total THMs (adjusted odd ratio = 2.0; 95% confidence limit 1.1-3.6). However, as pointed out by the authors themselves, (Swan *et al.* 1998 ; Waller, K. *et al.* 1998), it is noteworthy that :

- a THMs level > 75 $\mu\text{g/l}$ is not uncommon. The maximum contaminant level permissible for THMs is 100 $\mu\text{g/l}$ according to Federal Law. The mean THMs in Region I in the high tap water consumption group was 93 $\mu\text{g/l}$ (range 78-105 $\mu\text{g/l}$). For Region II, where women drinking tap water were not at extra risk for spontaneous abortion (see above, Swan, S.H. *et al.* 1998) the mean THMs level of 92 $\mu\text{g/l}$ (range 75-123 $\mu\text{g/l}$) was comparable to that of Region I.
- the practice of letting water stand before drinking it, which allows chlorination by-products to volatilise, should decrease the risk. On the contrary, the association in Region I appeared stronger in heavily exposed women who followed that practice (although numbers were small).

For the above reasons, Swan *et al.* believed that the association between spontaneous abortion and extensive cold tap water drinking recorded only in Region I cannot be explained by chlorination by-products.

A similar interpretation of the data was done by Williams, A. and Weiss, N.S. 1998, who concluded "since exposure to high levels of THMs in drinking water was more common in Region II than Region I, THMs would seem to be exonerated as a basis for the association in Region I."

4.1.2.8.3 Conclusion

There are no relevant studies of sodium hypochlorite *per se* looking at its reproductive toxicity potential in animals. However, relevant studies have been conducted using chlorine as the test substance, administered in solution by gavage or in drinking water.

In a teratogenicity study, in which exposure was confined to the gestation period, no significant differences in the incidence of skeletal or soft tissue abnormalities were observed in treated groups when compared to controls. A small, but statistically significant increase in sperm head abnormalities was seen in mice, although the effect was not dose-dependant. However, no effects were seen in a well conducted one-generation reproductive toxicity study in rats up to a concentration of 5 mg/kg bw of aqueous chlorine (expressed as HOCl - maximum dose tested) (Carlton, 1986). Even if the value is expressed as HOCl, it is equivalent to available chlorine since the measure method used detects all the chlorine species in water. Therefore, the value of **5 mg/kg bw** available chlorine is used in the risk characterisation as NOEL for reproductive toxicity. Long-term toxicity studies provide also additional assurance that the substance is not a reproductive toxicant as they did not identify the testes or ovaries as target organs.

The Carlton study appears relatively more updated and reliable with a number of animals more suitable for statistical analysis.

There are no studies performed at dose levels able to induce systemic toxicity.

A pragmatic approach is to accept the NOEL derived from the Carlton study because it is the best study available even if no severe effects are shown in all dosed groups.

Although limited data are available in animals, the available studies are sufficient in their design and quality to draw the conclusion that there is no evidence to suggest that sodium hypochlorite would present adverse effects on development or fertility. Similarly, no such evidence is forthcoming from epidemiological studies on populations consuming chlorinated drinking water.

4.1.3 Risk characterisation

4.1.3.1. General aspects

Human effects may occur mostly through dermal exposure to solutions of variable concentrations from 0.00001% (general public, drinking water) to 15-24% of available chlorine (occupational, production) leading to local effects on the skin due to corrosive/irritant effects of sodium hypochlorite solutions (classified as corrosive >10% and as irritant >5%). Consequently, appropriate personal protective equipment should be used as needed when exposure to such concentrations is possible. Due account should also be taken of the possibility of splashes of liquid coming into contact with eyes, again leading to the possibility of corrosive/irritant effects in the eyes. Generally, exposure to solutions above 10% occurs under occupational circumstances only.

Dermal exposure to solutions of sodium hypochlorite might also lead to dermal absorption. There are no data to indicate the degree of absorption of hypochlorite ions.

However, the potential of hypochlorite solutions to penetrate the skin is low given its reactivity to proteinaceous material. The absorption has therefore been assessed by assuming a default fraction of 10% that is penetrating the skin. This is considered to be a conservative assumption based on the indicated low potential for dermal penetration. Such absorption leads to the potential for systemic effects to occur, either from an acute exposure or from repeated exposures. The potential risks are characterised by comparing the resulting body burden with either the oral LD₀ in the rat of 626 mg/kg BW for acute effects and the NOAEL for the rat of 13.75 mg/kg BW/day for repeated-dose effects, the NOEL for the rat of 5 mg/kg bw/ day for reproductive toxicity. All values are expressed as available chlorine.

The possibility of local effects due to repeated dermal exposure to diluted hypochlorite solutions is taken into account. From the few dermal repeated dose animal studies available, a NOEL of 1% is chosen. From the information available, it is not possible to calculate a NOEL as a dose in mg/kg bw/day. Therefore, the approach chosen is to compare the concentration of sodium hypochlorite solutions to which consumers and workers can be repeatedly exposed in the different scenarios with the NOEL of 1%.

Inhalation exposure is only possible in case of formation of sodium hypochlorite aerosols, which could lead to local irritation effects of the respiratory tract. No repeated dose inhalation studies are available on sodium hypochlorite aerosol, either in animals or humans. It might be possible to use data that is available on chlorine gas as a surrogate, although it is recognised that this data will be derived following exposure to the gas and not to an aerosol. The use of data on chlorine gas is likely to be a conservative assessment of the potential effects of sodium hypochlorite aerosol.

Exposure to chlorine related to sodium hypochlorite is only likely to occur under accidental circumstances in case of contact of sodium hypochlorite solutions with acids. The primary effect of such exposures would be respiratory tract irritation. Workers can be exposed to chlorine in air only from chlorine production (since hypochlorite production is integrated in a Chlor-alkali plant). However, exposure to trichloramine (NCl₃), as insoluble, highly volatile, known irritant, will occur when there is a combination high chlorination of treated water with a high nitrogen content (i.e. swimming pool scenario).

Oral exposure is mainly thought to occur during drinking water use. Concentrations or total quantities absorbed are very low.

In the swimming pool scenario, a combined dermal and oral exposure is calculated.

Concerning disinfection by-products, some exposure data have been presented for some scenarios (swimming pool and drinking water). However, the available information is not sufficient to characterize the risk. Therefore, the effects on human health of disinfection by-products are not covered in this Risk Assessment, which only deals with sodium hypochlorite.

4.1.3.2 Systemic effects. Toxicity values used for risk characterisation

The LD₀/NOEL derived from the oral reliable studies expressed in mg/kg bw/day **as available chlorine** will be used for risk characterisation for all the exposure routes.

Acute toxicity

The Kaestner (1981) oral study is considered the key study for this end-point. Indeed it is based on rat and compared to the other studies it provides an exactly defined value.

For risk characterisation purposes a oral LD₀ value of 626 mg/kg BW of sodium hypochlorite expressed as av. Cl₂ is derived from the above mentioned oral study (see paragraph 4.1.2.2)

The minimal MOS for **workers** is derived taking into account the following Assessment Factors:

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

Hence the calculated minimal MOS is 50 (4 x 2.5 x 5)

The minimal MOS for **consumers** is derived taking into account the following Assessment Factors:

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

Hence the calculated minimal MOS is 100 (4 x 2.5 x 10)

Irritation/Corrosivity

The overall evaluation of both animal and human data supports the current EU classification as irritant above 5% and as corrosive above 10%.

Sensitization

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

Repeated dose toxicity

Also for RDT, reliable studies are available for the oral route only. For risk characterisation purposes the key study used for this end-point is the NTP study (1992) from which the lowest NOEL can be calculated. From this study the NOEL of 13.75 mg/kg of sodium hypochlorite expressed as av. Cl₂ is derived (see paragraph 4.1.2.5).

The minimal MOS for **workers** is derived taking into account the following Assessment Factors:

1. a factor of 4 allometric scaling factor for rats.
2. a factor of 2.5 for remaining interspecies differences

3. a factor of 5 for human intraspecies variation

Hence the calculated minimal MOS is 50 ($4 \times 2.5 \times 5$)

The minimal MOS for **consumers** is derived taking into account the following Assessment Factors:

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

Hence the calculated minimal MOS is 100 ($1.5 \times 4 \times 2.5 \times 10$)

For repeated dermal exposure, a concentration of 0.1% hypochlorite is chosen as a NOEL to evaluate local dermal effects. No additional safety margin seems to be required when comparing exposure to the NOEL:

- Local dermal effects, irritation, is the critical endpoint, which does not require a high margin of safety.
- Uncertainty and intra- and interspecies variation: Irritation levels have also been evaluated in humans. Assuming that 5% is the LOEL at which some irritation can be observed, there is an adequate margin of safety between LOEL and NOEL. No additional safety margin is needed.
- Although the animal test data is not optimal in design nor conducted to GLP, the confidence in the database is increased by the fact that sodium hypochlorite solutions have been in use for many years with relevant human exposure, without indication of problems.
- Chronic systemic effects through dermal exposure are not expected. No systemic effects have been observed in any of the oral dose studies reported.

For repeated inhalation exposure to hypochlorite aerosols, no specific studies are available. A conservative approach is to use data that is available on chlorine gas, which indicate a NOEL of 0.5 ppm of chlorine.

Mutagenicity

The available data are not conclusive with respect to genotoxicity. Although, since sodium hypochlorite has shown lack of carcinogenicity effects (see paragraph 4.1.2.7), no additional testing is required.

Carcinogenicity

Long term carcinogenicity studies with sodium hypochlorite administered in the drinking water didn't show a carcinogenic effect.

The human epidemiological data are not sufficient to suggest a causal relationship between the use of chlorinated drinking water and increased cancer risk.

The International Agency of Research on Cancer (IARC) 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. Based

on this assumption and the low exposure levels, there is currently no concern for the general population consuming treated drinking water.

Reprotoxicity

Only limited data is available on reproductive effects; however, there is no evidence to suggest that sodium hypochlorite would cause any adverse reproductive effects in humans, especially at current exposure levels.

The Carlton et al. study (1986) was used to derive a NOEL of 5.0 mg/kg/day of sodium hypochlorite expressed as av. Cl₂ for reprotoxicity.

The minimal MOS for **workers** is derived taking into account the following Assessment Factors:

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

Hence the calculated minimal MOS is 50 (4 x 2.5 x 5)

The minimal MOS for **consumers** is derived taking into account the following Assessment Factors:

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

Hence the calculated minimal MOS is 100 (4 x 2.5 x 5)

Table 4.25 Summary of effects

Substance name	Inhalation (N(L)OAEL)	Dermal (N(L)OAEL)	Oral (N(L)OAEL) mg/kg/day (as av. Cl ₂)
Acute toxicity			626 (LD ₀)
Irritation / corrositivity			
Sensitization			
Repeated dose toxicity (local)	0.5 ppm (NOEL for chlorine gas)	0.1% as sodium hypochlorite	
Repeated dose toxicity (systemic)			13.75
Mutagenicity			
Carcinogenicity			
Fertility impairment			
Developmental toxicity			5.0

4.1.3.3 Workers

The calculation of MOSs and the conclusions are presented in table 4.26 for acute toxicity, 4.27 for repeated dose toxicity and 4.28 for reproductive toxicity.

Dermal exposure

- **Production of hypochlorite and Production of other chemicals scenarios:** production processes are closed and tasks that could entail an exposure to hypochlorite (i.e. maintenance or sampling) are performed following strict safety procedures and wearing the appropriate personal protective equipment. It can be assumed that PPE are always used in these scenarios, since the hypochlorite solutions used are corrosive. Therefore dermal exposure is possible only in case of an accident.
- **Drinking water, Cooling water and Sewage treatment** scenarios: closed automatic systems are used; personal protective equipment is recommended to handle the corrosive concentrated solutions. EASE model is used to estimate dermal exposure when diluted solutions (<5%) are used and PPE are not worn.
- **Swimming pool** scenario: workers handling hypochlorite solutions shall wear appropriate personal protective equipment and follow strict safety procedures; high MOS was calculated for swimming pool instructors/competition swimmers (combined dermal+oral exposures).
EASE model is used to estimate dermal exposure when diluted solutions (<5%) are used and PPE are not worn. The lowest calculated MOS for this scenario is that of 877 derived for reproductive toxicity.
- **Institutional and Food industry (I&I) scenarios.** EASE model is used to estimate dermal exposure when diluted solutions (<5%) are used and PPE are

not worn. The lowest calculated MOS for this scenario is that of 877 derived for reproductive toxicity for the I&I scenarios a2, b1 and b2.

- **Pulp and paper scenario:** sodium hypochlorite is no longer used for bleaching purposes in Western Europe. In some cases, it can be used for water disinfection or surface cleaning. These uses are considered under the general I&I scenario.
- **Textile industry scenario:** closed automatic systems are used in the major plants; However in some minor plants where sodium hypochlorite is used as bleaching agent as well as for washing machinery, the transport of the substance from the reservoir tank to the machinery is not performed in a closed system; personal protective equipment is recommended to handle the corrosive concentrated solutions in all cases. EASE model is used to estimate dermal exposure when diluted solutions (<5%) are used and PPE are not worn. The lowest calculated MOS for this scenario is that of 5.9E+04 derived for reproductive toxicity.

Conclusion (ii) for all scenarios and all endpoints

Inhalation exposure

- **Production** of hypochlorite and Production of other chemicals: the production processes are normally integrated in Chlor-Alkali plants. Occupational exposure by inhalation to chlorine only could occur. Measured levels of chlorine in Chloro-Alkali plants are available and in most cases lower than the occupational exposure limit for chlorine (1.5 mg/m³ for 8 hours TWA, 0.5 ppm for the proposed STEL). In specific cases in which measured concentrations can be higher than the limit (i.e. during maintenance), adequate PPE are worn and strict safety procedure are applied.
- **Institutional and Food industry (I&I):** The exposure to hypochlorite from trigger spray use is small. An exposure study evaluating airborne aerosol exposure during the “open plant spraying” scenario demonstrated that the process is unlikely to result in significant hypochlorite exposure. Therefore it can be concluded that inhalation exposure to hypochlorite in I&I is likely to be very small and well below occupational exposure limits set for other similar respiratory irritants. The lowest calculated MOS for this scenario is that of 7.72E+04 derived for reproductive toxicity for the I&I scenario a2.

Conclusion (ii)

Irritation of skin, eye and respiratory tract:

- **Production:** As the skin, eye and respiratory tract exposure to sodium hypochlorite for workers during the production is negligible, the risk of irritant effects is considered very low.

- **Institutional and Food industry (I&I):** Similar to the consumer scenario (see 4.1.3.4 below), some mild irritation effects to skin and eye could be expected. However, personal protection is already recommended for most I&I scenarios, so the risk of irritation effects is considered to be very small.

