

**SODIUM**  

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**HYPOCHLORITE**



**THE SOAP AND DETERGENT ASSOCIATION**

# SODIUM HYPOCHLORITE

## INTRODUCTION

This monograph summarizes: 1) critical fate and effects data required for an environmental risk assessment on sodium hypochlorite; and 2) conclusions drawn from a risk assessment of sodium hypochlorite in the United States. Although focused on conditions in the U.S., data from other parts of the world that are relevant to a U.S. assessment are included in the monograph. The monograph is written for a technical audience, but not necessarily one familiar with environmental risk assessment.

The monograph is formatted into five sections. The first section describes sodium hypochlorite, its chemical structure and U.S. consumption volumes. The second section describes the function of sodium hypochlorite in cleaning products. The third section describes its fate and exposure concentrations in the environment. The fourth section presents environmental effects information. The fifth section presents a comparison of exposure and effects concentrations in the framework of an environmental risk assessment.

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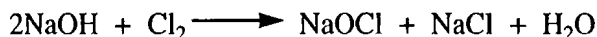
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## INGREDIENT IDENTIFICATION

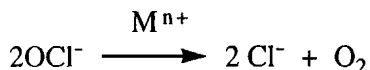
### *Chemical Description*

Sodium hypochlorite, NaOCl, better known as bleach, is an inorganic oxidizing agent. It is registered in the Toxic Substances Control Act (TSCA) Chemical Substance Inventory as hypochlorous acid, sodium salt (ClHO.Na) and is identified with the Chemical Abstracts Service (CAS) Registry Number 7681-52-9.

Sodium hypochlorite is formed under controlled conditions by reacting chlorine with aqueous solutions of sodium hydroxide as follows:



A small excess of sodium hydroxide is required to maintain the pH of sodium hypochlorite solutions between 11 and 13, thereby minimizing the decomposition of the sodium hypochlorite. Hypochlorite also decomposes as a result of catalysis by metal ions such as nickel, cobalt, iron and copper:



This reaction will lower the sodium hypochlorite concentration in a product, potentially reducing the product's performance, and produce oxygen gas which, if it occurs during storage, may deform or damage a closed container. That is why sodium hypochlorite solutions need to be measured as percent "available" chlorine. The percent available chlorine is 95% of the weight percent of sodium hypochlorite. "Available" chlorine is the equivalent concentration of chlorine needed to make sodium hypochlorite as shown above.

### *U.S. Consumption*

Approximately 500 million to 600 million pounds of sodium hypochlorite were produced and consumed in the U.S. in 1990 (Peters, Riepl, Leder and Sasano, 1992). About 40% is manufactured at 5.25% sodium hypochlorite, which is typical household strength. Many household cleaning products contain various concentrations of sodium hypochlorite. Drain openers, disinfectants, mildew stain removers and general purpose cleaners may contain 1-7% sodium hypochlorite. The remainder of the sodium hypochlorite is produced at industrial strength, 15-20% sodium hypochlorite. Industrial uses include drinking water, wastewater and swimming pool disinfection, and textile bleaching.

## INGREDIENT FUNCTION

### *Function*

Sodium hypochlorite reacts rapidly with a wide variety of inorganic and organic compounds. As a result, it is an effective stain remover, cleaner, sanitizer and disinfectant. Major uses of industrial strength sodium hypochlorite include disinfection of swimming pool water and wastewater generated by both municipalities and industry, and bleaching of chemical pulp, textiles and commercial laundry (Peters *et al.*, 1992).

Sodium hypochlorite bleach was introduced to U.S. consumers in 1916. Today, it is used in four out of five households in the U.S. (The Clorox Company, 1991). The major household use of sodium hypochlorite bleach is in laundering. Bleach boosts the cleaning power of all detergents. This is particularly important in cool water temperatures and in hard water. Sodium hypochlorite also ensures the destruction of contaminant microorganisms from cleaning towels, dish cloths, cloth diapers, etc.

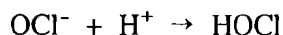
Sodium hypochlorite is one of the most effective disinfectant and bleaching agents known (Bloomfield, 1978; FIFE-AIS, 1993). It has broad spectrum action, being effective against bacteria (both Gram positive and Gram negative), bacterial spores, viruses and fungi both in laundry and on household surfaces. In addition to laundering, sodium hypochlorite bleaches are used to remove stains and soil, clean, sanitize and disinfect toilets, sinks, floors, showers, kitchen counters and other household surfaces. Bleach is also a deodorizer, killing the bacteria that cause odors and aiding in removing the soils that contribute to the odors themselves.

Sodium hypochlorite is approved for specific uses by the U.S. Environmental Protection Agency, Department of Agriculture and the Food and Drug Administration. These uses include disinfection of food and nonfood contact surfaces, including households and laundry (U.S. EPA, 1991; Cook, Hasler, Kim, deLeeuw, McCabe, Meehan, Mitchell, Shaheen, Smith and Stanislawski, 1996), dairy equipment (U.S. EPA, 1992), and washing fruit and vegetables (U.S. EPA, 1992; U.S. Department of Agriculture, 1991; Food and Drug Administration, 1991). Sodium hypochlorite is also used for a variety of sanitizing and disinfecting purposes in agriculture (U.S. EPA, 1991; U.S. EPA, 1992).

In the medical area, sodium hypochlorite bleach is used to disinfect kidney dialysis machines (U.S. EPA, 1992), to disinfect work surfaces in medical laboratories (U.S. EPA, 1992), and by dentists in the treatment of gum disease and root canals (Gilman, Goodman and Gilman, 1980).

