



Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien

**Technical Task Force
HYPOCHLORITE**

**BENEFITS AND SAFETY ASPECTS OF
HYPOCHLORITE
FORMULATED IN DOMESTIC PRODUCTS**

SCIENTIFIC DOSSIER

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TABLE OF CONTENTS

FOREWORD	10
1. GENERAL INTRODUCTION	10
1.1. Background information.....	10
1.2. Chemistry	12
1.3. Hypochlorite manufacture	14
1.3.1. Power consumption and efficiencies.....	14
1.3.2. Mercury emissions	15
1.4. References	17
2. NEEDS AND BENEFITS	18
2.1. Domestic applications - overview	18
2.2. Cleaning.....	18
2.2.1. Bleaching - Laundry benefits of hypochlorite.....	18
2.2.2. Stain removal.....	20
2.2.3. Malodour removal	20
2.3. Disinfection	20
2.3.1. Sources of infection and disease	21
2.3.1.1. Evidence of pathogens in the house and in the workplace	21
2.3.1.2. Transmission of pathogens.....	23
2.3.2. Disease statistics.....	26
2.3.2.1. Food poisoning.....	26
2.3.2.2 Other diseases	28
2.3.3. Disinfectant efficiency	29
2.3.3.1. Disinfection through cleaning.....	29
2.3.3.2. Disinfection with hypochlorite	29
2.3.4. Conclusions about disinfection	33
2.4. Other uses of hypochlorite	34
2.5. General conclusions	34
2.6. References	35
3. HUMAN SAFETY	40
3.1. Concentration and regulatory labelling.....	40
3.2. Exposure routes	41
3.2.1. Normal.....	41
3.2.2. Accidental.....	42

3.3. Toxicological data	42
3.3.1. Acute toxicity	42
3.3.2. Skin irritation	42
3.3.3. Eye irritation.....	43
3.3.4. Sensitisation	43
3.3.5. Chronic toxicity	43
3.3.6. Genotoxicity	44
3.3.7. Reproductive toxicity	45
3.3.8. Toxicity of main by-products	45
3.4. Consumer safety experience.....	46
3.4.1. Effects of misuse	46
3.4.1.1. Effects on eyes and skin.....	46
3.4.1.2. Ingestion.....	47
3.4.1.3. Inhalation.....	47
3.4.2. Data from Poison Control Centres	48
3.4.3. Child resistant packaging	51
3.5. Summary.....	52
3.6. References	53-54
4. ENVIRONMENTAL SAFETY	56
4.1. Physico-chemical properties of hypochlorite.....	56
4.2. Fate & Exposure.....	57
4.2.1. General Chemistry of hypochlorite- reaction products and impurities.....	57
4.2.2. Reactions of hypochlorite during domestic use	58
4.2.2.1. Reactions during toilet bowl cleaning.....	59
4.2.2.2. Reactions during laundry bleaching.....	61
4.2.2.3. Reactions during hard surface cleaning	64
4.2.3. Reactions of hypochlorite after use.....	65
4.2.3.1. Reactions with sewage	65
4.2.3.2. Decay kinetics of hypochlorite in sewage and surface waters.....	68
4.2.3.3. Reactions in the atmosphere	70
4.2.4. Field study results - in situ monitoring of AOX formation from hypochlorite.....	71
4.2.5. Fate of halogenated by-products	72
4.2.5.1. Atmospheric reactions of the volatile halogenated by-products.....	72
4.2.5.2. (Bio)degradability and treatability.....	74
4.2.5.3. Adsorption – Desorption.....	76
4.2.6. Summary of AOX predicted environmental concentrations	76
4.2.6.1. General	76
4.2.6.2. For toilet bowl cleaning	76
4.2.6.3. During laundry cycle.....	76
4.2.6.4. In household cleaning	78
4.2.6.5. From total domestic bleach use.....	78

4.3. Effects	79
4.3.1. Effects of hypochlorite on sewage treatment	79
4.3.2. Ecotoxicological effects	80
4.2.3.1. Hypochlorite and chloroamines	80
4.2.3.2. Organohalogen compounds.....	81
4.4. Organohalogens in the environment	84
4.4.1. Natural organohalogens.....	84
4.4.2. Background organohalogen levels	86
4.5. Summary.....	86
4.6. References	88-97

Appendix contents list	99-100
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Appendix with Environmental Safety data

LIST OF TABLES

Table 1.1.	Domestic hypochlorite consumption in Europe (as 3-5% commercial product)	p 11
Table 1.2.	Power demand in hypochlorite production (in kWh/te)	p 15
Table 1.3.	Hypochlorite production - mercury balance	p 15
Table 2.1.	Relative abundance of pathogens generally found in the home	p 21
Table 2.2.	Infections which can be caused by contaminated food and water	p 24
Table 2.3.	Activity of anti-microbial agents on various microbial types	p 30
Table 2.4.	Effectiveness of a range of disinfectants against <i>Bacillus subtilis</i> spores (log kills)	p 33
Table 3.1.	Overview of hypochlorite concentrations in European countries	p 40
Table 3.2.	Exposure Routes to hypochlorite reported by Poison Control Centres	p 48
Table 3.3.	Accidents with cleaning agents in the Netherlands (1988)	p 49
Table 3.4.	Exposures to cleaners and bleaches in the UK	p 50
Table 3.5.	Sources of bleach ingestion in the UK (HASS, unpublished)	p 51
Table 4.1.	Physico-chemical properties of 15 % (w/w) sodium hypochlorite solution.	p 56
Table 4.2.	Typical in-use NaOCl concentrations and reaction conditions	p 59
Table 4.3.	Expected formation of OBPs in the toilet bowl according to Peeters (1991) for a contact time >20 minutes.	p 61
Table 4.4.	Overview of organohalogens formed during laundry bleaching	p 63
Table 4.5.	Measured versus calculated chloroform levels in air after domestic use of hypochlorite.	p 73

Table 4.6. Overview of freshwater acute ecotoxicity and microcosm MATC data for hypochlorite and monochloramine p 80

Table 4.7. Overview of sea water acute and chronic ecotoxicity data for hypochlorite, chlorine gas and monochloramine. p 81

Tables A1-A27 in appendix of Environmental Safety data

LIST OF FIGURES

Figure 1.1.	Simulated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M Cl ₂ in water at standard temperature and pressure.	p. 13
Figure 2.1.	Reported cases of food poisoning in the UK (FAO/WHO, 1992).	p. 27
Figure 4.1.	Schematic overview of hypochlorite-related reaction routes.	p. 58
Figure 4.2.	Disinfection by-products in drinking water (Krasner <i>et al</i> , 1989).	p. 60
Figure 4.3.	Identification of the major OBPs in a laundry bleaching experiment	p. 62
Figure 4.4.	AOX formation in raw domestic sewage as a function of the NaOCl added.	p. 67
Figure 4.5.	Modelling of the decay of FAC and formation/decay of chloramine during transport in the environment.	p. 70
Figure 4.6.	Estimation of AOX (non-volatile) and THM levels after toilet bowl cleaning in various environmental compartments.	p. 77
Figure 4.7.	AOX after laundry cycle.	p. 78
Figure 4.8.	AOX levels in the environmental compartments, sewage, secondary effluent and surface water, after total domestic use of bleach	p. 79

GLOSSARY OF TERMS AND UNITS IN THIS DOSSIER

- * **FAC** = Free Available Chlorine
- * **CAC** = Combined Available Chlorine
- * **TAC** = FAC + CAC = Total Available Chlorine

These chemical species are expressed as Cl₂ concentration
(Mass Cl₂/Mass or Mass Cl₂/Volume) :

- * **TRO** = Total Residual Oxidant

The term 'active chlorine' is sometimes used as a synonym of 'available chlorine' (Av. Cl₂).

Conversion between Av.Cl₂ (FAC) and NaOCl concentration: **1.05 x Av.Cl₂ (%) = NaOCl (%)**

The hypochlorite concentration is ideally expressed as % NaOCl and not as available Cl₂ or active chlorine.

However, to allow a comparison between this document and legal criteria (expressing NaOCl solutions in available Cl₂ or active chlorine content) we used available Cl₂ and active chlorine in this dossier.

- * **AOX** = Adsorbable Organic Halogens
- * **AOXFP** = AOX Formation Potential (of a molecule or a solution)
- * **POX** = Purgeable Organic Halogens
(POX can be part of AOX if the sample is not purged prior to analysis)
- * **EOX** = Extractable Organic Halogens (solvent: pentane, cyclohexane, petroleum-ether,)

These analytical parameters have as units halide (X) concentration (Mass X/Mass, or Mass X/Volume) :

- * **THMs** = Trihalomethanes
- * **THMFP** = THM Formation Potential
- * **TOX** = Total Organic Halogen
- * **OBPs** = Organohalogen By-Products (including possible (bio)degradation products)
- * **VOCs** = Volatile Organic Compounds
- * **TOC** = Total Organic Carbon

The units of these parameters are as halogenated molecule concentration
(Mass/Mass or Mass/Volume) :

- * **COD** = Chemical Oxygen Demand (mg O₂/l)
- * **BOD** = Biochemical Oxygen Demand

FOREWORD

In many European countries, hypochlorite solutions have widespread household applications in surface cleaning, laundry and disinfection. The acceptability these household uses is currently the subject of an intensive debate. Constructive discussions require a good database on relevant aspects of the use of such chemicals. This Support Dossier deals with information on the environmental and human safety evaluation of

hypochlorite, and on its benefits as a disinfecting, deodorising and stain removing agent. The objective was to summarise a large body of non-aggregated data into a clear and systematic review, backed up wherever possible by reliable references. The dossier is intended as a 'living document', and will be updated at regular intervals.

1. GENERAL INTRODUCTION

1.1. BACKGROUND INFORMATION

Following the discovery of “dephlogisticated salt spirit” gas by Swedish chemist Carl Wilhelm Scheele in 1774, the French chemist, Claude-Louis Berthollet worked on bleaching solutions of this gas in 1787. In 1810 the gas was named chlorine by the English chemist, Davy.

A chemical factory in Paris managed by Léonard Alban, the Javel company, adapted the Berthollet process. The factory had been set up in 1778 on the river Seine. It was financed by a group of noblemen from the court of Louis XVI. The King's brother, the Count of Artois, gave his name to the factory.

The decision was taken here in 1787 to dissolve chlorine gas in a solution of “pot ash” lye, and a stable concentrated solution was obtained, called “liqueur de Javel” by Alban. This product, potassium hypochlorite, was rapidly advertised and stored in various places in France and England (Smith, 1979).

Berthollet would initially not accept that chlorine, “oxydated muriatic acid” gas, was a diatom. He accepted this fact only after Davy's publications in 1816.

Berthollet thought that chlorine was a molecule, and the name for this molecule is hypochlorous acid (HOCl).

Davy and Berthollet had, in fact, discovered the two forms of chlorine: in water at pH 7 it is mainly HOCl, whilst in the atmosphere it is Cl₂ (Sadoun-Goupil, 1978).

In 1820, Labarraque replaced potash liquor by the cheaper caustic soda liquor and obtained sodium hypochlorite solutions which were called “Eau de Labarraque” and used for disinfection (Holleman & Wiberg, 1976). The product was also used for the bleaching in paper making.

Today, hypochlorite is often chosen instead of chlorine for commercial bleaching, where it is largely produced on-site for captive consumption.

It is used as a laundry and household bleach and disinfectant, as a sanitiser for swimming pools, and as a disinfectant for municipal drinking water and sewage.

In food processing, sodium hypochlorite is widely

employed as a disinfectant.

Another important use for hypochlorite solutions is the prevention of microbial growth in sea water used for secondary oil recovery. This is necessary because otherwise slime growth would clog the oil-bearing strata (Ullmann, 1986).

Sodium hypochlorite is known to be one of the most effective and fast-acting germicides. It is effective against a wide spectrum of micro-organisms. The correct use of disinfectants containing sodium hypochlorite controls infection by breaking the cycle of disease transmission from infected to healthy people or animals. The right to health is a key aspect of human rights declarations, including those of the United Nations. Control of disease-causing organisms is a step towards safeguarding this right.

Sodium hypochlorite is a proven active ingredient used in hygiene cleansers, and since early in the twentieth century it has been accepted throughout the developed world as a safe way of helping to ensure that diseases such as cholera and typhoid do not claim any more victims. The cholera pandemic currently (1993-1994) raging

unchecked in South America (Peru, Ecuador and other countries) illustrates that without adequate disinfection of the public water supply, deaths can rapidly reach tens of thousands even in the closing years of the twentieth century.

The hypochlorite ion itself is a relatively poor disinfectant in comparison with hypochlorous acid, but it serves as a reservoir for the latter by hydrolysis. The detailed mechanism by which HOCl kills micro-organisms has not been well established, but sufficient experimental evidence has been obtained to strongly suggest that the mode of action involves penetration of the cell membrane followed by reaction with enzyme systems.

Hypochlorite is a widely used domestic chemical. Apart from its disinfecting properties, the chemical has benefits in cleaning, removing stains and in deodorising. The household consumption varies in Europe over a wide range from 0.22-11.8 kg commercial product per inhabitant and per year in 1994 (*Table 1.1*).

The domestic use of hypochlorite represents on average 39% of total hypochlorite production.

Table 1.1. Domestic hypochlorite consumption in Europe (as 3-5% commercial product)

Country	Total Consumption (‘000 te/year)	Per capita consumption (kg/year/inhabitant)
Belgium & Luxembourg	62	6.0
The Netherlands	26	1.7
Scandinavia	5.8	0.25
Spain	464	11.8
France	350	6.2
Greece	50	4.9
Italy	320	5.4
Portugal	95	9.5
Germany (East & West)	19	0.22
United Kingdom	175	2.9

Data based on AISE/Euro Chlor statistics (1996, unpublished)

NB: 1 metric tonne (te) = 1000 kg

In the second chapter of this dossier, a detailed evaluation is made of the requirements and performance of hypochlorite in the household. In particular, attention is given to the risk posed by pathogens in the home, and the potential of hypochlorite to reduce infection.

Disease organisms can spread in kitchens, bathrooms, toilets and all other areas in private houses used by several individuals, as well as in public buildings, the catering industry, swimming pools and hospitals. There is therefore a need for products based on hypochlorites which can successfully prevent the transmission of disease.

The third chapter deals with human and consumer safety aspects, classification and labelling, toxicology and Poison Control Centre experience. In addition to human safety, environmental aspects of chemicals are increasingly attracting attention. This is dealt with in the fourth chapter.

1.2. CHEMISTRY

When gaseous chlorine is passed into water it first of all dissolves and then disproportionates into hydrochloric acid and hypochlorous acid in a specific reversible reaction, of which the equilibrium position is mainly on the left-hand side, as shown in *Reaction 1* (Ullmann, 1986).

When Cl_2 is added to strong bases such as caustic or lime the reaction occurs stepwise, as illustrated in *Reaction 2* (Kirk-Othmer 1979).

Hypochlorous acid exists only in aqueous solutions and cannot be isolated as a pure substance. Any attempt to dehydrate

A Risk Assessment is currently being carried out on behalf of the European Commission, covering all aspects of human and environmental safety. One part of the risk assessment discussion is the interaction of hypochlorite itself with the environment.

In addition, studies are continuously underway to determine the fate and effects of reaction by-products, such as the small amounts of organic halogenated by-products formed during the use of hypochlorite.

These are of special interest, as some organohalogens are relatively resistant to degradation and can be associated with adverse ecotoxicological effects.

The formation and ecotoxicological assessment of by-products receives considerable attention in this dossier.

hypochlorous acid leads to the formation of Cl_2O . Dilute aqueous solutions of hypochlorous acid decompose slowly in the dark by two routes, to hydrochloric acid and chlorate (*Reaction 3*), and to hydrochloric acid and oxygen (*Reaction 4*). The latter reaction is accelerated by light and metal impurities.

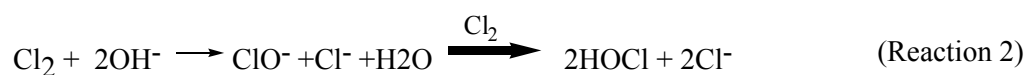
Though hypochlorous acid is a strong oxidising agent, its salts are less strongly oxidising. Hypochlorous acid is a very weak acid in aqueous solution and its salts hydrolyse easily to free hypochlorous acid as shown in *Reaction 5*.

Thus, in solution the oxidising potential of hypochlorites depends on the extent to which such hydrolysis takes place. In alkaline conditions, the equilibrium is shifted to the left and the oxidising potential is lower. If the solution is neutral, the equilibrium in *Reaction 5* shifts to the right, and under acid conditions the further equilibrium of *Reaction 2* is established.

It is important to know that chlorine can be found in water in three different chemical forms: Cl_2 , HOCl or OCl^- (*Figure 1.1*).

When the $\text{pH} < 4$, a mix of Cl_2 and HOCl occurs. At $\text{pH} 4$ 100% is HOCl. Between $\text{pH} 5$ and 10, a mixing of HOCl and OCl^- occurs. At $\text{pH} 7.5$, the ratio OCl^-/HOCl is 1. For a $\text{pH} > 11$, 100% is OCl^- . The reaction capacity of the different forms of chlorine in water increases from ClO^- to Cl_2 , and decreases with the pH . At $\text{pH} 7.5$ the ratio OCl^-/HOCl is 1. On the other hand, the solubility of Cl_2 in water is very low.

Key chemical reactions



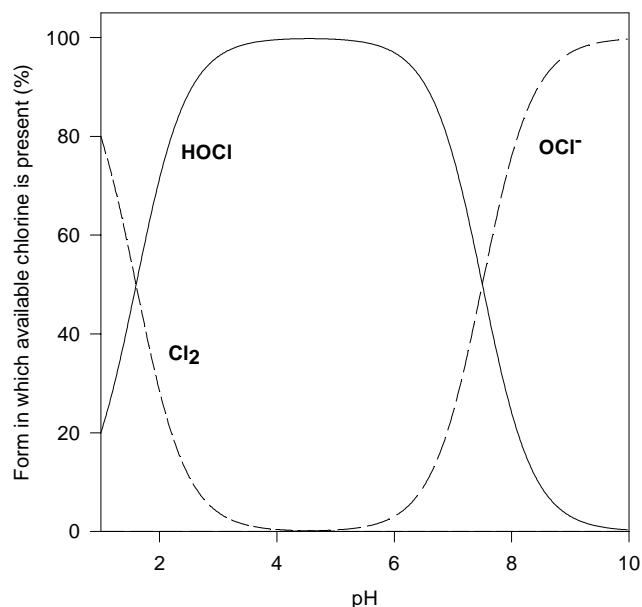


Figure 1.1. Simulated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M Cl₂ in water at standard temperature and pressure.

1.3. HYPOCHLORITE MANUFACTURE

The electrolytic preparation of hypochlorite from sodium chloride has taken place since the early nineteenth century. Most of the major developments in mercury cell and diaphragm cell technologies for the production of chlorine and caustic soda liquor took place between 1883 and 1893 (Jackson, 1983). Industrial scale use began between 1890 and 1899. At the beginning of the 20th century the traditional routes for the manufacture of bleach liquors were used less as the chlorine-caustic soda industry expanded rapidly, making available large quantities of reasonably-priced chlorine (Holleman & Wiberg, 1976).

Today, sodium hypochlorite is manufactured by the absorption of chlorine in 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 up with chlorine to provide finished material.

In recent years, concern regarding the safety hazards associated with liquid chlorine has grown. Several major cities now restrict transportation of chlorine (as Cl₂) within their boundaries. This has increased the popularity of sodium hypochlorite solutions as a source of chlorine, in spite of the relatively high cost.

1.3.1. POWER CONSUMPTION AND EFFICIENCIES

The major power requirement in the manufacture

of sodium hypochlorite solution is the production

of chlorine and sodium hydroxide solution (caustic soda liquor) in the electrolyser, although credit should also be given for the fuel value of the hydrogen produced. The power required to make the brine can generally be ignored although it will be larger if white crystal salt is used instead of solution-mined brine. The use of white crystal salts, however, can give less environmental impact if the crystallisation process is used to recover impurities from the parent solution-mined brine.

These and many other factors will obviously lead to a wide site-to-site variation in the energy required to manufacture sodium hypochlorite. The power consumption will also vary significantly with the load on the cell-room which makes it even more difficult to give precise figures. The data given here are therefore a guideline only, although they also allow a comparison between the three cell technologies.

Good estimates can be obtained from reported power consumptions such as those given in a series of books entitled “Modern Chlor-alkali Technology” (1992, 1994). It will be assumed that the hydrogen co-produced in the chlor-alkali cell

is burnt in an on-site electricity power station and that one-third of the thermal energy is recovered as electrical energy. This works out to 50 kWh/te of 16% sodium hypochlorite solution. It is also assumed that exactly two moles of caustic are used for one mole of chlorine in sodium hypochlorite solution production. This avoids the need to attribute energy requirements to each chemical individually, although it makes no allowance for the slight excess of sodium hydroxide in the final product. However this sodium hydroxide excess is unlikely to distort the result very much.

It should be noted that the diaphragm technology figure in *Table 1.2* is slightly misleading. Diaphragm cell caustic soda liquor is relatively dilute and contains substantial amounts of sodium chloride. Before conversion to hypochlorite, the solution is concentrated by evaporation, which is energy-intensive. The energy cost for this evaporation has not been included in the calculation of the table. Although membrane cell caustic liquor is also weaker than mercury cell caustic liquor and it is concentrated for many purposes by evaporation, this is not necessary for the manufacture of sodium hypochlorite solution.

Table 1.2. Power demand in hypochlorite production (in kWh/te)

Cell technology	Power demand	Total power demand for 16% hypo liquor
Membrane	2200-2500 (as 100% NaOH)	350 - 400
Diaphragm	2700	440
Mercury	3800	560 - 610

1.3.2. MERCURY EMISSIONS

The manufacture of bleach with mercury cell technology is associated with some mercury

emission.

Over the years, a significant reduction of this emission has been realised by improved treatment technologies.

The data presented below (*Table 1.3*) are the Euro Chlor Mercury Balance Figures for 1977 versus

1994 for manufacturing sites in the European Community. The figures are expressed as grams of mercury per te of chlorine capacity, weighted averages. The approximate number of manufacturing sites involved was 70.

Table 1.3. Hypochlorite production - mercury balance

	g Hg/te Cl ₂ capacity	
	1977	1994
Mercury emission in products	5.5	0.4
Mercury emission in aqueous effluents	9.4	0.2
Mercury emission in waste gases		
Process exhaust gases	4.9	0.5
Cell-room ventilation air	6.8	1.32
Mercury contained in waste disposal	21.7	11.44
Mercury consumption unaccounted for	46.4	2.6
Total Mercury consumption	94.7	16.6

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 73.0g Hg/te Cl₂ in 1977, and have decreased considerably to 5.2g Hg/te Cl₂ in 1994.

There are no measured data for mercury emissions related to hypochlorite production. However, assuming that 16% hypochlorite liquor consumes 0.16 te of chlorine per te of liquor and that 70% mercury cells are used, the figures for mercury emissions per te of hypo liquor become 0.83g in 1994, versus 11.68g in 1977.

In comparison, natural mercury cycles involve about 150,000 te per year on a world scale; 10,000 te per year are emitted by metal processing and fuel burning, and 7,000 te of mercury are mined every year.

In the context of OSPARCOM (Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic), the recommendation has been made to reduce by 1996 the atmospheric Hg emissions for each site to below 2g/te chlorine capacity.

Of the total amount of chlorine produced by electrolysis, around 1% ends up in domestic hypochlorite bleach products (based on FIFE 1995, unpublished & AISE/Euro Chlor statistics 1996, unpublished).

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2. NEEDS AND BENEFITS

The contents of this chapter have been peer reviewed by Prof P.A.D. Grimont from the Institut Pasteur (Paris).

2.1. DOMESTIC APPLICATIONS - OVERVIEW

Sodium hypochlorite is widely used as a cleaning agent in diverse domestic applications worldwide, due to a unique combination of properties:

- * *excellent stain removal*
- * *removal of odours (by eliminating micro-organisms and oxidising odorous compounds)*
- * *bleaching properties*
- * *highly-effective disinfectant action*

These are combined with cost-effectiveness and ready availability.

In the home, the cleaning and hygienic properties of hypochlorite are useful on floors, kitchen and bathroom surfaces, and fabrics, where its low-temperature bleaching properties contribute to energy savings.

2.2. CLEANING

The performance of hypochlorite in removing stains and bad odours, as well as in the bleaching

of laundry, are all associated with hypochlorite's strong oxidative power.

2.2.1. BLEACHING - LAUNDRY BENEFITS OF HYPOCHLORITE

A 3-5% sodium hypochlorite solution has been sold for many years to bleach fabrics. Its ability to "whiten" cotton is well known and appreciated by the consumer. It can remove many stains that cause garments to be discarded prematurely (Wentz *et al*, 1975).

With the move to energy conservation and greater concentration on environmental issues, cooler wash temperatures are being used more frequently than ever before in fabric laundering.

This inevitably leads to a deterioration in whiteness of fabrics, which can be compensated for by hypochlorite bleach treatment.

The low temperature reactivity of hypochlorite (Simpson, 1983) contributes to optimum fabric whitening and overall energy saving.

At 40°C in fabric washing, germs are not killed and laundry can remain contaminated. If hypochlorite is used virtually all germs are destroyed (Walter & Schillinger, 1975; Gamper & Riggs, 1983).

There are a variety of hypochlorite uses in laundry, depending on geographical location and other issues. It is mostly used with white or light-coloured cotton or polyester fabrics. The product may damage some synthetic fibres like nylon and it is not suitable for use with silk or wool.

In addition to its routine use with many white

fabric items - like underwear, nappies, kitchen cloths, handkerchiefs, towels or heavily soiled items - hypochlorite is often the product on which the consumer relies when dealing with stubborn stains that detergent alone fails to remove.

The product can be used:

a) In **hand washing**: A very widespread practice is to soak white garments in a bleach solution containing 250-500 ppm of sodium hypochlorite, although higher concentrations may be used in some cases. In the past, it was a common practice to soak garments overnight. Today, garments are rarely soaked for more than 20-30 minutes before washing with or without detergent.

b) In the **washing machine**:

- * When the washing machine has a bleach dispenser, hypochlorite can be added here. This means in most cases that the product will be added in the second rinse cycle, releasing a bleach solution to provide 200-250 ppm of hypochlorite, provided a standard product containing 4-5% active chlorine is used.
- * If the washing machine has no bleach dispenser, the user has various options. A short complete wash cycle may be used, dosing only hypochlorite in the dispenser. As a next step a standard wash cycle with detergent may be used. Alternatively, hypochlorite may be used in the pre-wash cycle available on many washing machines, or it may be added manually during the rinse cycle.

Hypochlorite may be added together with the detergent. It provides bleaching capacity, specially when the wash is performed at low temperature (40°C or below). In any case, hypochlorite disinfects, a process not carried out to the same extent by detergent alone, especially at low temperatures.

Summary of benefits:

- Tests show that hypochlorite is unmatched in removing bleachable stains and soils from white fabrics.
- It is an unparalleled laundry disinfectant, not only from an efficacy point of view but also from an economic one.
- The continuous use of detergent alone on white garments leads to a gradual greying, making garments appear dull, dingy and prematurely old. Hypochlorite is very efficient in removing this greyness.
- The combined bleaching and disinfecting effect of hypochlorite make it a very efficient odour removal agent, eliminating both the smell of food residues and offensive odours produced when traces of organic material are decomposed by micro-organisms.
- Many detergents - even those containing alternatives to bleach such as perborate and percarbonate with activators - need to be used at 50-60°C to reach a good efficacy. Hypochlorite enables consumers to wash laundry at lower temperatures, saving energy, which benefits the consumer in the short term and the environment in the long term.

2.2.2. STAIN REMOVAL

Hypochlorite's high chemical reactivity towards complex organic chromophoric structures which make up coloured soils (such as unsaturated fatty acids and esters, carbohydrates and proteins) makes it a good stain remover (Smith, 1983).

Whether stains are on fabrics, household surfaces or toilets, hypochlorite is widely recognised as superior to other products for keeping surfaces clean and stain-free.

For example, mould and mildew - which are regarded as stains by many people - can successfully be removed by hypochlorite, which also kills the micro-organisms. Hypochlorite products can often restore stained surfaces to their original appearance.

2.2.3. MALODOUR REMOVAL

Areas of the home known to be breeding sites for bacteria which produce unpleasant odours (such as drains, sinks, discharge pipes, toilets and waste bins) have been traditional areas for hypochlorite application. The high organic content of bad-smelling soils makes bleach particularly effective. Odorous components such as sulphide, reduced organic sulphur compounds, aldehydes and esters are effectively oxidised by hypochlorite.