Conclusion (ii)

Table 4.26 Occupational risk assessment for acute toxicity

Minimal MOS = 50	Inhalation				Dermal				Combined (Dermal+oral)			
	Exposure (mg/kg/day) as Cl ₂ eq.	LD0 (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	LD0 (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	LD0 (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion
Production and Production of other chemicals												
No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3.												
Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided												
Formulation												
Swimming pools operators handling 5% solutions					0.0057	626	1.1E+05	ii				
I&I (a2, b1 and b2)					0.0057	626	1.1E+05	ii				
I&I (d1, d2, e1 and e2)					0.0038	626	1.6E+05	ii				
Uses												
Swimming pools instructors/comp. swim.									0.0049	626	1.3E+05	ii
Textile Bleaching					0.000085	626	7.4E+06	ii				
STP, DW and CW					0.0057	626	1.1E+05	ii				

Table 4.27 Occupational risk assessment for repeated dose toxicity

Minimal MOS = 50	Inhalation				Dermal				Combined			
	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion
Production and Production of other chemicals												
No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3.												
Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided												
Formulation												
Swimming pool operators handling starting solutions (5%)					0.0057	13.75	2.4E+03	ii				
I&I a2, b1, b2					0.0057	13.75	2.4E+03	ii				
I&I d1, d2, e1, e2					0.004	13.75	3.4E+03	ii				
Uses												
Swimming pools instructors/comp. swim.									0.0205	13.75	670	ii
Textile Bleaching					0.000085	13.75	1.6E+05	ii				
STP, DW and CW					0.0057	13.75	2.4E+03	ii				
I&I (b1,b2)					0.010	13.75	1310	ii				
I&I (d1+d2)					0.010	13.75	1310	ii				
I&I (a2)	6.48E-05	13.75	2.12E+05	ii								
I&I (b3)	5.7E-07	13.75	2.41E+07	ii								

Table 4.28 Occupational risk assessment for reproductive toxicity

Minimal MOS = 50	Inhalation				Dermal				Combined			
	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion
Production and Production of other chemicals												
No sodium hypochlorite inhalation is expected during production operations see par. 4.1.1.3.												
Potential dermal exposure is not calculated for production because only corrosive solutions are used and the use of PPE is mandatory. Information on the efficacy of PPE is provided												
Formulation												
Swimming pool operators handling starting solutions (5%)					0.0057	5	877	ii				
I&I a2, b1, b2					0.0057	5	877	ii				
I&I d1, d2, e1, e2					0.004	5	1250	ii				
Uses												
Swimming pools instructors/comp. swim.									0.0205	5	244	ii
Textile Bleaching					0.000085	5	5.9E+04	ii				
STP, DW and CW					0.0057	5	877	ii				
I&I (b1,b2)					0.0105	5	476	ii				
I&I (d1+d2)					0.0105	5	476	ii				
I&I (a2)	6.48E-05	5	7.72E+04	ii								
I&I (b3)	5.7E-07	5	8.77E+06	ii								

4.1.3.4 Consumers

The calculation of MOSs and the conclusions are presented in table 4.29 for acute toxicity, 4.30 for repeated dose toxicity and 4.31 for reproductive toxicity.

Dermal exposure

Dermal/Ocular exposure of the general public is found under **Household, Swimming Pool** and **Drinking water** scenarios. In all cases diluted solutions are used from 0.00001% (drinking water) to 0.5% (household). A long historical experience of the use of hypochlorite in household products showed that no dermal risk is expected. However, some sensitive persons may develop irritant dermatitis which can be prevented by the wearing of gloves. MOS values of 1.8E+04 for acute toxicity, of 393 for chronic toxicity and of 143 for reproductive toxicity were calculated for **household** scenarios involving dermal exposure. For swimming pool swimmers combined dermal and oral exposure has been considered and the lowest MOS is that of 2083 derived for 1 year old childrens for reproductive toxicity.

Conclusion (ii) for all end points and all scenarios

Oral exposure:

Drinking water scenario:

The lowest MOS value derived for this scenario is that of 1.5E+03 for reproductive toxicity in 10 years old childrens. Oral exposure is also possible in connection with accidental ingestion. However current labelling is adequate (S1/2).

Conclusion (ii) for all end points

Inhalation exposure

Household scenario: The lowest MOS calculated for household bleach sprays is that of 1.7E+06 for reproductive toxicity. Accidental mixing with acids could generate chlorine gas. However current labelling is adequate (R31, S50).

Conclusion (ii)

Irritation of the skin, eye and respiratory tract

Skin and Eye

Consumer products containing > 5% hypochlorite may cause irritant effects to skin and eye, and concentrations of > 10% may lead to corrosive effects.

The overall evaluation of data on animal and human skin for concentrations < 5% which are typically marketed for consumer use leads to the conclusion that only mild irritating effects are caused at < 5% hypochlorite.

The evaluation of all available data on eye irritation including human exposure leads to the conclusion that in the event of an accidental exposure to concentrations of < 5% hypochlorite, the risk for pronounced irritant effects is low.

Respiratory tract

Aerosols generated from a 10% solution of sodium hypochlorite have been shown to cause respiratory irritation in mice. These aerosols had a much smaller particle size than domestic aerosol products (approximately 3.3 µm compared to an average of >75 µm). They also contained higher concentrations of available chlorine than would be expected in a domestic product that is formulated with sodium hypochlorite at concentrations no greater than 3.0%. It is anticipated that exposure to domestic aerosols formulated with sodium hypochlorite solutions of less than 3.0% would not present a significant respiratory irritation hazard.

Overall the evaluation of both animal and human data supports the current EU classification.

Conclusion

(ii)

Table 4.29 Consumer risk assessment for Acute toxicity

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

¹ Inhalation

² Oral

Table 4.30 Consumer risk assessment for Repeated dose toxicity

Minimal MOS = 100	Inhalation ¹ /Oral ²				Dermal				Combined (Dermal+oral)			
	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion	Exposure (mg/kg/day) as Cl ₂ eq.	NOAEL (mg/kg/day) as Cl ₂ eq.	MOS	Conclusion
Uses												
Household	0.000003 ¹	13.75 ¹	4.6E+06	ii	0.035	13.75	393	ii				
Swimming									0.0021	13.75	6.5E+03	ii

pool swimmers	Childrens 1 y								0.00235	13.75	5.7E+03	ii
	Childrens 10 y								0.0016	13.75	9.0E+03	ii
Drinking water	Adults	0.003 ²	13.75 ²	4.6E+03	ii							
	Childrens 10 y	0.0033	13.75	4.2E+03	ii							

¹ Inhalation

² Oral

Table 4.31 Consumer risk assessment for Reproductive toxicity

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

¹ Inhalation

² Oral

4.1.3.5. Man exposed via the environment

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

Conclusion (ii)

4.1.3.6. Combined exposure

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

4.1.3.7 Risk Characterization for local effects

4.1.3.7.1 Inhalation

For local irritation effects, no study is available to determine a NOAEL for hypochlorite. As a surrogate, a respiratory inhalation study conducted for chlorine gas is used (Klonne et al, 1987, see also section 4.1.2.5.3). NOAEL in that study is 0.5 ppm chlorine, or 1.5 mg/m³ chlorine.

Consumers:

$$\rightarrow \text{MOS} = 1.5 / 0.00168 \text{ mg} / \text{m}^3 = 892$$

I&I scenario b.3):

$$\rightarrow \text{MOS} = 1.5 / 0.00168 \text{ mg} / \text{m}^3 = 892$$

The obtained values for the MOS in both scenario could still be considered conservative based on the assumptions used:

- not all particles measured in the volume considered the breathing zone might enter the nose, mouth and respiratory system.
- the irritancy of a 3% hypochlorite aerosol is considered equal to that of chlorine gas, while it is estimated to be lower based on the general irritation profile of hypochlorite solutions.

An additional safeguard exists against the possibility of respiratory irritation among consumers. Industry designs household trigger sprayers such as to emit large droplets of product to avoid eliciting any kind of transient 'coughing' response. Experience gained during the long history of marketing trigger sprays, including those based on hypochlorite, shows that a transient 'coughing' reflex response can be induced in some consumers during use if substantial numbers of small particles are emitted that can remain airborne long enough to be breathed in. Consumer use experience, especially with products containing more potent irritants than hypochlorite, shows that the cough reflex is a very sensitive response that consumers will begin to experience and complain about at much lower exposure levels than would be required to produce respiratory irritation.

Formulations and trigger design are now chosen to limit the number of small particles to ensure a cough reflex response is not triggered. Before marketing a new product formulation or packaging for this type of spray product, which is outside the boundaries of experience, a

clinical safety test would typically be conducted to directly confirm no adverse respiratory responses under normal use conditions compared to the previous product. The use of current hypochlorite trigger sprays does not give rise to complaints about cough induction.

This approach provides a more relevant and direct approach to safety assurance than, for example, attempting to define a universal LOEL for humans. This would be difficult to define as people have different thresholds based on status of health. The LOEL/NOEL would also be dependent on the formulation and the interacting effects of the other ingredients contained in a formulation as well as the product viscosity, such that different hypochlorite-based products would have different LOELs.

4.1.3.7.2 Dermal

The critical endpoint for repeated dermal exposure to sodium hypochlorite is irritation. The NOEL for this effect depends on the concentration of the solution.

For the evaluation of the risk of local dermal effects, the NOAEL of 0.1% (as sodium hypochlorite) derived in section 4.1.2.5.3 is of limited use. While this is the only value that can be proposed based on the available studies, these studies generally expose test animals in ways that are very different to the way humans are exposed. For example, the studies using 0.1% concentrations (Cotter et al., 1985; Robinson et al., 1986) expose subjects continuously for many hours per day over a period of many days whereas cleaning tasks involve at most intermittent exposure for a period of minutes followed by washing. That this NOAEL is very conservative as regards human effects is reinforced by the study of Habets et al.(1986), who found that the application of 1% and 0.5% sodium hypochlorite to human skin for long periods of time evokes no signs of irritation in sensitive individuals (Habets et al., 1986, 69 patients with suspected allergic contact dermatitis).

Repeated exposure is only likely to involve dilute solutions of sodium hypochlorite. When handling concentrated solutions, PPEs are generally used and closed systems are available. In such cases, exposure to concentrated solutions will only be accidental and is unlikely to occur repeatedly. The tables below compare concentrations to which users are exposed and derive MOS figures against the above NOAEL. Since this NOAEL is very conservative, the assessment for use scenarios where a possible risk from repeated dermal exposure is indicated is then refined by further consideration.

Workers

Table 4.32 shows the results of the Risk Characterisation for workers repeated dermal exposure to sodium hypochlorite. For concentrations above the irritation limit (5%) it can be assumed that PPE are always used.

Table 4.32 Workers risk assessment for repeated dermal exposure

Scenarios	Repeated Dermal exposure			
	Exposure to neat solution (% as available chlorine)	Exposure to in-use solution (% as available chlorine)	MOS	Conclusion
Minimal MOS = 1 NOAEL = 0.1%				

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

(1) The cleaning operation is a wet exercise and operators are dressed up with watertight clothing, boots and facial masks (see chapter 4.1.1.3.6.1)

For swimming pool scenario (lifeguards and swimming instructors): the maximum allowable concentration of sodium hypochlorite (as available chlorine) in European swimming pools is 5 mg/l as available chlorine (Denmark). This can be considered equivalent to a concentration of 0.0005%. The I&I exposure scenarios are detailed in chapter 4.1.1.3.6.

Exposure to neat solution is not of concern for all scenarios: even if PPE are not used, the exposure can only be accidental and not repeated.

Consumers

Table 4.33 shows the the results of the Risk Characterisation for consumer repeated dermal exposure to sodium hypochlorite.

The lack of an MOS against the very conservative NOAEL for consumers using concentrations of product above 0.1% in household cleaning needs further consideration. Exposure to neat product or concentrated solutions (>0.5%) will only occur accidentally and is thus not relevant for repeated dose exposure. Use of hypochlorite solutions 0.1% < <=0.5% in a way that would generate exposure for several minutes is uncommon. Even though such exposure is considered as a worst case as regards acute dermal toxicity, products normally recommend dilution below 0.1% for such uses. Rinsing after exposure is recommended. The end-point being considered here is irritation, which will be self-evident to the user. Hypochlorite solutions are very widely used for cleaning tasks, and have been for several decades, yet product manufacturers have experienced no comments or complaints that would lead them to believe such irritation is being experienced. This suggests either that the derived NOAEL of 0.1% is indeed too low as an indicator of concentrations that might lead to irritation through repeated exposure or that the frequency, duration and conditions of

exposure to such solutions experienced by consumers, is below that which might produce such effects.

In the absence of evidence to suggest such self-evident effects are occurring to a significant extent, the conservative NOAEL alone provides insufficient basis to declare a conclusion iii, and a conclusion ii is felt appropriate.

Table 4.33 Consumer risk assessment for repeated dermal exposure

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

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

Conclusion

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

Conclusion (ii)

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

4.2.1. Exposure assessment

4.2.1.1. Occupational exposure

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

4.2.1.2. Consumer exposure

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

4.2.1.3. Indirect exposure via the environment

No such exposure is thought to occur.

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

4.2.2.1. Explosivity

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

4.2.2.2. Flammability

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

4.2.2.3. Oxidizing potential

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

4.2.3. Risk Characterisation

4.2.3.1 Workers

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

Conclusion (ii)

4.2.3.2 Consumers

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

Conclusion (ii)

4.2.3.3. Man exposed indirectly via the environment

No risk is identified due to no potential exposure.

Conclusion (ii)

5 RESULTS

5.1 INTRODUCTION

5.2 ENVIRONMENT

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

5.3 HUMAN HEALTH

5.3.1 Human health (toxicity)

5.3.1.1 Workers

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

Conclusion (ii) applies to all scenarios.

5.3.1.2 Consumers

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

Conclusion (ii) applies to all scenarios.

5.3.1.3 Humans exposed via the environment

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

Conclusion (ii) applies to all scenarios.

5.3.1.4 Combined exposure

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

Conclusion (ii) applies to all scenarios.

5.3.2 Human health (risks from physico-chemical properties)

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

Conclusion (ii) applies to all scenarios.

Glossary of terms

ABBREVIATIONS

AOX	Adsorbable Organic Halogens
BAT	Best Available Technique
CAC	Combined Available Chlorine
CIP	Cleaning in place
COD	Chemical Oxygen Demand
CPO	Chlorine Produced Oxidants
DOC	Dissolved Organic Carbon
ECF	Elemental Chlorine Free
GLP	Good Laboratory Practice
FAC	Free Available Chlorine
FO	Free Oxidant
FRC	FAC measured after a reaction
HRIPT	Human Repeated Insult Patch Test
I&I	Institutional and Food industry
MAC	Maximum Allowable Concentration
MAK	Maximal Arbeitsplatz Konzentration
OBP	Organohalogen By-Products
OEL	Occupational exposure limit
TAC	Total Available Chlorine
TCF	Total Chlorine Free
TGD	Technical Guidance Document
THM	Trihalomethanes
TLV	Threshold limit value
TRC	Total Residual Chlorine
TRO	Total Residual Oxidant

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The report provides the comprehensive risk assessment of the substance Sodium hypochlorite. 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.

Appendix 1

Mercury hypochlorite-related emissions

Mercury emissions

In the chlorine-caustic soda production plants using the mercury-cell technology, the sodium ion is discharged on the cathode as metal forming an amalgam; afterwards the amalgam is added to water, thus leading to caustic soda, hydrogen production and metallic mercury, which is then recycled.

The sodium hydroxide solution contains traces of mercury suspended. The hypochlorite is produced adding chlorine and maintaining the sodium hydroxide solution in excess (5 to 10 g/kg), so that the disproportion speed of hypochlorite will be reduced obtaining a stabilising effect.

The filtration is a system used to remove mercury from sodium hydroxide solutions; the final product will contain more or less mercury depending on the accuracy of this process.

The manufacture of chlorine and caustic soda using mercury cell technology is associated with some mercury emissions in air, water and products. Over the years, a significant reduction of these emissions has been realised by improved treatment technologies. The mercury contained in waste disposal can be discounted from the environmental point of view since virtually all of it is either recovered or it is disposed of to high-integrity sealed landfill sites from which it cannot escape. Thus, the total unconfined emissions to all parts of the environment were 26.6g Hg/t Cl₂ in 1977, and have decreased considerably to 2.5g Hg/t Cl₂ in 1994 and 1.25 g Hg/t Cl₂ in 2000.

There are no measured data for mercury emissions related specifically to hypochlorite production as it is included in the chlorine production figures.

Table 1. Hypochlorite production – mercury balance (g Hg/t Cl₂ capacity)

	1977	1994	2000
Mercury emission in products	5.5	0.4	0.09
Mercury emission in aqueous effluents	9.4	0.2	0.08
Mercury emission in waste gases			
Process exhaust gases	4.9	0.6	0.08
Cell-room ventilation air	6.8	1.3	1.00
Total mercury emissions	26.6	2.5	1.25
Mercury contained in waste disposal	21.7	11.4	15.58
Mercury consumption unaccounted for	46.4	2.6	2.63
Total Mercury consumption	94.7	16.6	16.60

The data presented above are the Euro Chlor Mercury Balance for 1977 versus 1994 and 2000 for manufacturing sites in the European Community. The figures are expressed as grams of mercury per tonne of chlorine capacity, weighted averages. The approximated number of manufacturing sites involved was 70.