The presence of bacteria on wet soiled areas leads to development of unpleasant odours.

In addition to breaking down soil molecules into more easily removable components, hypochlorite also kills the bacteria responsible for malodour generation. Hypochlorite products are recognised by the consumer as the only cleaning agents which both deodorise and disinfect such areas.

2.3. DISINFECTION

In this section, the need for effective hygiene in the home is reviewed, together with the role hypochlorite can play in maintenance of hygiene. Although hygiene education can significantly increase the awareness of the population of the habits needed for better health, it is clear that good hygiene practice needs to

be accompanied by effective disinfectant products to deliver hygiene where there is any real risk of infection. The fact that this chapter is more elaborate than the cleaning section reflects the fact that more data of scientific quality is available on disinfection than on the other applications.

2.3.1. SOURCES OF INFECTION AND DISEASE

2.3.1.1. EVIDENCE OF PATHOGENS IN THE HOME AND THE WORKPLACE

Pathogens are ubiquitous and can be found all over the home, on surfaces, in the air and on and within the human body. Most pathogens can survive for periods varying from several minutes to weeks depending on the humidity and their ability to form biofilms.

Numerous surveys have been carried out to assess the number and types of micro-organisms found in the home and in public places. It has been found that *Salmonella*, *Pseudomonas* and *Enterobacter spp* occur in most homes (Scott, 1990). The presence of potentially harmful micro-organisms in sufficient numbers to cause disease is well established (Darlow & Bale, 1959; Mendes & Lynch, 1976; Mendes, 1977; Mendes *et al*, 1978; Finch *et al*, 1978; Bloomfield, 1978; Scott *et al*, 1981; Scott *et al*, 1982; Scott & Bloomfield, 1985; Borneff *et al*, 1988a,b; Scott, 1996).

Studies on the bacteriological flora in the kitchen revealed for example a high degree of contamination (>100 colonies/25 cm²) in places such as surfaces, sinks and cloths. The types of pathogens generally present in the domestic environment are given in Table 2.1 below.

Toilet bowls and fittings may be reservoirs of infection. Faecal bacteria have been found on toilet seats (> 1000 cfu/ 25 cm² - Mendes and Lynch, 1976), door handles and hand-towels (Scott, 1990). Floors and mats can also be contaminated. Waste bins are also a serious reservoir of pathogens. They are visited by insects which allow transportation of the micro-organisms to food surfaces (Mayr, 1983).

Domestic animals such as cats can transmit pathogens to contaminate foods (Smith, 1996).

Table 2.1: Relative abundance of pathogens generally found in the home

Type of potential pathogen	Relative abundance
Vegetative bacteria	+++
Bacterial spores	++
Viruses	++
Fungi	
- Moulds	++
- Yeasts	++
Lice / Mites	+

All of the above groups of potentially pathogenic organisms can be associated with human infections. There are numerous routes by which contamination can occur.

Guidelines on acceptable levels of microbes vary, but can be based on those for the food and beverage industry: <10-20 micro-organisms/cm² (Niskanen & Poha, 1977).

In a healthy person, a typical intake level of micro-organisms needed to cause infection is generally $>10^5$. However, in susceptible groups (the sick, elderly, pregnant women, children), intake levels as low as 10^3 germs can cause infection. For example, kitchen cloths can contain up to 10^6 germs per cm^2 (Mendes *et al*, 1978), and therefore can be a source of transmission and infection.

Microbial infections due to lack of hygiene or poor quality drinking water are considered by WHO to be number one priority in protecting humans from environmental hazards (WHO, 1992).

Concern has been expressed that a reduction in standards in the hospital environment had led to an increase in cross-infection (Rel-Calero, 1991). In hospitals where susceptible groups are centralised, pathogenic bacteria are found in fractions over 60%, compared with the population norm, which is 6% (Bloomfield, 1978). Under favourable conditions bacteria can multiply rapidly, 1 bacterium becoming 10^6 in less than 24 hours. Thus, even the presence of less than 10 bacteria can potentially become harmful under favourable growth conditions. Assessments have been made in wet areas (kitchens, bathrooms and toilets) and also on dry surfaces such as door handles, floors and work surfaces. For example, *Pseudomonas spp.* were shown to be viable for several days on dry surfaces, due to the formation of biofilms (McEldowney & Fletcher, 1988).

In toilets, significant numbers of bacteria are found (Newsom, 1972; Mendes & Lynch, 1976; Mendes, 1977). The areas of highest risk are those where there is a likelihood of cross infection, such as the toilet seat (Scott *et al*, 1982). Splashing of water during flushing is another potential source of infection (Gerba *et al*, 1975).

In the UK more than 50% of schools have too few toilets to comply with government regulations. In addition, many primary schools are still using outside toilets (NUT, 1992).

With inadequate cleaning, this has been seen as contributory to the spread of diseases such as dysentery which thrives in cold damp conditions.

The relationship between damp housing, mould growth and symptomatic health state has been well established (Strachan & Elton, 1986; Martin *et al*, 1987; Hunter & Grant, 1988; Platt *et al*, 1989; Strachan *et al*, 1990).

In a recent survey, damp was found in 31% of dwellings and actual mould growth in 46%. The greater the mould growth, the higher the proportion of respondents reporting symptoms of illness.

The concentration of spores in the air is directly correlated to high blood pressure, nervous problems, palpitations and breathlessness.

It was concluded that damp and mouldy living conditions have an adverse effect on symptomatic health, particularly among children. Moulds can exacerbate asthma and other respiratory diseases.

The extent to which damp and moulds occur in homes is unknown, but the problem is increasing as double-glazed, insulated and draught-free homes allow condensation to form. If allowed to build up on porous surfaces, this leads inevitably to mould.

The Institute of Environmental Health Officers recommends that mould should be "wiped away with a solution of diluted bleach", at least as a temporary solution.

Epidemiological investigations have shown that increasing health problems, especially gastroenteritis, are caused by contaminated food. This contamination can occur either because the product (such as meat, offal or milk) comes from contaminated animals, or during its preparation. Inadequate hygiene in the home increases the infectious risk by cross-contamination from foods to surfaces to other foods. In Germany there are 100,000-1 million cases of such diseases per year (Borneff, 1989). Pets can also be a source of cross-contamination. They can contaminate floors, seats, tables or toys, and indirectly, children or food. Insects can also be carriers of

2.3.1.2. TRANSMISSION OF PATHOGENS

There are three major sources of infection: directly through consumption of contaminated food and water; indirectly via the hands; or cross-infection from contaminated items such as cloths, surfaces, pets or house mites.

Direct from food, water and air

Analysis of raw and cooked meats shows potentially pathogenic bacteria in the food and on the premises (Tebbutt, 1986). Bakery products and salads are also a potential source of food poisoning; sandwiches in particular have been linked with food poisoning outbreaks. These items require considerable handling during preparation, and storage at ambient temperature is common.

Coleslaw salads have also been implicated in outbreaks of food poisoning (Greenwood *et al*, 1985).

Food poisoning outbreaks of *Salmonella enteritidis* are often due to contamination of eggs or chickens.

pathogens, for example cockroaches in towns or flies in the country. Diseases related to the house dust mite (e.g. *Dermatophagoides farinae*) have been studied (for example, Sporik & Platts-Mills, 1992).

Evidence shows that house dust mite exposure is not only associated with the majority of asthma cases in children and young adults, but is also related to asthma development.

Hypochlorite is not particularly suited to reducing house mite populations or eliminating insects, however.

In the catering industry, the increase of bacteria can occur in dishes used for preparing omelettes. Therefore, contamination of other dishes or food is foreseeable. Different *Salmonella spp* can contaminate minced meat, cream, sauces and cakes. *Listeria spp* in cheeses are also a well-known contaminants of food. Recent food poisoning outbreaks with haemorrhagic diarrhoea or haemolytic uremic syndrome are attributed to pathogenic *Escherichia coli* (such as type O157:H7).

Rinsing vegetables in polluted water can contaminate them. *Shigella sonnei* on imported lettuce caused dysentery outbreaks in the UK, Sweden and Norway (Kapperud *et al*, 1995).

Shigella contamination is always associated with human activity (faecal contamination of hands). In Italy and the Netherlands, high levels of lettuce and other vegetables (68% and 22%, respectively) contain *Salmonella spp*. (Ercolani, 1976; Tamminga *et al*, 1978).

Water can also cause disease if it is untreated or polluted (Green *et al*, 1966). In Spain, hypochlorite (without additives) is prescribed for disinfecting polluted domestic drinking water (Spanish Sanitary Regulation on Bleaches, B.O.A, 1993).

Infections caused by contaminated food and water are illustrated in *Table 2.2*. Numerous examples of widespread food poisoning and their sources are detailed by WHO (1992) and others (Danielson *et al*, 1979; Anon, 1984; Hewitt *et al*, 1986; Acheson, 1988; Barrow, 1991).

Table 2.2. Infections which can be caused by contaminated food and water

Source	Organism	Disease
FOOD / WATER	<i>Salmonella spp</i>	Typhoid, Gastro-enteritis
	Pathogenic <i>Escherichia coli</i>	Gastro-enteritis, haemorrhagic diarrhoea, haemolytic uremic syndrome
	<i>Vibrio cholera</i>	Cholera
	<i>Yersinia enterocolitica</i>	Gastro-enteritis, Enterocolitis
	<i>Staphylococcus aureus</i>	Wound infections
	<i>Shigella sp.</i>	Bacillary dysentery
	<i>Clostridium botulinum</i>	Botulism
	<i>Clostridium perfringens</i>	Food poisoning
	Hepatitis Virus A	Infectious hepatitis
	<i>Bacillus cereus</i>	Food poisoning
	<i>Yersinia pseudo-tuberculosis</i>	Mesenteric lymphadenitis
	<i>Entamoeba histolytica</i>	Amoebic dysentery
	Viruses	Non-bacterial gastro-enteritis
	<i>Listeria monocytogenes</i>	Listeriosis
<i>Mycobacterium tuberculosis</i>	Tuberculosis	
<i>Coxiella burnetti</i>	Q Fever	

Contamination of foodstuffs can happen before they reach the household. However, pathogens from contaminated food can be spread in the kitchen during food preparation or storage. In this way, uncontaminated food can also get infected in the household.

A general higher level of hygiene in the kitchen or where the food is stored, will help prevent food-related infections.

Hypochlorite (or any other disinfectant) is not used in the home to disinfect food as such. However, vegetables such as lettuce can be soaked for a few minutes in water with a few drops of bleach to kill bacteria and then rinsed with tap water.

Hypochlorite is also effective for the disinfection of baby feeding utensils.

Transmission of contaminated aerosol droplets leading to cross infection (Favorova, 1969) and the role of airborne spores of fungi associated with allergic alveolitis have been reported (Flannigan *et al*, 1991).

Cross- and indirect contamination

Many cases of food poisoning are caused by infected food handlers. During food handling with the bare hands, there is a greater risk that food products will be contaminated, especially if these products are stored without cooling for long periods (Bryan, 1988).

Results suggest that where contaminated surfaces come into even brief contact with fingers, significant numbers of organisms can be transferred (Scott & Bloomfield, 1990b). Cross-contamination can for example occur via cloths, surfaces, pets, and the house mite. It is especially likely in the kitchen, bathroom and toilet.

Kitchens are a central room in the house, in addition to being a place to prepare and cook food. Thus, the risk of infection from the kitchen has increased, as children, guests and pets enter.

Kitchen cloths are a prime source of micro-organisms and contamination may range from 10^3 - 10^6 /cm² (Mendes *et al*, 1978). Where contaminated cloths or surfaces carrying even relatively low numbers of organisms come into contact with fingers or surfaces, organisms may be transferred in sufficient numbers to represent a potential infection hazard (Scott *et al*, 1981; Scott & Bloomfield, 1990a).

During the preparation of chickens, 74% of kitchen dish cloths together with other kitchen surfaces became contaminated (Kampelmacher, 1963; De Wit *et al*, 1979). Even after "cleaning" or washing-up, a significant number of surfaces and cloths were still contaminated.

Dempster *et al* (1973) and Gilbert (1969, 1986) have also demonstrated how easily undercooked or raw meats, as well as eggs (Humphrey *et al*, 1994) can contaminate food preparation areas with pathogenic organisms.

Van Vaerenberg (1991) illustrated the relevance of cross-contamination in a study on slaughterhouses, where *Salmonella spp* and Enterobacteria were transferred from contaminated to uncontaminated meat via working. As well as cleaning, a strict disinfection policy was recommended.

The results of an epidemiological investigation indicated that increasing health problems are caused by inadequate domestic hygiene. The study concluded that the use of household cleaners with germicidal properties does reduce the distribution of unwanted micro-organisms in the kitchen, and on surfaces in particular (Borneff, 1989).

Another study by Borneff *et al* (1988a,b) was carried out on cross-contamination by pathogens introduced into the kitchen from outdoors.

The authors found that only half the organisms introduced in the kitchen are removed by common cleaning procedures. However, when replaced by a hypochlorite product, bacteriologically clean surfaces were found.

It was concluded that infection links could be interrupted by household cleaners with biocidal activity, like hypochlorite. This was confirmed by analysing household utensils and surfaces. Kitchen work surfaces showed a high degree of cross-contamination. Disinfection with a 0.5% hypochlorite solution was found to eliminate the contamination.

In a study by Roberts (1982) of factors contributing to outbreaks of food poisoning in England and Wales, *Salmonella* was involved in 40% of all known cases; 25% of these cases were attributed to contamination in the home.

Of the factors contributing to the outbreak, about 10% could be attributed to infected food handlers and cross-contamination.

The report concludes that the general standard of hygiene in food premises could be improved to prevent cross-contamination by thorough cleaning and disinfection, especially when raw and cooked foods are being processed.

Many families have pets (cats, dogs, birds, turtles, hamsters), which can carry large numbers of germs on their paws from the outside, such as *Campylobacter spp.* This bacterium is often found on their coats and can be transferred easily by touch.

Cats and dogs carry a wide range of organisms which are also found in man (Bruner & Gillespie, 1966). Pets will not normally be disinfected before they enter the house. However, the regular use of a disinfectant to clean the areas which are visited by pets will help to reduce microbial contamination of floors and other areas.

2.3.2. DISEASE STATISTICS

2.3.2.1. FOOD POISONING

Food-borne disease data suggests that food poisoning is on the increase throughout the Western world. Data from the UK (FAO/WHO, 1992), Netherlands (Sockett, 1993), Germany (Kusch & Klare, 1992) and Spain (FAO/WHO, 1992) indicate that 50-80% of all outbreaks of food-borne disease originate in the home. Surveillance programmes and national data collection systems vary in quality within Europe. At present, the most accurate data are provided by the UK and the Netherlands.

The surveillance and control of *Campylobacter* infection has been carried out (Pearson & Healing, 1992).

Transfer of microbes from toilets to surrounding areas has been assessed (Darlow & Bale, 1959; Bound & Atkinson, 1966; Gerba *et al.*, 1975). Reports of diarrhoea outbreaks from the spread of *Shigella sonnei* have been made (Hutchinson, 1956). Houseflies are known mechanical vectors of *Shigella spp.* Seasons when flies and dysentery cases are prevalent often coincide. Houseflies can readily contaminate food and eating utensils (Levine & Levine, 1991).

The accumulation of waste in urban areas and increase in vermin level are further sources of potential infection in the home. For example, cockroaches (*Periplaneta americana*) transmit large numbers of bacteria, viruses, fungi and worm eggs (Agbodaze & Owusu, 1989).

In hospitals, floors and bedding can be a source of microbial contamination; rules specify distances between beds to restrict cross-contamination (Walter & Kundsinn, 1960). Obviously, shared instruments cause infection and it is important that these are sterilised between patients.

In the UK, statistics show a significant increase over 10 years (FAO/WHO, 1992) to over 70,000 cases in England and Wales in 1992 (*Figure 2.1*). Due to under-recording, this is thought to be an underestimate by a factor of 5-100. Surveys are planned to establish the true figure. These surveys will be based on those recently completed in the Netherlands, which indicate some 2.5 million cases of gastro-enteritis per year, whereas the data collection system identified only 300 cases per year (Hoogenboom - Verdegaal, 1992).

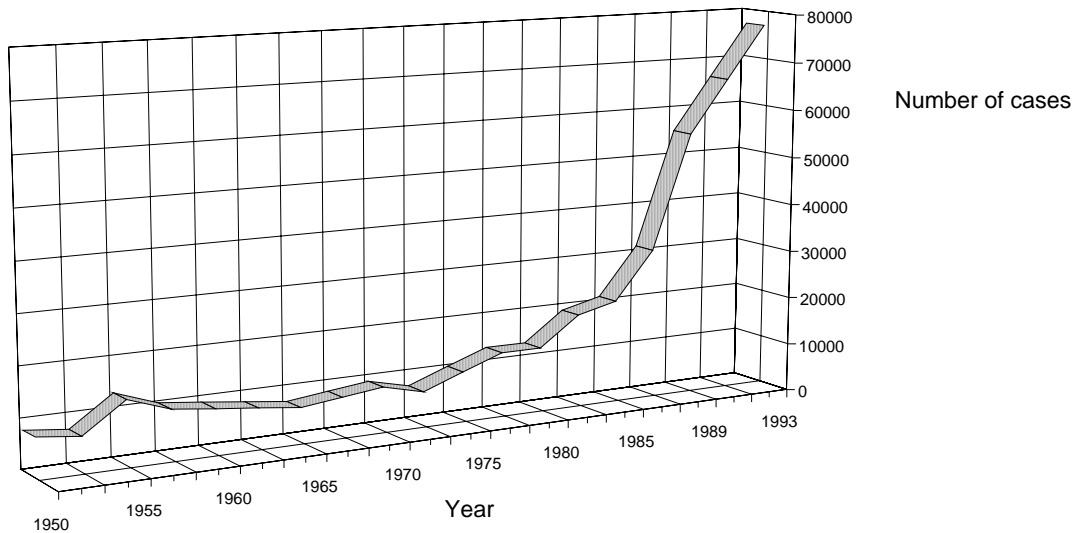


Figure 2.1. Reported cases of food poisoning in the UK (FAO/WHO, 1992).

In England and Wales, 1000-2000 meningitis and 3000-9000 dysentery cases are reported every year. A dysentery epidemic caused by *Shigella sonnei* was seen in Britain, with 7518 cases reported in the first 15 weeks of 1992 compared with 1708 for the same period in 1991.

Improved domestic hygiene can help reduce incidence and spread of such diseases.

Incidence of *Haemophilus meningitis* in four Welsh counties in children aged under 5 was found to be 12-44% higher than previously published for the UK (Howard *et al.*, 1991). Data available from France (FAO/WHO, 1992), Germany (Institute for Social Medicine and Epidemiology, Berlin) and Sweden (Andersson & de Jong, 1991; Sockett, 1993) show similar increases in reported incidence of food-borne illness during the 1980s.

Salmonellosis and *Campylobacter*-related enteritis are now the most important food borne infections (Sockett *et al.*, 1993). Salmonellosis and *Campylobacter*-related enteritis, which are self-limiting diseases in man, can last up to 3 days. Salmonellosis necessitates admission to hospital in about 20% of cases. The young, elderly, pregnant and immunologically suppressed are most susceptible and will hence suffer most. In extreme cases this can lead to death.

Several new water- and food-borne pathogens are emerging, the most important of which are *Listeria monocytogenes*, viruses such as Hepatitis A, *Yersinia spp* and infection due to *Cryptosporidium* (Galbraith, 1990).

Food poisoning does not only result from "eating out". Indeed, figures indicate greater incidence of food poisoning originating in the home (Communicable Disease Surveillance Centre, CDSC). However, take-away outlets have been suggested as posing high levels of health risk by the Audit Commission (The Audit Commission for Local Authorities in England and Wales, 1990).

The likelihood of food poisoning increases as food production and retailing becomes more sophisticated so that a contamination at one part of the chain can lead to severe consequences over a wide geographic area.

The trend towards more "natural" food has led to reduced processing and preservation, with greater emphasis on correct storage and reheating.

This contributes to the levels of bacterial contamination found in certain food (Greenwood *et al*, 1985; Galbraith *et al*, 1987; Anon., 1988; Galbraith, 1990). For example, increased consumption of fresh chicken, which is more likely to be contaminated than frozen chicken has taken place in the last decade (PHLS, British Food Information Service).

2.3.2.2. OTHER DISEASES

Other diseases continue to represent a threat, including dysentery, meningitis, legionellosis and typhoid. These are still prevalent in Europe and typhoid and other bacterial, viral and intestinal diseases continue to cause deaths (Green *et al*, 1966). In developing countries, several diseases and epidemics are still related to a lack of basic hygiene.

The number of microwave ovens has increased, but surveys show that a significant proportion fail to heat food properly and many consumers are unaware of how to use them correctly (Saunders & Blair, 1992). This can lead to incorrect temperatures in the reheating of pre-cooked chilled food, which may result in food poisoning. The UK Department of Health has advised that pre-cooked chilled food should be safe if reheated to a uniform temperature of 70°C for at least two minutes (Department of Health, London, 1989) but this can be difficult to assess in a domestic situation.

In addition to the human costs of ill health, food poisoning also involves the financial costs of lost working days and medical care. Public health officials recognise that costs associated with food poisoning, and Salmonellosis in particular, are high. Estimates are billions of dollars in the US (Archer & Krenberg 1985) and millions of pounds in the UK (Sockett, 1991). These figures include 1) industry losses through embargoes, 2) voluntary destruction of contaminated sources, 3) public bodies' investigations into the source of food poisoning, and 4) subsequent containment and treatment of patients.

Recently, outbreaks of the so-called Ebola virus were reported in central Africa. This lethal virus is only transmitted by blood or human secretions. The use of hypochlorite against the virus is to prevent indirect contamination (Instituut Antwerpen, oral communication). The use of hypochlorite as a cleaner and disinfectant could help to reduce these countries' disease statistics.

2.3.3. DISINFECTANT EFFICIENCY

2.3.3.1. DISINFECTION THROUGH CLEANING

To destroy bacteria on surfaces it is first necessary to remove the biofilm with a surfactant. Although surfactant cleaning may also remove some bacteria, it will leave viable bacteria behind.

This is not sufficient to achieve disinfection, which involves reducing bacterial populations to very low and safe levels (Niskanen & Poha, 1977; Borneff, 1989).

2.3.3.2. DISINFECTION WITH HYPOCHLORITE

Trials in the home and hospitals have shown that hypochlorite is an effective germicide, giving superior performance to other agents (Bloomfield, 1978; Bansemir, 1979; Scott & Bloomfield, 1985; 1990a,b; Borneff *et al*, 1988a,b; Bloomfield & Arthur, 1991, 1992). In hospitals, the use of hypochlorite is recommended for the disinfection of floors, cloths, clothing and surfaces (Darlow & Bale, 1959).

In Europe various disinfectants are approved for use in food preparation areas, whilst in the US, only hypochlorite is currently approved for this application.

Sodium hypochlorite is highly effective across the complete range of micro-organisms, including bacteria (including Gram-positive and Gram-negative species), fungi, viruses and spores.

Table 2.3. identifies the activity of a range of anti-microbial agents on various types of micro-organism.

Of the common anti-microbial agents, only glutaraldehyde and iodine compounds match the spectrum of efficacy of sodium hypochlorite. These are not appropriate for use in the household, however, for reasons such as stability and colour.

Phenolics, quaternary ammonium compounds, formalin, hydrogen peroxide, chloramines and chlorhexidine do not kill the complete spectrum of micro-organisms. Quaternary ammonium salts or chlorhexidine solutions may be contaminated (*Acinetobacter*, *Pseudomonas*, *Serratia*) and therefore may contaminate surfaces and man. Data for peracetic acid indicate that this material is also an effective sporicidal and germicidal agent at low concentrations (especially at pH 5), and therefore a potent disinfectant. Due to instability and odour issues it has not been possible to formulate the chemical into household disinfectants.

Table 2.3. Activity of anti-microbial agents on various microbial types

Disinfectant Type	TYPE OF MICRO-ORGANISM								Mode of Action
	<i>Salmonella</i>	<i>Campylobacter</i>	Vegetative bacteria		Myco-bacteria	Fungi	Viruses	Bact. Spores	
			Gram+	Gram-					
Sodium Hypochlorite	+	+	+	+	+	+	+	+	Potent oxidiser of biological molecules such as proteins, nucleic acids
Phenolics	+	+	+	+	±	+	±	-	Combine with and denature proteins
Quaternary Ammonium Compounds	+	+	+	±	-	+	±	-	Not fully elucidated but affects proteins, metabolic reactions, cell permeability etc.
Formalin	+	+	+	+	±	+	+	±	Affects the cell wall and reacts readily with amino groups of proteins, denaturing them.
Glutaraldehyde	+	+	+	+	+	+	+	+	Not fully elucidated but affects proteins such as enzymes, transport of nutrients & cell walls.
Hydrogen Peroxide / Potassium Permanganate	+	+	+	+	(+)	±	±	(+)	Generates hydroxyl free radicals which attack biological molecules. Peroxide may have a less important effect.
Iodine Compounds	+	+	+	+	+	+	+	+	Attacks N-H and S-S/S-H bonds in proteins etc.
Alcohols	+	+	+	+	±	±	±	-	Denatures proteins and affects cell membrane permeability
Chloramines	+	+	+	+	(+)	(+)	(+)	(+)	See hypochlorite, but less active
Chlorhexidine	+	+	+	±	-	+	?	-	Probably causes leakage of semi-permeable membrane.
Peracetic Acid	+	+	+	+	+	+	+	+	Potent oxidiser (considerably more active than H ₂ O ₂).

+ : Susceptible ; - : Resistant ; ± : Some susceptibility ; (+) : Susceptible at high concentrations.

For many bacteria, under ideal conditions where soil levels are very low, a constant level of 1 ppm of sodium hypochlorite is sufficient to achieve kill. However, 5 ppm is sufficient to achieve greater than 99% kill across a range of temperatures, times and pH values.

A study by Scott & Bloomfield (1985) in particular demonstrated a significant reduction in bacteria in the toilet bowl water and surrounding sites from daily cleaning of college toilets with hypochlorite compared to non-disinfectant cleaning agents. The same authors (Scott, Bloomfield & Barlow, 1984) demonstrated that detergent and hot water produced no observable reduction in microbial contamination in kitchen, toilet and bathroom sites. However, single and daily cleaning with hypochlorite gave a substantial reduction in bacterial contamination.

Sodium hypochlorite has been shown to reduce cross-contamination with micro-organisms in mechanical dish-washing at low temperatures (Kilsby *et al* 1982). Fungi are more resistant to biocides than bacteria. A high density of spores of *Aspergillus niger* and *Trichophyte rosaceum* were inactivated by 135-500 ppm sodium hypochlorite in a few minutes (Block, 1991).

Of increasing importance today are viruses. Children can easily be affected and can transmit viruses either directly or indirectly by surfaces contaminated (for example, toys, tables or spoons) with saliva or secretions.

Hypochlorite kills rhinovirus (Sattar *et al*, 1993), Respiratory Syncytial Virus (Krillov *et al* 1993), rotavirus, enterovirus and hepatitis A virus. It has been shown that sodium hypochlorite will kill the most resistant viral types, such as entero-viruses, Hepatitis A (Springthorpe & Sutter, 1990), and many others.

Many other biocides, such as biguanides and Q.A.Cs, kill only the less resistant enveloped virus (Russell *et al*, 1992).

For general sanitation purposes, sodium hypochlorite is probably the most effective and inexpensive virucide provided the organic load is not significant (Block, 1991).

The evaluation of sodium hypochlorite has also been carried out against the human immunodeficiency virus (HIV) and satisfactory disinfection conferred (Bloomfield *et al*, 1990). Hypochlorite is therefore recommended by the WHO for the disinfection of this virus.

Sobsey (1988) and Sobsey *et al* (1988) investigated the parameters inactivating the rotavirus and Hepatitis A virus with low levels of hypochlorite.

Bacterial spores are the most resistant form of microbial life and the ultimate criterion of a sterilising agent is its sporicidal activity. Sodium hypochlorite will kill spores at concentrations of 25 ppm, if long contact times are used.

The rates of kill can be raised by increasing levels to 500 ppm, in clean conditions. Many recent studies have also investigated the sporicidal properties of hypochlorite (Best *et al*, 1994; Sagripanti & Bonifacino, 1996). As an indication of hypochlorite effectiveness, a range of disinfectants has been compared against *Bacillus subtilis* spores in *Table 2.4*.