Natural mercury cycles involve about 150,000 t per year on a world scale; in comparison, 10,000 t per year are emitted by metal processing and fuel burning, and 7,000 t of mercury are mined every year.

In the context of OSPARCOM (Oslo and Paris Convention for the Protection of the North-East Atlantic), the recommendation has been made to reduce by 1996 the atmospheric Hg emissions for each site to below 2 g/t chlorine capacity.

The PARCOM Decision 90/3 of 14 June 1990 on reducing atmospheric emissions from existing chloro-alkali plants states in its point 3 that:

“Contracting Parties to the Paris Convention for the Prevention of Marine Pollution from Land-Base Sources.....*recommend that existing mercury cell chloro-alkali plants be phased out as soon as practicable. The objective is that they should be phased-out completely by 2010*”.

Three Member States (Austria, Greece and Italy) with mercury cell capacity are not committed to the PARCOM Decision. Also, the wording of PARCOM Decision 90/3 part 3 could result in some Member States that are Contracting Parties to the Paris Convention allowing the operation of mercury cells after 2010 on the basis that it is not practicable to phase them out by the date signalled as the objective.

In March 1998 the the Italian chemical industry (EniChem S.p.A.) in agreement with Italian Government decided to substitute in Marghera plant, in the Venezia lagoon, the mercury cell technology with a membrane cells technology having same capacity.

Under the UN/ECE Convention on Long-Range Transboundary Air Pollution (LRTAP) a Protocol on Heavy Metals (HMs) is being developed, the aim of which is to reduce atmospheric emissions. There will be Best Available Technology (BAT) and/or emission limit values for mercury emissions from chlor-alkali installations, which will also affect Eastern Europe, where emissions are sometimes higher than in the EU.

It has been estimated that the EU chlor-alkali industry has invested 800 million EUR since 1970s and revised procedures in order to improve the performance of mercury cell plants, and over this period closed or replaced 1.94 million tonnes of mercury cell chlorine capacity, leaving 6.0 million tonnes mercury cell chlorine capacity in 2000. Some further investment would be required in order to achieve a reduction in reported emissions, for an economically driven scenario.

The levels and the average mercury in hypochlorite present solutions from 42 plants in EU are reported to be in the range of 0.004 to 0.707 mg/kg with a mean value of 0.105 mg/kg (Euro Chlor personal communication 2001 – mercury levels in hypochlorite solutions from producers) .

IPPC BREF recommendations mentioned caustic soda supplied from mercury cells should contain a maximum concentration of mercury of about 0.05 g Hg per tonne chlorine produced.

Emission scenarios

Swimming pools

In swimming pools, mercury in sodium hypochlorite is not retained by filters; purge in sewers can release mercury which will then adsorbed to activated sludge used in the depuration system of waste urban waters.

Antifouling use

The oil rigs offshore use sodium hypochlorite as antifouling agent for fire pumps; the 130 Italian oil rigs in the Adriatic sea employ 440-660 kg of active chlorine/year for each oil rig. As the hypochlorite employed is derived from chloroisocyanurate there is not immission of mercury or chlorates in the sea.

Institutional use

An Italian regional Authority prescribed that the mercury concentration in sodium hypochlorite bought for hospital uses must not exceeded 5×10^{-3} mg/l. **Editorial note: I heard this is no longer true!**

The Italian Government has established to limit the presence of toxic substances in drinking waters due to the potabilization treatment or to the formation of such substances in the waterworks. The limit is 1/50 of the MAC allowed for each toxic substance in the Italian and European legislation (Directive 98/83/CE). Considering the high mercury levels found in the commercial products, the Waterworks Association indicated some difficulties in the potabilization treatment related to the quantity of sodium hypochlorite needed.

The European Normation Committee is producing technical data sheets for chemicals used for treatment of water intended for human consumption: the limit of mercury in sodium hypochlorite is: 3.5 and 5 mg/kg of available chlorine for Type 1 hypochlorite and Type 2 hypochlorite respectively. Hence, to respect the limit of 1/50 of the MAC (0.02×10^{-3} mg/l) not more than 5.5 or 4 ppm of active chlorine should be applied for Type 1 and Type 2, respectively.

Household scenario

When sodium hypochlorite is used in the home, the final rejects go into the waste water network. Impurities and by-products of hypo will be part of the waste water.

Estimate content of mercury in waste water and final sludge

We know today the different contents of total mercury in the sodium hypochlorite used by the consumer. When it comes from an electrolysis process using no mercury the maximum content is **5 µg/kg**; when the mercury cathode process is used the average content is **100 µg/kg (or approximately 120 µg/l)**. These figures are known for 150 gCl₂/kg industrial concentrated product having a density of about 1.2.

Regulation about mercury content in sludge

Depending on the countries and keeping in mind the eventual evolution of the regulations, we know the maximum possible content of total mercury in this sludge.

The French norm NF U 44041 used in 1988, proposed for the European Regulation (directive 86/278/EEC) establish the following values:

- limit content in the soil 1 mgHg/ kg dry matter
- reference value in the sludge 10 mgHg/kg dry matter
- limit value in the sludge 20 mgHg/kg dry matter

To obtain these sludge the most widely used technique in urban waste water treatment works is the digestion of sludge by activated fluid bed process. Some towns are making anaerobic digestion. The highest efficiency of these two processes is over 50% of digestion by transformation of organic solids (volatile solids) in methane and CO₂.

Farmers and the food industry have proposed a diminution of the figures concerning the content of heavy metals and especially mercury in these applied sludge.

The new EU proposed figures are **5 mgHg/kg dm for 2015** or **2 for 2025**.

The geological content of total mercury in the soils is between 0.08 and 0.3 mg/kg dm. The objective for the soil content (NF U 44041) of 1mg/kg is not really far from the geological ranges.

Appendix 2

**Kinetic Model on the Long Term Hypochlorite Decay
in the Environment**

A Specific Model for Use in the HOCl Risk Assessment

Vincent Vandepitte and Diederik Schowanek

INTRODUCTION

Questions about the environmental effects of residual oxidants resulting from domestic or industrial use of hypochlorite has prompted efforts to model the decay of hypochlorite in the environment. There have been several efforts to model the kinetics of chlorine decay in estuarine and sea water near power plants (Lietzke 1975; Abarnou and Miossec, 1991;). However, the availability of reports dealing with the decay of HOCl (Free Available Chlorine (FAC)) and RH_2Cl (Combined Available Chlorine (CAC)) in river water is much less (Heinemann et al., 1975). There is hardly any data available on the disappearance of HOCl in sewage and activated sludge (Haas and Karra, 1984). In general, described models to simulate TRO (total residual oxidant (= CAC+FAC)) in the environment are empirical i.e. they are mathematical descriptions which are not related to the mechanisms driving the TRO decay (Heinemann et al., 1975; Qualls and Johnson, 1983; Haas and Karra, 1984; Yamamoto et al., 1988). The here proposed model is at the contrary chemical reactions based and tries to model the real chemical processes involved in the environmental decay of TRO. The advantage of models based on chemical reactions is that these apply at any concentration.

OBJECTIVE

The general objective of this study was to develop 1) a simple but relatively accurate kinetic model that could predict the consumption of HOCl in the sewer, the activated sludge unit and the river and 2) to predict the concentration TRO below analytical detection limits (i.e. ± 10 ppb in environmental samples).

MATERIAL AND METHODS

Model setup

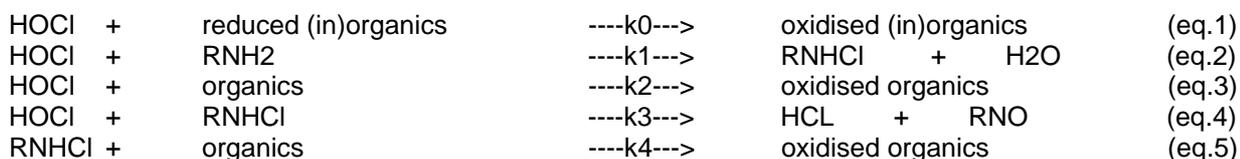
HOCl decay in the environment occurs in 4 "environmental compartments": 1) during use, 2) during sewer transport, 3) during sewage treatment, and 4) in surface water (characterised by a dilution phase). Every environmental compartment is characterised by the presence of specific reaction partners and a specific reaction time. Overall, HOCl decay can be described by the following chemical reactions (eq 1-5). This is a purely chemical process, no biodegradation occurs.

Simplification

For simplification and especially to avoid over-parameterisation of the model it was assumed that 1) the pH was 7 and that 2) The reaction products of HOCl with NH_3 were limited to NH_2Cl or its organic form as these will be the predominant species in the environment.

Conservatism

Some other additional simplification assumptions were chosen in the interest of the conservatism of the model. They are 1) No decay of HOCl during the use phase; 2) No volatilisation of FAC/CAC and 3) No decay of FAC/CAC due to light. The results of the model is therefore only a conservative approximation and will generally give an overestimation of the TRO in the environment.



These chemical equations can be translated to the following mass balance kinetic equations (eq.6-10) (equations are summarised and simplified from: Lawler, 1984; Birch and Fletcher, 1980; Hostgaard-Jensen et al., 1977; Lietzke, 1975 and Schowanek et al., 1996).

$$\frac{d[HOCl]}{dt} = -k_0 \cdot [HOCl] \cdot [red.inorganics] - k_1 \cdot [HOCl] \cdot [RNH_2] - k_3 \cdot [HOCl] \cdot [RNHCl] - k_2 \cdot [HOCl] \cdot [organics] \quad (\text{eq.6})$$

$$\frac{d[RNHCl]}{dt} = k_1 \cdot [HOCl] \cdot [RNH_2] - k_3 \cdot [HOCl] \cdot [RNHCl] - k_4 \cdot [RNHCl] \cdot [organics] \quad (\text{eq.7})$$

$$\frac{d[RNH_2]}{dt} = k_1 \cdot [HOCl] \cdot [RNH_2] \quad (\text{eq.8})$$

$$\frac{d[organic]}{dt} = -k_4 \cdot [RNHCl] \cdot [organic] - k_2 \cdot [HOCl] \cdot [organic] \quad (\text{eq.9})$$

$$\frac{d[red.inorganics]}{dt} = -k_0 \cdot [HOCl] \cdot [red.inorganics] \quad (\text{eq.10})$$

An analytical solution for this type of multiple order competition reactions is not existing. Therefore, the differential equations 6-10 were numerically solved by a variable-step 5th order Runge-Kutta routine. The mathematical problem was programmed in the ISIM (interactive simulator) program.

RESULTS AND DISCUSSION

A) Model evaluation/validation:

The appropriateness of the model for estimating the decay of HOCl was evaluated by simulating the available experimental HOCl decay data of Birch and Fletcher (1980) for activated sludge and of Yamamoto et al., 1985 for river water. Results are shown in Figure 1A and 1B respectively. The given initial environmental parameters are shown in Table 1.

Table 1: Given initial environmental parameters

PARAMETER	ACTIVATED SLUDGE (AS)	RIVER
NaOCl conc. (mg/l)	6	11
Ammonium conc. (mg/l)	1	0.1
Chloramine (mg/l)	calculated (model)	calculated (model)
Reduced compounds (mg/l S ²⁻)	0	0
Organic material (mg/l) (suspended solids)	3000	19

The kinetic parameters (Table 2) were estimated by visual fitting of the simulation curves to the experimental datapoints:

Table 2: Estimated kinetic parameters (units: l/mol.s)

PARAMETER	ACTIVATED SLUDGE (AS)	RIVER
k ₀	not involved (no reduced compounds present)	not involved (no reduced compounds present)
k ₁	100	12
k ₂	10	1
k ₃	1.5	0.025
k ₄	0.07	0.01

For comparison, literature data with respect to the general reaction kinetics of the considered data are: k₀ = 25, k₁ = 12, k₂ = 1, k₃ = 2, k₄ = 0.1 (units: l/mol.s) (These reaction constants are the

slowest values summarised from: Lawler, 1984; Birch and Fletcher, 1980; Hostgaard-Jensen et al., 1977; Lietzke, 1975 and Schowanek et al., 1996). These parameters are in the same order of magnitude as the estimated ones.

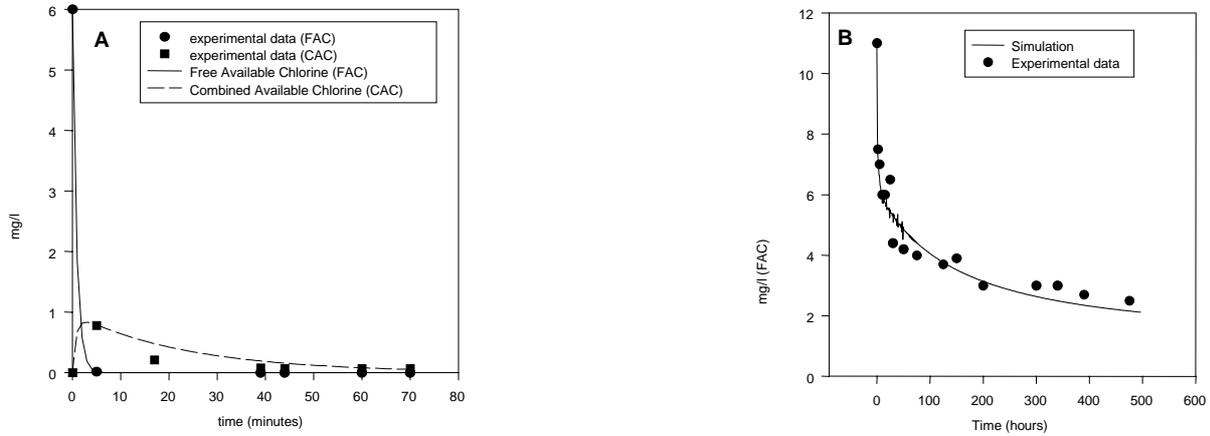


Figure 1: Experimental and simulated decay of FAC and CAC in activated sludge (A) and in fresh river water (B)

It becomes clear from Figure 1 that the model predicts quite well the decay of HOCl (FAC) and RH_2Cl (CAC) in river water and sludge. An even better fit is expected by mathematically fitting the differential equations to the data by minimizing the sum of squares of errors. A more precise parameter estimation requires additional software and was out of the scope of this work since it would be more of theoretical interest.

B) Simulation of the FAC/CAC decay in the "environmental compartments" for purpose of risk assessment

The model was used to estimate the level of FAC and CAC after transport in the environment incl. sewer, activated sludge processing and river water transport. A worst case scenario was adopted, and all HOCl was considered to arrive in the sewer, i.e. assuming no decay during application. As all estimated reaction constants appeared to be similar within an order of magnitude (cfr. supra) we assumed the following reaction constants $k_0 = 25$, $k_1 = 12$, $k_2 = 1$, $k_3 = 2$, $k_4 = 0.1$ (units: l/mol.s) throughout the three exposure scenarios; sewer, activated sludge and river water. The decay trough the 3 environmental compartments sewer, activated sludge and river, was simulated using the following initial parameters (Table 3):

Table 3: Assumed initial environmental parameters

	SEWER	ACTIVATED SLUDGE (AS)	RIVER
Ammonium conc. (mg/l)	36	1	0.1
FAC mg/l	7.5 (<u>max. value</u> as estimated from HOCl consumption data)	calculated (model)	calculated (model)
Chloramine (mg/l)	0	calculated (model)	calculated (model)
Reduced compounds (mg/l S^{2-})	0.00015	0	0
Organic material (mg/l)	300	3000	50
Dilution factor in the river			10
Residence time	1 h (3600 sec)	8 h (28800 sec)	10 min (600 sec)

Simulations show a quick elimination of $\text{NaOCl}/\text{ClO}^-$ (expressed as FAC) (Fig. 2 a) during transport in the sewer. The abundance of reduced reaction partners allows a fast initial FAC elimination

reaction. The FAC concentration estimated at the end of the sewer drops below 1.10^{-32} $\mu\text{g/l}$. The drop in FAC is in parallel with a sharp increase of the chloramine concentration, which can be explained by the high availability of ammonia in the sewer and the rapid reaction of NaOCl with NH_3 (within minutes). Chloramine further reacts as an oxidant during further transport in the sewer (Fig. 2 a), the activated sludge unit (Fig. 2. b) and in the river (Fig. 2 c). The extensive degradation of chloramine in the activated sludge unit can be explained by the presence of organic material acting as reductant. Chloramine is estimated to fall below 5.10^{-10} $\mu\text{g/l}$ in the river.