This test is used as a reference: effectiveness against bacterial spores implies effectiveness against a large number of bacteria. These results clearly show that hypochlorite is a much more effective sporicidal agent than most other common disinfectants.

In summary, whilst alternative disinfectants are available with good anti-microbial properties, hypochlorite is the only one combining excellent biocidal properties with ready availability, cost-effectiveness and ease of use in the home.

It is a highly effective household disinfectant on a wide spectrum of micro-organisms (bacteria, fungi, viruses and spores) at lower concentrations than most other disinfectants.

In addition, due to its mode of action (oxidation), no genetic resistance has been reported to hypochlorite. This also implies lower emissions to the environment for the same application. Hypochlorite can easily be formulated into domestic cleaning products.

However, the correct dosage must be used, taking into account the possible presence of organic matter which can reduce the disinfection efficacy.

Table 2.4. Effectiveness of a range of disinfectants against *Bacillus subtilis* spores (log kills, where 1 log kill = 90% of spores inactivated)

Disinfectant	Concentration	pH	Time (Minutes)				
			15	30	60	120	240
Sodium hypochlorite solution (as Av.Cl ₂)	375 ppm	10.00	2.21	4.20	Complete Kill		
	750 ppm	10.45	2.23	4.23	Complete Kill		
	1500 ppm	10.95	2.42	4.51	Complete Kill		
Peracetic acid (Mrozek, 1978)	100 ppm		2.5		2.50		
	200 ppm		2.5		3.50		
	400 ppm		3.5		3.50		
Peracetic acid (Baldry & Dickenson, 1986)	375 ppm	5.0			4.98	Kill	Kill
	375	7.0			2.90	2.90	2.92
	750	5.0			Kill	Kill	Kill
	750	7.0			4.04	4.64	Kill
Isopropyl alcohol	70%	6.65	0.92	0.92	0.93	0.97	0.97
Household disinfectant containing DCMX*	1%	8.18	0.78	-	0.79	0.79	0.79
	10%	8.80	0.94	0.97	-	0.98	1.02
Soluble phenolic	0.5%	7.45	1.06	1.38	1.41	1.78	1.92
	1.0%	7.60	1.07	1.32	1.43	1.87	1.96
	2.0%	7.85	1.21	1.30	1.83	1.86	1.98
Product containing 20% chlorhexidine gluconate	0.5%	6.35	0.75	0.76	1.90	2.01	2.11
	1.0%	6.50	1.19	1.19	2.56	2.71	2.93
	2.0%	6.60	1.21	1.21	2.01	2.78	2.98
Product containing 50% benzalkonium chloride	1.0%	7.20	0.71	0.75	0.82	0.84	0.91
Glutaraldehyde (BDH) buffered by 0.1 M NaHCO ₃	1.0%	7.50	1.48	1.40	1.86	1.85	2.14
	2.0%	7.50	1.53	1.56	2.21	2.93	-

* DCMX : Dichloro meta xylenol

* Inoculum and test temperature : 3.24×10^5 organisms/ml, 20°C.

2.3.4. CONCLUSIONS ABOUT DISINFECTION

Pathogens occur in several places in the home, at levels which may be sufficient to cause infection.

Whilst general domestic disinfection is not achievable, the risk of food poisoning from indirect contamination can be reduced by regular use of a wide-spectrum disinfectant in areas such as kitchen surfaces and cloths, bathrooms, toilets and floors.

Through home hygiene education and availability of effective cleaner-disinfectants, incidence of infections could be reduced (Scott, 1996).

Hypochlorite is one of the most potent disinfectants, and it is also very suitable for use in domestic cleaning products. Other powerful disinfectants are generally not appropriate for household use.

2.4. OTHER USES OF HYPOCHLORITE

Hypochlorite is commonly used in industry as a disinfectant. Some regulations require the use of sodium hypochlorite.

Examples of industrial and institutional use are:

- Cleaning of dairy equipment
- In restaurants/public houses
- Disinfection of chicken eggs
- Control of water-borne infections in mains drinking water
- Water used for processing in factories is treated with sodium hypochlorite to deliver 1.5 ppm Available Chlorine

2.5. GENERAL CONCLUSIONS

Sodium hypochlorite has a long history of use in the home for bleaching of textiles, cleaning and deodorising toilet bowls and as a surface disinfectant agent.

A significant number of pathogenic micro-organisms can be found in the home, particularly in kitchens and bathrooms.

They are frequently brought into the home on raw food and can cause food poisoning by cross-contamination, leading to disruption of the household and lost working days.

Due to its cost-effectiveness and ready availability, hypochlorite can also contribute to improved hygiene in developing countries.

In this way, it can help reduce the potential for diseases and epidemics.

- Sodium hypochlorite is the most widely used disinfectant in swimming pools
- It is acceptable for general use in hospitals as a disinfectant
- Hypochlorite is recommended for special hazards, such as viral diseases (hepatitis, AIDS, Ebola) and to disinfect hospital equipment (such as haemodialysis apparatus)
- Sanitising industrial plant equipment and disinfection in cooling towers (risk for *Legionella*),
- Disinfection of sea water for secondary oil recovery.

Statistics show that incidence of food poisoning is increasing. The most vulnerable sectors of the population - such as the very old, the very young and those with reduced immunity - are particularly at risk.

To lower risks of infection, cleaning with detergents may not be sufficient and disinfectants may be required.

Sodium hypochlorite is the most effective biocidal product, with a unique ability to kill even the most persistent microbes; its use is recommended where hygiene is important.

2.6. REFERENCES

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3. HUMAN SAFETY

3.1. CONCENTRATION AND REGULATORY LABELLING

Household hypochlorite solutions are sold in Europe in concentrations which vary from one country to another between 2-12.5% available chlorine level, with a prevalence of 4-5%. Table

3.1. gives the mean concentrations of hypochlorite solutions in some European countries.

Table 3.1. Overview of hypochlorite concentrations in European countries

Country	Available Chlorine Concentration (%)
Spain	3.6 - 4.8
The Netherlands	4.6
Belgium	2 - 3.6
Italy	1.8 - 6
UK	4 - 5
France	3.6 and 12.5
Germany	3.6
Sweden	3.6
Portugal	4.0 - 6.0

Conversion between $Av.Cl_2$ and NaOCl concentration: $Av.Cl_2 (\%) \times 1.05 = NaOCl (\%)$; 'active chlorine' is often used to mean 'available chlorine'

Under the Dangerous Substances Directive 67/548/CEE and Dangerous Preparations Directive 88/379/CEE, hypochlorite solutions are classified as:

Above 10 % active chlorine. "Corrosive," with the risk phrases:

- R 31, contact with acids liberates toxic gas
- R 34, causes burns.

The "S" phrases to be added to the Corrosive classification are:

- S 1/2: Keep locked up and out of reach of children - obligatory for sales to the general public but not required for industrial supply
- S 28: After contact with skin, wash immediately with plenty of water

- S 45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)

- S 50: Do not mix with acids or ammonia.

Other S phrases can be used according to national regulations or professional rules.

For 5-10% active chlorine, "Irritant," with the risk phrases:

- R 31: contact with acids liberates toxic gas
- R 36/38: irritating to eyes and skin

Below 5 % active chlorine solutions: not classified.

All hypochlorite solutions above 1% active chlorine must be labelled with "Warning! Do not use together with other products. May release dangerous gases (chlorine)".

When classified as "Corrosive", hypochlorite solution packages must carry tactile warnings of danger according to the EN standard 272.

They must also be child-resistant under the standard EN 28317 for reclosable packages.

Under the European Commission Recommendation for the Labelling of Detergents and Cleaning Products (89/542/EEC), all

hypochlorite solutions above 0.2% must be labelled as containing chlorine-based agents and their level (below 5%, or 5-15%).

Under EEC Directives (67/548/CEE and 88/379/CEE), household hypochlorite bleaches are not classified as very toxic, toxic or harmful by ingestion.

Hypochlorite solutions above 5% active chlorine are classified for transportation as: Class 8 : Corrosive; U.N. 1791.

3.2. EXPOSURE ROUTES

3.2.1. NORMAL

Under normal use conditions, the key route of exposure to hypochlorite is dermal contact, usually where the bare hands are dipped into a diluted hypochlorite solution in hand laundry bleaching.

Typical dilution concentrations are given in Chapter 4, and range from 0.01% (100 mg NaOCl/l) to 0.5% (5000 mg NaOCl/l).

Exposure to concentrated solutions is less frequent, due to the limited use of undiluted product (normally only used in manual cleaning jobs, like toilet bowl cleaning).

Exposure to by-products may also occur during the use of the compound. The most significant by-products identified are chlorate, chloramines and chloroform (see Chapter 4). Other by-products may be formed in quantities so small that they are not thought to have a potential impact on human health.

Concentrations and exposure of the main by-products are estimated as follows:

- * **Chlorate:** concentration ~1.8 g/l in domestic bleach (3.6 % NaOCl average), corresponding to 0.005-0.25 g/l under conditions of use. Exposure occurs mainly via the dermal route.
- * **Chloramines:** not present in bleach, but may be formed during use if mixed with N-containing compounds. The concentration will depend on the type of application. Exposure occurs via dermal (mono-, dichloramine) and inhalation routes (trichloramine). There are no exposure data available for chloramines during domestic hypochlorite use. However, at 0.1 ppm (v/v), trichloramine can be smelled, and at 0.5 ppm irritation is intolerable (Gagnaire *et al*, 1994).
- * **Chloroform:** traces can be present in bleach (Smith, 1994), but are mainly formed during use. Concentrations are up to around 1.0 mg/l in the water. Exposure occurs via the dermal

and inhalation route. However, inhalation is likely to be insignificant due to the very low

estimated atmospheric concentrations (a maximum of 1.34 mg/m³, Smith, 1994).

3.2.2. ACCIDENTAL

Ingestion of small quantities of product is the most relevant route of exposure for children. Adults are exposed orally to hypochlorite either by accidental ingestion or in the case of suicide attempts via deliberate poisoning. In adults, the most relevant route of accidental exposure due to misuse is inhalation of chlorine gas or trichloroamine, which are released when hypochlorite-containing products are mixed with

acids or amines. Eye contact accounts for only a minority of exposure cases.

The type and relevance of exposure routes under accidental circumstances have been clearly demonstrated in surveys conducted by Poison Control Centers (Racioppi *et al*, 1994; see section 3.4).

3.3. TOXICOLOGICAL DATA

3.3.1. ACUTE TOXICITY

The acute oral LD50 (rats) is reported to be 13,000 mg/kg body weight for 5.25% hypochlorite solution (MSDS Chlorine Institute, 1982) and 8,200 mg/kg body weight for 12.5% hypochlorite solution (BIBRA 1990).

Colgate-Palmolive (unpublished data) reported the LD50 (rats) to be 9,360-11,700 mg/kg body weight for 12.5% hypochlorite solutions. For 3.6% hypochlorite solutions, the LD50 (rats) is reported as >11,800 mg/kg.

Accidental ingestion in humans resulted in gastrointestinal signs of irritation or corrosion depending on concentration and quantity absorbed (HEDSET, 1994). Acute dermal toxicity is above 2,000 mg/kg body weight for 5.25% NaOCl (Clorox, unpublished data).

In conclusion, the acute toxicity of sodium hypochlorite does not represent a threat to human life.

3.3.2. SKIN IRRITATION

Detailed studies in animals and human volunteers with formulations of about 5% or on more diluted products have shown that they are severely irritant under drastic experimental conditions (patch test for 4h) for the undiluted form.

Uncovered applications of a 4% product produced no skin irritation.

Dilute solutions (1% NaOCl) have only a negligible effect on skin when exposed under covered contact (e.g. reviews by BIBRA, 1990; Racioppi *et al*, 1994).

It can be concluded that, when diluted for use, hypochlorite solutions are not irritant or are only slightly irritant.

3.3.3. EYE IRRITATION

Animal studies have shown the following effect thresholds:

- no irritation up to 0.05% formulation
- slight irritation from 0.5% (effect on conjunctiva resolved within 24 hours)
- mild transient irritation at 5% (if rinsed out with water within 30 seconds)
- severe irritation at 5% (no rinsing,

effects involving cornea and conjunctiva, recovery after 3 weeks).

Human accidental exposure to a 5% formulation leads to a clear irritant effect. However, recovery takes place within 48 hours due to prompt rinsing (Griffith *et al*, 1980; reviews by BIBRA, 1990, and Racioppi *et al*, 1994).

3.3.4. SENSITISATION

Sodium hypochlorite is not considered as a sensitising agent. In the past, hypochlorite solutions from some countries (Belgium and France) were coloured with potassium bi/dichromate or permanganate, and to some extent gave rise to allergic reactions.

The allergic reactions were eliminated when these colorants were removed (Lachapelle *et al*, 1980).

Allergic reactions due to hypochlorite bleach are very rare. Some cases of allergenic contact dermatitis have been reported in multi-sensitised individuals from exposure to 0.04% hypochlorite. Long-term exposure seems to be a pre-requisite

for such reaction, but some cases of immediate-type sensitivity have also been recorded. Non-immunological contact urticaria has been described after exposure to 6% formulations.

Predictive sensitisation tests conducted with guinea-pigs and then on human volunteers with hypochlorite bleach formulations have shown no potential for allergenic contact dermatitis.

Overall, reports place hypochlorite in the category of non-sensitising chemicals that can, on rare occasions, be implicated in sensitising reactions (e.g. reviews by BIBRA, 1990; Racioppi *et al*, 1994).

3.3.5. CHRONIC TOXICITY

Recently, much attention has been paid to the possible carcinogenicity of sodium hypochlorite, also due to the fact that halogenated organic compounds can be formed in very small quantities from the in-use reactions of hypochlorite.

However, there is no evidence to suggest that sodium hypochlorite is carcinogenic to man. Some examples of experimental studies are given below.

Sub-chronic exposure of various experimental species to hypochlorite failed to show any adverse effect other than irritation (HEDSET, 1994).

In a more prolonged study, Hasegawa *et al* (1986) administered to groups of 50 Fisher344 rats sodium hypochlorite in drinking water (0.1 and 0.05% for males and 0.2 and 0.1% for females) for 104 weeks.

All animals receiving sodium hypochlorite had reduced body weight gain relative to control animals but haematology, biochemical examination of the blood and histopathology were not significantly altered.

In another study (Kurokawa *et al*, 1986), NaOCl was administered to groups of around 50 male and 50 female mice at doses of 1,000 or 500 ppm to either sex for 103 weeks. NaOCl was not found carcinogenic in either sex. The administration of sodium hypochlorite solutions in Fisher344 rats and B₆C₃F₁ mice (50 animals/sex-group) in drinking water for two at up to 275 ppm (as FAC) resulted in no observable pathological effects. Only a marginal incidence of leukaemia was found in female rats (not dose-related), but not in male rats or mice of both sexes. Survival was not affected (NTP, 1992).

Epidermal hyperplasia was found after continuous topical application of sodium hypochlorite solutions (1000 mg/l) on Sencar mouse or guinea pig skin. No such effect was noted when the treatment was discontinued (HEDSET, 1994).

In humans, several epidemiological studies have evaluated the carcinogenic effect of chlorinated

water consumption. When the data are examined on the basis of individual cancer sites, evidence of an elevated risk for urinary bladder, colon and rectum cancer is suggested. However, due to several methodological inadequacies no causal link between increased cancer risk and consumption of chlorinated drinking water can be found (International Agency for Research on Cancer (IARC), 1991).

The IARC (IARC, World Health Organisation monograph (1991) concluded that chlorinated water and hypochlorite salts are "not classified as to their carcinogenicity to humans" because of inadequate (meaning insufficient) evidence from animal tests and/or epidemiological studies.

For perspective, the classification adapted by IARC concerning carcinogenicity is as follows :

- Group 1: substance carcinogenic to humans
- Group 2A: probably carcinogenic to humans
- Group 2B: possibly carcinogenic to humans
- Group 3: not classified as carcinogenic to humans, because of inadequate evidence from animal tests and human experience
- Group 4: not carcinogenic

3.3.6. GENOTOXICITY

Detailed studies can be found in the NaOCl HEDSET (1994). Mutagenicity tests in bacteria appeared inconclusive with some tests being positive, others being negative. Mainly *Salmonella typhimurium* TA 100 and TA 1535 appeared to be reactive in the presence of metabolic activation. Cytogenetic and DNA damage assays in mammalian cells were also difficult to interpret since both positive and negative results were obtained depending on the test system. Most often, no details are available on the methodology used and on results observed

so that a correct interpretation of the data obtained is difficult. These results may be linked to the potential germicidal effect of sodium hypochlorite.

In vivo micronucleus or chromosome aberration tests via oral or intra-peritoneal route showed no genotoxic activity. Also, no *in-vivo* kidney DNA damage was found in the rat.

Ambiguous results were found in a mouse sperm-head abnormality test for which the relevance for genotoxicity is questionable.

3.3.7. REPRODUCTIVE TOXICITY

No fertility effects were noted in studies where sodium hypochlorite was administered to rodents, either by gavage or in the drinking water for up to several generations (HEDSET, 1994).

The only developmental study available with sodium hypochlorite administered in drinking water prior to and throughout gestation has shown a decrease in pups' weight and an increase in skeletal and soft tissues variations at the high dose (100 mg/l). However, the low number of animals used in the test and the lack of detailed data preclude any firm conclusion on this foetotoxic effect (HEDSET, 1994).

3.3.8. TOXICITY OF MAIN BY-PRODUCTS

During the use of hypochlorite, chlorate, chloramines and chloro-organic compounds can be formed. A short summary of the toxicological profile of the main by-products (chlorate, chloramines and chloroform) is given below.

Chlorate

Sodium chlorate is slightly irritating to the skin and the eyes, and is harmful by ingestion. It causes methemoglobinemia if ingested and subtle haematological changes have been found from 10 ppm in drinking water in rats exposed for a long period.

Human volunteers receiving 500 ml/day of a 5 ppm chlorate solution for 12 weeks did not demonstrate any clinically relevant toxic effects (EUCLID data sheet, 1994).

In conclusion, sodium hypochlorite is not to be considered as a genotoxic agent. The few effects found in *in vitro* systems are probably linked to its known bacterial and cytotoxic properties.

There is no data available on reproductive effects of hypochlorite in humans. A few preliminary studies exist on drinking water consumption and adverse reproductive and developmental outcome in humans. However, such studies are inadequate to determine a risk or a causality between foetal development or congenital malformation and exposure to chlorinated water and by-products (EPA, 1993).

The overall conclusion is that there is no indication that sodium hypochlorite exposure via drinking water would entail any reproductive effect at parental non-toxic levels.

Chloramines

Chloramines are irritant to the skin, eyes and respiratory tract, with trichloramine having the strongest effects (Grant, 1986). Acute exposure of mice to trichloramine by inhalation produces toxic effects after acute exposure for 1 hour to 1.2 ppm (Gagnaire, 1994). Long-term administration of chloraminated water to rats and mice up to a level of 200 ppm in drinking water did not lead to any remarkable toxic effect (NTP, 1992).

Haematological disturbances were found in patients receiving intravenous injections of water containing chloramines but this effect has never been demonstrated after other routes of exposure (Neilan *et al*, 1978; NTP, 1992). A short-term

occupational exposure limit of 0.3 ppm is suggested (Gagnaire, 1994).

Chloroform

Chloroform is harmful by the oral route and lightly irritant to the skin through its degreasing effect. Anaesthesia, effects on the kidney and liver have been found in both humans and animals after oral or inhalation exposure. Carcinogenic effects in the liver (mouse) and kidney (rat) are thought to be secondary to toxic effects (IPCS, 1994). The WHO guideline for drinking water is

200 µg/l. The American Conference of Governmental Industrial Hygienists (ACGIH) has proposed an occupational exposure limit of 10 ppm (49 mg/m³) for an 8 hour exposure scheme (TLV/TWA).

In conclusion, adverse effects due to the by-products of hypochlorite are not expected due to the by-products' very low concentrations and the non-continuous exposure which is characteristic of domestic use.

3.4. CONSUMER SAFETY EXPERIENCE

Hypochlorite solutions have been widely used in many countries (France, USA, Italy, Spain) for more than a century. Therefore, consumer exposure to them is highly frequent.

It is demonstrated below that the recommended use of hypochlorite is safe and no ill-effects have resulted throughout its history.

3.4.1. EFFECTS OF MISUSE

3.4.1.1. EFFECTS ON EYES AND SKIN

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

Given the corrosiveness of >10% Active Chlorine solutions, these may cause chemical burns to the eyes and skin if they are not rinsed immediately with plenty of water. In practice, however, no permanent damage has been reported from accidental exposures to hypochlorite. Solutions of 5% hypochlorite can cause irritation to the eye upon direct contact and to the skin upon prolonged contact. The effects are reversible.

Dufier (unpublished data) and Lavaud *et al* (1989, unpublished data) reported 100 ocular exposures,

with hypochlorite solutions containing 3.6% and 12.5% active chlorine.

Total recovery was obtained within 48 hours for 98% of the cases. In the remaining 2%, which all were with concentrated hypochlorite solutions, total recovery was obtained within 10-30 days.

Only a minority of cases reported to Poison Control Centers (PCCs) relate to eye and skin irritation. Ocular exposures may occur while pouring hypochlorite solution for dilution and use.

Table 3.2 gives average percentages (1989-1992) of these two exposure routes, as reported by Poison Control Centers (calculated from Racioppi *et al*, 1994). In Belgium (1987), of the total accidental hypochlorite exposures, 2.5% were

skin contacts and 5% were ocular exposures (Govaerts, unpublished 1989). Italy gives only

eye exposures, 4.6% Milan (1990) and 2% Rome (1990). No permanent effects are reported.

3.4.1.2. INGESTION

Ingestion by children is very rarely of concern because in most cases, the unpleasant taste and emetic effect prevent intake of large volumes (CSNEJ, 1987; Riboulet-Delmas, 1989; Govaerts, 1989). In most cases, volumes ingested by children are very low.

Another fatal suicide case was reported by Hilbert and Bedry (1994) by ingestion of 121g of NaOCl. In those cases, hypochlorite was in prolonged contact (several hours) with the oesophagus and stomach mucous membrane before medical aid was administered, and probably in many cases it was mixed with other products.

Suicide attempts by adults can lead to death in case of ingestion of at least 250-500 ml of 12.5% hypochlorite solutions (Riboulet-Delmas, 1989). Litovitz *et al* (1987) reported a death by suicide with a 5.25% solution in the USA.

Table 3.2 shows average percentages (1989-1992) of accidental exposure via ingestion, as reported by Poison Control Centers (calculated from Racioppi *et al*, 1994).

3.4.1.3. INHALATION

Under misuse conditions, hypochlorite can react with other household cleaning products, particularly with acidic products and ammonia. The gases liberated (chlorine or chloramines) are very irritant and warn the user immediately, significantly reducing the risk of prolonged contact.

result of household cleaning with a mixture of ammonia and bleach.

No mention to the population size or relative frequency of such events was made.

Chlorine gas from mixing with acids

Occupational Exposure Limits (OEL) for chlorine at the workplace are:

In most cases, levels of chlorine are too low to cause tissue damage (Reisz & Gammon, 1986) but in rare cases, it can cause tracheobronchitis or acute respiratory distress (Ellenhorn & Barceloux, 1988).

- Time Weighted Average (TWA) Long-term exposure limit (8h weighted average reference period) : 0.5 ppm v/v (1.5 mg/m³) (ACGIH booklet, 1996)

Chloramines from mixing with ammonia

- Short Term Exposure Limit (STEL) (10-minute reference period) : 1 ppm (3 mg/m³). Many people would not tolerate 1 ppm chlorine because of its irritating action on lungs.

In very rare cases, chloramine compounds, with predominance of monochloramine, can cause life threatening pneumonitis in the event of prolonged contact in closed areas. In one year, three cases were reported by Reisz & Gammon (1986), as a

Olfactory threshold of chloramine: ~ 0.1 ppm v/v (0.3 mg/m³) (Gagnaire *et al*, 1994)

Inhalation of toxic gases represents a significant percentage of the total exposures, as reported by Poison Control Centers from various countries:

Spain 1988, 16% (Segura Abad, 1989); Belgium, 36% (Govaerts 1989); UK, 2% (HASS, 1992). Table 3.2. shows average percentages (1989-1992) of exposure via ingestion, as reported by

Poison Control Centers (calculated from Racioppi *et al*, 1994).

All household hypochlorite solutions are sold with an instruction not to mix hypochlorite with any product, in order to minimise inhalations.

3.4.2. DATA FROM POISON CONTROL CENTRES

In recent years, many European and American Poison Control Centres (PCCs) have reviewed their hypochlorite data concerning involuntary accidents and voluntary poisoning.

not considered a major issue for Poison Control Centers (Efthymiou & Riboulet-Delmas, unpublished data 1989; Racioppi *et al*, 1994).

In some countries, hypochlorite is the source of a large number of exposures, which can be explained by its very wide use. However, involuntary exposures to hypochlorite solution are

An overview of the key conclusions from various PCCs is given below. Table 3.2 gives average percentages (1989-1992) of different exposure routes reported by a number of Poison Control Centers (calculated from Racioppi *et al*, 1994).

Table 3.2. Exposure routes to hypochlorite reported by Poison Control Centers

	Lyon, France	Milan, Italy	Rome, Italy	Brussels, Belgium	Athens, Greece	Ankara, Turkey*	Madrid, Spain*
Ingestion	74.1%	72.7%	63.6%	37.3%	53.3%	74.9%	32.2%
Inhalation	16.8%	17.0%	33.9%	49.4%	46.0%	21.9%	25.7%
Skin	3.8%	1.8%	1.1%	3.7%	0.2%	2.5%	1.7%
Eyes	4.4%	1.8%	1.4%	5.8%	0.6%	0.8%	9.1%

* period 1991-1992

An average of 2.9% of calls to Poison Control Centres are about hypochlorite exposure (data from Litovitz *et al*, 1987, 1988, 1989, 1990; Riboulet-Delmas, 1989; HASS, 1992; Racioppi *et al*, 1994).

Belgium

The percentages vary from 0.1% (UK, 1989) to 7.3% (Spain, 1996; Report 0180/96 Instituto Nacional de Toxicología 16/2/1996), with the majority between 2.5% and 4.5%.

In 1989-92, an annual average of 1,021 exposures to hypochlorite were reported. Of these, 95% were accidental, and 3% suicide attempts. Adults were more frequently involved (62%) than children (38%) (Racioppi *et al*, 1994). Exposure routes are listed in Table 3.2. Inhalation is of most concern in Belgium. Children swallow only very small quantities (Govaerts, 1989).

Canada

A survey from 1978-83 reported 5,103 incidents involving sodium hypochlorite solutions and children under five.

About 25% of the total reported involved some form of treatment or advice at a hospital, but no evidence of severe injury to children directly due to exposure to household hypochlorite has been found (Cotterill & Harrison, 1986).

France

A survey recording all exposures to sodium hypochlorite (1974-1988) was made by the PCC of Paris (Riboulet-Delmas, 1989). 91% of exposures to hypochlorite were accidental, while 9% were suicide attempts. Eight deaths occurred after ingestion of at least 250 ml of hypochlorite at 12.5% active chlorine. Child exposure represented 46% of the accidental exposures. Only 38 children presented a positive endoscopy, but no permanent effects were reported.

In 1994, the PCC of Paris reported 1825 hypochlorite exposures (Riboulet-Delmas, 1996). Child accidental ingestion represented 36% of total exposures. 5% were adult suicide attempts with no permanent damage. Accidental exposures by inhalation (only adults) represented 16% of total exposures versus 36% for adult accidental ingestion.

From 1989 to 1992, on average 640 yearly exposures to hypochlorite were reported at the PCC of Lyon. 89% were accidental exposures (Racioppi *et al*, 1994). The main exposure route was oral ingestion (Table 3.2).

Italy

In Italy, the two major Poison Control Centres reported on average 600 (Milan) and 200 (Rome) hypochlorite exposures per year, with no deaths recorded (Racioppi *et al*, 1994). Ingestion is the predominant exposure route (Table 3.2).

Children under five years of age are most frequently involved in accidental swallowing. No serious or long-term consequences were noted for victims of either accidental or voluntary ingestion (Ruggerone, unpublished data).

The Rome Poison Control Centre recorded from 1982 to 1990 a total of 1,002 accidents related to hypochlorite bleach. None of these contacts appears to have had significant health consequences (Magalini, 1991).

The Netherlands

Dutch data are provided by the Private Accident Registration System (PORS 1988), which involves 10% of Dutch hospitals.

Results are summarised in Table 3.3.

Table 3.3. Accidents with cleaning agents in The Netherlands (1988)

	Accidents per 1 million people
Total accidents with cleaning agents	72
Accidents with bleach involving children (< 5 years)	13
Ingestions of cleaning agents by children (< 5 years)	15

Portugal

In 1989-92, the PCC of Lisbon, the Centro de Informacao Antivenemos, recorded an average of 660 exposures to sodium hypochlorite solutions. These represented the second most frequent agent.

In the vast majority of cases the exposure was accidental, and the main exposure route was oral ingestion.

Young children (0-3 years) were mainly involved in accidental ingestion (Racioppi *et al*, 1994).

A communication to the EU Commission from the Portuguese Ministry of Industry (002863 14/03/91) stated that no corrosive effects were observed with household hypochlorite solutions (Borges, 1990).

Spain

In 1991-1992, the Spanish Poison Control Centre, the Instituto Nacional de Toxicologia (Madrid), reported on average 1172 hypochlorite exposures per year, of which 97% were accidental. Ingestion was the predominant exposure route (Table 3.2). Of the total, 71% were reported free of symptoms (Racioppi *et al*, 1994). No sequels were reported (Segura Abad, 1989).

United Kingdom

The UK data are provided by the Home Accident Surveillance Scheme (HASS, 1992). This scheme is run by the UK Government, via the Department of Trade and Industry. The source of data represents 10% of the total number of cases in hospitals (Table 3.4).

Table 3.4. Exposures to cleaners and bleaches in the UK

	Accidents per 1 million people
Total cleaner exposures	131
Bleach exposures involving children (< 5 years)	16
Ingestion of cleaning product (< 5 years)	68
Ingestion of bleaches (< 5 years)	15

Table 3.4 shows that bleach accounts for a small proportion (around 25%) of cleaning product

exposures and a very small proportion of all UK accidents (25,955 per million people per year). (Litovitz *et al*, 1987, 1988, 1989, 1990). One death by suicide was reported in 1989.

USA

The percentage of human exposures to sodium hypochlorite solutions stays under 2% of total exposures. The outcome of accidents are classified as: no effect, minor effect, moderate effect, major effect, death. Major effects reported were, on average, 12 per year in 1986-1989

Conclusion: Despite the fact that many calls relate to hypochlorite, the conclusion of Poison Control Centres is that hypochlorite is generally

not considered to be a major issue, even for 12.5% hypochlorite solutions. This is due to the reversibility of the observed effects.

3.4.3. CHILD RESISTANT PACKAGING

Child resistant packaging (child resistant closures, CRCs) is compulsory for preparations classified as "Corrosive"; hypochlorite solutions above 10% Active Chlorine fall into this category. After the publication of the Dangerous Preparations Directive, consideration was given at the European level to extending child resistant packaging to hypochlorite solutions containing less than 10% active chlorine (classified as "Irritant", or not classified; FIFE, unpublished data 1989). In many countries, Poison Control Centres were contacted to review all data on ingestion by children, and were asked to advise.

For Belgium, Govaerts (1989) reported that children swallow only small quantities of product, and that ingestion by children represents 38% of the exposures. In spite of this relatively high number of exposures, it was concluded that the use of CRC is unnecessary for non-corrosive hypochlorite solutions, due to the absence of

serious consequences and the small accidental ingestion volumes.

In Canada, an evaluation of a child-resistant container requirement for liquid household bleach was made in 1986 (Cotterill & Harrison, 1986). This concluded that mandatory child-resistant containers for sodium hypochlorite household bleach were not warranted, since in many cases children were exposed to it during use, when it was not in the original container.

CRCs were introduced by some bleach manufacturers for the UK market in the 1980s. By the late 1980s more than 50% of bleaches sold in the UK had CRCs. However, analysis of the UK HASS data does not support the view that the introduction of CRCs reduced the rate of bleach accidents. Table 3.5 shows that the majority of bleach ingestion cases did not occur from the original container.

Table 3.5. Sources of bleach ingestion in the UK (HASS, unpublished)

Bleach Source	% of Bleach Ingestion cases
Original bottle	16%
Not in the original container (cup, mug, etc)	27%
Toilet bowl/sink	4%
Sucked article dipped in bleach	6%
Source not specified	18%

In 1990, CRCs were introduced onto household bleach products in Holland. Following this introduction, industry sources cited a 10-fold

increase in consumer complaints. As a result there is now a general move to non-CRCs.

In some countries there is still a debate among experts about the necessity of CRCs. In Germany, a voluntary agreement stipulates that

3.5. SUMMARY

Household hypochlorite solutions generally contain 2-12.5% Available Chlorine, but 4-5% solutions are most widely used.

These solutions have to be considered as irritant or corrosive depending on the concentration. They are not sensitising. No systemic effects have been observed after repeated administration to laboratory animals. Hypochlorite is not considered as genotoxic, carcinogenic or affecting reproduction.

Exposure to hypochlorite under normal circumstances would be topical. As the product is used diluted, only occasional irritancy is expected to occur.

By-products like chlorate, chloramines or chloroform are either formed during storage or under use conditions. Due to the very low level exposure to these by-products during domestic

hypochlorite solutions above 1% Active Chlorine should use child-resistant caps.

use of hypochlorite is not thought to have an impact on human health.

Exposure under misuse conditions results in dermal or ocular irritation or burns which are reversible. Accidental ingestion only occurs in children but is rarely of concern due to the unpleasant taste and emetic effects.

Inhalation of chloramines or chlorine may result when the compound is mixed with ammonia or acidic products. Although many calls to Poison Control Centres related to hypochlorite (due to the widespread use of the product) they are not considered as major issues due to the reversibility of the observed effects.

Hypochlorite solutions are regulated under European Directives 67/548, 88/379 and 89/542 for labelling. No child-resistant packaging is mandatory for solutions up to 10%.

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4. ENVIRONMENTAL SAFETY

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the Swedish Environmental Research Institute, IVL, Stockholm, Sweden.

4.1 PHYSICO-CHEMICAL PROPERTIES OF HYPOCHLORITE

The physico-chemical properties of a 15% (w/w) solution of sodium hypochlorite (CAS # 7681-52-

9; EINECS 231-668-3) are summarised in Table 4.1.

Table 4.1: Physico-chemical properties of 15% (w/w) sodium hypochlorite solution.

Property	Value	Conditions	Reference
Molecular weight (NaOCl)	74.44 g/M		HEDSET (1994) Hays Chemicals (1995)
Melting point	Solidifies at around - 25°C		
Crystallisation temperature	- 33°C		
Boiling point	107°C		ICI data (1995)
Density	1.193 g/cm ³	20°C	
Vapour pressure	20 hPa	20°C	
Water solubility	Totally miscible		
log Po/w	-	Not measurable	
Henry's coefficient (Cl ₂)	0.6 (= 767 atm, 777 x 10E3 hPa)	20°C	Blatchley <i>et al</i> (1992)
Henry's coefficient (HOCl)	4.52 x 10E-5 (= 0.06 atm, 60.8 hPa)	20°C	
Viscosity	2.6 mPa.s	20°C	Smeets & Van Kesteren (1994)

4.2. FATE & EXPOSURE

4.2.1. GENERAL CHEMISTRY OF HYPOCHLORITE - REACTION PRODUCTS AND IMPURITIES

Hypochlorite is a strongly oxidative chemical which during and after use forms various types of reaction products. The nature of these products depends on the reaction conditions and reaction partners (*Figure 4.1*):

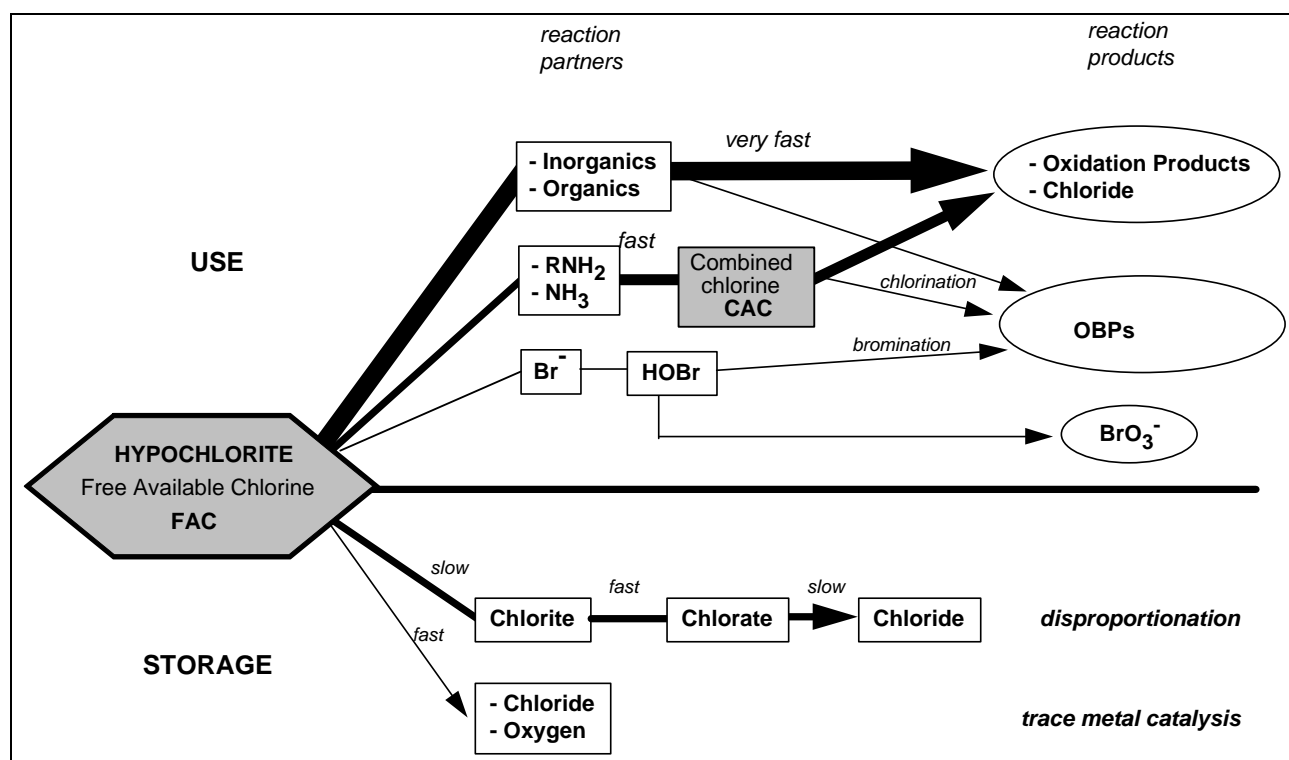
- * **Oxidation** - Under all usage conditions the major reaction mechanism is oxidation of inorganic and organic compounds, yielding various oxidation products and chloride ions. Active oxygen species are generated by hypochlorite as intermediates in the reaction (eg Atkinson & Palin, 1973)
- * **N-chlorination** - In the presence of N-containing compounds (ammonia, amino acids, proteins), the formation of labile N-chlorinated compounds such as chloramines is also an important reaction (eg Johnson, 1975; Pierce, 1978)
- * **Disproportionation-decomposition** - During storage, hypochlorite can disproportionate and decompose. Chlorate, chloride and small amounts of chlorite ions are formed by the disproportionation, while oxygen and chloride are the end-products of the metal catalysed decomposition. The most active metal catalysts are Ni, Co and Cu (eg Lister, 1956; Jolley & Carpenter, 1981, Church, 1994).

- * **Halogenation** - The formation of organohalogen by-products (OBPs) can also occur. Halogenated organics, containing both chlorinated and brominated species, may be produced by substitution reactions at carbon atoms. Bromination may take place in the presence of bromine species as found, for example, in sea water (eg Jolley and Carpenter, 1981; Ghanbari *et al*, 1983). As most of the OBPs are longer-lived in the environment than the parent chemical, hypochlorite, considerable attention is given in this dossier to the OBPs, rather than to hypochlorite itself or its main oxidised reaction products. A safety assessment for hypochlorite would be incomplete without an evaluation of the identity, fate and toxicity profile of these OBPs.

Organohalogens are often quantified as a single group, based on their ability to adsorb to activated charcoal. They can be measured collectively as AOX, but have individually very different environmental fates and behaviours.

Hypochlorite solutions contain a background AOX level of 0.5-50 mg AOX/l (Kolb & Schulz, 1990; Schowanek *et al*, 1996).

Figure 4.1. Schematic overview of hypochlorite-related reaction routes



4.2.2. REACTIONS OF HYPOCHLORITE DURING DOMESTIC USE

There are three main applications for hypochlorite in the home, which determine its domestic reaction conditions: toilet bowl cleaning, laundry bleaching and hard surface cleaning.

In addition, all uses may result in the discharge of residual hypochlorite, which will react in the sewer system. An overview of the expected reaction conditions is shown in *Table 4.2*, based on consumer usage data from AISE member companies.

The chemistry is discussed in the text below. The ratio of NaOCl and the organic material (characterised as COD) gives a rough indication of whether hypochlorite is chemically in excess over its reaction partners under a given set of reaction conditions.

The higher the NaOCl:COD ratio, the more the reactions will shift towards the formation of smaller end-products such as CO₂, chlorinated acids and THMs (Peeters, 1991).

Table 4.2. Typical in-use NaOCl concentrations and reaction conditions

Use	NaOCl (mg/l)	Contact time	Temperature (°C)	pH	NaOCl: COD
Toilet bowl	250 - 50,000 (average: 5,000)	5 - 20 min. (8 h worst case)	15 - 20	9 -13	very high (10 - 500)
Laundry	100 - 500 (average: 200)	3 - 30 min (90 exceptionally)	20 - 40 (60)	8-11	low (< 1)
Hard surface cleaning	100 - 2,500	5 - 30 min.	15 - 40	8 - 11	high->low
Sewage	up to 500	until exhaustion	5 - 25	7 - 9	low (<<1)

4.2.2.1. REACTIONS DURING TOILET BOWL CLEANING

Experimental data which apply specifically to this situation are to our knowledge presently not available. To predict which OBPs could potentially be formed in the toilet bowl, data from use of hypochlorite for drinking water disinfection were used as the best available model, as they also represent situations with an elevated NaOCl:COD ratio ($\geq 1:1$). In the toilet bowl the NaOCl:COD ratio can be much greater than 1:1 and the pH is considerably higher, but still the reaction chemistry is expected to produce overall the same groups of OBPs.

Empirical equations describing the *quantitative* formation of OBPs from a single type of organic precursor (humic acids) in drinking water were

proposed by Urano & Takemasa (1986). The equations illustrate that the amount of chlorinated compounds formed is proportional to the concentration of organic material, active chlorine, and time (*Reaction 1* in the box below).

THM formation is also stimulated by a higher pH (*Reaction 2*). Values for the parameters (k, a, b) in the equations are given in the Urano & Takemasa (1986) paper for different media and reaction conditions.

It should be noted that THMs, unlike TOX, are only formed from specific organic precursors, and that Reaction 2 is therefore not generally applicable.

Key chemical reactions

$$[\text{TOX}] = k_{\text{TOX}} \cdot [\text{TOC}] \cdot [\text{Av Cl}_2]^a \cdot t^b \quad (\text{Reaction 1})$$

$$[\text{THM}] = k_{\text{THM}} \cdot (\text{pH}-a) [\text{TOC}] \cdot [\text{Av Cl}_2]^m \cdot t^n \quad (\text{Reaction 2})$$

t = time

a, m, k_{TOX} , k_{THM} : constants

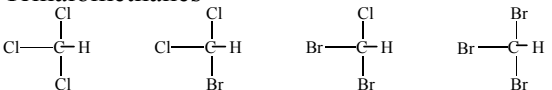
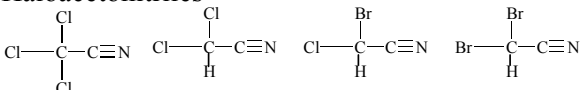

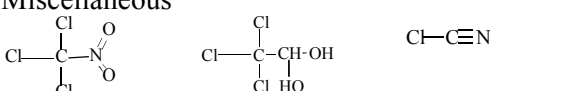
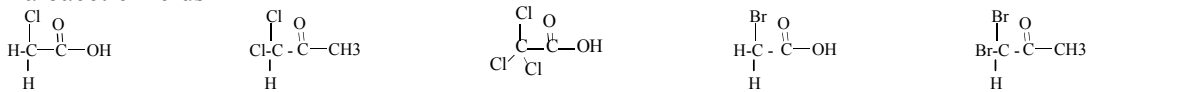


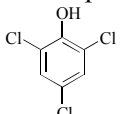


A *qualitative* overview of the OBPs found in chlorinated drinking water is presented in *Figure 4.2*.

In order of decreasing importance, the major classes of compounds identified in drinking water are the THMs, the haloacetic acids and the halogenated aldehydes (Krasner *et al*, 1989).

The main precursors for these OBPs are humic, carboxylic and amino acids.

Additional information is given in Coulston & Kolbye (1994-Chapter 7). According to the Overleggroep Deskundigen Wasmiddelen-Milieu (1989), the expected concentration of the THM fraction in the Dutch drinking water distribution system is 3-45 µg/l. In addition, the non-volatile fraction in this tap water (such as chlorophenolics, di- and trichloroacetic acid and chloromaleic acid) would be 25-200 µg/l. A THM:Total OBP ratio of 1:3-1:4 is suggested by eg Singer & Chang (1989) and Peeters (1991).

Figure 4.2. Disinfection by-products in drinking water (Krasner et al, 1989)

Trihalomethanes 				Haloacetonitriles 					
Chloroform	Dichlorobromomethane	Dibromochloromethane	Bromoform	Trichloroacetonitrile	Dichlorobromoacetonitrile	Bromochloroacetonitrile	Dibromoacetonitrile		
Haloacetones 			Miscellaneous 						
1,1-Dichloropropanone		1,1,1-Trichloropropanone		Chloropicrin (trichloro-nitromethane)	Chloral hydrate	Cyanogen chloride			
Haloacetic Acids 									
Monochloroacetic acid	Dichloroacetic acid		Trichloroacetic acid	Monobromoacetic acid	Dibromoacetic acid				
Chlorophenols 				Aldehydes 					
2,4,6-Trichlorophenol				Formaldehyde		Acetaldehyde			

The contact time in the toilet is considered of prime importance in the prediction of type and amount of OBPs; if limited to around 10 minutes, OBP formation in the toilet can be largely avoided.

The elevated pH, the low solubility of the organic matter and presence of reduced compounds will retard chlorination. As a result, the AOX formed will be only a small fraction of the AOXFP of the solution (Overleggroep Deskundigen Wasmiddelen-Milieu, 1989).

Under normal usage conditions (contact time around 20 minutes) the average THM formation

in the toilet is estimated to be 1-15 µg/l (HOV-Studie, 1987; Overleggroep Deskundigen Wasmiddelen-Milieu, 1989).

However, with reaction times of 30 minutes or longer, the AOXFP will be extensively exploited and the newly formed OBPs may equal or exceed the background levels in tap water.

Table 4.3 presents another expert judgement of the types of OBPs that may be formed in the toilet (Peeters, 1991). The predicted concentrations depend on the contact time, and are somewhat higher than in the former estimate.

Table 4.3. Expected formation of OBPs in the toilet bowl according to Peeters (1991) for a contact time > 20 minutes

CLASS OF COMPOUNDS	COMPOUND	PREDICTED CONCENTRATION (µg/l)
Trihalomethanes	Chloroform	15 - 75
	Bromodichloromethane	3 - 10
Dihaloacetonitriles	Dichloroacetonitrile	1 - 2
Haloketones	1,1,1-trichloroacetone	1 - 2
Haloaldehydes	Chloral	1 - 5
Halocarboxylic acids	Dichloroacetic acid	7 - 20
	Trichloroacetic acids	5 - 75
	Dibromoacetic acid	3 - 5
	Dichlorinated acids	2 - 20
Halophenols	Chlorophenols	0.1 - 0.2

4.2.2.2. REACTIONS DURING LAUNDRY BLEACHING

This area is covered in part by experimental work by Colgate-Palmolive (1990, unpublished) and Smith (1994). In addition, the reactions taking place in drinking water preparation and pulp & paper bleaching may to some extent serve as model systems to aid understanding. Colgate-Palmolive (1990, unpublished) investigated AOX

as well as chloroform formation during laundry washing at 60°C and 90°C with regular detergents and hypochlorite (125 ml of a 4.4% active chlorine solution) added in the pre-wash or main wash. The experiments showed a small but statistically significant increase in AOX, situated between 0.15 and 1.7 % of the added NaOCl.

Indications were found that soil present on the fabrics could enhance AOX formation. This effect could be explained by the presence of some catalysts. The study showed also that on average 48% (range 27-67) of the formed AOX in laundry wash waters, after the use of bleach or bleach + detergent to clean clothes, was eliminated when the wash waters were tested in a 28-day ready biodegradation test (OECD 301C).

Similarly, Smith (1994) reported that the total AOX formed per job (15 minute wash at 38-50°C, sealed machine, 69 litre wash water) ranged from

55-539 mg (= 800-7800 µg/l), of which chloroform represented 5-13%. The NaOCl to AOX conversion efficiency in these experiments was 0.7-4% (6.2% in one sample). The above results are shown in more detail in *Table 4.4*.

Variations in parameters such as wash time, temperature and concentration of hypochlorite had only a small effect on the AOX produced. However, AOX was found to correlate closely with the organic load of laundry wash water (*Equation 1* below).

Key equation

$$\text{AOX (mg/l)} = 0.0155 \times \text{TOC (mg/l)} \quad (\text{correlation coefficient } r^2 = 0.95) \quad (\text{Equation 1})$$

A large proportion of the individual OBPs constituting the AOX in laundry wash water remains to be identified. Volatile compounds that represented more than 1% of the laundry-AOX were chloroform (10-20% typically), dichloroacetonitrile and bromodichloromethane. Haloacetic acids (eg dichloroacetic acids 6.2%, trichloroacetic acid 5.2%) were reported by Smith

(1994) and Colgate-Palmolive in wash water extracts (*Figure 4.3*). Traces of mono-, di- and trichlorinated phenols were detected in one test, but it is not certain that they were related to hypochlorite bleaching (Colgate-Palmolive, 1990 - unpublished).

Smith (1994) detected no chlorophenols.

Figure 4.3. Identification of the major OBPs in a laundry bleaching experiment (Smith, 1994)

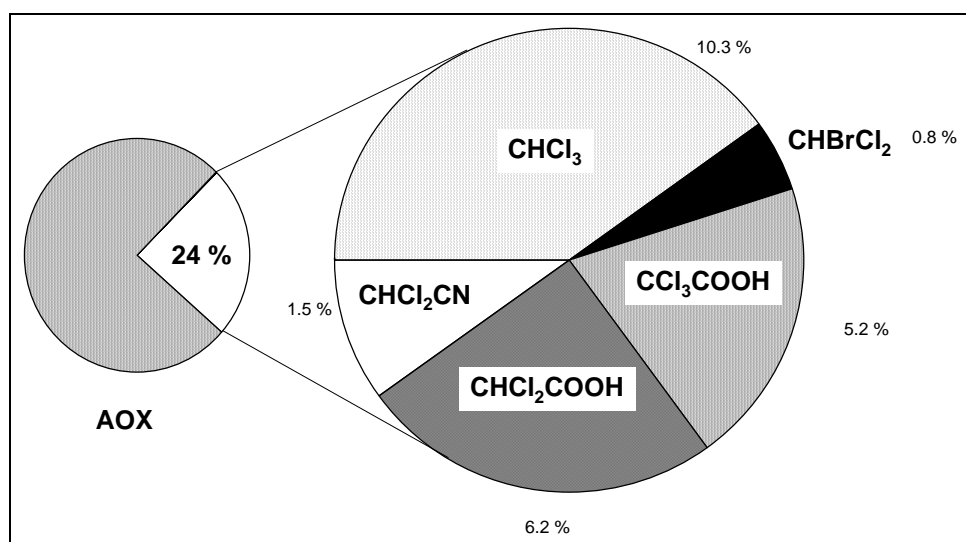


Table 4.4. Overview of organohalogenes formed during laundry bleaching (Smith, 1994 and Colgate Palmolive, 1990 - unpublished)

Compound	Total/wash (mg)	Concentration (mg/l)	NaOCl-AOX Conversion (%)	% of AOX	% of POX
Colgate-Palmolive data (*)			5-158 mg/l NaOCl dosed		
AOX (average)	80	1.1	0.6		
AOX (max.)	366	5.3	1.7		
- CHCl ₃	69 (max)	1.0		17	majority
Smith (1994) data			120-200 mg/l NaOCl dosed		
AOX	258 (average) 55 - 539 (min-max)	3.74 0.8-7.8	2.6 0.7-6.2		
- CHCl ₃	37 (average) 16 - 61 (min-max)	0.54 0.23-0.88		10 5-13	77 64-86
- CHCl ₂ CN	8 2 - 20 (min-max)	0.12 0.03-0.29			16 6-31
CHBrCl ₂	1.3	0.02			7
CHBr ₂ Cl	<0.1				<1

* Calculated for 69 litre wash water

Domestic reaction conditions for bleach are much milder than those in pulp bleaching, and the reaction partners differ.

The hypothesis can be made that fat, protein and humic-acid type material from soiled laundry and tap water will give rise to traces of chlorinated acids and possibly chlorophenols, but also to a considerable high molecular weight AOX fraction (ie >600-1000 Dalton).

This part is difficult to identify analytically and may account for a large part of the currently undefined AOX (see *Figure 4.3*).

Following this hypothesis, from a safety perspective the latter material can be considered as virtually biologically inert, because the potential to penetrate the cell membrane and the

bioavailability of any molecule of that size is very limited (Gobas *et al*, 1986; EEC 1993).

It is important to note that studies in the laboratory of Professor Rappe, University of Umel, Sweden demonstrated that hypochlorite bleach used for washing does not give rise to dioxin formation (Rappe *et al*. 1990; unpublished results reported by Colgate-Palmolive, 1991; Office of Nature Conservancy, Sweden, Report 4009, 1992).

This outcome was also expected on the basis of the prevalent reaction conditions in the home and mechanistic/chemical considerations.

The same studies showed also that dioxins, if analytically detectable in the commercial bleach formulation, are present at levels equivalent to or less than the general environmental background.

4.2.2.3. REACTIONS DURING HARD SURFACE CLEANING

A series of quantitative experiments by Henkel (1992, unpublished) studied AOX formation during household tasks such as cleaning floors, counters and toilet floors.

Key conclusions were:

- * If bleach is the only cleaning agent, the amount of AOX in the spent cleaning liquor remains below 1.5 mg/l
- * If bleach is mixed with other cleaners (this may occur, for instance, if bleach is added occasionally during hand dish-washing), there may be a significant increase in the AOX formed. In this case, average AOX was 10 ppm with two outliers close to 50 mg/l. Considering the amount of bleach used for each sample (average 73 ml), the average degree of conversion of NaOCl to AOX was high, at 1.26% (0.8%-1.7% for 95% available Cl).
- * Additional testing in control experiments carried out without soil proved that these high AOX values were mainly linked to the presence of efficient AOX precursors in some dish-washing products.
- * The relationship between organic material and newly-formed AOX is very similar to that seen in laundry bleaching: $\text{AOX (mg/l)} = 0.015 \times \text{TOC (mg/l)}$. A preliminary estimate for the average degree of NaOCl-to-AOX conversion for the various jobs was 0.2-0.4%.

As indicated in *Table 4.2*, the initial NaOCl:COD ratio in hard surface cleaning solution is high, but drops rapidly with the introduction of soil. As such, a wide variety of OBPs is to be expected. Initially, some volatile compounds (type THMs) will be produced.

With the further soiling of the solution, the reactions will become incomplete and the OBP pattern will shift from small volatile compounds towards formation of intermediate chlorination products.

These will probably include haloacetic acids, mono- and dichlorinated phenols and complex chlorinated organic material which may resemble the products formed in sewage (see below).

No data on the exact identity of the OBPs are currently available.

Preliminary work on the interaction of hypochlorite with casein, maize oil and starch has suggested that more AOX is produced when hypochlorite reacts with proteins than with fats or hydrocarbons. The interaction of hypochlorite (0.35%) with specific amino acid solutions (0.1%) has now been investigated in more detail. This indicated that the more complex the amino acid, the greater the amount of AOX formed, varying from 0.3 mg AOX/l for glycine (similar to hypochlorite alone) to 21.5 mg AOX/l for arginine, and up to 101.5 mg/l for proline (Lever, 1996 - unpublished).