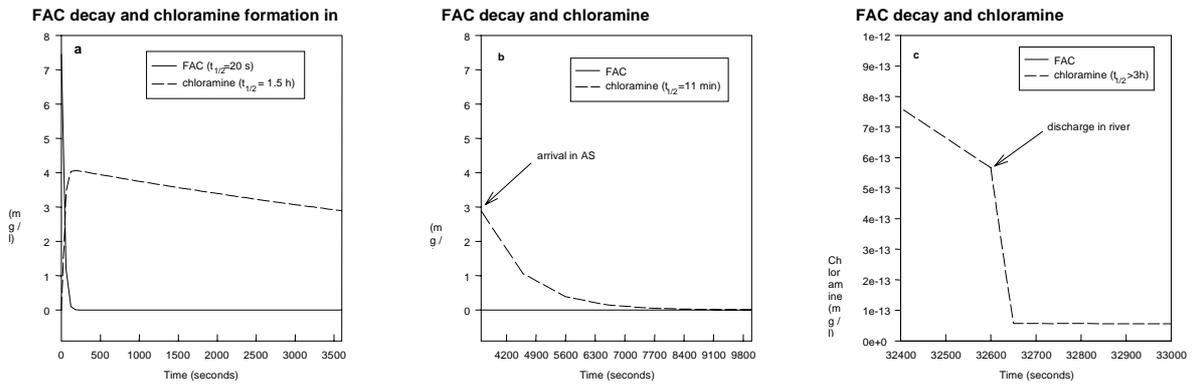


Figure 2: Simulation of the decay of FAC and formation/decay of chloramine during transport in the environment.

It has to be clear that due to the assumptions made during the setup of the model (i.e. 1: No decay of HOCl during the use phase; 2) No volatilisation of FAC/CAC and 3) No decay of FAC/CAC due to light). The model is expected to predict an overestimated environmental HOCl concentration i.e actual data may be lower.

C) Sensitivity analysis of the model

Variation of the HOCl influent concentration:

The above specified parameters were used to simulate the effect of the initial NaOCl concentration on the estimated environmental concentration. In a first set of simulations the NaOCl in the influent was varied between 7.5 mg NaOCl/l to 75 mg NaOCl/l. Results on the NaOCl decay during the first 300 sec i.e. in the sewer are represented in Figure 3a. The decay of the NaOCl is dependent on the concentration with a faster decay rate at higher NaOCl concentrations. In all cases the NaOCl concentration dropped below 4.10^{-27} (virtually nil) $\mu\text{g NaOCl / l}$ when extrapolating the data to the river and taking into account the above specified assumptions. The evolution of chloramines at different NaOCl concentrations is represented in Figure 3b. The decay is most important in the activated sludge unit and drops to 1.10^{-10} $\mu\text{g/l}$ in the river even at a NaOCl dosage in the sewer of 75 mg/l.

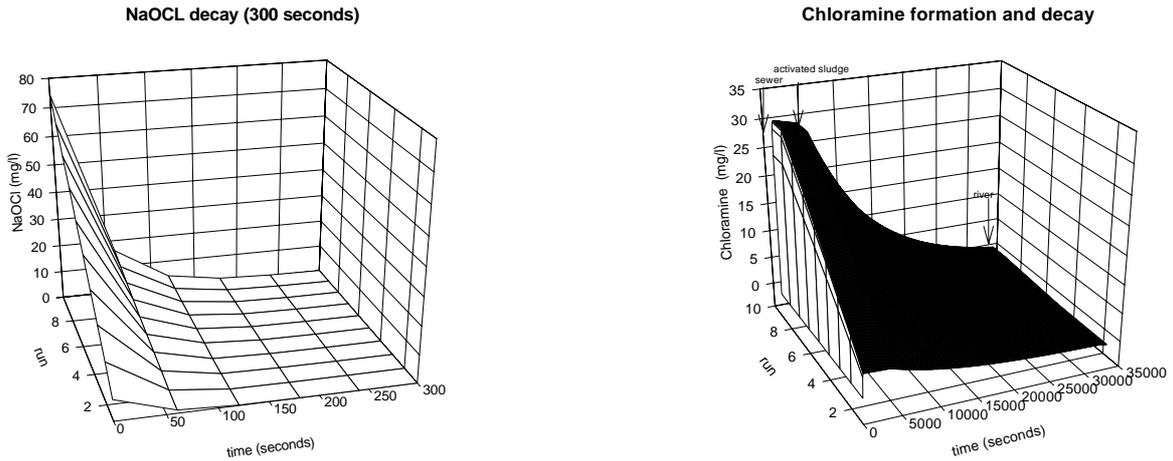


Figure 3: NaOCl and chloramine decay in function of the initial NaOCl concentration (7.5, 15, 22.5, 30, 37.5, 45, 52.5, 60, 67.5 and 75 mg/l; run 1 to run 10).

Variation of the reaction kinetics:

The effect of decreasing the reaction kinetics by a factor 10 was assessed to evaluate sensitivity of the model for changes in reaction rate. The dosed NaOCl concentration was set at 7.5 mg/l. In all cases the NaOCl concentration in the river drops below 4.10^{-27} $\mu\text{g/l}$ when extrapolating the data to the river. The chloramine evolution for different reaction constants is given in Figure 4. According to the simulation, the chloramine concentration in the river varies from $< 1.10^{-10}$ $\mu\text{g/l}$ (run 1) to 15 $\mu\text{g/l}$ (run 10) in an unrealistic worst case scenario i.e. all reaction constants 10 times slower (Figure 4).

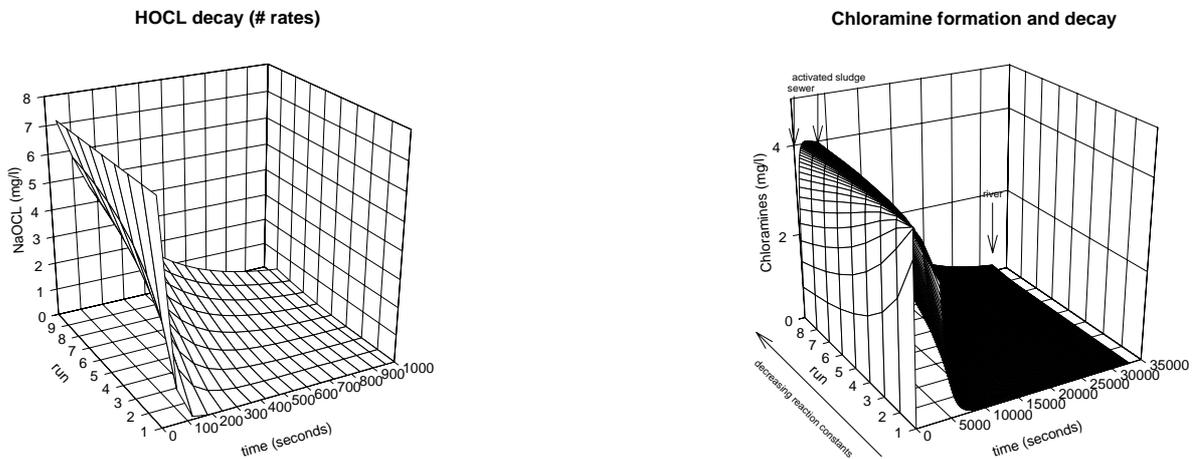


Figure 4: NaOCl decay (initial 7.5 mg/l) in function of decreasing reaction constants (run 10 is 10 times slower compared to run 1)

CONCLUSIONS

It was shown that the presented model describes quite well the decay of FAC and CAC in the different "environmental compartments" activated sludge and river water. By using the same reaction mechanisms and kinetics, an attempt was made to estimate the FAC/CAC decay in sewage. In a reasonable case for the environment, the FAC concentration estimated at the end of the sewer drops to 0 $\mu\text{g/l}$. Chloramine is estimated to fall below 5.10^{-10} (virtually nil) $\mu\text{g/l}$ in the river. These data have to be compared with the PNEC values in the risk assessment.

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SUMMARY OF ECOTOXICOLOGY STUDY RESULTS WITH SODIUM HYPOCHLORITE IN SEA WATER

Algae

Species	System	Comments T°/pH	Duration	Anal. meas.	Parameter	Results (mg/l)	Val	Hedset	Reference
Short term studies									
<i>Dunaliella primolecta</i>	S	20°C	24 h	(+)/TRO	50% mortality	0.4	3	(+)	Videau et al. (1978.79)
<i>Pavlova lutheri</i>	S	20°C	24 h	(+)/TRO	50% mortality	4	3	(+)	Videau et al. (1978.79)
<i>Phaeodactylum tricornutum</i>	S	20°C	24 h	(+)/TRO	100% mortality	0.8	3	(+)	Videau et al. (1978.79)
<i>Skeletonema costatum</i>	S	20°C/	24h	(+) (a)	LC50	0.095	3	(-)	Gentile et al. (1976)
<i>Rhodomonas baltica</i>	S	20°C/	24h	(+) (a)	LC50	0.11	3	(-)	Gentile (1976)
<i>Dunaliella tertiolecta</i>	S	20°C/	24h	(+) (a)	LC50	0.11	3	(-)	Gentile (1976)
<i>Monochrysis lutheri</i>	S	20°C/	24h	(+) (a)	LC50	0.200	3	(-)	Gentile (1976)
<i>Thalassiosira pseudonana</i>	S	20°C/	24h	(+) (a)	LC50	0.075	3	(-)	Gentile (1976)
<i>Thalassiosira pseudonana</i>	S		20 min		60% effect at 48h	0,2	3	(-)	Gentile (1976)
<i>Chaetoceros decipiens</i>	S	10°C/	24h	(+) (a)	LC50	0.140	3	(-)	Gentile (1976)
<i>Thalassiora nordensholdii</i>	S	10°C/	24h	(+) (a)	LC50	0.195	3	(-)	Gentile (1976)
<i>Thalassiosira rotula</i>	S	10°C/	24h	(+) (a)	LC50	0.330	3	(-)	Gentile (1976)
<i>Asterionella japonica</i>	S	10°C/	24h	(+) (a)	LC50	0.250	3	(-)	Gentile (1976)
<i>Chaetoceros didyum</i>	S	10°C/	24h	(+) (a)	LC50	0.125	3	(-)	Gentile (1976)
<i>Detonula confervacea</i>	S	10°C/	24h	(+) (a)	LC50	0.200	3	(-)	Gentile (1976)
Phytoplankton	FT	9-18°C//8.4	12h	(+)/TRO	Primary productivity(EC98	1.2	3	(-)	Carpenter (1972)
Phytoplankton	SS	7-19.7°C//8.4	3x1.5h	(+)/TRO	Primary productivity(EC86	1.2	3	(-)	Carpenter (1972)
General review							3	(+)	White (1972)
General review					Any parameter		4	(-)	Mattice (1976)

SUMMARY OF ECOTOXICOLOGY STUDY RESULTS WITH SODIUM HYPOCHLORITE IN SEA WATER

Algae

Species	System	Comments T°/pH	Duration	Anal. meas.	Parameter	Results (mg/l)	Val	Hedset	Reference
Long-term studies									
Phytoplankton (microcosm)	FT, DA	6-8°C/7.7-7.9	21 d	(+TRC (b))	50% cell density reduction	0.001-0.01	s	(+)	Sanders et al. (1981)
<i>General review</i>					Any parameter		4	(-)	Mattice (1976)
Phyto- and Zoo-plankton									
Microcosm study	FT	10.1- 30.8 °C/	1 y	(+TRC	13-58% ATP reduction	< 0.01	s	(-)	Ericksson and Foulk (1980)

Validity

1 = valid without restriction

S = Static

TRO = total residual oxidant

2 = valid with restriction

SS = Semi static

TRC = total residual chlorine

3 = invalid

FT = flow-through

Cl₂ = available chlorine

4 = not assignable

DA = daily chemical addition

(a) only the stock solution (100 mg/l)+A22 was measured

(b) free chlorine as HOCL was administered

SUMMARY OF ECOTOXICOLOGY STUDY RESULTS WITH SODIUM HYPOCHLORITE IN FRESHWATER

Microorganisms										
corretto										
Species	System	Hardness	Comments T°//pH	Duration	Anal. meas.	Parameter	Results (mg/l)	Val	Hedset	Reference
Microcosm	FT	n.r.	19.4°C// 8.08	7 d	(+) TRC	ba species richn	0,0027	2	(+)	Cairns et al (1990)
Microcosm	FT	n.r.	19.4°C// 8.08	7 d	(+) TRC	a species richn	0,006	2	(+)	Cairns et al (1990)
Microcosm	FT	n.r.	19.4°C// 8.08	7 d	(+) TRC	f Protozoa taxa/	0,006	2	(+)	Cairns et al (1990)
Microcosm	FT	60	9.6-17°C//7.7	28 d	(+)TRC	TP Biomass/NO	0.100	2	(-)	Pratt et al (1988)
Microcosm	FT	60	9.6-17°C//7.7	28 d	(+)TRC	rotein level/NO	0.025	2	(-)	Pratt et al (1988)
Microcosm	FT	60	9.6-17°C//7.7	28 d	(+)TRC	Potassium/NOE	0,1	2	(-)	Pratt et al (1988)
Microcosm	FT	60	9.6-17°C//7.7	28 d	(+)TRC	phosphatase/N	0.0021	2	(-)	Pratt et al (1988)
Microcosm	FT	60	9.6-17°C//7.7	28 d	(+)TRC	otozoa species/	0.0021	2	(-)	Pratt et al (1988)
Mesocosm (fie	SS	197	22.5°C//8.0	24 d	(+)TRC	rotein level/NO	0.079	2	(-)	Pratt et al (1988)
Mesocosm (fie	SS	197	22.5°C//8.0	24 d	(+)TRC	phosphatase/N	> 0.261	2	(-)	Pratt et al (1988)
Mesocosm (fie	SS	197	22.5°C//8.0	24 d	(+)TRC	cies number/NO	0,079	2	(-)	Pratt et al (1988)
Mesocosm (fie	SS	197	22.5°C//8.0	24 d	(+)TRC	ankton density/	0.0015	2	(-)	Pratt et al (1988)

Validity

1 = valid without restriction
 2 = valid with restriction
 3 = invalid
 4 = not assignable
 S=supportive information

S = Static
 SS = Semi static
 FT = flow-through
 TRO = total residual oxidant
 TRC = total residual chlorine
 Cl2 = available chlorine

Appendix 4

Active/Available chlorine and hypochlorite

ACTIVE/AVAILABLE CHLORINE AND HYPOCHLORITE

Two terms are used for defining the concentration of bleach in the lay-man literature and the market:

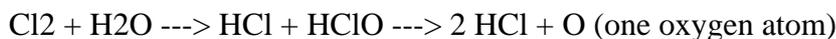
- Active chlorine is by definition the amount of pure (100%) chlorine, in aqueous solution, which has the same oxidizing power (= the same amount of available oxygen) as a unit quantity of that substance. In other words, that means that the oxidizing properties of a substance are compared with chlorine itself and expressed as such. In practice this corresponds to $\text{Cl}_2 + \text{HOCl}$. However, it is often used for available chlorine which is the sum of $\text{Cl}_2 + \text{HOCl} + \text{ClO}^-$. Both active and available chlorine are expressed as equivalent content of Cl_2 (molecular weight: 71g).
- Sodium hypochlorite is the word used to give the concentration of bleach in North America. The molecular weight of NaOCl is 74.5 g.