4.2.3. REACTIONS OF HYPOCHLORITE AFTER USE

4.2.3.1. REACTIONS WITH SEWAGE

Due to its domestic use, some residual hypochlorite may be present in the discharged

waste water. In drains and sewers, residual hypochlorite will further react with inorganic and

organic sewage components, which are in excess over hypochlorite. The hydraulic residence time in these systems is typically 1-24 hours.

The *theoretical* average NaOCl concentration in sewage can be calculated on the basis of total usage figures (*Table 1.1* - right-hand column) and the mean EU water consumption (200 l per capita per day). This leads to around 0.12 mg/l for Germany (lowest value) and 6.5 mg/l for Spain (highest value). These values represent an unrealistic worst case situation, assuming that no reaction has taken place during application.

In practice, the hypochlorite emission of an individual household will be nil most of the time, but short and local peak concentrations up to 500 mg/l unreacted NaOCl may occur in individual household discharges, immediately after discharge of spent solutions (for example, after toilet bowl cleaning). In a large sewer system, these individual peaks will be averaged by dilution, rapid decay will occur, and actual in-sewage concentrations will be much lower and show less variability (see section on decay, 4.2.3.2.).

The pH of well-buffered municipal sewage (7-8.5) is not affected by the discharge of hypochlorite at the above mentioned concentrations. A pH of 7.5 implies a 50:50 ratio of HOCl and OCl⁻, and the presence of the more reactive hypochlorous acid (HOCl) than in the toilet bowl, with its elevated pH conditions.

A typical COD value of domestic waste water would be around 400 mg/l, versus 0.25-4 mg NaOCl/l. The average ratio of hypochlorite to other sewage constituents is therefore very low (<<1). During peak emissions only, it can reach up to 1:1 locally.

The following organic sewage constituents were found in mechanically treated sewage, in decreasing order of concentration (Painter, 1971):

- * Fats and greases, free and esterified, saturated and unsaturated fatty acids (174 mg/l),
- * Carbohydrates, ranging from simple sugars to complex polysaccharides, starch, etc. (104 mg/l),
- * Proteins and their breakdown products like amino acids (60 mg/l), volatile acids (25 mg/l),
- * Surfactants (23 mg/l),
- * Soluble acids (12.5 mg/l),
- * Urea and its breakdown products (2-16 mg/l),
- * Creatine (6 mg/l),
- * Phenols (0.2 mg/l),
- * Aliphatic amine (0.1 mg/l).

Reduced inorganic constituents are present at a rather low concentration in municipal sewage (mostly <0.1 mg/l), except for ammonia (Painter, 1971). In municipal sewage up to 70 mg/l total-N can be recorded, mainly in the form of urea and proteins (Rueffer, 1964) which are degraded to ammonia. An analysis of sewage in the UK showed 46 mg/l NH₃-N and 22 mg/l organic N (Painter, 1971). Hence, ammonia will on average be present at a 10-fold stoichiometric concentration versus hypochlorite, and N-chlorination will be a major process. Monochloramine will be the predominant species.

Formation of THMs and other volatile organohalogens, which require high concentrations of FAC and the completion of a long reaction sequence, is virtually impossible in sewers (Overleggroep Deskundigen Wasmiddelen-Milieu, 1989). At high NaOCl doses (> 10 mg/l) CHCl₃ represents 5-15% of the AOX (Raff *et al*, 1987).

A chlorination study of primary and secondary sewage by Jolley (1975) showed that 99% of the added FAC is consumed in oxidation reactions

and only <1% (on Cl weight basis) is incorporated into organic compounds (Jolley, 1975). Forty-six additional OBPs were identified after chlorination. It should be added that the studies were conducted in such a way that a residual FAC content of 2 mg/l was maintained with 60 minutes reaction time to simulate a worst-case situation. A figure around or below 1% AOX formation yield is also cited independently by Mills (1978) and Hull and Reckow (1993).

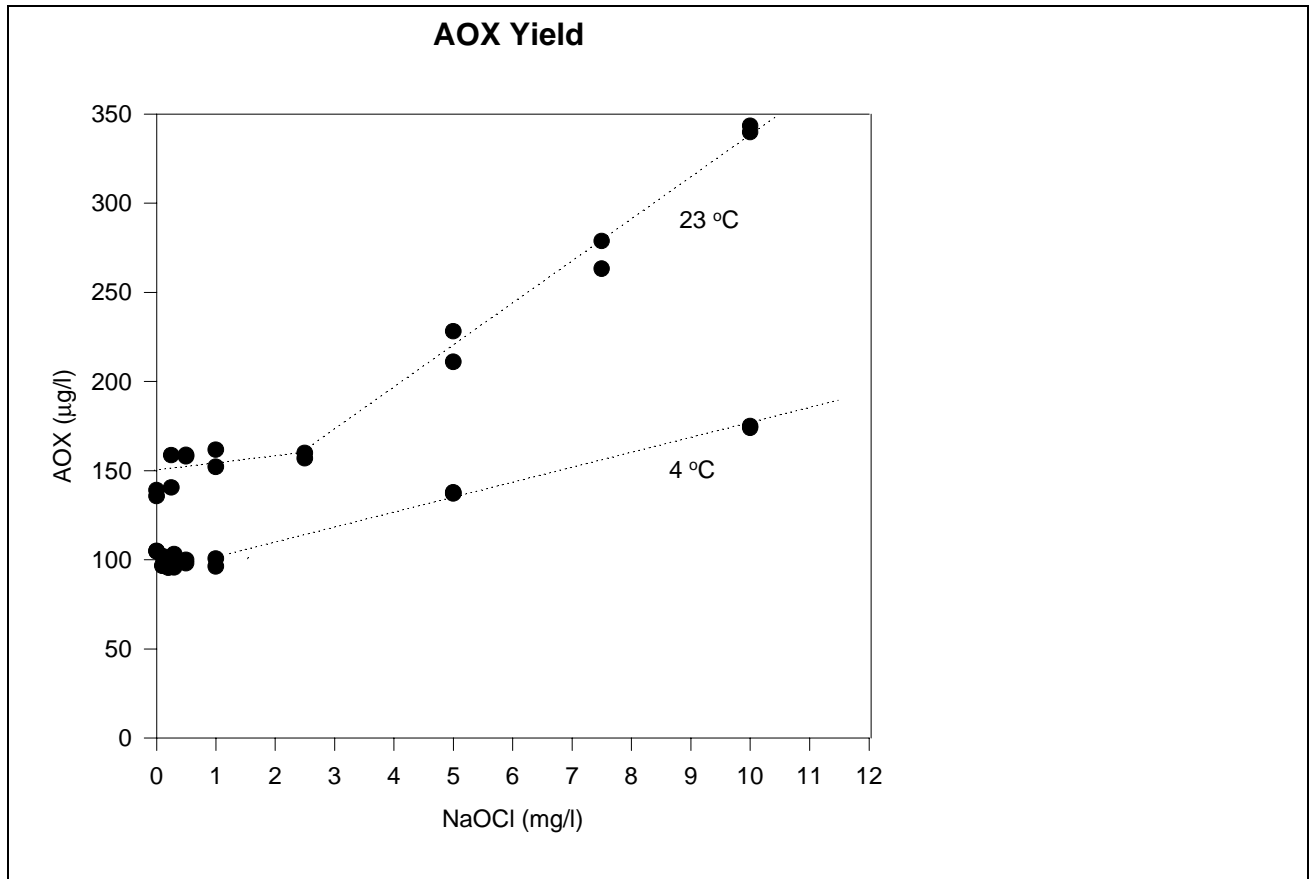
Studies with secondary effluent, using a NaO^{36}Cl tracer, gave comparable results of <1% and 1.4% incorporation of the chlorine into organic sewage constituents (Faith *et al*, 1980; Koczwara *et al*, 1983). Mori *et al* (1978) found that 0.01% of the FAC applied to primary effluents ends up as volatile halogenated compounds.

Raff *et al* (1987) reported a 0.6% NaOCl-to-AOX conversion upon continuous dosage of 7-10 mg NaOCl/l in an activated sludge unit. The authors noted that the AOX formed was of a polar and macromolecular nature.

Figure 4.4 shows another experiment on AOX formation in sewage (Schowanek *et al*, 1996). Under these experimental conditions there seems to be a threshold effect before chlorination starts. This can probably be attributed to a buffer effect from the presence of reduced compounds, which up to a certain dose are immediately oxidised by the hypochlorite added. The slope of the curve suggests a degree of NaOCl-to-AOX conversion of 0.75-2.25%, depending on the reaction conditions.

In summary, the degree of conversion of NaOCl (FAC) to AOX in sewage is around 1%. This is the same order of magnitude as in laundry wash water. Virtually all identified non-volatile chloroorganic compounds identified in sewage under realistic formation conditions were monochlorinated ones. 5-chlorouracil, 5-chlorouridine, 8-chlorocaffeine, 2-chlorophenol and 8-chloroxanthine were the five compounds present at the highest concentration in the Jolley study (Jolley, 1975). Peeters (1991) suggests that halogenated carboxylic acids, dichloroacetonitrile, chlorocyanide and chloropicrin can also be formed in sewage.

Figure 4.4. AOX formation in raw domestic sewage as a function of the NaOCl added. The test was run at 4 and 23°C (NB: the sewage samples were not the same). The reaction time was 1 h.



4.2.3.2. DECAY KINETICS OF HYPOCHLORITE IN SEWAGE AND SURFACE WATERS

a) Chemical kinetics

In the environment, hypochlorite is involved in a range of reactions (*Reactions 1-5* below).

Key reactions

1. Fast oxidation of inorganic and organic substances (eg reduced sulfur compound, nitrite, bromide, reactive amino acids and other organic constituents). Hypochlorite itself is reduced to chloride.

HOCl	+	reduced inorganics	---k0--->	oxidised inorganics	+	Cl ⁻	(Reaction 1)
HOCl	+	organics	---k2--->	oxidised organics	+	Cl ⁻	(Reaction 2)

2. Reactions with inorganic and organic nitrogen compounds forming inorganic and organic monochloramines.

HOCl	+	RNH ₂	---k1--->	RNHCl	+	H ₂ O	(Reaction 3)
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The monochloramines have a further oxidation and chlorination ability due to much slower reaction kinetics. They have also the potential to be further oxidised by HOCl.

RNHCl	+	organics	---k4--->	oxidised organics	(Reaction 4)		
HOCl	+	RNHCl	---k3--->	HCl	+	RNO	(Reaction 5)

3. Slower oxidation reactions with organic substances, and substitution and addition reactions in which chlorine is incorporated in the organic molecule.

Various model studies with phenols, ammonia, amino acids and other reactive organic compounds showed predominantly an oxidation of these substances within about 2 h reaction time.

Chlorination of organics is clearly retarded by the presence of ammonia but could take place after a longer reaction time (Murphy *et al*, 1975).

The chlorination of ammonia is about 1000 times faster than chlorination of phenol (Lee & Morris, 1962). The CAC gives rise to very little THMs, but non-volatiles may still be formed (Peeters, 1991).

In the presence of a large excess of reaction partners, hypochlorite decays very fast in sewage and activated sludge. A dose of 10.7 mg/l NaOCl added to mechanically treated **sewage** disappeared within 2 minutes (Topping, 1985). Johnson (1978) measured the kinetics of chlorine residuals in **water** and found that FAC disappearance in sewage follows a first order pattern in FAC, with a rate constant > 2.8 h⁻¹ (i.e. a half-life < 15 min). TAC (FAC + CAC) decay in **river water** equally behaves approximately according to a first order model, with half-lives in the order of 45-60 minutes (k = 0.83-1.17 1/h; Milne *et al*, 1993).

Reported half-lives for the stability of monochloramine vary between 10-70 minutes in chlorinated waste water treatment facility samples kept in a laboratory (Yoon & Jensen, 1995), 2-23 hours in effluent containing ammonia (Johnson,

1978), and 9-157 hours in river water (Lin *et al*, 1983) with the longer half-lives being from samples kept in the dark. This indicates that photolysis is a mechanism by which monochloramine is degraded.

b) Decay modelling

The decay of HOCl in sea water has been described before by using chemical models (Haag & Lietzke, 1980).

By using the above chemical reactions (equations; 1, 2, 3, 4 and 5) a kinetic model was developed to describe the HOCl and chloramine concentration in the sewer, the waste water

treatment and river. The reaction constants $k_0=25$, $k_1=12$, $k_2=1$, $k_3=2$, $k_4=0.1$ (units: l/mol.s) were chosen based on Lawler (1984), Unilever (unpublished, 1996), and Schowanek *et al* (1996).

Calculations were made using the following assumptions:

Assumed data:

	SEWER	ACTIVATED SLUDGE AERATION TANK	RIVER
Ammonium conc. (mg/l)	36	1	0.1
FAC (mg/l)	8	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 FAC (Fig. 4.5a) during transport in the sewer. An abundance of reaction partners allows a fast reaction. The HOCl/OCl⁻ (expressed as FAC) concentration estimated at the end of the sewer drops below 1.E-32 µg/l.

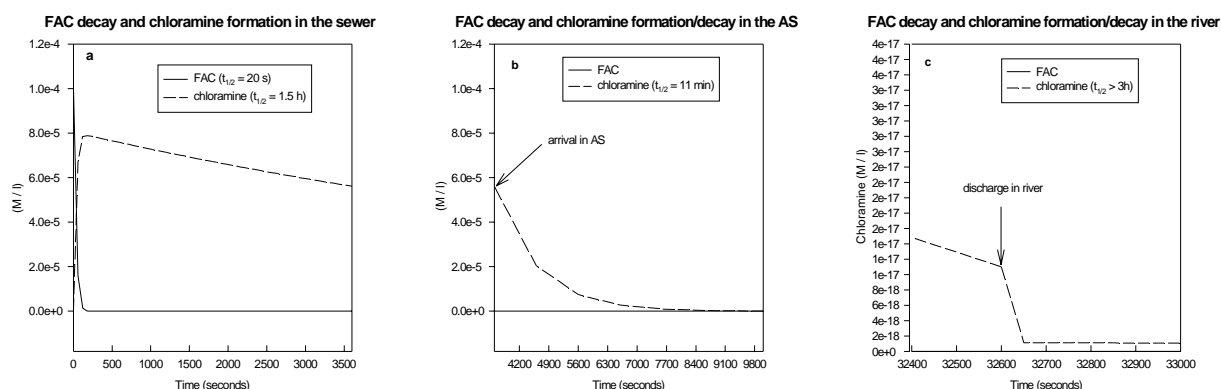
The drop in FAC is in parallel with a sharp increase of the chloramine concentration, which can be explained by the high availability of ammonia in the sewer.

Chloramine further reacts as an oxidant during additional transport in the sewer, the activated sludge unit (Fig. 4.5b) and in the river (Fig. 4.5c).

The extensive degradation of chloramine in the activated sludge unit can be explained by the presence of reduced organic material.

Chloramine is estimated to fall below 5 E-10 µg/l in the river.

Figure 4.5. Modelling of the decay of FAC and formation/decay of chloramine during transport in the environment.



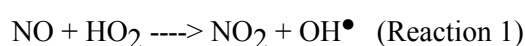
4.2.3.3. REACTIONS IN THE ATMOSPHERE

Sodium hypochlorite has negligible volatility, whilst hypochlorous acid has a low volatility. The dimensionless Henry's coefficient for HOCl is estimated as 4.52×10^{-5} (Blatchley *et al*, 1992), and measured as 0.3 for NCl_3 at pH 7.5 and 20°C by Holzwarth *et al* (1984). The equilibrium concentration of hypochlorous acid vapour in the gaseous phase above a solution of 0.85g NaOCl/l depends upon the solution pH, as expected from the fact that hypochlorous acid is volatile but the hypochlorite anion is not. It increases from ~ 0.001 ppm when the solution pH is 11 (similar to usage pH), up to ~ 10 ppm when the solution pH falls to 7.5 (typical of after-use effluent) (P&G, 1992 - unpublished). The value of 10 ppm is equivalent to $\sim 6 \text{ mg/m}^3$ hypochlorous acid vapour in the gaseous phase immediately above a litre of a 0.85g NaOCl/l solution.

Any hypochlorous acid vapour reaching the troposphere is likely to undergo rapid photolysis, forming OH^\bullet and Cl^\bullet radicals (Graedel, 1980).

Hydroxyl radicals are the initiators in the majority of atmospheric chemical processes in the troposphere. They can lead to the creation of ozone via reactions with organic compounds (Atkinson, 1989), the production of nitric and sulfuric acids (contributors to acid rain) and the formation, from hydrocarbons, of aliphatic aldehydes (eye irritants present in smog). However hydroxyl radicals present in urban atmospheres are primarily formed by *Reaction 1* below (Graedel, 1980), and the contribution from the photolysis of bleach-derived hypochlorous acid can be shown to be negligible via a tropospheric budget of reactive chlorine (Graedel & Keene, 1995).

Key reaction



This budget indicates that the background level of about 1.5 ppb is made up from nine species, with one of these, inorganic chlorine (ie HOCl from all

uses and/or Cl_2), representing just a few percent of that total. Data recorded above eastern North America gave a value for HOCl + Cl_2 of <26 ppt,

and indicated that anthropogenic activities including water purification apparently do not directly emit significant amounts of HOCl to the troposphere (Maben *et al*, 1993).

Chlorinated species, predominantly hydrogen chloride, exist in the troposphere, mainly above the open oceans, and can upon reaction with OH[•] also produce chlorine radicals/atoms.

The reactions of these radicals have been reviewed in some detail. Available data show that most chlorine atoms in the troposphere are likely to be consumed by organic compounds. This occurs via the abstraction of hydrogen to form hydrogen chloride, rather than by addition to the organic species (Graedel, 1980; Chlorine Institute Pamphlet, 1990; Keene, 1995). This indicates that the chlorination of organic compounds in the atmosphere is likely to be insignificant.

4.2.4. FIELD STUDY RESULTS - *IN SITU* MONITORING OF AOX FORMATION FROM HYPOCHLORITE

A field monitoring program was carried out on the sewage of five large apartment blocks in the city of Parma, Italy, to quantify *in situ* the organohalogen compounds emitted as a result of the domestic use of bleach containing sodium hypochlorite (Schowanek *et al*, 1996). The halogenated by-products present in the sewage were determined as AOX. The average AOX level was determined for three distinct experimental phases, each lasting 21 days: an "undisturbed period", a "no bleach period", and a "period with monitored bleach consumption". The study involved the participation of the site inhabitants in the second and the third phase. This design allowed in a highly realistic way to 1) compare a bleach-use situation with a no-bleach use situation, and 2) to quantify the fraction of NaOCl involved in halogenation reactions.

While all average AOX concentrations observed in this study fell within the typical range for domestic sewage across Europe (around ca. 50-250 µg AOX/l), an effect from the use of

hypochlorite bleach on the AOX concentration in domestic sewage was detected. In absolute terms, the difference in average sewage concentration between a "no bleach" (106 µg AOX/l) and an "undisturbed" bleach use situation (143 µg AOX/l) was 37 µg AOX/l (P<0.05). In relative terms, hypochlorite bleach contributed around 26% of the total AOX level in sewage at this particular site. Other sources of AOX in sewage were not quantified in this study. The POX fraction of the AOX was not measured separately.

The degree of NaOCl-to-AOX conversion was of the order of 1.5% (w/w). For perspective, this corresponds to a conversion of 0.075% (w/w) for bleach containing 5% NaOCl. These values are in good agreement with literature data. The average bleach-related AOX emission at the study site was around 7 mg per inhabitant per day. The EOX/AOX ratio, and the identity of the organohalogen was not further investigated in this study (EOX/AOX ratios have been published by Bakker *et al*, 1995).

4.2.5. FATE OF HALOGENATED BY-PRODUCTS

4.2.5.1. ATMOSPHERIC REACTIONS OF THE VOLATILE HALOGENATED BY-PRODUCTS

In domestic use hypochlorite can react with many of the chemical species present in a soil, producing a variety of volatile halogenated compounds. Photolysis is a well-described and efficient degradation mechanism for many of these (Atkinson, 1989; Zetzsch & Becker, 1989).

Chloramines

Initial contact between a high concentration of hypochlorite and ammonium salts is likely to result in the short-term production, via monochloramine and dichloramine, of a small amount of trichloramine. Although this compound is rapidly hydrolysed to dichloramine (Heltz, 1980), a low level of trichloramine would be expected to reach the atmosphere due to its high volatility - it has a Henry's constant of 0.3 at 20°C (Holzwarth *et al*, 1984; this paper quotes Henry's constants in dimensionless units, but by comparison with the Blatchley *et al*, 1992, it is believed that they should be in atmospheres). In the atmosphere trichloramine is believed to undergo photolysis. The total maximum discharge, through ventilation, of trichloramine from the use of chlorinated compounds in swimming pools in France, could be around 2.5 tonnes, and only about 0.2% of the total chlorine consumed (Verhille, personal communication; Mannschott *et al*, 1995).

Upon dilution of the hypochlorite and lowering of the pH, which occurs during use, only the less chlorinated chloramines are likely to continue to form, with monochloramine being substantially more abundant than dichloramine. Monochloramine is volatile, with a Henry's constant of 0.45 atm at 20°C (Holzwarth *et al*, 1984, see above) and a dimensionless value of 3.4×10^{-4} .

However, monochloramine is unstable - at 0°C it will decompose to nitrogen, ammonium chloride and trichloramine (Mellor, 1931). In solution it will decompose by hydrolysis to ammonia and hypochlorous acid with a half-life of 10 hours (Margerum *et al*, 1978). Monochloramine can also break down in the presence of nitrogenous organics, such as proteins, via the transfer of chlorine to form organic chloramines (Yoon & Jensen, 1995). In view of the instability of monochloramine in solution, the levels in the gas phase above it are likely to be low.

Chloroform

The most abundant of the volatile AOXs formed in the household use of hypochlorite is chloroform, which has been predicted to be present at 15-75 µg/l in toilet cleaning waste water (Peeters, 1991) and measured at levels of 230-1000 µg/l in laundry bleach wash waste water; Smith, 1994; Colgate-Palmolive, 1991 unpublished).

Chloroform has a high vapour pressure of 160 mm Hg (0.21 atm.) at 20°C (Verschueren, 1983) and is thus likely to evaporate during use, in sewage treatment and from natural water. The half-life for the evaporation of chloroform from a 6.5 cm depth of a 1 mg/l solution is around 35 minutes at 1-2°C, and around 22 minutes at 25°C (Dilling, 1977). A half-life of 36 h has also been reported by Euro Chlor (1994). Almost complete volatilisation of chloroform can be expected. From its vapour pressure and water solubility of ~8000 mg/l at 20°C (Verschueren, 1983) a dimensionless Henry's constant of 0.13 can be calculated. Thus, at equilibrium the concentration of chloroform in the gas phase above one litre of a waste water solution containing chloroform can be calculated.

A comparison of calculated levels with the measured data is given in *Table 4.5* below:

Table 4.5. Measured versus calculated chloroform levels in air after domestic use of hypochlorite.

Domestic Use of NaOCl	Measured Conc CHCl ₃ in waste water	Calculated Conc CHCl ₃ in air directly above	Max Measured Conc CHCl ₃ in air in ~7.7 m ³ room [1]
Toilet Cleaning	15-75 µg/l	2-10 mg/m ³	---
Laundry Bleach	230-1000 µg/l	30-130 mg/m ³	1.2 mg/m ³
Hard Surface Cleaning (Shower)	---	---	1.4 mg/m ³

[1] Smith, 1994

The calculated concentrations represent a worst-case scenario, as no dispersion of the chloroform with air flow is incorporated. Measured values are significantly lower, and well below the Permissible Occupational Exposure Limits in the US and Germany of 50 mg/m³.

Substantial further reductions in the chloroform concentration would be expected upon mixing within the atmosphere.

There are also many natural sources of chloroform, such as volcanoes, plants (barley, lemon, orange, cedar, moss) (Euro Chlor, 1994), seaweeds (Gribble, 1995) and algae (Siuda, 1979). However, the measured levels of chloroform in air vary from <0.015 to only 15 µg/m³, depending on locality.

Far away from anthropogenic sources, chloroform levels range from <0.015-0.225 µg/m³ (van der Heijden *et al*, 1986), whilst those at urban sites in the US range from 0.3- ~10 µg/m³ (ATSDR, 1991/1993), and in Japanese and European cities from 1 to 15 µg/m³ (Su & Goldberg, 1976).

For a total European consumption of commercial hypochlorite product of 1500 x 10E3 te per annum containing 5% NaOCl (Table 1.1), a conversion to AOX of 1.5% (Schowanek *et al*, 1996), and the assumption that around 30% of the AOX formed is volatile and could be chloroform, then the maximum emission of chloroform to the atmosphere is ~ 340 te. This quantity is insignificant when compared to either the yearly emission of VOCs from natural sources (around 2 million te) or the total yearly emission of VOCs (around 20 million te) in Europe in 1985 (Corinair, 1995).

Available data indicate that chloroform has a residence time in the atmosphere of several months, with a calculated half-life of 100-180 days for its degradation. The probable underlying mechanisms are direct photolysis and reactions with strong oxidants such as singlet oxygen or hydroxyl radicals (van der Heijden *et al*, 1986, Euro Chlor 1994, Zetzsch & Becker, 1989). Chloroform deposition half-life has been estimated to vary from more than 20 days to 900 years (IPCS EHC 163, 1994).

During its presence in the atmosphere, chloroform is not expected to affect ozone levels significantly. It has a Photochemical Ozone Creation Potential (POCP) cited in the VOCs protocol of 0.7, which puts it in the lowest category for VOC controls and with materials whose reduction in emissions are not mandated under the protocol.

As chloroform has a life-time of at most around six months, little or none will reach the

stratosphere. Hence if an Ozone Depletion Potential (ODP) were to be assigned to chloroform, under the UNEP Science Assessments for the Montreal Protocol, 1994, its ODP would be defined as zero.

In addition, chloroform has been assigned a low Global Warming Potential (GWP) of 25 for a 100 years time horizon, and qualitatively is shown to have a negative indirect contribution (Houghton *et al*, 1992).

4.2.5.2. BIODEGRADABILITY AND TREATABILITY

General

Hypochlorite in itself represents no BOD/COD load. In fact it reduces the COD by oxidising organic matter.

The biodegradability of individual halogenated organic compounds depends mainly on:

- (1) their degree of halogenation (it decreases with increasing halogenation)
- (2) the positions of the halogen atoms and other substituents, as this is important for the degradation pathway
- (3) the molecular weight (Neilson *et al*, 1991).

Sewage Treatment

Activated Sludge: The average practical elimination of AOX formed from domestic bleach, as tested in a Semi Continuous Activated Sludge (SCAS) test, is moderate to good. Smith (1994) observed a 59-73% removal of this type of AOX, with little adsorption measured. Similar removal figures were measured by Colgate-Palmolive (1990 unpublished).

Enzymatic (hydrolytic, oxidative and reductive) as well as non-biological (photolytic, radical) dehalogenation mechanisms have been described (eg Leisinger & Brunner, 1986; Stora Teknik, 1990, Janssen *et al*, 1991). As a rough guideline, aerobic biological metabolism can cope with 2-3 halogen substituents, while reductive (anaerobic) dehalogenation may cope with higher substitutions (Gottschal & Gerritse, 1996). However, an individual assessment of each compound based on the number and position of the substituents is needed to predict more exactly the biodegradation potential and route (Neilson *et al*, 1991).

Degradation of up to 85-90 % can be reached after acclimation of the biomass and with prolonged contact times (Henkel Metabolites Test, 1993 unpublished). This degradation potential is in the same range as for the other organics present in domestic effluent. For volatile OBPs, stripping results in a high level of removal (>90 %) in aerobic sewage treatment.

A qualitative and semi-quantitative overview of halogenated compounds remaining in secondary effluents after chlorination of domestic sewage is given for example by Clark *et al* (1991). All compounds were present at low ppb levels, or below, and the total level of organohalogenes varied between 5-100 µg/l, depending on the source of the waste water and period concerned.

After discharge, a slow but consistent degradation is expected to reduce environmental concentrations further. This degradation was demonstrated by mass balances for pulp and paper AOX in lake sediments (Grimvall *et al*,

Examples of Degradation of Organohalogenes

Inherent degradability, and a high potential for removal in sewage treatment under optimal operational conditions has been demonstrated for the majority of AOX compounds identified in domestic bleaching. A detailed discussion for each individual compound falls outside the scope of this dossier. Instead, a number of examples and guidelines are given per class of relevant organohalogenes.

The spectrum of known or predictable OBPs ranges from aliphatic C1 to C6 compounds, as well as larger compounds such as halogenated long chain fatty acids, aromatic compounds, humic material and proteins.

According to Janssen *et al* (1991), most of the chlorinated short-chain aliphatic compounds are biodegradable under aerobic conditions. This includes, for example, mono-, di- and trichloroacetic acid and dichloromethane, which

1991). The rates will depend on the ambient conditions and the type of chemical (structure, degree of halogenation, (de)sorption properties, etc).

Septic Tank: Smith *et al* (1995) reports 87-94% removal of AOX associated with the use of hypochlorite in bleached laundry wash water, when treated in a domestic septic tank system followed by soil leaching. As adsorption was found to be insignificant, it was concluded that AOX was removed by biodegradation or by chemical decomposition.

are typical organohalogenes in bleached effluents. Halogenated aliphatic compounds such as disubstituted alkanes and substituted fatty acids and their esters are dehalogenated by bacteria isolated from sewage and soil extracts (Omori & Alexander, 1978a, b).

Mono- and dichlorobenzoates, and dichlorophenoxyacetic acid are inherently biodegradable. Monochloroanilines have equally been shown to be biodegradable by activated sludge micro-organisms (Pitter, 1976; Shamat & Maier, 1980). By contrast, no organism utilising chloroform as a growth substrate has been isolated so far.

In comparison with chlorinated compounds the brominated analogues are in general less chemically stable in the environment (Mills, 1978).

4.2.5.3. ADSORPTION - DESORPTION

The (de)sorption coefficient of AOX in general to secondary sludge is not very well defined for domestic sewage. However, it is reported that AOX adsorption to primary sludge is negligible (Böhnke & Li, 1992).

This may indicate an overall low degree of hydrophobicity. Some additional research on the sorption behaviour of bleach related AOX is needed to complete the picture.

4.2.6. SUMMARY OF AOX PREDICTED ENVIRONMENTAL CONCENTRATIONS

4.2.6.1. GENERAL

In this section a tentative mass-balance of the AOX formed under realistic conditions from domestic use of hypochlorite is made, based on currently available AOX formation data. Estimations are made of AOX levels in the different environmental compartments, starting with formation in the household and following the AOX levels during discharge. It is assumed that the AOX is transported via domestic sewage to a sewage treatment plant, and then to surface water. Given a) the large differences in bleach use

among countries and individual households and b) the data gaps in some areas, only general estimations can be made. It is expected that this mass-balance can be refined and completed as more data become available.

Starting assumptions were that the degree of AOX degradation in sewage treatment was 60% (Smith, 1994) and dilution of the effluent in the river 1:3.

4.2.6.2. FOR TOILET BOWL CLEANING

Consumer research throughout Europe indicates that toilet bowls are probably the most important cleaning application. At least 20% of the volume of hypochlorite sold in Europe is used in the toilet (AISE unpublished, 1996).

A worst-case scenario calculated that 15 µg/l THM formation may occur during domestic application in the toilet (Overleggroep Deskundigen Wasmiddelen-Milieu, 1989). Assumptions were that 5% of the THMFP of the solution was used under realistic cleaning conditions, with 20 minutes contact time. With a THM:Total OBP ratio of around 1:4, the non-

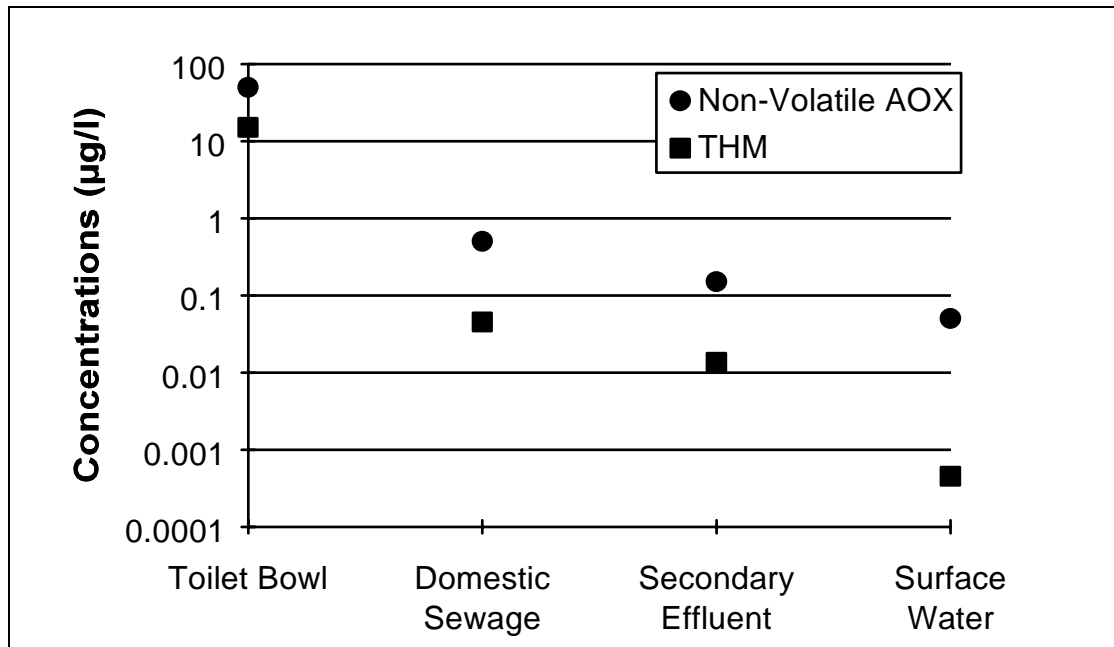
volatile AOX fraction (= Total OBP - THM) formed in toilets may amount to around $15 \times 3 = 45$ µg/l.

Taking into account the fraction of the water which is chlorinated in the toilet (1% of total daily use, or around 2 l/capita.day), this results in about 11 mg THM/inhabitant.year ($2 \times 15 \times 365$), and 45 mg total AOX/inhabitant.year ($2 \times (15 + 45) \times 365$). Due to volatilisation underway (around 60 %), only a small fraction of the THMs is expected to reach the treatment systems.

The estimated final concentrations of toilet-bowl related AOX in sewage, secondary effluent and

surface water are given in *Figure 4.6*.

Figure 4.6. Estimation of AOX (non-volatile) and THM levels after toilet bowl cleaning in various environmental compartments.



4.2.6.3. DURING LAUNDRY CYCLE

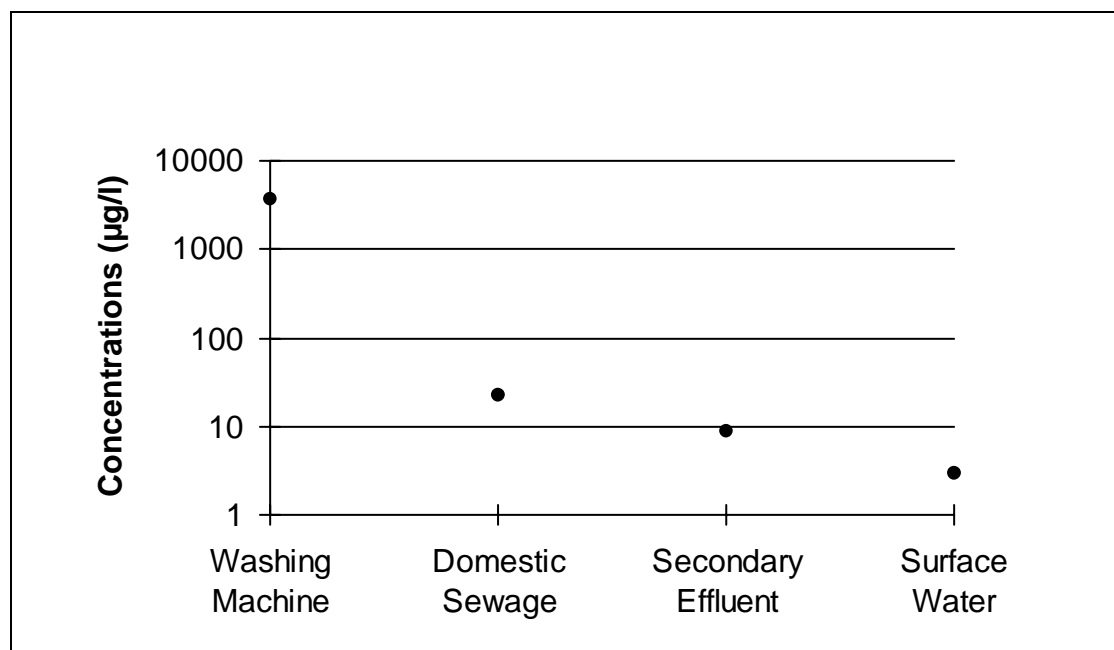
A calculation comparable to that for the toilet bowl was made for laundry bleaching. Laundry bleaching accounts for 5-30 % of the volume of bleach used, with large regional differences.

Smith (1994) measured an average AOX formation of 3.7 mg/l (258 mg/bleached wash). Assuming 15 bleached laundry cycles per person per year (corresponding to a total of 15 x 125 (normal dosage) = 1875 ml), the AOX emitted from this application would be of the order of

3900 mg (15 x 258) per person per year. The concentration of this AOX at different stages is shown in *Figure 4.7*. It is assumed that the bleached wash waters represent 0.6% on average of the total flow.

Taking into account the fact that chloroform represents 10-30 % of the AOX, and at least 60% volatilises, the AOX concentrations in raw sewage and effluent may be 6-20 % lower than that shown here.

Figure 4.7. AOX after laundry cycle



4.2.6.4. IN HOUSEHOLD CLEANING

Hard surface cleaning tasks (such as floors, bathrooms, kitchens, fridges and waste-bins) represents the major use of hypochlorite, typically accounting for more than 50% of the volume used (AISE unpublished, 1996). Insufficient data are

presently available on consumer habits and the degree of NaOCl-to-AOX conversion for these specific cleaning tasks for a precise estimation to be made of the AOX formed.

4.2.6.5. TOTAL DOMESTIC BLEACH USE

On the basis that the overall NaOCl-to-AOX conversion degree is 1.5% (as reported in the Parma field study by Schowanek *et al* (1996)), with the total NaOCl consumption figures from *Table 1.1* (assuming an average bleach strength of 4%), the AOX that may be formed daily from domestic bleach by one person ranges between:

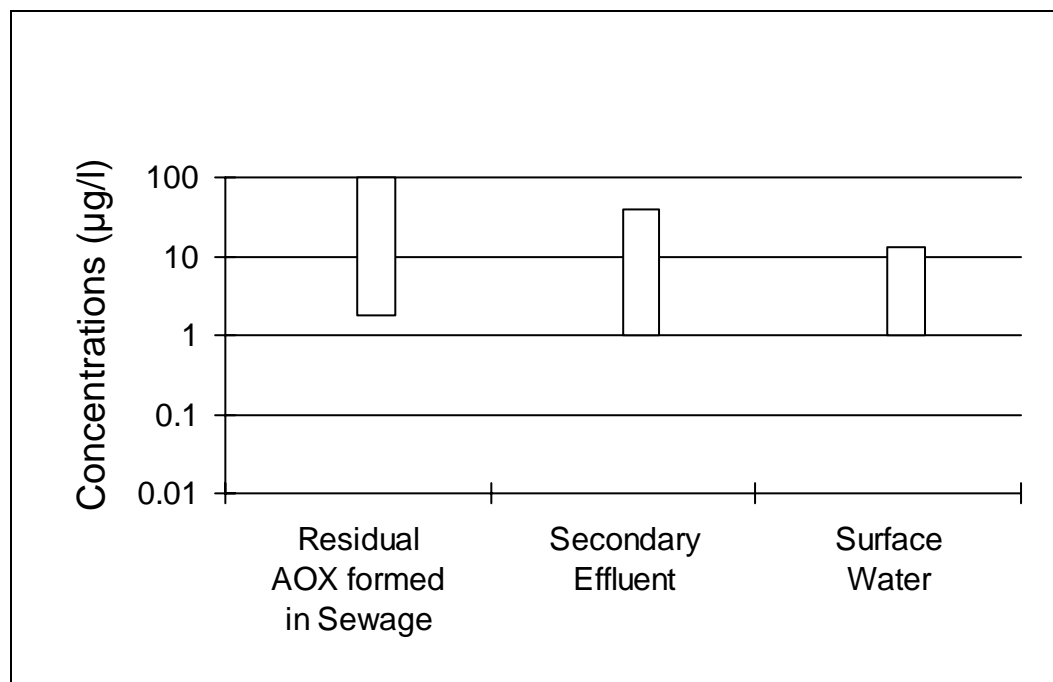
* Germany: $0.22 \times 0.04 \times 0.015 = 132 \text{ mg AOX/person.year (0.36 mg/day)}$

* Spain: $11.8 \times 0.04 \times 0.015 = 7080 \text{ mg AOX/person.year (19.4 mg/day)}$

The bleach-related AOX concentration in sewage is situated between the extremes of 1.8-97 µg/l for water consumption of 200 l/person.day.

The average for Europe is likely to be 10-25 µg/l. The fate of this AOX can be summarised as follows in *Figure 4.8*.

Figure 4.8. AOX levels in the environmental compartments, sewage, secondary effluent and surface water, after total domestic use of bleach



4.3. EFFECTS

4.3.1. EFFECTS OF HYPOCHLORITE ON SEWAGE TREATMENT

Despite the strong antimicrobial potential of hypochlorite and chloramines, there is little need for concern about possible inhibition effects on biological sewage treatment with the current hypochlorite use pattern. First, NaOCl (FAC) will normally disappear before reaching the treatment plant. Small concentrations of monochloramine may be present in the influent (see section 4.2.3.2), but circumstantial evidence in bleach using countries indicates that no adverse effects on sewage treatment functioning occur in practice (IFREMER, 1990).

Further evidence comes from the fact that activated sludge flocs are not very sensitive to NaOCl, probably due to protection by their glycocalix made out of polysaccharides. Small, frequent additions of NaOCl to activated sludge up to 25 mg/l did not affect BOD-, COD-, NH₃-

N- and suspended solids removal. A loading of about 50 mg/l every fifth day showed a marginal effect on COD-removal. A shock-loading of 100-125 mg/l NaOCl gave a small and temporary effect on COD- and NH₃-N removal (Birch & Fletcher, Unilever 1980, unpublished). The EC₅₀ for the inhibition of activated sludge respiration is situated around 3 mg/l for a continuous hypochlorite dosage, with a NOEC of around 0.375 mg/l (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 for batch doses of 1.5 mg NaOCl/mg sludge suspended solids.

Sludge from sewage treatment plants is sometimes deliberately treated with NaOCl in order to avoid unpleasant smells, to improve

primary sludge settleability or the performance of trickling filters. Bulking sludge can be corrected by inactivating the filamentous bacteria outside

the flocs with hypochlorite (Jenkins *et al*, 1984), Marstaller *et al*, 1992). The addition can be as high as 30 mg FAC/l.

4.3.2. ECOTOXICOLOGICAL EFFECTS

4.3.2.1. HYPOCHLORITE AND CHLORAMINES

Ample acute data for hypochlorite are available. However, the scientific quality of these data is highly variable. Only a few sets of data meet current state-of-the-art testing criteria (such as verification of exposure conditions and chemical species during the test). Little chronic data are presently available. In the context of the EU Hypochlorite Risk Assessment a selection of the most relevant data was made (Tables A1-A25).

A summary is presented in Table 4.6 of the most relevant acute ecotoxicity data for sodium hypochlorite and monochloramine (NH₂Cl) to

fish, crustaceans and algae, respectively. It should be noted that in fact most studies have measured the toxicity of TRO, which may include chloramines, depending on the medium. Similar data are presented in Table 4.7 for sea water.

As illustrated in section 4.2.3.2. monochloramine is the most environmentally-relevant species of interest, as the FAC will have disappeared. An excellent review of hypochlorite fate and toxicology has been prepared by Abarnou & Miossec (1992).

Table 4.6. Overview of freshwater acute ecotoxicity and microcosm MATC data for hypochlorite, and monochloramine (references in appendix).

		NaOCl	NH ₂ Cl
	(E)LC50 (µg/l)		
Organism			
- Fish		60 (1)	85 (1)
- Invertebrates		5 (1)	16 (1)
- Algae	(IC27)	200 (3)	NA
Microcosm	(MATC) (µg/l)	6 (2)	NA

NA: not available - The number (1 - 4) in brackets represents the IUCLID validity criterion.

Using the EU terminology for substances, hypochlorite and monochloramine are 'very toxic' to aquatic organisms ((E)LC50 typically <1 mg/l). Sensitivity may vary considerably with factors such as species, life stage, test duration and pH.

Adverse effects on some sensitive freshwater aquatic species in laboratory systems, particularly on eggs and larval stages, are observed at concentrations of about 1 µg/l hypochlorite. Avoidance effects by fish were observed at 50 µg/l (Brungs *et al*, 1980).

Table 4.7. Overview of sea water acute and chronic ecotoxicity data for hypochlorite and monochloramine (references in appendix).

		NaOCl	NH ₂ Cl
Organism	(E)LC50 (µg/l)		
- Fish		32 (1)	NA
- Invertebrates		27 (2)	NA
- Algae		75 (2)	NA
Chronic			
- Microcosm	(NOEC) (µg/l)	3 (3)	12 (2)
- Invertebrate	(NOEC) (µg/l)	16 (3)	

NA: not available - The number (1 - 4) in brackets represents the IUCLID validity criterion.

Sublethal effects of hypochlorite or chloramines on aquatic species and plants have been reported. These include reduced growth, reproductive impairment, reduced photosynthesis, membrane permeability changes, and effects on respiration and osmoregulation (Abarnou & Miossec, 1992). The most reliable microcosm MATC is 6 µg/l.

As all the EC50/LC50/LOEC/NOEC values mentioned above for hypochlorite are around the µg/l level, there is a substantial safety margin between them and the predicted concentration of hypochlorite at the end of the sewer (1.E-32 µg/l, see section 4.2.3.2 (b)) even before further degradation in sewage treatment is included. A risk assessment for hypochlorite is currently underway, in the framework of the EU second priority list for existing chemicals.

4.3.2.2. ORGANOHALOGEN COMPOUNDS

Some groups or individual organochlorine compounds of anthropogenic origin have been identified as potentially harmful to the environment on the basis of their acute or chronic toxicity, mutagenicity/genotoxicity or bioaccumulation characteristics.

The acute toxicity of chloramines is comparable or slightly less than that of free chlorine (when expressed as NaOCl equivalents), but chloramines may exist longer in the environment (Heath, 1978).

As for any chemical, the direct discharge of hypochlorite or chloramines in amounts that would exceed the toxic concentrations in natural ecosystems should be avoided.

However, with disposal down the drain, rapid reduction of the TAC level in sewage generally takes place before such ecosystems are reached.

Any accidental direct discharges, such as spills, would take place locally in the mixing zone, and be temporary in nature.

Effects such as chronic aquatic toxicity, developmental damage, malformations, reduced viability of eggs and reduced reproduction, and ecosystem changes, have been associated with chlorinated organics (such as PCBs, DDT and

dioxins) released into the environment. Of most concern are those which are *persistent*, *bioaccumulative* and *toxic* (the so-called PBTs), as they tend to accumulate in sediments, living

organisms, and biomagnify in the food chain (eg Paasivirta, 1990; Coulston & Kolbeye 1994).

The possible environmental effects of the main PBT organohalogenes have recently been reviewed by Ballschmitter (1996) in the IUPAC White

A wide range of toxicity studies on the most common disinfection by-products present in chlorinated drinking water has been critically reviewed by the Foundation for Water Research (O'Neill *et al*, 1994).

This report also summarises current WHO Guideline Values for acceptable levels of these species in drinking water, and some international regulatory levels. Generally, the WHO Guideline Values (WHO, 1993) for individual species in drinking water (ranging from 1-200 µg/l) are two orders of magnitude or more higher than the concentrations of those species that would be expected to be present in secondary-treated sewage effluent arising from domestic bleach use.

Estimating the environmental hazard of complex mixtures of trace concentrations of halogenated organics, as formed by chlorine bleaching, is complicated and associated with great uncertainty. Recent studies on the fractionation of the mixture produced when hypochlorite interacts with a household soil (milk) have been presented (DIFF 96/5/2-E). Assessments of secondarily-treated pulp and paper industry effluents indicate that no clear-cut concentration-response relationship exists between the "surrogate" parameter AOX and acute or chronic aquatic toxic effects, provided that adequate secondary waste water treatment has been used to eliminating to a large extent the biodegradable

Book on Chlorine, and the toxicology of the main persistent chlorinated organic compounds is reviewed by Hanberg (1996) in the same publication.

Table A26 shows a summary of ecotoxicological data for a number of organohalogen compounds which are potential by-products of domestic hypochlorite use (taken from Overleggroep Deskundigen Wasmiddelen Milieu, 1989).

AOX (Borton *et al*, 1990; Owens, 1991). Similarly, no correlation was found between total chlorinated compounds found in drinking water and chronic toxicity in humans (Drinking Water Health Effects Task Force, 1990; IARC, 1991; Flaten, 1992).

Acute toxicity of organohalogenes from domestic bleach use

Some attempts have been made to investigate whether the AOX formed from domestic bleach was toxic to aquatic organisms. Waste waters containing 'typical' AOX were generated under realistic usage conditions for testing purposes. These waste waters were tested as a whole in 'limit tests', without attempting to derive a AOX concentration-response relationship. According to Abarnou & Miossec (1992) the concentrations of the various individual OBPs measured or estimated in treated chlorinated effluents (typically <1 µg/l), are expected to be well below lethal concentrations.

In separate studies, Smith (1994) and Colgate-Palmolive (unpublished, 1990) observed that the more recalcitrant AOX fractions concentrated from biologically treated bleached domestic waste water were not acutely toxic to fish (fathead minnow) and invertebrates (*Ceriodaphnia* spp, *Daphnia* spp) at 250 and 143 µg/l (highest concentrations tested) respectively.

Chronic toxicity of organohalogens from domestic bleach use

It is more relevant to assess the hazards associated with chlorinated by-products at the chronic level. Research from Henkel (unpublished - 1995) showed no biological effects up to 140 µg/l of the recalcitrant AOX fraction (after waste water treatment in the metabolite test) in a *Daphnia* spp life-cycle test. With the same sample the NOEC for growth of the alga *Scenedesmus subspicatus* was >100 µg/l (Henkel unpublished, 1996). Smith (1994) observed that 143 µg AOX/l (highest concentration tested) did not affect the growth or the reproduction of *Ceriodaphnia dubia*.

These AOX concentrations are far higher than those likely to occur in treated domestic effluents as a result of normal domestic use. It can therefore be concluded that adequately treated sewage containing residual AOX from domestic bleaching is unlikely to be acutely or chronically toxic to aquatic organisms at concentrations up to 100-200 µg AOX/l. Experimental evidence suggests that effluents from adequately operating domestic sewage treatment plants in bleach-using countries are non-toxic to sensitive aquatic species at realistic dilutions (Hagendorf & Rode, 1990). Smith (1994) demonstrated that bleached laundry wash water mixed with municipal sewage (1:4) after biological treatment showed no increased acute or chronic toxicity versus domestic sewage alone. AOX remaining in effluents was shown to be biologically very inert, probably because uptake by living cells is limited due to bioavailability (Grimvall *et al*, 1991).

Bioaccumulation

Among chlorinated compounds found in the environment, increased body burden has been observed for example with chlorophenols.

Bioconcentration factors for chlorophenolic compounds range from 5-5370, depending essentially on the degree of chlorination (Owens, 1991).

However Colgate (unpublished, 1990) and Smith (1994) have shown that:

- a) Chlorophenols are not a very important fraction of the AOX formed from domestic bleach
- b) Chlorophenols are often metabolised and therefore their accumulation is less than would be expected from their octanol/water coefficients
- c) The main AOX fraction (> 95%) is water soluble and therefore unlikely to bioaccumulate.

The same Colgate study, which was performed with biologically stabilised waste water from bleach use in laundry washing, showed the presence of one chlorinated neutral compound (tentatively identified as: ethane, 2-chloro-1, 1-diethoxy), two monochlorinated compounds (tentatively identified as: monochloropropionic acid and monochlorinated fatty acid) and three other dichlorinated fatty acids. These chlorinated fatty acids are all believed to be of low molecular weight, and elute off a GC DP-5 column before unchlorinated C8 fatty acid.

Secondary treated effluents from laundry bleaching contained no compounds listed by the US EPA as "Chemicals of highest concern" (such as DDT, PCBs or dioxins) at a 10 ng/l detection limit. No other potentially bioaccumulative compounds or lipophilic chlorinated organics were found in the same effluent with a detection limit of 100 ng/l.

Thus, using hypochlorite does not increase the bioaccumulative potential of the chemicals in

treated domestic sewage (Smith, 1994; Kee Ong et al, 1996).

Mutagenicity/Genotoxicity

According to Abarnou and Miossec (1992), the mutagenic character of some OBPs may represent the main hazard associated with chlorinated effluents.

The Ames test is often applied to investigate the mutagenicity of mixtures (such as urine or sewage), in some cases with pre-treatment by liver enzymes (S-9 mix) for metabolic activation. Fukui et al (1990) observed a 5-50-fold increase of the response of the Ames test for domestic sewage after chlorination (FAC/carbon 1:1, reaction time 1 h, 7000-30,000 revertants/l). Ames mutagenic activity is also frequently detected in concentrates of chlorinated drinking water (Coleman *et al*, 1984).

However, many epidemiological and animal studies have also looked for evidence of possible carcinogenicity to humans of chlorinated drinking water, compared with non-chlorinated supplies. No such conclusive evidence has been found. IARC concluded that “there is inadequate evidence for the carcinogenicity of chlorinated drinking water” in humans or in experimental

animals and that “chlorinated drinking water is not classifiable as to its carcinogenicity to humans” (IARC, 1994).

A compound of particular importance regarding mutagenicity is 3-chloro-2-dichloromethyl-5hydroxy-2(5H) furanone (the so-called MX). It has been detected in chlorinated pulp and paper effluents and surface waters and accounts for a large fraction (20-50%) of the mutagenicity detected (Overleggroep Deskundigen Wasmiddelen-Milieu, 1989).

Samples of settled primary municipal sewage treatment works effluent diluted in sea-water, which would *de facto* contain OBPs from bleach use and tap water, have, however, recently been tested for genotoxicity by *in vivo* exposure of embryo-larvae of the marine worm, *Platynereis dumerilii*. Examination of cells for chromosomal aberrations demonstrated the absence of cytogenic damage in all samples tested (Jha *et al*, 1996).

At present, there are no indications that the domestic use of hypochlorite bleach is the source of OBPs which could be classified as persistent, bioaccumulative and toxic.

4.4. ORGANOHALOGENS IN THE ENVIRONMENT

In this section, some perspective is given on the amounts and fluxes of organohalogens that can be measured in various environmental

compartments, and how this compares to the amounts of organohalogens formed by domestic hypochlorite usage.

4.4.1. NATURAL ORGANOHALOGENS

Organohalogen compounds are by no means entirely anthropogenic. It is often overlooked that another source of AOX in surface waters or sewage will be natural halogenated molecules. In

fact, natural AOX does occur in all environmental compartments. This AOX should be compared in terms of quantity, ecotoxicity and exposure with bleach-derived halogens to bring perspective to

the environmental hazard assessment for the latter source.

A natural organohalogen cycle has been clearly reported, with apparently most activity in acidic peat ecosystems (in areas such as Scandinavia), forest soils and in the marine environment. Several types of fungi, marine algae and lichens produce organohalogens (Grimvall, 1993). Their biological significance is still poorly understood, but to the micro-organisms these organohalogen compounds may serve as protective toxins, secondary metabolites (such as hormones) and biosynthesis aids.

More than 2400 naturally-produced organohalogens are known to date (Grimvall *et al*, 1990; Gribble, 1994). The biochemistry of their formation and degradation is under active investigation (Neidleman & Geigert, 1986; Stora Teknik, 1990; Fleming, 1991; etc.).

The enzymes responsible for the formation of natural AOX are the haloperoxidases, of which several types exist. It is interesting to note that they form hypochlorite as the chlorinating agent on the basis of peroxide and chloride ions (Hodin *et al*, 1991).

On a global basis, one of the most significant sources of natural AOX are the halomethanes (CH₃Cl, CH₃Br) generated by marine micro-organisms (Fleming, 1991; Harper, 1993).

In the seas, about 4-5 million te chloromethane are generated yearly, which gives rise to a CH₃Cl background concentration of 16-47 ng/l in the marine environment.