Since the 2 molecular weights of Cl_2 and NaOCl are slightly different, the way of expressing the concentration is only slightly different.

In fact for those chemicals, the difference is small; the active chlorine equivalent content is:

- for chlorine Cl_2 : 100 % (by definition)
- for sodium hypochlorite NaOCl : 95 % (by calculation)

1- For pure chlorine in aqueous solution, the reactions are:



Mol. Weight of Cl_2 is 71

Cl_2 contains 100 % of active chlorine.

2- For sodium hypochlorite in aqueous solution the reaction is :



Mol Weight of NaOCl : 74.5

active chlorine content : $71 * 100 / 74.5 = 95 \%$

As conclusion, we can say that in the case of sodium hypochlorite, due to small difference in figures expressed in active chlorine or in weight of substance (i.e. % act. Cl_2 = % weight), there is no consequence for the labelling related to the concentration limits defined in Annex I .

DEFINITION OF “ACTIVE CHLORINE”

"The active chlorine content of a chlorinated substance (in g/kg) is the amount of pure (100%) chlorine (in g) that has the same oxidizing power than one kg of the substance.

Example: 1 kg of a sodium hypochlorite solution containing 12.5% of active chlorine (125 g/kg) has the same oxidizing power than 125 g of pure chlorine.

The oxidizing power of a substance characterizes the number of electrons exchanged during reaction of this substance.

While transforming in chloride ions (Cl^-), 1 molecule of the following substances exchanges.

- Chlorine (Cl_2) : 2 electrons

- Hypochlorite ion (ClO^-) or hypochlorous acid (HClO) : 2 electrons

-> 1 mole of pure NaClO (74.5 g) has the same oxidizing power than 1 mole of Chlorine (71 g)

Example: The active chlorine content of a sodium hypochlorite solution containing 15 % (150 g/kg) of NaClO is : $150 * 71 / 74.5 = 143 \text{ g act. Cl}_2 / \text{kg}$

What is measured in environmental media like surface fresh water is generally expressed as free available chlorine (FAC) or total residual chlorine (TRC) which encompass free and combined chlorine (like chloramines). In saltwater what is measured is generally called total residual oxidant (TRO) including free chlorine and bromine or chlorine produced oxidant (CPO) which encompass free and combined chlorine and bromine species.

Appendix 5 – Former use of hypochlorite for paper pulp bleaching

Generalities of the pulping process

The pulping process in the paper manufacturing started with the treatment of wood chips in a 'white liquor' solution of sodium sulfide and sodium hydroxide at high temperature (160-180 °C) to cleave lignin ether bonds and to dissolve 90%-95% of the lignin. The “black liquor” produced in this process was refined into tall oil and was either used as an energy source by incineration or was disposed of. The evaporate was trapped in a condenser and was converted to a sulfur wastewater stream referred to as evaporate condensate. This pulping process was continued until the pulp contained 5% to 10% lignin.

Bleaching was done to remove the colour due to the remaining lignin from the pulp. In the bleaching process, the pulp was made into a 3% slurry and treated with a bleaching agent, usually chlorine, hypochlorite or chlorine dioxide. This was followed by filtration and alkali treatment. After each treatment, the pulp was filtered and the process liquids were combined as bleach effluent. The pulping process was done to release cellulose fibers from the wood, for the production of paper and other materials.

Chlorine, hypochlorite and chlorine dioxide bleaching chemistry

Elemental chlorine (Cl_2), in addition to acting as an oxidizing agent, acted as a chlorinating agent. In the first stage of bleaching, about half the elemental chlorine applied to pulp combined with the lignin and the remainder oxidized the lignin and was converted to chloride ion (Kempf and Dence, 1970; Hardell and de Sousa, 1977). Following alkaline extraction, about 90% of the original elemental chlorine applied to pulp had been converted to chloride ion, the rest remaining as solubilized chlorinated organic material.

The relative concentration of Cl_2 , HOCl and OCl^- is sensitive to pH and careful control of the pH was required to reduce the formation of Chlorinated organic by-products. Hypochlorous acid and elemental chlorine react differently with the chemical structures present in lignin (McKague and Reeve, 1995): hypochlorous acid reacts with double bonds to produce chlorohydrins, while elemental chlorine reacts with double bonds to produce dichlorinated products. Chlorine was eliminated from chlorohydrins during subsequent alkaline extraction more readily than from dichlorinated products.

If chlorine dioxide is used as bleaching agent, hypochlorous acid is generated as a secondary product by reduction of chlorine dioxide as the lignin is oxidized. Therefore, the lignin that is available to react with hypochlorous acid is more highly oxidized and contains fewer aromatic structures than lignin which reacts with elemental chlorine or hypochlorite as the primary oxidant (McKague and Reeve, 1994). As a result, more of the hypochlorous acid is consumed by reaction with non-aromatic structures and thus less chlorinated aromatic material is formed.

From the above consideration it appears that the amount of chlorinated organic produced as by-product of the bleaching process may be ranked in the following order:



The ClO_2 bleaching is the safest among the chlorine based processes. The process based on the use of ClO_2 instead of Cl_2 has been called Elemental Chlorine Free (ECF); due to its better environmental performance.

Chlorinated compounds in the pulp process effluents

In order to quantify the amount of chlorinated compounds produced by the pulp bleaching, it is important to recall that nearly 10% of the elemental chlorine applied during bleaching remained as solubilised chlorinated organic material. Studies (Solomon et. al, 1993) reported a 5-10 fold decrease in the production of chlorinated organics if ClO_2 was utilized instead of Cl_2 . It may be assumed that the production of chlorinated organics in the hypochlorite bleaching process was almost the half the quantity produced in the elemental chlorine process. The chlorinated organic material deriving from the pulp bleaching process was generally a complex mixture of different compounds, ranging from degradable to persistent and from relatively non toxic to more toxic. The chlorinated organic material in the effluent was generally measured as AOX (Adsorbable Organic Halogens). The Adsorbable Organic Halogen (AOX) method determines the quantity of chlorine in a sample which is retained on activated carbon. It is viewed as determining the total quantity of organically bound chlorine.

The presence of several chlorinated compounds was reported in the pulp mill effluent. In table [Number] the compounds identified in the effluent from the chlorine bleaching process are reported.

Environmental fate and distribution of chemicals produced during bleaching

Several studies deal with the fate and distribution of by-products of the chlorine based bleaching process, like dioxins and furans. (Muir *et al.*, 1992; Buser *et al.*, 1989) and chlorophenolic substances (Allard *et al.* (1988); Carey *et al.* (1993); Neilsen *et al.* (1991); Passivirta *et al.* (1985)).

For persistent hydrophobic substances such as the dioxins, environmental degradation is very slow and, in some cases, half lives can be measured in years. These compounds strongly adsorb to sediment and soil, which may continue to slowly release them in the environment long after the pollution source has been removed.

For highly substituted chlorophenols, biodegradation and biotransformation are key processes and it appears that these substances have half-lives from days to months. They do bioconcentrate but to a lesser extent than the dioxins, presumably because of their lower K_{ow} values and greater susceptibility to metabolism and/or excretion.

High and low molecular mass AOX, which comprised the bulk of the chlorinated organic by-products discharged, are hydrophilic. The dominant transport process for these compounds appeared to be simple advective transport and attachment to solid surfaces. Several reports are available on plant performance and on laboratory-scale

systems with removal efficiencies being determined for AOX, chlorophenols, chloroform, and hydrophobic compounds such as the dioxins, as well as toxicity reduction (Wilson *et al.*, 1992). Hydrophobic organics partition strongly to biomass and were removed by sedimentation with possible subsequent mineralization by aerobic or anaerobic processes. The unmineralized portion may have been retained in sludges and their ultimate fate was determined by sludge management practices. Chlorophenols were substantially biodegraded in aerated lagoons, and typical removals in activated sludge ranged from 50% to 90% and 80% to 90% in anaerobic systems. There are differences between phenols, guaiacols, catechols and vanillins and with chlorine number (i.e., di-, tri-) with lower chlorine number compounds being more readily degraded.

Table Number Compounds detected in pulp mill final effluents (before and after treatment) and expected environmental behavior (AET 1998; Rantio 1995)

	<i>1. Low molecular weight (MW) compounds</i>	<i>2. Intermediate MW moderately polar chlorinated compounds⁽¹⁾</i>	<i>3. Intermediate MW non-polar, chlorinated compounds</i>
Examples	chlorate ion, chloroform, dichloromethane, carbon tetrachloride, 1,2-dichloroethane, dichloroacetonitrile	chlorophenols, chlorocatechols, chloroguaiacols, chlorosyringols. Chlorovanillins, chlorinated hydroxybutanoic acids, 2,3,4,4-tetrachloro-3-hydroxybutanoic acid, 3-methoxy-5-dichloromethylene-2(5H)-furanone	PCDDs/PCDFs ² , chlorinated resin acids, chlorinated dibenzothiophenes, chlorinated thiophenes chlorocymenes ³ , chlorocymenes ³ . Chloronaphthalenes, chlorophenanthrenes, 2,5-dichlorothiophene
Log K_{OW} range (at least for compounds in the class for which K_{OW} has been determined)	<<1-3	2 - 5	4 - 9
Aqueous solubility	Moderate to High	Moderate to High	Extremely Low
Primary environmental compartment where found under equilibrium conditions	Water column	dissolved and particulate organic matter, suspended and deposited sediment	Dissolved and particulate organic matter, suspended and deposited sediment
Principle Exposure Pathway	Water (dissolved)	Water and sediment	Sediment and particulates; food-chain mediated
Pathway of Entry into Organisms	Respiratory and other external epithelia	Respiratory and other external epithelia	Diet; directly from surrounding media
Amenable to Biomagnification ?	No	Limited	Yes
Expected Environmental Half Life (where known)	minutes to days	days to weeks	Years
Primary Mechanism of Removal from Aquatic Environment	Volatilization and Photolysis, Biodegradation, Chemical degradation	Biodegradation and Biotransformation	Burial in sediment

1. Molecular weight from ca. 100 to 1000 Daltons
2. 2,3,7,8-TCDD and 2,3,7,8-TCDF not present at concentrations exceeding analytical detection limits in most effluent samples from mills employing 100% ClO₂ substitution in 1995/96.
3. Substantially reduced following conversion from Cl₂ to ClO₂ bleaching (Rantio, 1995).

The overall hypochlorite consumption reported by Euro Chlor in 1994 was 8.53 kt/year as available chlorine. On the basis of this figure, if 1995 production data still applied, it may be estimated that $8.53 \text{ kt NaClO} / (36000 \text{ kt pulp} \times (1 - 0.995)) = 0.046 \text{ t NaClO}$ were required for each ton of pulp treated. This approximate estimate is in agreement with data concerning the bleaching process (NaClO ratio in the range 2.5% - 5%).

On the basis of data concerning NaClO reactivity in the presence of organic compounds, as supported also by the model calculation reported in Appendix 2, it may however be expected that a negligible concentration of NaClO would be found at the process effluent a short time after discharge. **Thus, a null PEC for NaClO at the end of bleaching plant could be assumed.**

By-products formation is linked to the oxidation potential of hypochlorite and depends on the chemical species present. The main reaction product (99%) was the chloride ion (Jolley, 1975). Generally trihalomethanes (THM) were found with variable ranges.

Literature data shows that 5%-10% of the NaClO used in the bleaching process could form chlorinated by-products of the bleaching process; thus an AOX/pulp ratio in the range of 0.125% - 0.5% (1.25 – 5 kg per ton dry weight of pulp treated) would have been expected. U.S. EPA effluent concentration limits in term of kg AOX per ton dry wt of pulp treated for BAT technologies (conventional delignification followed by complete substitution like ClO₂ or TCF processes) are 0.448 as monthly average or 0.769 as maximum value. As recognised by U. S. EPA, hypochlorite bleaching did not allow these limits to be met.

On the basis of data reported from CEPI, the average pulp produced at one site per year was equal to 460 t/day which can be used to estimate a consumption of NaClO of approximately 23 t/day at one average pulp mill performing NaClO pulp bleaching. Assuming a 5% solution, a ratio NaClO/pulp of 5% corresponds to 50 kg of NaClO per tonne of pulp bleached. Considering an NaClO-AOX conversion of 10% (see Section 3.1.1.8) and that the chlorinated by-products were typically removed with about 50% efficiency, probably by settling and subsequent mineralization/degradation in the sludge (Wilson *et al.*, 1992) a PEC local for surface water could be determined as indicated in the calculation below.

PEC calculation:

In conventional pulp manufacturing as Cl₂ or NaClO is used, the AOX formation (and emission to effluent) has been ca. 2-5 kg/ton pulp. From these figures a daily AOX emission to waste water can be calculated to be 920-2300 kg/d for the average

production site. Taking an average characteristic emission 3.5 kg AOX/ton pulp a C_{local} is calculated.

$$AOX E_{localwater} = 460 \text{ t/d} * 3.5 \text{ kg/t} = 1610 \text{ kg /d}$$

The amount of water (= effluent load) needed to manufacture a tonne dry pulp is ca. 60 m^3 (Hynninen 1998). Based on $60 \text{ m}^3/\text{t}$ water consumption, a simplified calculation for $C_{localwater}$ is as follows:

$$C_{localinf} = E_{localwater} * 10^6 / \text{EFFLUENT}_{stp}$$

$$AOX C_{localinf} = 1610 \text{ kg} * 10^6 / (430 \text{ t} * 60000 \text{ l/t}) = 62 \text{ mg/l}$$

$$AOX C_{localeff} = C_{localinf} * F_{stpwater}$$

Considering a factor of 0.5 for removal in STP ($F_{stpwater}$) the $C_{localeff}$ value would be 31 mg/l

$$C_{localwater} = C_{localeff} / \text{DILUTION} = 3.1 \text{ mg/l} \text{ considering a dilution factor of 10.}$$

This latter AOX concentration value of 3.1 mg/l could be assumed to be equivalent to the average PEC_{local} considering the $PEC_{regional}$ in surface water level to be negligible.

PEC local surface water = 3.1 mg/l (AOX)

Appendix 6. Information on discharges from production sites and tentative PEC_{local} calculation

Introduction to questionnaire

In the context of preparing the risk assessment of chlorine in 1998 a questionnaire was sent to the Euro Chlor members requesting information from production sites *inter alia* about water influent and effluent data, including data on the characteristics of the receiving water. The questions were restricted to the discharge of active oxidants and COD. These data have been analysed to determine initial PEC_{local} values, if possible. For this analysis only sites were considered that are still in operation (situation end 2003). An up to date overview of the current chlorine production sites is presented in the Table below (Source: Euro Chlor, 2004). Based on this most recent list of 84 production sites the 1998 questionnaire provided information mostly for 1996 and some for 1997, covering 52 plants (62% of current total). 44 sites reported on the WWTP question, and WWTP's were present at 15 sites, while 4 plants reported not to have water emissions.

However, there are a number of issues and important caveats related to the interpretation of these data which need to be well understood to allow a meaningful evaluation.