Chloroform, of which several million te are believed to be produced annually as well, is also

amongst the more important small natural organohalogens. Halomethanes are believed to play a role in the regulation of the ozone layer.

The main degradation mechanism of CH₃Cl is via photodegradation. Volcanic activity (0.4 x 10⁶ te/yr average) and forest fires also contribute to the natural AOX background.

It is now well-established that hypochlorous acid is involved as a microbicidal agent in the operation of the human immune system. When an immune response is produced by the recognition of "non-self" proteins in an invading micro-organisms, mammalian neutrophil cells (a type of white blood cell) generate hypochlorous acid from hydrogen peroxide and chloride ions in a reaction catalysed by the enzyme, myeloperoxidase (Weiss, 1989; Babior, 1984; IARC, 1991).

This hypochlorous acid plays a key role in the process of phagocytosis through which bacteria, for example, are killed, probably by degradation of a variety of functionally important molecules.

To what extent are bleach-related and natural AOX sources comparable? A key difference from natural AOX (such as that in humus) may be that bleach-AOX contains a larger fraction of low- and medium molecular weight compounds. However, increasing similarity is being found between natural and man-made organohalogens.

For example, chloroform and other halomethanes, as well as chlorophenols, are known to occur naturally. This is after all not so surprising, as natural chlorination processes involve hypochlorous acid.

4.4.2. BACKGROUND ORGANOHALOGEN LEVELS

Natural halogenated molecules have been detected in surface waters, groundwater and soil remote from industrial activities, and even in "old" ground waters (Asplund *et al*, 1989; Grimvall *et al*, 1990). These quote 25 µg AOX/l on average, and a maximum of up to 200 µg/l in unpolluted Swedish waters (*Table A27*). Between 0.2 and 3 g AOX/kg C was found in the soil organic matter fraction at these locations. The natural AOX pool in Sweden is estimated to be at least 300,000 te, and is mainly found in humic material. This humus-AOX would be randomly distributed in a myriad of different macromolecules.

AOX levels of 10-20 µg/l are a typical natural background level in rivers. The River Rhine has a natural background level of 1-2 µg/l AOX near its source, and about 15 µg/l in the Netherlands (Euro Chlor, 1995; Hoekstra & Leer, 1994). The River Seine's natural organohalogen background level is about 10-15 µg/l AOX (Durand, 1995).

For perspective, the total yearly AOX emission by the pulp and paper industry reached 10,000 te in Finland in 1987 and 4000 te in Sweden in 1990 (Wigilius *et al*, 1988; Owens, personal communication). A remarkable observation is that unpolluted rivers can contain levels of natural AOX similar to polluted ones (although this does not imply that the AOX compounds are identical or would have similar ecotoxicity profiles).

4.5. SUMMARY

Hypochlorite is a highly reactive chemical which, during and after its use in household scenarios, undergoes a variety of reactions. The major one is the oxidation of inorganic and organic species. A minor reaction, which consumes about 1.5% of the chlorine atoms from hypochlorite, is

In addition, human urine typically contains more AOX than chlorinated tap water. This may be due to the concentration of drinking water by evaporation, or to AOX intake with food, with excretion via the urine. There are indications that food contains a background level of AOX, and is a significant overall contributor to AOX levels in domestic sewage. Elevated levels of AOX have been measured in bleached flour and smoked foods (Monzain & Durand, 1995).

There is also mounting evidence that suggests that some organochlorine species will be produced in the body as by-products during the process of phagocytosis (Fleming, 1991). As well as many N-chlorinated products, derived from proteins, bases and amino acids for example, chlorohydrins of unsaturated fatty acids (Winterbourn, 1992) and chlorinated sterols (Hazen *et al*, 1996) have been identified as by-products of *in vitro* reactions of the myeloperoxidase/peroxide/chloride system.

Haas (1994) has estimated that perhaps 5.7-28 µg/day AOX might be produced by the human immune system.

Table A27 aims at providing more perspective to the estimated emissions of bleach-related AOX, by means of a comparison with measured AOX levels in various unpolluted and polluted environments.

chlorination, which leads to formation of organohalogen by-products that are often measured by the group parameter, AOX.

Hypochlorite itself is rapidly broken down during use, in the sewer, and if any does reach sewage

treatment it will further degrade (half-life of around 0.6 minutes). Predictions have indicated that its concentration will fall to below 1.E-32 μ g/l by the end of the sewer, partially due to its reaction with ammonia in the sewer which leads to a subsequent increase in chloramine.

The level of chloramine reaching surface water is estimated to be below 5.E-10 μ g/l. Both these concentrations are orders of magnitude below the lowest acute EC50s determined for sodium hypochlorite (EC50 to invertebrates = 5 μ g/l) and monochloramine (EC50 to invertebrates = 16 μ g/l).

The organohalogen by-products formed from the use of hypochlorite are currently receiving much attention. However, the levels of AOX produced are low (for example, 37 μ g/l from bleach use compared to a sewage background level of 106 μ g/l), and the organohalogens produced from domestic use of hypochlorite are not believed to have an adverse effect on the environment. Available data indicate that no dioxins are produced, and that the identified AOXs are typically small molecules with a low degree of

chlorination and for which ecotoxicological properties are known or can be predicted.

Where drinking water is disinfected by chlorination, the levels of organohalogens in sewage effluent arising from bleach use will be comparable with, and sometimes only a fraction of, those arising from the tap-water. After secondary sewage treatment, the levels entering receiving waters will be of the same order of magnitude as background levels typically present in rivers, though the total flux in rivers from natural sources will be much greater.

The majority of the measured AOX is unidentified, but thought to consist of high molecular weight components formed from fats, proteins and humic acids which are too large to bioaccumulate.

In addition, studies on the whole AOX mixture in laundry waste-water indicated that the level of AOX present did not effect growth or reproduction of *Ceriodaphnia*, and that around 70% is removed in activated sludge.

4.6. REFERENCES

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LIST OF TABLES IN APPENDIX

- Table A1. Summary of ecotoxicological data for sodium hypochlorite - brackish and sea water invertebrates (acute studies)
- Table A2. Summary of ecotoxicological data for sodium hypochlorite - fresh water invertebrates (acute studies)
- Table A3. Summary of ecotoxicological data for sodium hypochlorite - sea water invertebrates (chronic studies)
- Table A4. Summary of ecotoxicological data for sodium hypochlorite - fresh water invertebrates (chronic studies)
- Table A5. Summary of ecotoxicological data for chlorine - brackish and sea water invertebrates (acute studies)
- Table A6. Summary of ecotoxicological data for chlorine - fresh water invertebrates (acute studies)
- Table A7. Summary of ecotoxicological data for chlorine - sea water invertebrates (chronic studies)
- Table A8. Summary of ecotoxicological data for monochloramine - brackish and sea water invertebrates (acute studies)
- Table A9. Summary of ecotoxicological data for monochloramine - fresh water invertebrates (acute studies)
- Table A10. Summary of ecotoxicological data for sodium hypochlorite - brackish and sea water fish (acute studies)
- Table A11. Summary of ecotoxicological data for sodium hypochlorite - fresh water fish (acute studies)
- Table A12. Summary of ecotoxicological data for sodium hypochlorite - brackish and sea water fish (chronic studies)
- Table A13. Summary of ecotoxicological data for chlorine - fresh water fish (acute studies)
- Table A14. Summary of ecotoxicological data for chlorine - sea water fish (acute studies)
- Table A15. Summary of ecotoxicological data for chloramine - fresh water fish (acute studies)
- Table A16. Summary of ecotoxicological data for chloramine - brackish and sea water fish (acute studies)
- Table A17. Summary of ecotoxicological data for sodium hypochlorite - fresh water algae (acute studies)

- Table A18. Summary of ecotoxicological data for sodium hypochlorite - sea water algae (acute studies)
- Table A19. Summary of ecotoxicological data for sodium hypochlorite - sea water algae (chronic studies)
- Table A20. Summary of ecotoxicological data for sodium hypochlorite - fresh water microcosm (chronic studies)
- Table A21. Summary of ecotoxicological data for sodium hypochlorite - sea water plankton (chronic studies)
- Table A22. Summary of ecotoxicological data for chlorine - fresh water algae (acute studies)
- Table A23. Summary of ecotoxicological data for chlorine - sea water algae (chronic studies)
- Table A24. Summary of ecotoxicological data for chlorine - sea water microcosm (chronic studies)
- Table A25. Summary of ecotoxicological data for chloramine - sea water algal microcosm (chronic studies)
- Table A26. Ecotoxicity of Organohalogenes (After Overleggroep Deskundigen Wasmiddelen-Milieu, 1989).
- Table A27. Examples of average organohalogen concentrations in various compartments or med

Table A1. Summary of ecotoxicological data for sodium hypochlorite
- brackish and sea water -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Crassostrea virginica (MB)</i>	Larvae (7 d)	FT	20°/25°C//8.0	30 min *	(+)TRO	LC50	0.08-0.12	2	(-)	Capuzzo (1979)a
<i>Crassostrea virginica (MB)</i>	Larvae (7 d)	FT	20°/25°C//8.0	30 min *	(+)TRO	LC100	0.86-1.40	2	(-)	Capuzzo (1979)a
<i>Brachionus calyciflorus (R)</i>	Juvenile	S	25°C/7.5	24 h	(-)	LC50	0.37	3	(+)	Snell (1991)
<i>Brachionus plicatilis (R)</i>		FT	20°/25°/27.5°C//8.0	30 min*	(+) TRO	LC50	0.01-0.18	2	(-)	Capuzzo (1979)b
<i>Brachionus plicatilis (R)</i>		FT	20°/25°/27.5°C//8.0	30 min*	(+) TRO	LC100	0.46-1.76	2	(-)	Capuzzo (1979)b
<i>Pandalus goniurus (CD)</i>	Adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.090	2	(+)	Thatcher (1977)
<i>Crangon nigricauda (CD)</i>	Adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.134	2	(+)	Thatcher (1977)
<i>Hemigrammus nudus (CD)</i>	Juvenile/adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	1.418	2	(+)	Thatcher (1977)
<i>Hemigrammus oregonensis (CD)</i>	Juvenile/adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	1.418	2	(+)	Thatcher (1977)
<i>Pandalus danae (CD)</i>	Juvenile/adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.178	2	(+)	Thatcher (1977)
<i>Palaemonetes pugio (CD)</i>	Adult	S	22°C/8.5	96 h	(+) TRO	LC50	5.90	2	(+)	Curtis (1981)
<i>Homarus americanus (CD)</i>	Larvae (stage I)	FT	20°/25°/30°C//8.0	60 min**	(+) TRC	LC50	0.41-2.89	2	(-)	Capuzzo (1976)
<i>Neomy sp. (CD)</i>	Adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.162	2	(+)	Thatcher (1977)
<i>Anonyx sp. (CA)</i>	Adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.145	2	(+)	Thatcher (1977)
<i>Pontogenia sp. (CA)</i>	Juvenile	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.687	2	(+)	Thatcher (1977)
<i>Gammarus fasciatus (CA)</i>	Juvenile	S	20°C/7.5	96 h	(-)	LC50	4.0	3	(+)	Ewell (1986)
<i>Asella intermedius (CA)</i>	Juvenile	S	20°C/7.5	96 h	(-)	LC50	32	3	(+)	Ewell (1986)
<i>Nitocra spinipes (CCP)</i>	Adult	SS	10°C/7.8	96 h	(-)	LC50	40	3	(+)	Bengtsson (1983)
<i>Nitocra spinipes (CCP)</i>	Adult	S	10°C/7.8	96 h	(-)	LC50	40	3	(+)	Linden (1979)
<i>Acartia tonsa (CCP)</i>		FT	10°/15°/20°/25°/28°C/8.0	30 min*	(+) TRO	LC50	0.82-0.86	2	(-)	Capuzzo (1979)a
<i>Acartia tonsa (CCP)</i>		FT	10°/15°/20°/25°/28°C/8.0	30 min*	(+) TRO	LC100	3.5-3.6	2	(-)	Capuzzo (1979)a
General review								3	(-)	Abarnou (1992)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

*30 min exposure & 48 h observation

** 60 min exposure & 48 h observation

MB = Mollusc bivalve; MG = Mollusc gasteropode; FW = Flat worm, SW = Segmented worm; R = Rotifer

4 = not assignable

CD = Crustacea decapod; CA = Crustacea amphipod; CPP = Crustacea copepod; CCL = Crustacea cladocere

**Table A2. Summary of ecotoxicological data for sodium hypochlorite
- freshwater -**

Invertebrates

Species	Stage at test	System	Comments	Duration	Analy	Parameter	Results	Val	Hedset	Reference
Acute studies	initiation		T°/pH		meas		(mg/l)			
<i>Ceriodaphnia dubia (CCL)</i>	Juvenile	S	25°C/8.0	24 h	(+) TRC	LC50	0.048	2	(+)	Taylor (1993)
<i>Ceriodaphnia dubia (CCL)</i>	Juvenile	S	25°C/7.0	24 h	(+)TRC	LC50	0.035	2	(+)	Taylor (1993)
<i>Ceriodaphnia dubia (CCL)</i>	Juvenile	FT	25°C/8.0	24 h	(+) TRC	LC50	0.006	1	(+)	Taylor (1993)
<i>Ceriodaphnia dubia (CCL)</i>	Juvenile	FT	25°C/7.0	24 h	(+)TRC	LC50	0.005	1	(+)	Taylor (1993)
<i>Daphnia magna (CCL)</i>	1st & 2nd larvae	S	20°C/7.5	96 h	(-)	LC50	2.1	3	(+)	Ewell (1986)
<i>Daphnia magna (CCL)</i>	Juvenile (<24 h)	S	17.5-19°C/8.4	48 h	(-)	EC50	0.02	2	(-)	Unilever (1992)
<i>Daphnia magna (CCL)</i>	Juvenile	S	20 +/- 1°C	24 h		EC50	0.06 <x<0.1	3	(+)	Rhone-Poulenc (1979)
<i>Daphnia magna (CCL)</i>	Juvenile	S	20°C/7.8	48 h	(-)	EC50	1.7	3	(-)	INERIS (1992a)
<i>Dreissena polymorpha (MB)</i>	Larvae (veligers)	FT	20°C/8.3	18 h	(+) TRC	LC100	1.00	3	(-)	Benschotten (1993)
<i>Goniobasis liviscens (MG)</i>	Adult	SS	24 °C/(+)	24 h	(-)	LC50	10.4	2	(+)	Cairns (1976)
<i>Goniobasis liviscens (MG)</i>	Adult	SS	24 °C/(+)	48 h	(-)	LC50	6.2	2	(+)	Cairns (1976)
<i>Physa integra (MG)</i>	Adult	SS	24 °C/(+)	24 h	(-)	LC50	2.0	2	(+)	Cairns (1976)
<i>Physa integra (MG)</i>	Adult	SS	24 °C/(+)	48 h	(-)	LC50	1.8	2	(+)	Cairns (1976)
<i>Lymnacea emarginata (MG)</i>	Adult	SS	24 °C/(+)	24 h	(-)	LC50	21.8	2	(+)	Cairns (1976)
<i>Lymnacea emarginata (MG)</i>	Adult	SS	24 °C/(+)	48 h	(-)	LC50	13.6	2	(+)	Cairns (1976)
<i>Helisoma trivolis (MG)</i>	Juvenile	S	20°C/7.5	96 h	(-)	LC50	59	3	(+)	Ewell (1986)
<i>Dugesia tigrina (FW)</i>	Juvenile	S	20°C/7.5	96 h	(-)	LC50	32	3	(+)	Ewell (1986)
<i>Lumbriculus variegatus (SW)</i>	Juvenile	S	20°C/7.5	96 h	(-)	LC50	3.2	3	(+)	Ewell (1986)
General review								4	(-)	Kalmaz (1981)

Validity

- 1 = valid without restriction
- 2 = valid with restriction
- 3 = invalid
- 4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

MB = Mollusc bivalve; MG = Mollusc gasteropode; FW = Flat worm, SW = Segmented worm; R = Rotifer

CD = Crustacea decapod; CA = Crustacea amphipod; CPP = Crustacea copepod; CCL = Crustacea cladocere

Table A3. Summary of ecotoxicological data for sodium hypochlorite
- sea water -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Crassostrea virginica (MB)</i>	Adult	S	24-31°C/7.4-8.3	60 d	(+) Cl2	LC98	0.66	3	(+)	Scott (1979)
<i>Crassostrea virginica (MB)</i>	Adult	S	24-31°C/7.4-8.3	60d	(+) Cl2	LC58	0.21	3	(+)	Scott (1979)
<i>Crassostrea virginica (MB)</i>	Adult	S	24-31°C/7.4-8.3	60 d	(+) Cl2	LC46	0.11	3	(+)	Scott (1979)

Validity

- 1 = valid without restriction
- 2 = valid with restriction
- 3 = invalid
- 4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

(+) Cl2 = Available chlorine

MB = Mollusc bivalve; *MG* = Mollusc gasteropode; *FW* = Flat worm, *SW* = Segmented worm; *R* = Rotifer

CD = Crustacea decapod; *CA* = Crustacea amphipod; *CPP* = Crustacea copepod; *CCL* = Crustacea cladocera

Table A4. Summary of ecotoxicological data for sodium hypochlorite
- freshwater -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Corbicula fluminea (MB)</i>	Adult	FT	25°C/7.7	13 d	(+) TRC	LC100	0.2	3	(+)	Ramsay (1988)
<i>Corbicula fluminea (MB)</i>	Adult	FT	25°C/7.7	26 d	(+) TRC	LC100	0.10	3	(+)	Ramsay (1988)
<i>Corbicula fluminea (MB)</i>	Adult	FT	25°C/7.7	36 d	(+) TRC	LC100	0.05	3	(+)	Ramsay (1988)
<i>Dreissena polymorpha (MB)</i>	Juvenile	S	21°C/7.8	460 h	(+)Cl2	LC10	<1.00	2	(+)	Martin (1993)
<i>Dreissena polymorpha (MB)</i>	Juvenile	S	21°C/7.8	295 h	(+)Cl2	LC50	1.00	2	(+)	Martin (1993)
<i>Dreissena polymorpha (MB)</i>	Juvenile	S	21°C/7.8	178 h	(+)Cl2	LC50	2.5	2	(+)	Martin (1993)
<i>Dreissena polymorpha (MB)</i>	Juvenile	S	21°C/7.8	360 h	(+)Cl2	LC100	2.5	2	(+)	Martin (1993)
<i>Dreissena polymorpha (MB)</i>	Juvenile	S	21°C/7.8	157 h	(+)Cl2	LC50	5.00	2	(+)	Martin (1993)
<i>Dreissena polymorpha (MB)</i>	Juvenile	S	21°C/7.8	264 h	(+)Cl2	LC100	5.00	2	(+)	Martin (1993)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

(+) Cl2 = Available chlorine

MB = Mollusc bivalve; *MG* = Mollusc gasteropode; *FW* = Flat worm; *SW* = Segmented worm; *R* = Rotifer

CD = Crustacea decapod; *CA* = Crustacea amphipod; *CPP* = Crustacea copepod; *CCL* = Crustacea cladocere

Table A5. Summary of ecotoxicological data for chlorine
- brackish and sea water-

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Crassostrea virginica (MB)</i>	Larvae	S		48 h	(+)TRO	LC50	<0.005	3	(-)	Bellanca (1977)
<i>Mercenaria mercenaria (MB)</i>	Larvae	S		48 h	(+)TRO	LC50	<0.005	3	(-)	Bellanca (1977)
<i>Palaemonetes pesis (CD)</i>		FT		96 h	(+)TRO	LC50	0.22	3	(-)	Bellanca (1977)
<i>Acartia tonsa</i>		S		48 h	(+)TRO	LC50	<0.005	3	(-)	Bellanca (1977)
<i>Arcatia tonsa (CCP)</i>	Adult	FT	31°C	24 h	(+) TRO	LC40	0.085	3	(-)	Liden (1980)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

MB = Mollusc bivalve; *MG* = Mollusc gasteropode; *FW* = Flat worm, *SW* = Segmented worm; *R* = Rotifer

CD = Crustacea decapod; *CA* = Crustacea amphipod; *CPP* = Crustacea copepod; *CCL* = Crustacea cladocere

Table A6. Summary of ecotoxicological data for chlorine
- freshwater -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Daphnia magna (CCL)</i>	Juvenile	FT	21°C/7.4	30 min	(+) TRC	LC50	0.097	2	(-)	Mattice (1981)
<i>Daphnia magna (CCL)</i>	Juvenile	FT	21°C/7.4	60 min	(+) TRC	LC50	0.063	2	(-)	Mattice (1981)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

MB = Mollusc bivalve; *MG* = Mollusc gasteropode; *FW* = Flat worm, *SW* = Segmented worm; *R* = Rotifer

CD = Crustacea decapod; *CA* = Crustacea amphipod; *CPP* = Crustacea copepod; *CCL* = Crustacea cladocere

Table A7. Summary of ecotoxicological data for chlorine
- sea water -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Crassostrea virginica (MB)</i>	Juvenile	FT	30.9 °C/7.0	15 d	(+) TRO	LC10	0.032	3	(-)	Liden (1980)
<i>Rangia cuneata (MB)</i>	Juvenile	FT	30.9 °C/7.0	15 d	(+) TRO	LC20	0.032	3	(-)	Liden (1980)

Validity

- 1 = valid without restriction
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- 3 = invalid
- 4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

MB = Mollusc bivalve; MG = Mollusc gasteropode; FW = Flat worm, SW = Segmented worm; R = Rotifer

CD = Crustacea decapod; CA = Crustacea amphipod; CPP = Crustacea copepod; CCL = Crustacea cladocere

Table A8. Summary of ecotoxicological data for monochloramine
- brackish and sea water -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Crassostrea virginica</i> (MB)	Larvae (7 d)	FT	20°/25°C//8.0	30 min*	(+) TRO	LC50	0.01	2	(-)	Capuzzo (1979)a
<i>Crassostrea virginica</i> (MB)	Larvae (7 d)	FT	20°/25°C//8.0	30 min*	(+) TRO	LC100	0.16-0.48	2	(-)	Capuzzo (1979)a
<i>Gammarus pseudolimnaeus</i> (CA)	Juvenile	FT	17 +/- 1°C	96 h	(+)	TLm	0.220	2	(-)	Arthur (1971)
<i>Acartia tonsa</i> (CCP)		FT	10°/15°/20°25°/28°C//8.0	30 min*	(+) TRO	LC50	0.23-0.34	2	(-)	Capuzzo (1979)a
<i>Acartia tonsa</i> (CCP)		FT	10°/15°/20°25°/28°C//8.0	30 min*	(+) TRO	LC100	1.05-1.22	2	(-)	Capuzzo (1979)a
<i>Brachionus plicatilis</i> (R)		FT	20°/25°/27.5°C//8.0	30 min*	(+) TRO	LC50	0.01-0.02	2	(-)	Capuzzo (1979)b
<i>Brachionus plicatilis</i> (R)		FT	20°/25°/27.5°C//8.0	30 min*	(+) TRO	LC100	0.19-0.82	2	(-)	Capuzzo (1979)b
<i>Homarus americanus</i> (CD)	Larvae (stage I)	FT	20°/25°/30°C//8.0	60 min	(+) TRC	LC50	0.06-0.69	2	(-)	Capuzzo (1976)

Validity

- 1 = valid without restriction
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- 3 = invalid
- 4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

*30 min exposure & 48 h observation

MB = Mollusc bivalve; MG = Mollusc gasteropode; FW = Flat worm, SW = Segmented worm; R = Rotifer

CD = Crustacea decapod; CA = Crustacea amphipod; CPP = Crustacea copepod; CCL = Crustacea cladocere

Table A9. Summary of ecotoxicology data for monochloramine
- freshwater -

Invertebrates

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Ceriodaphnia dubia (CCL)</i>	Juvenile	S	25°C	24 h	(+)TRC	LC50	0.012	2	(+)	Taylor (1993)
<i>Ceriodaphnia dubia (CCL)</i>	Juvenile	FT	25°C	24 h	(+) TRC	LC50	0.016	1	(+)	Taylor (1993)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

TRO = total residual oxidant/TRC = total residual chlorine

MB = Mollusc bivalve; *MG* = Mollusc gasteropode; *FW* = Flat worm, *SW* = Segmented worm; *R* = Rotifer

CD = Crustacea decapod; *CA* = Crustacea amphipod; *CPP* = Crustacea copepod; *CCL* = Crustacea cladocere

Table A10. Summary of ecotoxicological data for sodium hypochlorite
- brackish and sea water -

Fish

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Oncorhynchus kisutch</i>	Juvenile	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.032	1	(+)	Thatcher (1977)
<i>Oncorhynchus kisutch</i>	Adult	FT	13°C/7.9	60 min	(+)TRO	LC50	0.208	2	(-)	Stober (1980)
<i>Oncorhynchus kisutch</i>	Adult	FT	20°C/7.9	60 min	(+)TRO	LC50	0.130	2	(-)	Stober (1980)
<i>Oncorhynchus gorbuscha</i>	Juvenile	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.052<x>0.023	1	(+)	Thatcher (1977)
<i>Oncorhynchus tshawytscha</i>	Juvenile	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.065<x>0.038	1	(+)	Thatcher (1977)
<i>Oncorhynchus gorbuscha</i>	Juvenile	FT	13.6°C/7.53	7.5 min	(+)CI2	LC50	0.5	3	(-)	Stober (1974)
<i>Oncorhynchus tshawytscha</i>	Juvenile	FT	11.7°C/7.53	30/60 min	(+)CI2	LC50	0.25	3	(-)	Stober (1974)
<i>Clupea harengus</i>	Juvenile	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.065	1	(+)	Thatcher (1977)
<i>Cymatogaster aggregata</i>	Juvenile/adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.071	1	(+)	Thatcher (1977)
<i>Cymatogaster aggregata</i>	Juvenile	FT	13°C/8.0	60 min	(+)TRO	LC50	0.308	2	(-)	Stober (1980)
<i>Cymatogaster aggregata</i>	Juvenile	FT	20°C/8.0	60 min	(+)TRO	LC50	0.230	2	(-)	Stober (1980)
<i>Ammodytes hexapterus</i>	Juvenile/adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.082	1	(+)	Thatcher (1977)
<i>Gasterosteus aculeatus</i>	Juvenile/adult	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.167	2	(+)	Thatcher (1977)
<i>Pseudopleuronectes americanus</i>	Juvenile	FT	24°C/8.0	30 min*	(+) TRO	LC100	0.55	2	(-)	Capuzzo (1977)
<i>Parophrys vetulus</i>	Juvenile	FT	14.8°C/8.0	96 h	(+) TRO	LC50	0.073	1	(+)	Thatcher (1977)
<i>Fundulus heteroclitus</i>	Juvenile	FT	24°C/8.0	30 min*	(+) TRO	LC100	0.65	2	(-)	Capuzzo (1977)
<i>Stenotomus versicolor</i>	Juvenile	FT	24°C/8.0	30 min*	(+) TRO	LC100	0.65	2	(-)	Capuzzo (1977)
<i>Cynoscion nebulosus</i>	Larvae (1 h)	S	25°C/7.8	48 h	(+) TRO	LC50	0.17 +/- 0.28	2	(-)	Johnson (1977)
<i>Cynoscion nebulosus</i>	Eggs (2 h)	S	25°C/7.8	48 h	(+) TRO	Hatch (LC50)	0.21 +/- 0.01	2	(-)	Johnson (1977)
<i>Cynoscion nebulosus</i>	Eggs (10 h)	S	25°C/7.8	48 h	(+) TRO	Hatch (LC50)	0.21 +/- 0.01	2	(-)	Johnson (1977)
<i>Alburnus alburnus</i>	Adult	S	10°C/7.8	96 h	(-)	LC50	34.5 +/- 2.5	3	(+)	Linden (1979)
<i>Morone saxatilis</i>	Larvae (2d old)	FT	18°C/6.8	48 h	(+) TRC	LC50	0.04	2	(-)	Middaugh (1977)
<i>Morone saxatilis</i>	Larvae (12d old)	FT	18°C/6.8	48 h	(+) TRC	LC50	0.07	2	(-)	Middaugh (1977)
<i>Morone saxatilis</i>	Juvenile (30d old)	FT	18°C/6.8	48 h	(+) TRC	LC50	0.04	2	(-)	Middaugh (1977)
<i>Morone saxatilis</i>	Larvae (24d old)	FT	18°C/6.8	25 min	(+) TRC	Avoidance test	0.29-079	2	(-)	Middaugh (1977)
<i>Morone saxatilis</i>	Eggs(8/9h old)	FT	18°C/6.8	48 h	(+) TRC	100% no hatch	0.21	2	(-)	Middaugh (1977)