- Not all information was completed for all plants, for example because not all requested data are measured on all sites.
- It is also important to note that the reported data are not directly comparable because they do not necessarily represent similar methodology, accuracy, detection limits, etc., It is difficult or impossible to measure active oxidants with reasonable accuracy in effluents at low concentrations (see also chapter 2.6) Great uncertainty will thus attach to any comparison of such measurements with the PNEC (determined as 0.06 ug/l) based on measurements in different circumstances, and the result can only be regarded as a tentative indication
- Hypochlorite releases from chlorine production plants in effluent is measured as TRC (Total Residual Chlorine). However, it cannot be determined to what extent this TRC value in the final effluent is related to hypochlorite production or to other oxidative compounds that are produced in the same plant or result from various reactions underway.
- Final effluents of production plants are usually a combination of effluents from different processes and may also contain sewer waste. Considering the properties of active oxidants such as hypochlorite, it is expected they will rapidly react with other substances present in the process effluent or the sewer at the site (COD) and thereby be eliminated.
- In the calculations it is thus assumed that when COD was measured the (final) effluent will in fact have no TRC left (i.e. PEC_{local} is zero). In some cases both TRC and COD have been reported for the same effluent, which is unexpected, but could for example be due to different sampling points for the measurements (e.g. COD measured more towards the final discharge) or because TRC which is not in fact detected is formally reported in terms of 'less than' values.
- Any residual oxidant which did reach the surface water in certain cases would be expected to disappear rapidly as is illustrated for example by the model calculations in Appendix 2 used for other scenarios.

Tentative PEC_{local} calculations

COD values were reported for 32 plants (38% of total) and "active chlorine" for 32 plants (39% of total). Flow data for the receiving water are available for 35 sites (67% of respondents), representing rivers, canals, a lake and marine and estuarine tidal waters.

Most of the active chlorine measurements reported are low (less than 1 mg/l TRC) or under the detection limit. Three plants reported active chlorine concentrations higher than expected (4, 7.7 and 3100 mg/L) and have been followed up to obtain more details:

- The site originally reporting 7.7 mg/l Cl_2 (site 18) could not check their 1996-1997 data anymore, but their data from 2000 until 2003 (annual average) were 1.9, 2.1, 1.6 and 1.8 mg/l, so a better estimation of the tentative PEC_{local} for this site would be 0,01 mg/l TRC.

They also indicated that the site did install a neutralisation system in 2004, so the final effluent will not contain significant TRC.

- The plant reporting 4 mg/l did not respond and the plant reporting 3100 mg/L supplied additionally statistically treated data for July 1997 until September 2004. The average concentration over this period was 1 mg/L and the maximum value was 46 mg/L. They reported an estimated COD of 30 mg/l and indicated that they do not need a permit for discharging chlorine to sea.

In summary:

- An initial tentative PEC_{local} could be estimated for 46 sites. For 38 of these sites, the COD reported in the effluent will eliminate TRC and the PEC_{local} is considered to be zero.
- For the 8 remaining sites for which a PEC_{local} was calculated and which did not report a COD value of the effluent, 3 of these reported measurements of TRC below the detection limit, which could lie between the reported detection limit and zero. For some, additional information was also obtained (see above). This leaves 4 sites for which a concern could not be excluded based on the tentative PEC_{local} . However, it should be considered that these initial values are effectively worst-case assumptions. Any TRC in the final effluent will be subject to further reaction immediately on encountering oxidisable matter in the receiving water such that the very small concentrations of TRC potentially remaining will be eliminated close to the point of discharge.

An additional measure to ensure that significant adverse effects do not occur from discharge of TRC is now provided by the IPPC Directive. 'Best Available Technique' (BAT) practices under this directive stipulate removal of free oxidant and can be required at a particular site if adverse effects are observed. Removal of oxidant is also promoted as common practice for chlorine production sites in Europe in the chlor-alkali BREF (BREF Chlor-Alkali Manufacturing industry). In the BREF several technical options to reduce active oxidants have been described i.e. chemical oxidation, catalytic reduction, thermal decomposition and recycling of hypochlorite. Additionally the removal of free oxidants is regulated by several EU Member States, sometimes initiated by the EU Urban Waste Water Treatment Directive [Directive 91/271/EEC]. For example Italy has a decree in its National law limiting the discharge of free oxidants to 0.004 mg/l. In Germany there are limits for the chlor-alkali sector to be applied before discharge (also to WWTPs) of 0.2 mg/l 'free chlorine' (analysed according to DIN 38480-G 4-1), which is in the similar range as applied and discharged from cooling water application (see 3.1.1.9). The levels at which these limits are set, many times above the calculated PNEC, will reflect partly the difficulties and inherent uncertainties in measuring TRC in effluents as well as experience of what analytical limits are effective in avoiding adverse effects.

Code	Water												Dilution factor (average)	Tentative PEClocal TRC*
	Influent				effluent			Receiving water						
	m³/sec			m³/sec	TRC (mg/l)	mg COD/l	Type	m³/sec	m³/sec	m³/sec	Year			
	WWTP	Influent	mg Cl2/l	mg COD/l				effluent flow average	Flow:Low	10 perc.		Average		
17	Yes	1.08	< 0.01		1.8	< 0.01		river	280	288		1995	>160	<0,00006
18	No				0.069	7.7	na	river	10				145	0.05
20	No				0.0066	0.05	100	estuary	na					0
21	No						30	river	0.1		0.13	1997		0
22	No				0.3	< 0.1	< 10	other	0.3					0
23	No					0		marine			(m)			0
24	Yes				0.05		142	?			4.2	1996	84	0
25	Yes				0.31		219	river			100	1996	323	0
26	Yes				4.69	0	87	river		734			157	0
27	No				0.4	na	20	river	25~30				63	0
28	No				3	< 0.01	3	marine			(m)	1996		0
29	Yes				0.056	< 0.5	200	river	5		10	1996	179	0
30	Yes				2.4	< 0.05	30	river	20		162	1996	68	0
31	No				0.18	< 0.05	163	river	1.2		18	1996	100	0
32	No				0.52	< 0.50	71	river	200		350	1996	673	0
33	No				1.1	< 1	31	marine			(m)	1996		0
34	Yes				1	0.00008	19	river	1000		2870	1996	2870	0
36	No				0.023	< 0.6	93	river			160	1996	6957	0
37	No/Yes	No water emissions												0
38	No/Yes	No water emissions												0
39	No/Yes	No water emissions												0
40	No/Yes	No water emissions												0
41	No				2		15	river	25		30	1996	15	0
42	No				0.7	0.09	12	river	10		30	1996	43	0
43	No				0.043	< 0.1	5	Sea			(m)			0
44	Yes/No				0.05	< 0.025	0	Sea			(m)	1996		-
45	No				0.28	< 0.008	60	river	2		2.6	1996	9	0
46	No				0.15		65	river	1030		900	1996	6000	0
47	No				4.3	0.1		estuary/marine	tidal system	na	(m) 1500	1996	349	0.0003
49	No				0.0284	< 0.1	363	other	na	na	na	1996		0
50	No				0.002	~ 0								-
51	No							lake	0.4		4.1	1996		-
52	Yes	0.006	< 1	650 kg/day	0.006	< 1	~65 kg/day	river	~0.4				67	0
57	No				0.11			river	04-10				4-97	-

Code	Water												Dilution factor (average)	Tentative PEClocal TRC*
	WWTP	Influent			effluent			Receiving water						
		m ³ /sec	mg Cl ₂ /l	mg COD/l	m ³ /sec	TRC (mg/l)	mg COD/l	Type	m ³ /sec	m ³ /sec	m ³ /sec	Year		
		Influent			effluent flow average			Flow:Low	10 perc.	Average				
58	No					100	river	0.6		1	1996		0	
60	Yes	0.0022	0	170	0.00016	3100	<30	marine		(m)	1996		0	
61	No				0.26	4		estuary	9.5		15.8	1996	61	0.06582
62	No				0.25			river	0.8-13		2.51	1996	10	0
74					0.2			estuary/lake	0.2		100000	1996	500000	0

M=marine, dilution factor mostly not exactly known, but relatively high

*Tentative because based on reasoning as explained in section 3.1.2.1., a zero is used to express that no TRC is expected to be present

*Values in italics have TRC values but also COD and should be considered to contain no TRC

Appendix 7 Definitive study of the effects of chlorination/dechlorination of raw settled sewage

1. Introduction

As a key step in finalising the Risk Assessment of sodium hypochlorite under the EU Existing Chemicals legislation, Euro Chlor has been requested to make an assessment of the potential for toxic effects to aquatic life that may arise from chlorinated organic by-products formed by reaction of hypochlorite with organic matter in various use scenarios. While the concentrations and potential effects of certain identified species, such as haloacetic acids and trihalomethanes have been assessed directly in conventional PEC/PNEC terms, the purpose of this work is to assess potential effects of unidentified chlorinated species as well as to provide an additional perspective on the identified components.

The agreed concept is to conduct comparative toxicity tests on a whole effluent with and without the use of hypochlorite. Initially it is agreed to test an unbiodegraded effluent from simulated chlorination of raw settled sewage on the basis that this would also provide a 'worst case' example, often an extreme one, in respect of many of the other use scenarios being considered, viz

- Wastes from household bleach use discharged to a sewage treatment works (STW);
- Wastes from Industrial and institutional cleaning (IIP) discharged to a STW;
- Water from swimming pools discharged to a STW;
- Wastes from drinking water treatment facilities discharged to a STW;
- Treated cooling waters discharged directly to a receiving water;
- Treated swimming pool water discharged directly to a receiving water;
- Sewage disinfected prior to discharge to a receiving water.

Whole effluent toxicity data are already available for household use of hypochlorite for the freshwater invertebrate *Daphnia* and fish and these will provide additional reference points for the Risk Assessment. To ensure the potential toxic effects of chlorinated organic by-products are not obscured by those of free or combined available chlorine, residual chlorine will be destroyed with excess sulphite before testing.

A tiered approach has been adopted for the testing such that the perceived "worst-case" scenario is investigated first with others being assessed in a sequential manner based on the evaluation of the accumulated data, should the 'worst-case' not show clear results.

The first step in the tiered approach for the risk assessment is an assessment of the extent to which the disinfection of raw settled sewage with hypochlorite can result in changes (increases or decreases) in potentially bioaccumulative chlorinated by-products and in toxicity, relative to that observed in unchlorinated raw settled sewage. This report describes the approaches adopted and the results of this study.

It is important to re-iterate at this stage that the study was designed to assess the potential environmental impacts of chlorinated reaction products but is not designed to assess the toxicity of residual chlorine. As such the study programme includes a dechlorination stage.

2. Methodology

2.1 Sample preparation

On 16th February 2004 a 40 litre sample of raw settled sewage from Henley STW was collected in two 25 litre plastic containers which had been rinsed with the sample prior to filling. The sample was returned to the WRc-NSF laboratory and two 20 litre aliquots were prepared in large glass containers. One of the aliquots served as an untreated control (Raw settled sewage or RSS) whilst the other aliquot was chlorinated (with 50 mg chlorine l⁻¹ for 1 hour) and then residual chlorine removed (referred hereafter as 'dechlorinated') by the addition of an excess concentration (40 mg l⁻¹) of sulphite (coding C/D-RSS). The procedures for the chlorination and dechlorination are described below.

A 1 litre volume of a 1000 mg l⁻¹ sodium hypochlorite solution was prepared from a stock 10-12% Analar sodium hypochlorite solution by dilution of 10 ml of stock with groundwater. This 1 litre solution was then added to one of the 20 litre aliquot of raw settled sewage (C/D-RSS). A 1 litre sample of groundwater was added to the other 20 litre raw settled sewage aliquot which was acting as the unmodified control (RSS). The samples were then stirred for a period of 1 h.

Measurements of free residual chlorine in the samples were made in the raw settled sewage aliquots before and after the addition of either groundwater or sodium hypochlorite using the DPD method. Residual chlorine concentrations (mg l⁻¹) were determined by adding 0.12g of DPD (diethyl-p-phenylenediamine) to 8 ml of each sample. The Merck SQ 118 spectrophotometer was calibrated at a wavelength of 550nm and zeroed using a groundwater blank (2ml of groundwater in 1 cm cuvette). Two ml aliquots of the samples were then transferred to a 1 cm cuvette and the resulting concentration determined.

The chlorinated sample (C/D-RSS) was then 'dechlorinated' by the addition of a 1000 ml volume of an 800 mg sulphite l⁻¹ solution (1260 mg sodium sulphite l⁻¹) to achieve a final sulphite concentration of 40 mg sulphite l⁻¹ (see Table 2.1). A 1000 ml volume of groundwater containing 35 mg l⁻¹ of calcium sulphate was added to the unmodified raw settled sewage aliquot (RSS). The samples were again stirred for a period of 1 hour after addition of the sulphite solution. At the end of this period the residual chlorine level in each test vessel was measured.

Table 2.1 Preparation of different chlorinated/dechlorinated raw settled sewage treatments

Sample	Volume of raw settled sewage	Volume of 1000 mg Cl ₂ l ⁻¹ solution	Volume of 800 mg sulphite l ⁻¹ solution
Untreated raw settled sewage (RSS)	20000 ml	0 ml (1000ml groundwater added)	0 ml (1000ml groundwater added)
Chlorinated/Dechlorinated raw settled sewage (C/D-RSS)	20000 ml	1000 ml	1000 ml

The 22 litre samples of raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS) were then each subdivided into two aliquots:

- 17 litre aliquots which were centrifuged at 3500 rpm for 15 minutes in a Sigma 6K10 cooled centrifuge to provide material for the bacterial (*Vibrio fischeri*) bioluminescence, algal (*Pseudokirchnerella subcapitata*) growth inhibition and *Daphnia magna* immobilisation/reproduction toxicity tests. The samples were initially centrifuged to reduce suspended solids concentrations to < 20 mg l⁻¹ (a level which would not affect the conduct of the test). The supernatants (and solids) resulting from the centrifugation of each sample were retained.
- 5 litre aliquots which were not centrifuged and which were used for the biodegradation and bioaccumulation studies.

The samples were stored at 2 °C until the results of an analysis of chlorinated organic by-products (as Adsorbable Organic Halide - see Section 2.2) had confirmed that there had been a several-fold increase in the level of these by-products in the chlorinated/dechlorinated RSS. A 48h *Daphnia magna* immobilisation test was conducted on the freshly prepared samples so that any changes in toxicity which occurred during storage could be quantified.

2.2 Chemical analysis

Two 500 ml aliquots of the untreated raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS) were taken for analysis for biological oxygen demand (BOD), chemical oxygen demand (COD), ammonia (NH₃), dissolved organic carbon (DOC), total organic carbon (TOC), suspended solids, chloride and sulphate. Replicate samples (250 ml) of the unmodified and centrifuged raw settled sewage and chlorinated/dechlorinated samples were taken for AOX analysis.

2.3 Test framework and procedures

2.3.1 Test framework

Table 2.2 summarises the dates on which different tests within the framework were started and ended.

Table 2.2 Start and end dates for different tests

Test procedure	Start date	End date
Bacterial (<i>Vibrio fischeri</i>) bioluminescence test	9-10 March 2004	9-10 March 2004
Algal (<i>Pseudokirchnerella subcapitata</i>) growth inhibition test	9 March 2004	12 March 2004
<i>Daphnia magna</i> immobilisation and reproduction test	10 March 2004	24 March 2004
Zahn Wellens biodegradation test and SPME bioaccumulation study	10 March 2004	7 April 2004

2.3.2 Bacterial (*Vibrio fischeri*) bioluminescence test

The toxicity of the RSS and C/D-RSS samples to the Microtox[®] test system after a 30 minute exposure period was determined on two occasions (9th and 10th March 2004) according to procedure PROC/ECO/005 which is accredited by the United Kingdom Accreditation Service (UKAS). The Microtox test system utilizes the bioluminescent marine bacterium, *Vibrio fischeri* and measures the change in bioluminescence upon exposure to the sample. The Microtox[®] toxicity test reagent was supplied as a commercial package by SDI Europe Ltd.

Conductivity, temperature and pH measurements were taken on the sample submitted for testing, to establish the appropriate degree of salinity and pH adjustment necessary in order to comply with the Microtox[®] assay protocol.

In order to ensure that the response of the Microtox[®] reagent was consistent with similar studies undertaken previously at WRc-NSF, it was also tested with the reference substances phenol and zinc.

A model 500 Microtox[®] analyser was switched on at least 30 minutes before testing so that the test cuvette wells could reach their pre-set temperatures. Clean unused cuvettes were placed into all 30 test wells and in the reagent well. A fresh vial of freeze-dried Microtox[®] reagent (freeze-dried *Vibrio fischeri*) was reconstituted into a clean cuvette containing 1 ml of reconstitution solution. Ten microlitres of reagent were pipetted into each of ten cuvettes containing 0.5 ml of Microtox[®] diluent (2% sodium chloride solution). The reagent was allowed fifteen minutes to stabilise and then the initial light output (I_0) was measured for each cuvette. Dilution series of the RSS and C/D-RSS samples were prepared with Microtox[®] diluent and appropriate volumes of sample were then added to duplicate cuvettes to achieve the concentration range, 5.7, 11.4, 22.8 and 45.5% sample in 2% NaCl. The light output from the cuvettes was then determined after 5, 15 and 30 minutes exposure. Two control cuvettes containing 2% sodium chloride solution were tested in parallel. EC_{50} values were calculated using the appropriate statistical method menu of computer software supplied by Microbics Corporation (Version 7.8).

2.3.3 Algal (*Pseudokirchneriella subcapitata*) growth inhibition test

A culture of *Pseudokirchneriella subcapitata* was obtained from the Institute of Freshwater Ecology, Culture and Collection of Algae and Protozoa Centre on the 5th March and was used within 6 days of receipt. The algal test was initiated on 9th March 2004 according to the Organisation for Economic Cooperation and Development (OECD) Test Guideline Method 201 (OECD, 1984a) in a temperature controlled orbital incubator.

For each test concentration of the RSS and C/D-RSS samples, four flasks were prepared. Three replicate flasks were inoculated with algae whilst algae were omitted from the fourth, which served as a blank to monitor any background changes in non-algal particles. Algae were added immediately after preparing the test solutions. The algal cell density of the starter culture was determined using an electronic particle counter, and the three replicate algal containing flasks were inoculated to achieve an initial cell density of approximately 10000 cells per ml.

The background particle concentration and pH of each stock solution contained in the volumetric flasks were measured using an electronic particle counter and a pH meter,

respectively. All flasks (inoculated and un-inoculated) were then plugged with sterile foam bungs and placed under constant illumination (6000 - 10,000 lux) and rotation (100 - 130 r.p.m.) at $23 \pm 2^\circ\text{C}$.

After 24, 48 and 72 h the particle density of each flask was measured. These measurements were taken by removing 0.5 ml of solution from each flask using a sterile pipette and adding this to 50 ml of Isoton, before determining the particle density using an electronic particle counter. At the end of the test, the pH of each sample concentration was measured in the solution from a replicate flask.

In order to ensure that the response of the algae was consistent with similar studies undertaken previously at WRc-NSF a test with the reference substance zinc was also conducted at nominal concentrations of 100, 320 and 1000 $\mu\text{g Zn l}^{-1}$. The actual exposure concentrations were confirmed by chemical analysis

Counting procedure for the test:

The measurements of cell density in each replicate of an exposure concentration were used to derive growth rates using the equation;

$$u = (\ln N_n - \ln N_o) / t_n$$

Where:

- t_n is the time of the final measurement after the beginning of the test;
- N_o is the nominal or measured initial cell density (after correction for background particles);
- N_n is the measured final cell density (after correction for background particles).

The mean values of u for each test concentration and control were then used to calculate the percentage inhibition for each test concentration from the equation:

$$Iu_i = [(U_c - U_i) / U_c] \times 100$$

- Iu_i is the percentage inhibition (growth rate) for test concentration i ;
- U_i is the mean growth rate for test concentration i ;
- U_c is the mean growth rate for the control.

The test concentration corresponding to 50 % inhibition of growth (EC_{50}) was then determined using a statistical software package ToxCalc5 (Tidepool Scientific).

2.3.4 *Daphnia magna* immobilisation and reproduction test

The 14 day *Daphnia magna* immobilisation and reproduction test was initiated on 10th March 2004 according to the Organisation for Economic Cooperation and Development (OECD) Test Guideline Methods 202 and 211 (OECD, 1984b, 1998). The juvenile *Daphnia magna* used in the test were obtained from the in-house cultures. The concentration series used for the raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS) samples were 0 (control), 1.0, 3.2, 10, 32 and 100% sample.

Fifty ml aliquots of each concentration were added to 100 ml glass beakers and one juvenile (<24 h old) daphnid was added to each test vessel. Twenty control vessels

of groundwater were also used in the test. Observations of the number of mobile and immobile daphnids in each vessel were made daily and the number of juveniles in each vessel was noted from day 9 onwards. Water quality parameters (pH, temperature, dissolved oxygen and hardness) were measured at the beginning of the test. If pH and/or dissolved oxygen levels in the test solutions were outside acceptable test ranges then modifications were made to ensure they were within range at the start of the test. The animals were fed each day with an algal suspension and the test solutions were replaced every Monday, Wednesday and Friday prepared from the stored RSS and C/D-RSS samples.

A zinc reference toxicant test accompanied the *Daphnia magna* immobilisation and reproduction test to ensure the sensitivity of the test organisms was consistent with previous studies at WRc-NSF using this test organism. The following nominal concentrations were used, expressed as zinc: 0.0 (control), 0.2, 0.4, 0.8, 1.6 and 3.2 mg l⁻¹. The actual exposure concentrations were confirmed by chemical analysis.

2.3.5 Biodegradation and bioaccumulation tests

Zahn-Wellens biodegradation test

The Zahn-Wellens test is a static 'die-away' method measuring disappearance of dissolved organic carbon (DOC). The method identifies substances that have the potential to undergo ultimate biodegradation in an aerobic environment. The test material is dissolved in a buffered mineral salts medium and inoculated with activated sludge not previously exposed to the test material and incubated in darkness at constant temperature for 28 days. Analyses of DOC are made at intervals and compared against the concentration present at the start of the test. Biodegradation is indicated by DOC removal. The procedure and the activity of the inoculum are checked using a functional control substance whose pattern of biodegradation is well established.

The Zahn-Wellens biodegradation test was carried out according to OECD Test Guideline 302 B (OECD, 1992). Duplicate solutions containing the test substance (raw settled sewage and chlorinated/dechlorinated raw settled sewage) mineral nutrients and activated sludge in aqueous medium was agitated and aerated at 20-25 °C in the dark for 28 days. A blank control containing activated sludge, mineral nutrients but no test substance and a reference test, containing activated sludge, mineral nutrients and diethylene glycol were tested in parallel.

Mineral medium was prepared according to test guideline OECD 302B the day before the tests were initiated and allowed to stand overnight at the test temperature.

For the blank control, 5 ml of the concentrated mineral medium was added to a volumetric flask and made up to 2000 ml with distilled water before being transferred to the test vessel.

For the reference test, 2.22 g of diethylene glycol was weighed into a glass weighing dish and made up to 1000 ml with distilled water (nominal concentration 1000 mg organic carbon per litre). A 200 ml aliquot of the diethylene glycol stock solution and 5 ml of the concentrated mineral medium were added to a 2000 ml volumetric flask and made up to a final volume of 2000 ml with distilled water before being transferred to the test vessel.

Duplicate test vessels were prepared for each of the test substances (raw settled sewage and chlorinated/dechlorinated raw settled sewage) where 5 ml of the concentrated mineral medium was added to make up to a total volume of 2000 ml.

Each of the test vessels were inoculated with 5 ml l⁻¹ micro-organisms of a mixed population obtained from the activated sludge of Henley Sewage Treatment Works on the day of test initiation. Each of the test vessels contained a large PTFE-coated magnetic follower and was connected to an air line which provided an even distribution of fine bubbles from the aeration tubes.

After recording the pH (and adjusting, if necessary, to within a pH range of 6.5-8.0) for each of the treatments (Day 0) the remaining test solutions were kept in the dark at a constant temperature (20 - 25°C). In the test, degradation was followed by analysis of DOC (see Tables 2.3 and 2.4) over a 28-day period. Samples were taken for the determination of DOC at test intervals of 0 (after 0 and 3 hours), 1, 2, 7, 14, 21 and 28 days for the control, reference substance (diethylene glycol) and each of the test substances (raw settled sewage and chlorinated-dechlorinated raw settled sewage).

Table 2.3 Procedure for the analysis of DOC

Determinand	Dissolved Organic Carbon
Method	UV - Persulphate Oxidation / NDIR
Sample Types	Potable waters, Surface & Groundwaters, Sewage Samples and Seawater.
Principle	A portion of the sample is filtered through a GF/C filter, acidified to pH2 with phosphoric acid and purged with argon. Inorganic carbonates and bicarbonates are converted to carbon dioxide and removed. Volatile or purgeable organic carbon is also removed at this stage. A known volume of the purged sample is injected into the instrument, where the organic carbon reacts with acidified potassium persulphate in the presence of UV radiation to generate carbon dioxide. The carbon dioxide is measured using non-dispersive infra red detection.
Reference	SCA publication : "The Instrumental Determination of Total Organic Carbon, Total Oxygen Demand and Related Determinands, 1989" , Methods for the Examination of Waters and Associated Materials, HMSO

Table 2.4 Performance Characteristics of DOC measurements

Range of Application	0 - 20mg/l C (undiluted samples)	
Reporting Limit	0.2 mg/l C	
Precision Data	Concentration (mg/l C)	Standard Deviation (mg/l C)
Standards	2.0	0.05
	18.0	0.33
QC Standard	5.0	0.15

Notes: All precision data are based on estimates with at least 10 degrees of freedom

The biodegradation process during the 28 day test period was monitored by determination of DOC taken at regular intervals and the ratio of eliminated DOC corrected for the blank, after each time interval, to the initial DOC value is expressed as the percentage biodegradation at the sampling time.

To calculate the percentage degradation at time t;

$$D_t = \left(1 - \frac{C_t - C_B}{C_A - C_{BA}} \right) \times 100$$

Where:

- D_t = percentage at time t;
- C_A = concentration (mg/l) of DOC in the test suspension measured after 3h of incubation;
- C_t = mean concentration (mg/l) of DOC in the test suspension at time t;
- C_{BA} = mean concentration (mg.l) of DOC in the blanks measured after 3h of incubation;
- C_B = mean concentration (mg/l) of DOC in the blanks at time t.

The pH of the solutions in each of the test vessels were monitored at regular intervals and adjusted with acid or alkali to be within the pH range 6.5-8.

Bioaccumulation tests

At the start (day 0) and end (day 28) of the biodegradation tests on the RSS and C/D-RSS samples the presence of chlorinated by-products with the potential to bioaccumulate was investigated using Solid Phase Micro-Extraction (SPME) fibres. This involved using polyacrylate fibres (Supelco, Bellafonte, CA, USA) having a length of 1 cm and an internal diameter of 55 μm . On the fibre there was a coating of 100 μm polydimethylsiloxane (PDMS) . The volume of the PDMS phase is 0.621 μl . The fibres were conditioned prior to use according to the manufacturers instructions

On day 0, replicates of the RSS and C/D-RSS samples were dispensed into 250 ml glass bottles. One fibre was placed in the middle of each sample bottle. There was no headspace in the bottle and the fibres were brought into the solution through a seal in the cap of the bottle. The extraction period, lasted for 24 hours and the solutions were continually stirred during this period. After the exposure period the fibre was removed from the bottle, dried gently with a tissue and stored at 4°C in a sealed container until analysis. The same procedure was repeated on RSS and C/D-RSS samples after 28 days degradation. These fibres were used for the analysis of TOX.

A corresponding study was carried out in which a series of fibres were exposed to 25 ml of each of the test solutions for 24 hours. These fibres were used to determine total extractable chlorinated organics by direct injection into a GC-MS in ECD mode. The data are expressed in terms of the concentration of chlorinated organic compounds recovered from an SPME fibre exposed for 24 hours to a 25 ml sample of standard mixture of chlorinated paraffins (45% chlorine, CAS Number 63449-39-8) at a concentration of 0.5 mg l⁻¹.

3. Results and Discussion

3.1 Sample preparation phase

3.1.1 Chlorine (free and residual) measurements

Analysis of the free chlorine concentration in the sodium hypochlorite solution used to chlorinate the raw settled sewage resulted in a value of 980 mg l⁻¹, meaning that the initial free chlorine concentration in the test vessels was estimated to be 46.7 mg l⁻¹. Table 3.1 summarises the residual chlorine concentrations measured in the different treatments after chlorination and dechlorination. Following reaction of the sodium hypochlorite solution with raw settled sewage for an hour the resulting level of residual chlorine was 8.2 (8.0 – 8.4) mg l⁻¹. The addition of 40 mg l⁻¹ sulphite concentration resulted in a reduced residual chlorine concentrations in the C/D-RSS sample that was similar to that in the raw settled sewage (RSS).

Table 3.1 Residual chlorine levels in unchlorinated and chlorinated/dechlorinated raw settled sewage

Sample	Residual chlorine concentration (mg l ⁻¹)	
	After 1 h chlorination	After 1 h dechlorination
Raw settled sewage (RSS)	0.58	0.58
Chlorinated/dechlorinated raw settled sewage (C/D-RSS) (~50 mg Cl ₂ l ⁻¹ and 40 mg sulphite l ⁻¹)	8.20	0.56

3.1.2 Chemical analysis

Table 3.2 summarises the analytical chemistry data for a range of determinands (BOD, COD, NH₃, TOC, suspended solids, AOX, chloride and sulphate) in the raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS) samples. The chlorinated/dechlorinated raw settled sewage sample had a lower ammonia concentration than the RSS. Higher concentrations of BOD, COD, DOC, TOC and suspended solids were measured in the C/D-RSS compared to the raw settled sewage.

Table 3.3 summarises the AOX measurements in raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS). Separate analysis by two laboratories confirmed that there had been a 6.5-7.0 fold increase in AOX in the C/D-RSS sample relative to the RSS sample.

The AOX levels in the centrifuged raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS) samples were measured at the start of the toxicity tests and were found to be compatible with those in the freshly prepared samples. The AOX concentration in the centrifuged RSS was 110 µg l⁻¹ and there was 900 µg l⁻¹ in the C/D-RSS.

Table 3.2 Analytical chemistry data for a range of determinands (BOD, COD, NH₃, DOC, TOC, suspended solids, chloride and sulphate in the raw settled sewage (RSS) and chlorinated/dechlorinated raw settled sewage (C/D-RSS) samples

Sample	BOD (mg l ⁻¹)	COD (mg l ⁻¹)	Ammonia (mg l ⁻¹)	DOC (mg l ⁻¹)	TOC (mg l ⁻¹)	Suspended solids (mg l ⁻¹)	Chloride (mg l ⁻¹)	Sulphate (mg l ⁻¹)
Raw settled sewage (RSS)	170	349	32.8	43.2	43.2	118	117	50.0
Chlorinated/dechlorinated raw settled sewage (C/D-RSS)	194	388	23.6	59.4	59.4	158	328	85.7

Table 3.3 Summary of the AOX values on freshly prepared samples

Sample	Laboratory	Uncentrifuged samples		Supernatants	
		Mean AOX (µg l ⁻¹)	Range of AOX values (µg l ⁻¹)	Mean AOX (µg l ⁻¹)	Range of AOX values (µg l ⁻¹)
Raw settled sewage (RSS)	A	210	200 – 220	180	170 – 190
	B	174	148 – 200	153	151 – 155
Chlorinated/ dechlorinated raw settled sewage (C/D-RSS)	A	1355	1300 – 1410	1025	950 – 1100
	B	1223	1149 – 1296	1100	1075 – 1125

3.1.3 Initial *Daphnia magna* immobilisation test

Table 3.4 summarises the results of the initial *Daphnia magna* immobilisation test on the freshly prepared samples. These showed that the toxicity of the RSS sample (48h EC₅₀ value = 17.9%) was slightly greater than that of the C/D-RSS sample (48h EC₅₀ value = 47.6%).