Table A10 - footnotes

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

TRO = total residual oxidant/TRC = total residual chlorine

*30 min exposure & 48 h observation

(+) Cl₂ = available chlorine

Table A11. Summary of ecotoxicological data for sodium hypochlorite
- freshwater -

Fish

Species	Stage at test initiation	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Salmo gairdneri</i>	Juvenile	FT	5°/12°/17°C//7.35	24 h	(+) TRC	LC50	0.26-0.29	2	(-)	Heath (1978)
<i>Salmo gairdneri</i>	Juvenile	FT	5°/12°/17°C//7.35	48 h	(+) TRC	LC50	0.09-0.16	2	(-)	Heath (1978)
<i>Salmo gairdneri</i>	Juvenile	FT	5°/12°/17°C//7.35	72 h	(+) TRC	LC50	0.07-0.10	2	(-)	Heath (1978)
<i>Salmo gairdneri</i>	Juvenile	FT	5°/12°/17°C//7.35	96 h	(+) TRC	LC50	0.06-0.09	1	(-)	Heath (1978)
<i>Salmo gairdneri</i>	Juvenile	SS	15°C/7.0	24 h	(+) Cl2	LC50	0.43	2	(-)	Soivio (1988)
<i>Salmo gairdneri</i>	Juvenile	SS	15°C/7.0	24/48 h	(+) Cl2	LC50	0.35	2	(-)	Soivio (1988)
<i>Salmo gairdneri</i>	Juvenile	FT	10/15/20°C//7.81-8.33	30 min**	(+)TRC	LC0	0.30-0.65	2	(-)	Brooks (1977)
<i>Salmo gairdneri</i>	Juvenile	FT	10/15/20°C//7.81-8.33	30 min**	(+)TRC	LC100	0.56-1.60	2	(-)	Brooks (1977)
<i>Salmo gairdneri</i>	Juvenile	FT	10/15/20°C//7.81-8.33	30 min**	(+)TRC	LC50	0.43-0.99	2	(-)	Brooks (1977)
<i>Salmo gairdneri</i>	Juvenile	FT	10/20°C//7.86-8.45	3 times 5 min**	(+)TRC	LC0	1.0-1.7	2	(-)	Brooks (1977)
<i>Salmo gairdneri</i>	Juvenile	FT	10/20°C//7.86-8.45	3 times 5 min**	(+)TRC	LC100	1.5-2.5	2	(-)	Brooks (1977)
<i>Salmo gairdneri</i>	Juvenile	FT	10/20°C//7.86-8.45	3 times 5 min**	(+)TRC	LC50	0.82-2.87	2	(-)	Brooks (1977)
<i>Salmo gairdneri</i>	Juvenile	FT	5°/12°/17°C//7.35	120 h	(+) TRC	LC50	0.05-0.09	2	(-)	Heath (1978)
<i>Oncorhynchus kisutch</i>	Juvenile	S	10/15/20°C//8.16-8.33	30 min*	(+) TRC	EC0	0.21-0.91	2	(-)	Seegert (1978)
<i>Oncorhynchus kisutch</i>	Juvenile	S	10/15/20°C//8.16-8.33	30 min*	(+) TRC	LC100	0.54-1.7	2	(-)	Seegert (1978)
<i>Oncorhynchus kisutch</i>	Juvenile	S	10/15/20°C//8.16-8.33	30 min*	(+) TRC	LC50	0.29-1.38	2	(-)	Seegert (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	30 h	(+) TRC	LC50	0.26-0.84	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	48 h	(+) TRC	LC50	0.22-0.55	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	72 h	(+) TRC	LC50	0.21-0.39	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	96 h	(+) TRC	LC50	0.19-0.27	1	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	120 h	(+) TRC	LC50	0.18-0.21	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	144 h	(+) TRC	LC50	0.18-0.18	2	(-)	Heath (1978)
<i>Lepomis macrochirus</i>	Juvenile	FT	6°/15°/25°/32°C//7.35	48 h	(+) TRC	LC50	0.47-0.54	2	(-)	Heath (1978)
<i>Lepomis macrochirus</i>	Juvenile	FT	6°/15°/25°/32°C//7.35	72 h	(+) TRC	LC50	0.41-0.53	2	(-)	Heath (1978)
<i>Lepomis macrochirus</i>	Juvenile	FT	6°/15°/25°/32°C//7.35	96 h	(+) TRC	LC50	0.39-0.46	1	(-)	Heath (1978)
<i>Lepomis macrochirus</i>	Juvenile	FT	6°/15°/25°/32°C//7.35	168 h	(+) TRC	LC50	0.33-0.41	2	(-)	Heath (1978)
<i>Lepomis macrochirus</i>	Adult	FT	21.1/7.0	96 h	(+) TRC	LC50	1.93-2.34	1	(+)	Wilde (1983a)

Table A11. Summary of ecotoxicological data for sodium hypochlorite - freshwater - (continued)

Species	Stage at test	System	Comments	Duration	Analy	Parameter	Results	Val	Hedset	Reference
Acute studies	initiation		T°/pH		meas		(mg/l)			
<i>Ictalurus punctatus</i>	Juvenile	FT	5°/24°C//7.35	48 h	(+) TRC	LC50	0.14-0.20	2	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	5°/24°C//7.35	72 h	(+) TRC	LC50	0.09-0.12	2	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	5°/24°C//7.35	96 h	(+) TRC	LC50	0.06-0.08	1	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	5°/24°C//7.35	120 h	(+) TRC	LC50	0.05-0.05	2	(-)	Heath (1978)
<i>Pimephales promelas</i>	Juvenile	FT	21.1/7.0	96 h	(+) TRC	LC50	0.21-0.53	1	(+)	Wilde (1983a)
<i>Pimephales promelas</i>	Adult	FT	21.1/7.0	96 h	(+) TRC	LC50	1.19-1.55	1	(+)	Wilde (1983a)
<i>Pimephales promelas</i>	Juvenile	FT	27°C//7.0	96 h	(+)TRC	LC50	0.08	1	(-)	Wilde (1983b)
<i>Pimephales promelas</i>	Adult	FT	27°C//7.0	96 h	(+)TRC	LC50	0.35	1	(-)	Wilde (1983b)
<i>Pimephales promelas</i>	Adult	S	22°C/7.2-7.9	96 h	(+) TRC	LC50	4.8-8.0	2	(+)	Curtis (1981)
<i>Pimephales promelas</i>	Juvenile	S	20°C/6.5-8.5	96 h	(-)	LC50	10	3	(+)	Ewell (1986)
<i>Puntius sarana</i>		SS		96 h	(+) TRC	LC50	0.39-0.87	3	(-)	Nimbargi (1987)
<i>Alosa pseudoharengus</i>	Juvenile	S	10/15/20/25/30°C//8.23-8.53	30 min*	(+) TRC	EC0	0.8-1.1	2	(-)	Seegert (1978)
<i>Alosa pseudoharengus</i>	Juvenile	S	10/15/20/25/30°C//8.23-8.53	30 min*	(+) TRC	LC100	0.63-4.6	2	(-)	Seegert (1978)
<i>Alosa pseudoharengus</i>	Juvenile	S	10/15/20/25/30°C//8.23-8.53	30 min*	(+) TRC	LC50	0.30-2.15	2	(-)	Seegert (1978)
<i>Notropis hudsonius</i>	Juvenile	S	10/15/20°C//8.28-8.41	30 min*	(+) TRC	EC0	0.38	2	(-)	Seegert (1978)
<i>Notropis hudsonius</i>	Juvenile	S	10/15/20°C//8.28-8.41	30 min*	(+) TRC	LC100	0.83	2	(-)	Seegert (1978)
<i>Notropis hudsonius</i>	Juvenile	S	10/15/20°C//8.28-8.41	30 min*	(+) TRC	LC50	0.53-2.41	2	(-)	Seegert (1978)
<i>Osmerus mordax</i>	Adult	S	10°C/8.46	30 min*	(+) TRC	LC10	0.72	2	(-)	Seegert (1978)
<i>Osmerus mordax</i>	Adult	S	10°C/8.46	30 min*	(+) TRC	LC50	1.27	2	(-)	Seegert (1978)

Table A11. Summary of ecotoxicological data for sodium hypochlorite - freshwater - (continued)

<i>Perca flavescens</i>	Juvenile	FT	10/15/20/25/30°C//8.2-8.8	30 min**	(+)TRC	LC0	0.48-5.1	2	(-)	Brooks (1977)
<i>Perca flavescens</i>	Juvenile	FT	10/15/20/25/30°C//8.2-8.8	30 min**	(+)TRC	LC100	0.95-15	2	(-)	Brooks (1977)
<i>Perca flavescens</i>	Juvenile	FT	10/15/20/25/30°C//8.2-8.8	30 min**	(+)TRC	LC50	0.7-8.0	2	(-)	Brooks (1977)
<i>Perca flavescens</i>	Juvenile	FT	10/20°C//8.0-8.52	3 times 5 min**	(+)TRC	LC0	17	2	(-)	Brooks (1977)
<i>Perca flavescens</i>	Juvenile	FT	10/20°C//8.0-8.52	3 times 5 min**	(+)TRC	LC100	37	2	(-)	Brooks (1977)
<i>Perca flavescens</i>	Juvenile	FT	10/20°C//8.0-8.52	3 times 5 min**	(+)TRC	LC50	22.6	2	(-)	Brooks (1977)
<i>Carassius auratus</i>	Adult	S	17/22.5°C//7.4-8.7	24 h ²	(+)TRC	LC50	0.27	2	(-)	Dickson (1977)
<i>Osmerus mordax</i>	Adult	S	10°C/8.46	30 min*	(+) TRC	LC90	2	2	(-)	Seegert (1978)
<i>Brachydanio rerio</i>	Adult	S	23°C/7.6	96 h	(-)	LC50	8.7	3	(-)	INERIS (1992b)
General review								3	(-)	Brungs (1973)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

TRO = total residual oxidant/TRC = total residual chlorine

*30 min exposure & 48 h observation

(+) Cl₂ = available chlorine

** Mortality assessed after 24-72 h in recovery tanks

² 15 min exposure every 4 h during 24 h

Table A12. Summary of ecotoxicological data for sodium hypochlorite
- brackish and sea water -

Fish

Species	Stage at test	System	Comments	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Chronic studies	initiation		T°/pH							
<i>Brevoortia tyrannus</i> *	Juvenile	FT	30.9°C/7.0	19 d	(+) TRO	LC100	0.032	2	(-)	Liden (1980)
<i>Leiostomus xanthurus</i> *	Juvenile	FT	30.9°C/7.0	20 d	(+) TRO	LC26	0.014	2	(-)	Liden (1980)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

TRO = total residual oxidant

TRC = total residual chlorine

**Table A13. Summary of ecotoxicological data for chlorine
- freshwater -**

Fish

Species	Stage at test	System	Comments	Duration	Analy	Parameter	Results	Val	Hedset	Reference
Acute studies		initiation	T°/pH		meas		(mg/l)			
<i>Rhinichthys atratulus</i>		FT FT	21°C/7.0		(+) TRC	Median Survival Time (MST)	0.15mg/l = 684min 6.6mg/l = 17min	3	(-)	Tompkins (1976)
Ocean spot		FT	14.2-16°C//7.5	96 h	(+)TRC	LC50	0.09	3	(-)	Bellanca (1977)
<i>Salmo gairdneri</i>	Adult	FT	20°C	48 h	(+) TRC	Avoidance test	total at 0.5	3	(-)	Schumacher (1980)
<i>Pimephales promelas</i>		FT	0.5-9°C/7.1-8.3	96 h	(+) TRC	100% kill	0.16-0.21	3	(-)	Zillich (1972)
<i>Pimephales promelas</i>		FT	25°C	96 h	(+) TRC	LC50	0.082/0.095	3	(-)	DeGraeve (1977)
<i>Pimephales promelas</i>		FT	25°C//7.08.2	up to 330 d	(+)TRC	% Survival		3	(-)	Ward (1978a)
<i>Pimephales promelas</i>		FT	25°C//7.08.2	up to 330 d	(+)TRC	% Survival		3	(-)	Ward (1978b)
<i>Lepomis macrochirus</i>	Adult	FT	15°C/25°C/32°C	96 h	(+) TRC	LC50	0.44 +/- 0.03	2	(-)	Bass (1977)
<i>Lepomis macrochirus</i>		FT	6/15/25/32°C	96 h	(-)	LC50	0.436	3	(-)	Bass (1975)
<i>Gambusia affinis</i>		FT	21°C/8.2	30 min	(+) TRC	LC50	1.59	2	(-)	Mattice (1981)
<i>Gambusia affinis</i>		FT	21°C/8.2	60 min	(+) TRC	LC50	0.84	2	(-)	Mattice (1981)

Validity

- 1 = valid without restriction
- 2 = valid with restriction
- 3 = invalid
- 4 = not assignable

- S = Static
- SS = Semi static
- FT = flow-through
- ND = no data

- TRO = total residual oxidant
- TRC = total residual chlorine

Table A14. Summary of ecotoxicological data for chlorine
- seawater -

Fish

Species	Stage at test	System	Comments	Duration	Analy	Parameter	Results	Val	Hedset	Reference
Acute studies	initiation		T°/pH		meas		(mg/l)			
<i>Syngnathus fuscus</i>		FT		96 h	(+)TRO	LC50	0.037-0.22	3	(-)	Bellanca (1977)
<i>Gobiosoma bosci</i>		FT		96 h	(+)TRO	LC50	0.037-0.22	3	(-)	Bellanca (1977)
<i>Menidia menidia</i>		FT		96 h	(+)TRO	LC50	0.037	3	(-)	Bellanca (1977)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

TRO = total residual oxidant

TRC = total residual chlorine

Table A15. Summary of ecotoxicological data for chloramine
- freshwater -

Fish

Species	Stage at test	System	Comments	Duration	Analy	Parameter	Results	Val	Hedset	Reference
Acute studies	initiation		T°/pH		meas		(mg/l)			
<i>Oncorhynchus kisutch</i>	Juvenile	FT	6°/12° C//7.35	96 h	(+) TRC	LC50	0.64-0.68	1	(-)	Heath (1978)
<i>Oncorhynchus kisutch</i>	Juvenile	FT	6°/12° C//7.35	120 h	(+) TRC	LC50	0.57-0.62	2	(-)	Heath (1978)
<i>Oncorhynchus kisutch</i>	Juvenile	FT	6°/12° C//7.35	144 h	(+) TRC	LC50	0.54-0.55	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	48 h	(+) TRC	LC50	0.99-1.09	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	96 h	(+) TRC	LC50	0.72-0.93	1	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	120 h	(+) TRC	LC50	0.67-0.92	2	(-)	Heath (1978)
<i>Notemigonus crysoleucas</i>	Juvenile	FT	5°/24°C//7.35	144 h	(+) TRC	LC50	0.64-0.92	2	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	6°/24°C//7.35	48 h	(+) TRC	LC50	0.45	2	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	6°/24°C//7.35	96 h	(+) TRC	LC50	0.28-0.33	1	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	6°/24°C//7.35	120 h	(+) TRC	LC50	0.23-0.26	2	(-)	Heath (1978)
<i>Ictalurus punctatus</i>	Juvenile	FT	6°/24°C//7.35	144 h	(+) TRC	LC50	0.21-0.25	2	(-)	Heath (1978)
<i>Pimephales promelas</i>	Juvenile	FT	23°C/7.2-8.6	96 h	(+) TRC	TLm	0.085-0.154	1	(-)	Arthur (1971)
<i>Rhinichthys atratulus</i>		FT	21°C		(+) TRC	Median Survival Time (MST)	0.19mg/l = 1048min 5.25mg/l = 11min	3	(-)	Tompkins (1976)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

TRO = total residual oxidant/TRC = total residual chlorine

*30 min exposure & 48 h observation

Table A16. Summary of ecotoxicological data for chloramine
- brackish and sea water -

Fish

Species	Stage at test	System	Comments	Duration	Analy	Parameter	Results	Val	Hedset	Reference
Acute studies	initiation		T°/pH		meas		(mg/l)			
<i>Pseudopleuronectes americanus</i>	Juvenile	FT	24°C/8.0	30 min*	(+) TRO	LC100	2.55	2	(-)	Capuzzo (1977)
<i>Stenotomus versicolor</i>	Juvenile	FT	24°C/8.0	30 min*	(+) TRO	LC100	3.10	2	(-)	Capuzzo (1977)
<i>Fundulus heteroclitus</i>	Juvenile	FT	24°C/8.0	30 min*	(+) TRO	LC100	1.20	2	(-)	Capuzzo (1977)
<i>Cynoscion nebulosus</i>	Larvae (1 h)	S	25°C/7.8	48 h	(+) TRO	LC50	5.75 +/- 3.01	2	(-)	Johnson (1977)
<i>Cynoscion nebulosus</i>	Eggs (2 h)	S	25°C/7.8	48 h	(+) TRO	Hatch (LC50)	14.14 +/- 1.13	2	(-)	Johnson (1977)
<i>Cynoscion nebulosus</i>	Eggs (10 h)	S	25°C/7.8	48 h	(+) TRO	Hatch (LC50)	0.57 +/- 0.28	2	(-)	Johnson (1977)

Validity

1 = valid without restriction
2 = valid with restriction
3 = invalid
4 = not assignable

S = Static
SS = Semi static
FT = flow-through
ND = no data

TRO = total residual oxidant/TRC = total residual chlorine
*30 min exposure & 48 h observation

**Table A17. Summary of ecotoxicological data for sodium hypochlorite
- freshwater -**

Algae

Species	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Chlorella sorokiniana</i>	S	30°C/7.0	20 h	(+)Cl2	Algae number (43% killed)	0.6	3	(+)	Kott (1969)
<i>Chlorella sorokiniana</i>	S	30°C/7.0	20 h	(+)Cl2	Algae number (27% killed)	0.2	3	(+)	Kott (1969)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

(+)Cl2 = available chlorine

Table A18. Summary of ecotoxicological data for sodium hypochlorite
- sea water -

Algae

Species	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Acute studies									
<i>Dunaliella primolecta</i>	S	20°C	24 h	(+)TRO	EC50	0.4	2	(+)	Videau (1978)
<i>Dunaliella primolecta</i>	S	20°C	24 h	(+)TRO	EC100	0.6	2	(+)	Videau (1978)
<i>Pavlova lutheri</i>	S	20°C	72 h	(+)TRO	EC50	4	2	(+)	Videau (1978)
<i>Phaeodactylum tricorutum</i>	S	20°C	72 h	(+)TRO	EC100	0.8	2	(+)	Videau (1978)
General review							3	(+)	White (1972)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A19. Summary of ecotoxicological data for sodium hypochlorite
 - sea water -

Algae

Species	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
<i>Chronic studies</i>									
<i>Phaeodactylum tricorutum</i>	S	20°C	72 h	(+)TRO	EC20	0.6	2	(+)	Videau (1978)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A20. Summary of ecotoxicological data for sodium hypochlorite
- freshwater -

Species	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Chronic studies									
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Chlorophyll a/NOEC	<0.0021	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Chlorophyll a/LOEC	0.0021	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Chlorophyll a/MATC	0.0021	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	ATP Biomass/NOEC	0.100	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	ATP Biomass/LOEC	0.308	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	ATP Biomass/MATC	0.175	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Protein level/NOEC	0.025	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Protein level/LOEC	0.100	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Protein level/MATC	0.050	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Potassium/NOEC	0.100	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Potassium/LOEC	0.308	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Potassium/MATC	0.175	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Alk. phosphatase/NOEC	0.0021	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Alk. phosphatase/NOEC	0.0061	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Alk. phosphatase/NOEC	0.0036	2	(-)	Pratt (1988)
Microcosm	FT	9.6°-->17.0°C/7.7	28 d	(+)TRC	Species number/MATC	0.0036	2	(-)	Pratt (1988)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

**Table A21. Summary of ecotoxicological data for sodium hypochlorite
- sea water -**

Species	System	Comments	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Chronic studies		T°/pH							
Plankton	FT	23°C	1 y	(+)TRC	ATP/EC87	0.125	3	(-)	Ericksson (1980)
Plankton	FT	23°C	1 y	(+)TRC	ATP/EC78	0.25	3	(-)	Ericksson (1980)
Plankton	FT	23°C	1 y	(+)TRC	ATP/EC67	0.5	3	(-)	Ericksson (1980)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A22. Summary of ecotoxicological data for chlorine
- freshwater-

Algae

Scientific name	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Acute studies									
Phytoplankton	S		30 min	(+)TRC	Chlorophyll a/EC100	1	3	(+)	Brooks (1979)
Phytoplankton	S		30 min	(+)TRC	Chlorophyll a/EC20	0.1	3	(+)	Brooks (1979)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A23. Summary of ecotoxicological data for chlorine

-sea water-

Algae

Scientific name	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Chronic studies									
Phytoplankton	FT	23.6-24.4°C/7.8	23 d	(+)TRC	Chlorophyll a/EC50	0.25	3	(+)	Sanders (1981)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A24. Summary of ecotoxicological data for chlorine
- sea water -

Algae

Scientific name	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Chronic studies									
Microcosm	FT	18.9-20.4°C	7 d	(+)TRC	IC20	0.0027	2	(+)	Cairns (1990)
Microcosm	FT	18.9-20.4°C	7 d	(+)TRC	IC50	0.0316	2	(+)	Cairns (1990)
Microcosm	FT	18.9-20.4°C	7 d	(+)TRC	IC80	0.491	2	(+)	Cairns (1990)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A25. Summary of ecotoxicological data for chloramine

- sea water -

Algae

Scientific name	System	Comments T°/pH	Duration	Analy meas	Parameter	Results (mg/l)	Val	Hedset	Reference
Chronic studies									
Microcosm	FT	18.9-20.4°C	7 d	(+)TRC	IC20	0.0012	2	(+)	Cairns (1990)

Validity

1 = valid without restriction

2 = valid with restriction

3 = invalid

4 = not assignable

S = Static

SS = Semi static

FT = flow-through

ND = no data

FW = freshwater

SW = salt water

BW = brackish water

TRO = total residual oxidant

TRC = total residual chlorine

Table A26. Ecotoxicity of Organohalogens (after Overleggroep Deskundigen Wasmiddelen-Milieu, 1989)

Chemical	Organism		Test		Result (mg/l)	Ref.
TCA						
	bacteria	<i>Pseudomonas putida</i>	LOEC		> 1000	1
	algae	<i>Microcystis aeruginosa</i>	LOEC		250	1
		<i>Scenedesmus quadricauda</i>	LOEC		200	1
	protozoa	<i>Entosiphon sulcatum</i>	LOEC		800	1
		<i>Uronema parduczi</i>	LOEC		435	
	crustacea	<i>Daphnia magna</i>	LC50	48h	2000	1
	fish	<i>Pimephales promelas</i>	LC50	96h	2000	1
5-chloro-uracil						
	fish	Carp eggs hatching	LOEC		0.001	3
2-chlorophenol						
	algae	<i>Chlorella pyrenoidosa</i>	?		96	1
		<i>Scenedesmus</i>	?		60	1
	bacteria	<i>Pseudomonas</i>	?		30	1
	protozoa	Colpoda	?		30	1
	fish	<i>Lepomis macrochirus</i>	LC50	96h	8.4	1
		<i>Lepomis macrochirus</i>	LC50	24h	8.2	1
		<i>Lepomis macrochirus</i>	LC50	24-96h	22-8	1
		<i>Pimephales promelas</i>	LC50	24-96h	22-11	1
		<i>Pimephales promelas</i>	LC50	96h	13.8	2
		<i>Carassius auratus</i>	LC50	24-96h	15-12	1
		<i>Carassius auratus</i>	LC50	24h	16	1
		<i>Poecilia reticulata</i>	LC50	24-96h	23-20	1
		<i>Poecilia reticulata</i>	LC50	24h	11	1
		<i>Idus idus melanotus</i>	LC50	48h	8.5	1

Table A26. Ecotoxicity of Organohalogens (Continued)

4-chlorophenol						
	bacteria	Pseudomonas	?		20	1
	algae	Scenedesmus	?		20	1
		Chlorella pyrenoidosa	?		40	1
	protozoa	Colpoda	?		5	1
	fish	Poecilia reticulata	LC50	24h	9.0	1
		Idus idus melanotus	LC50	48h	3.5	1
3-chlorophenol						
	algae	Chlorella pyrenoidosa	?		40	1
	fish	Poecilia reticulata	LC50	24h	6.5	1
		Idus idus melanotus	LC50	48h	3	1
4-chlororesorcinol						
	fish	Carp eggs hatching	LOEC		0.001	3
4-chloro-3-methylphenol						
	fish	Pimephales promelas	LC50	96h	0.1 - 0.01	1

Table A26. Ecotoxicity of Organohalogenes (Continued)

Chloroform						
	bacteria	<i>Pseudomonas putida</i>	LOEC		125	1
	algae	<i>Microcystis aeruginosa</i>	LOEC		185	1
		<i>Scenedesmus quadricauda</i>	LOEC		1100	1
	protozoa	<i>Entosiphon sulcatum</i>	LOEC		> 6560	1
		<i>Euronema parduczi</i>	LOEC		> 6560	1
	mollusca	<i>Crassostrea virginica</i> larvae	LC50	48h	1	1,7
	fish	<i>Salmo gairdneri</i>	LC50	27d	1.24	4
		<i>Salmo gairdneri</i>	LC50	ELS	1.24 / 2.03	6
		<i>Leuciscus idus melanotus</i>	LC50	48h	162 - 191	5
References: (1) Verschueren (1983), (2) Geiger et al. (1985), (3) EUR 5983 EN (1978), (4) EPA (1986), (5) Bringmann & Kuehn (1978), (6) Birge et al. (1979), (7) Stewart et al. (1979).						

Table A27 Examples of average organohalogen concentrations in various compartments or media (as AOX, unless otherwise specified)

Sample	Organohalogen Conc. (mg/l or mg/kg)	References
Natural Water (AOX)		
- Rivers		
Natural background (unpolluted river)		
Through peat soil	0.05 - 0.2	Asplund et al. (1989), Hasanen & Maninen (1989), Grimval et al. (1990)
Not through peat soil	< 0.015	
Rivers in polluted areas (Finland)	0.10 - 0.50	Hasanen & Maninen (1989), Asplund et al. (1989), Grimvall et al. (1990)
Rivers unpolluted & polluted (Sweden) (respective annual mean)	0.002 - 0.103	Enell & Wennberg (1991)
Specific: - Rhine	0.029 - 0.058	HOV studie (1987)
- Seine	0.010- 0.030 (0.3)	Monzain & Durand (1995)
- Marine environment		
Sea Water (general)	16e-6 - 47e-6 (CH ₃ Cl)	Fleming (1991)
Baltic sea	???	Enell (1993)
- Rain & Snow	0.002 - 0.010	Monzain & Durand (1995)
Swimming Pools		
POX (VOX)	0.2 - 0.5	Aggazzotti & Predieri (1986)
AOX	46-253	Manschott et al. (1995)

Table A27. Examples of average organohalogen concentrations in various compartments or media (as AOX, unless otherwise mentioned)-(continued)

Sample	Organohalogen Conc. (mg/l or mg/kg)	References
Drinking Water Europe & US		
POX (VOX)	0.005 - 0.05	Aggazzotti & Predieri (1986)
AOX	0.010 - 0.50 (0.100)	Kostyal et al. (1994)
Total OBPs	0.020 - 0.250	Krasner et al. (1989)
Mineral water	< 0.005	Kostyal et al. (1994)
Sewage Treatment (STP)		
- Domestic		
STP influent	0.05-0.25	Hoffmann et al. (1988),
activated sludge Mixed liquor	0.015-0.160	Laschka & Schall (1989),
activated sludge DM (mg/kg DM)	200-500	Laschka & Trumpp (1991),
STP effluent	0.01-0.05	Böhnke & Li (1992),
STP effluent	0.015-0.12	HOV studie (1987),
Chlorinated STP effluent	0.056-1,530	Hull & Reckow (1993)
- Industrial		
activated sludge DM (mg/kg DM)	Sometimes >1000	Norton (1991), Hoffmann et al. (1988)
Emission Pulp & Paper Industry		
Untreated effluents	up to 60 mg/l	Norton (1991)
Human body(AOX)		
urine	0.06 - 0.18	Fleming (1991)
breast milk	???	
Technical NaOCl Solutions	0.5-21	Kolb & Schulz (1990)