Table 3.4 Summary results of the initial *Daphnia magna* immobilisation test

Test concentration	Immobilisation after 48 hours (%)	
	RSS	C/D-RSS
Control	0	0
1.0	0	0
3.2	0	0
10	0	0
32	100	15
100	100	100

The test can be considered valid since the results of the accompanying zinc reference toxicant test were consistent with the mean EC₅₀ values from the in-house Shewart control chart for this test.

3.2 Test procedures

3.2.1 Bacterial (*Vibrio fischeri*) bioluminescence test

Table 3.5 summarises the results of the bacterial bioluminescence tests carried out on the RSS and C/D-RSS samples on 9th and 10th March 2004. On both occasions the RSS sample showed greater toxicity (i.e. lower EC₅₀ values) than the C/D-RSS sample. There was good agreement between the resulting EC₅₀ values from the two tests.

The results of both tests can be considered valid since the results of the zinc and phenol reference toxicant tests were consistent with the mean EC₅₀ values from the in-house Shewart control chart for this test.

Table 3.5 Bacterial (*Vibrio fischeri*) bioluminescence test data

Test number	Substance	EC ₅₀ value (95% Confidence intervals)		
		5 minutes	15 minutes	30 minutes
1 (9/3/04)	RSS	7.1 (6.5 - 7.9)	4.2 (3.6 - 4.9)	5.9 (5.2 - 6.6)
	C/D-RSS	37.3 (34.3 - 40.6)	33.0 (30.9 - 35.2)	33.1 (31.3 - 34.9)
	Zinc	-	-	0.45 (0.42 - 0.47)
	Phenol	-	16.1 (15.5 - 16.7)	-
2 (10/3/04)	RSS	10.1 (9.5 - 10.7)	7.4 (6.5 - 8.3)	8.5 (7.7 - 9.4)
	C/D-RSS	35.3 (32.6 - 38.1)	27.2 (26.1 - 28.4)	27.9 (26.6 - 29.2)
	Zinc	-	-	0.42 (0.40 - 0.44)
	Phenol	-	18.0 (16.9 - 19.1)	-

3.2.2 Algal (*Pseudokirchnerella subcapitata*) growth inhibition test

Table 3.6 summarises the results of the algal growth inhibition tests carried out on the RSS and C/D-RSS samples between 9th and 12th March 2004. From the data it is evident that the responses for both samples were similar with a reduction in algal growth being evident at concentrations exceeding 3.2% v/v. A greater than 50% reduction in algal growth was evident in both samples at concentrations of 32% v/v. No growth occurred in the 100% v/v concentrations which was probably due to reduced light attenuation in the test vessels due to the presence of fine particulates. The resulting 72h-NOEC, 72h-LOEC and 72h-EC₅₀ values for the RSS and C/D-RSS were as follows:

RSS: 72h-NOEC = 1.0%,
 72h-LOEC = 3.2%,
 72h-EC₅₀ = 19.5% (95% Confidence Interval = 15.9 - 24.0%)

C/D-RSS: 72h-NOEC = 1.0%,
 72h-LOEC = 3.2%,
 72h-EC₅₀ = 25.7% (95% Confidence Interval = 12.5 - 44.8%)

The results of the test can be considered valid since the result of the zinc reference toxicant test (EC₅₀ = 642 µg l⁻¹ with 95% Confidence Intervals of 570 – 742 µg l⁻¹) was consistent with the mean EC₅₀ values from the in-house Shewart control chart for this test.

Table 3.6 Algal (*Pseudokirchnerella subcapitata*) growth inhibition test data for test started on 9/3/04

Substance	Concentration	Mean growth rate	% Inhibition
RSS	Control	1.13	-
	1.0 %	1.10	2.7
	3.2 %	0.98	13.3
	10 %	0.76	33.3
	32 %	0.31	72.6
C/D-RSS	Control	1.13	-
	1.0 %	1.12	0.9
	3.2 %	1.02	9.7
	10 %	0.80	29.2
	32 %	0.47	58.4
Zinc reference	100 µg l ⁻¹	1.10	0.7
	320 µg l ⁻¹	0.86	23.9
	1000 µg l ⁻¹	0.24	78.8

Note: No algal growth occurred in 100% RSS and C/D-RSS solutions

3.2.3 *Daphnia magna* immobilisation and reproduction test

Table 3.7 summarises the results currently available for the *Daphnia magna* immobilisation and reproduction test on the RSS and C/D-RSS samples which was started on 10th March 2004. The extent of the immobilisation of daphnids was similar for both samples with no effects being observed at 32% v/v and high levels of immobilisation at 100% v/v. The results for the C/D-RSS sample are similar to those from the initial test on the freshly prepared sample (see Table 3.4). The RSS sample showed a slightly lower toxicity after storage.

For both samples production of juveniles was evident after 8-9 days. The numbers of juveniles per surviving adult shows a similar pattern for both samples; namely increasing numbers from 1.0 to 10% v/v sample with a reduction at 32% v/v back to the numbers found at 1.0% v/v sample. This bell shaped response is probably the result of the competition between two factors:

- The presence of increasing levels of nutrients and/or food items with increasing sample concentration
- The presence of increasing levels of contaminants with increasing sample concentration

At the exposure concentrations of 3.2 and 10% the enhanced effects of the nutrients and/or food items on juvenile production appear to outweigh the effects of the contaminants present. However, in contrast, at 32% v/v the effects of the contaminants appear to outweigh the effects of the nutrients and/or food items.

The levels of juvenile production observed in all the controls were markedly lower than in RSS and C/D-RSS treatments which presumably reflects the greater levels of nutrients and/or food items present in the treatments.

The test can be considered valid since the results of the accompanying zinc reference toxicant test were consistent with the mean EC₅₀ values from the in-house Shewart control chart for this test.

Table 3.7 *Daphnia magna* immobilisation and reproduction test for test started on 10/3/04

Test concentration (%)	Immobilisation (%) after 48 hours		Reproduction data			
	RSS	C/D-RSS	Time of first brood (days)		No. of juveniles per surviving adult	
			RSS	C/D-RSS	RSS	C/D-RSS
Control	0	0	9	9	36.4	36.4
1.0	0	0	8	8	115.1	116.7
3.2	0	0	8	8	127.2	132.4
10	0	0	8	8	146.6	141.6
32	0	0	8	8	86.6	117.2
100	80	100	-	-	-	-

The similarity in the responses observed in the RSS and C/D-RSS samples is indicates that the daphnids in the C/D-RSS sample were not evidently exposed to by-products formed during chlorination which bioaccumulated in the organisms resulting in enhanced toxic effects.

3.2.4 Biodegradation and bioaccumulation tests

Biodegradation test

After sample collection and preparation the RSS and C/D-RSS samples were stored at 4°C for 20 days whilst confirmatory AOX analyses were performed. During this period there was loss of DOC due to degradation. In the RSS sample DOC decreased from 43.2 to 21.7 mg l⁻¹ and in the C/D-RSS sample DOC decreased from 59.4 to 45.6 mg l⁻¹.

Table 3.8 shows the DOC (mg l⁻¹) values from the test vessels, the blank control and the reference test after 0, 1, 2, 7, 9 and 28 days which were determined by UV - Persulphate Oxidation / NDIR.

Table 3.8 Mean measured DOC in the biodegradation test over the 28 day exposure period

Treatment	DOC concentration (mg C l ⁻¹) over the 28 day exposure period						
	Day 0 (0 h)	Day 0 (3 h)	Day 1	Day 2	Day 7	Day 9	Day 28
Control blank	5.0	7.0	2.8	1.4	2.9	2.0	2.5
RSS	21.7	18.7	12.6	16.1	15.5	17.3	11.1
C/D-RSS	45.6	38.9	16.7	16.0	15.4	14.9	12.0
Diethylene glycol reference test	94.6	96.1	67.6	86.0	76.0	78.4	18.7

Whilst the initial DOC analysis results for the RSS and C/D –RSS treatments were different (21.7 and 45.6 mg l⁻¹ respectively) the samples taken on day 28 show that degradation has occurred and the remaining DOC concentration was similar in both treatments (11.1 mg l⁻¹ for RSS and 12.0 mg l⁻¹ for C/D-RSS).

In the diethylene glycol reference test the DOC levels decreased from an initial level of 94.6 mg l⁻¹ to 18.7 mg l⁻¹ after 28 days indicating there had been >80% degradation of the test material during the test. No marked changes in DOC were evident in the control blank throughout the exposure period.

Bioaccumulation tests

Table 3.9 summarises the results of the analysis of the Solid Phase MicroExtraction (SPME) fibres. SPME fibres which had been exposed to RSS and C/D-RSS solutions before (Day 0) and after 28 days biodegradation.

The analysis of lipophilic Organic Halide (as TOX) on the SPME fibres showed that the TOX concentration on the fibre exposed to the C/D-RSS sample on day 0 (510 µg) was higher compared to the concentration on the fibre exposed to the RSS (160 µg). After the samples had been degraded for 28 days in the Zahn-Wellens test the TOX concentrations on the fibres exposed to the RSS and C/D-RSS samples were the same (100 µg) indicating that any potentially bioaccumulable chlorinated by-

products which were present at day 0 were biodegradable. In the analysis of the TOX on the SPME fibres the precision of measurement of the low values (RSS_{d0}, RSS_{d28} and C/D-RSS_{d28} samples) was inevitably less than for the higher value C/D-RSS_{d0} sample, but this does not preclude drawing conclusions as to the changes in TOX on the fibres between exposure regimes.

The analysis of the total extractable chlorinated organics on the SPME fibres by their direct injection into a Gas Chromatograph in ECD mode provided data that was consistent with that for TOX. This showed that though the fibre exposed to the undegraded C/D-RSS sample contained more chlorinated organics than the fibre exposed to the unchlorinated RSS sample, levels in the fibres exposed to the two samples after biodegradation were similar

Table 3.9 Summary of the data from the analysis of SPME fibres

Treatment	Day of biodegradation test	TOX level from SPME fibre (μg per fibre)	Total achlorinated organics from SPME fibres (mg l^{-1})
RSS	0	160	0.19
	28	100	0.11
C/D-RSS	0	510	1.03
	28	100	0.06

4. Summary

In the study samples of raw settled sewage (RSS) which had not be treated and RSS that had been chlorinated and subsequently dechlorinated (i.e. residual chlorine was removed)(C/D-RSS) were prepared. These samples were then compared to assess whether chlorinated organic by-products formed in the chlorination process were toxic, or potentially bioaccumulable and persistent. The relative toxicity of the samples was assessed using a series of tests with representatives of different taxonomic groups (namely bacteria, algae and invertebrates). The persistence and potential for bioaccumulation of chlorinated organic by-products was assessed by exposing SPME fibres to samples of RSS and C/D-RSS before and after degradation in a Zahn-Wellens test. Table 4.1 summarises the results of studies assessing the toxicity, biodegradation and bioaccumulation of RSS and C/D-RSS samples.

Table 4.1 Summary of the results of the toxicity, biodegradation and bioaccumulation studies

Type of measurement	Description	Findings
Toxicity	Bacterial (<i>V. fischeri</i>) bioluminescence test	Replicate tests showed that the RSS sample exhibited greater toxicity (15 minute EC ₅₀ values of 4.2 – 7.4 %v/v) compared to the C/D-RSS sample (15 minute EC ₅₀ values of 27.2 – 33.0 %v/v).
	Algal (<i>P.subcapitata</i>) growth inhibition test	Both the RSS and C/D-RSS samples showed similar responses with a reduction in algal growth being evident at concentrations exceeding 3.2% v/v and greater than 50% reduction in algal growth being evident in both samples at concentrations of 32% v/v. Resulting EC ₅₀ values were 19.5 %v/v for the RSS sample and 25.7% v/v for the C/D-RSS sample.
	<i>D.magna</i> reproduction and survival test	Both the RSS and C/D-RSS samples showed similar responses with mortality of daphnids at 100% v/v. The numbers of juveniles per surviving adult showed a similar pattern for both samples; namely increasing numbers from 1.0 to 10% v/v sample with a reduction at 32% v/v back to the numbers found at 1.0% v/v sample.
Biodegradation	Zahn-Wellens test	Although the DOC level in the C/D-RSS sample was higher at the start of the test than in the RSS sample, levels in the two samples were the similar after 28 days degradation
Bioaccumulation	SPME fibres	Although the TOX level on the fibre exposed to the C/D-RSS sample was higher at the start of the test than in the RSS sample fibre, levels in the fibres from the two samples were the same after 28 days degradation. A similar pattern was observed for the total extractable chlorinated organics as measured by GC-MS in ECD mode

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.

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Appendix 8

Hypochlorite Trigger Spray Inhalable Particle Tests

[Background: In December 2004, additional analytical work was undertaken by industry to confirm and refine the inhalation exposure assessment for consumers.]

Test Method

The product tested was a trigger spray cleaner containing hypochlorite typical of products on the EU market.

The test samples were pumped, using 10 successive squeezes of the trigger, against the back wall of a 512 litre chamber (= 0.512 m³, dimensions 0.8m x 0.8m x 0.8m) to simulate its use in a confined environment. The number and mass of airborne particles in the “breathing zone” (the chamber) were determined by sampling the atmosphere from the chamber at a rate of five litres a minute via a short tube connected to a TSI Model 3320 Aerodynamic Particle Sizer (APS) which samples particles in the size range 0.5 to 20 µm. The sampling tube was positioned 15 cm above the base of the chamber and 40 cm from the back and to one side of the chamber. Sampling commenced just prior to spraying. The atmosphere in the chamber was analysed for a total of five minutes, in consecutive one-minute samples.

In each test, two packs of the test sample were tested simultaneously and three runs (of 10 squeezes each) were completed on each pack. Between each replicate test run the chamber was cleared of any airborne material using a high powered vacuum. The floor of the chamber was wiped with paper tissues to remove excess discharged material.

Various data relating to particle number and particle mass are automatically calculated by the APS and associated software; the relevant results from the breathing zone measurements were expressed as:

- a. Mean respirable and inhalable mass concentrations - (µg/m³).
- b. Mean inhalable particle number concentration (particles/cc).
- c. Mass Median Aerodynamic Diameter (µm)

Results

Aerodynamic Particle Sizer

The mean discharge rates were 1.18g per trigger squeeze, range for the 6 replicate tests 1.13 – 1.26g.

The mean particle number concentration was 38 particles / cc (range 29 – 56).

The mean mass concentration was 56 µg / m³ (range 26 – 92).

The mean Mass Median Aerodynamic Diameters produced by spraying the test product was 3.35 µm (range 3.18 – 3.66).

Run No. (Sub-sample)	Discharge rate (g/trigger squeeze)	MMAD (µm)	MEAN CONCENTRATIONS	
			Mass (µg/m ³)	No. (Particles/cc)
1 (001)	1.26	3.18	92	56
2 (001)	1.17	3.31	87	42
3 (001)	1.16	3.21	65	36
4 (002)	1.19	3.21	29	32
5 (002)	1.13	3.53	26	30
6 (002)	1.15	3.66	34	29
Mean value	1.18	3.35	56	38

Particles greater than 20 µm

In an attempt to measure any particles greater than 20 µm that might remain airborne and thus inhalable in the chamber, duplicate runs were conducted on each of the 10 spray bottles using an Andersen Cascade Impactor arranged as for the APS above. The size and mass of any airborne particles from the "breathing zone" (the chamber) were determined by sampling the atmosphere from the chamber at a rate of 28 litres a minute via a short tube connected to the Andersen Cascade Impactor. The atmosphere in the chamber was analysed for a total of five minutes, in consecutive one minute samples. The ten GF/C filters were reweighed after each test run.

The amounts of material collected using the ACI was too small for analysis indicating that no significant amounts of material remain suspended in the air and thus inhalable in particles greater than 20 µm. This confirms what would be expected because particles of 20 µm and above rapidly fall out of the air and are not available for breathing.