## Mechanism

In water, sodium hypochlorite exists as sodium,  $\text{Na}^+$ , and hypochlorite,  $\text{OCl}^-$ , ions. The hypochlorite ions are also in equilibrium with hypochlorous acid, as shown in the following equation:



The relative amounts of hypochlorite ions and hypochlorous acid vary with pH (Jolley and Carpenter, 1981). HOCl will predominate below pH 7.5, while  $\text{OCl}^-$  is predominant above this pH. Both HOCl and  $\text{OCl}^-$  are oxidizing species. The HOCl form is a stronger oxidant than the less electrophilic  $\text{OCl}^-$ .

Sodium hypochlorite and other products which produce hypochlorite species, such as chlorinated isocyanurates, hydantoin and calcium hypochlorite, will react rapidly with oxidizable inorganic and organic compounds (soils, stains), predominantly through nucleophilic or electron transfer reactions yielding primarily sodium chloride as the chlorine-containing product. Sodium hypochlorite may also react with some organic compounds to form small amounts of chlorinated organic compounds (Jolley *et al.*, 1981).

## ENVIRONMENTAL FATE AND EXPOSURE

### Fate

The route of environmental release of sodium hypochlorite from use in cleaning products is down-the-drain, with the product and/or its by-products being treated by on-site or municipal waste treatment systems. Studies conducted with bleached laundry wash water suggest that approximately 12% of the chlorinated organic compounds formed are volatile and that the majority of these volatile compounds, greater than 70%, remain in solution during the wash cycle (Ong, DeGraeve, Silva-Wilkinson, McCabe and Smith, 1996).

The fate of sodium hypochlorite during use and discharge to sewer systems has been investigated (FIFE-AIS, 1993; Consultative Expert Group Detergents-Environment, 1989). These studies reveal that hypochlorite is rapidly consumed, predominantly through oxidation reactions, with inorganic compounds and organic substances found in wash water and wastewater, and is converted to chloride. The rapid reactivity of sodium hypochlorite with the high concentrations of inorganic and organic materials already present in wastewater makes sodium hypochlorite safe for biological treatment plants. Unused consumer quantities of hypochlorite-containing cleaning products can be safely disposed of down-the-drain. Sodium hypochlorite will have reacted completely before reaching the treatment plant. Further, activated

sludge has been shown to be tolerant to hypochlorite (Larson and Schaeffer, 1982), and is often used at sewage treatment plants to control odor and improve the settling of primary sludge (Parker, Randall and King, 1972).

Sodium hypochlorite bleach is also safe for septic tank systems. Laboratory and field studies (Gross, 1987) concluded that a homeowner could pour more than 1.3 gallons of undiluted sodium hypochlorite bleach daily into a standard 1,000-gallon septic tank without causing any serious harm to the septic tank's bacteriologic action. This amount far exceeds the amount used by a consumer on a daily basis.

Since sodium hypochlorite-containing cleaning products are intended to be used and disposed of down-the-drain, the only way sodium hypochlorite-containing household products could reach the environment without first being treated by sewage or septic tank systems is through accidental spills or misuse of the product. These situations could include direct exposure to plants and animals.

### By-products Formation and Fate

To evaluate the environmental impact of the chlorinated organic by-products formed by the use of household bleach, it is necessary to identify all major chlorinated organic compound sources. Chlorinated organic compounds result from the direct and indirect use of chlorine. Some chlorinated organic compounds are formed intentionally, as in the manufacturing of chlorinated solvents and pesticides, while others are formed unintentionally as by-products. Further, chlorinated organic by-products may also result from the use of chlorine-containing compounds, like sodium hypochlorite.

The types of chlorinated organics formed and the amounts are dependent upon pH, which governs which available chlorine species will be present, the types of substrate, concentrations, temperature and reaction times (Jolley *et al.*, 1981). Under current wastewater treatment practices, about 1% of the hypochlorite species used in disinfection is converted into chlorinated organic compounds (Jolley, 1975). Conversion of hypochlorite species to chlorinated organics under drinking water disinfection conditions is approximately 3% (The Clorox Company, 1992). Similar conversion levels (2.6%) have been reported for sodium hypochlorite used in household laundering (The Clorox Company, 1992), and when sodium hypochlorite or chlorinated isocyanurate is used for household automatic dishwashing (2.8%) (Smith, 1993). Conversion of hypochlorite for cleaning kitchen floors, bathroom floors, kitchen counters and toilets is estimated at 0.5% (Smith, 1993).

The use of sodium hypochlorite under household conditions does not produce the type nor the quantity of chlorinated organic by-products formed as when chlorine

is used for pulp and paper bleaching. In the pulp and paper industry, wood pulp has traditionally been treated with molecular chlorine at low pH. These conditions result in about 10% of the chlorine being converted to chlorinated by-products (Leach, 1979). While chlorine is also used in water disinfection, the chlorine first reacts with the water to form hypochlorous acid, which is the predominant active species. With hypochlorous acid, much less chlorine is incorporated into organic compounds than with chlorine. About 3% of the chlorine used for drinking water disinfection is converted to chlorinated organics (Ong *et al.*, 1996). Sodium hypochlorite is the predominant species under household use conditions and it is somewhat less reactive than hypochlorous acid.

The form of available chlorine is also an important factor in determining the types of by-products formed. The by-products formed in treating wood pulp, where molecular chlorine is used, differ considerably from those in drinking water disinfection and household use of sodium hypochlorite. Only in the bleaching process of paper pulp can polychlorinated high molecular weight by-products be found. The conditions necessary to form high molecular weight polychlorinated organic compounds, like dioxin, PCB and DDT, are not present in the household use or disposal of hypochlorite-containing products (Smith, 1991). Recent findings by the Swedish government provide further evidence that no measurable amount of dioxin is formed from hypochlorite-containing products used for dishwashing or laundering (Swedish Office of Nature Conservancy, 1992).

The following table describes the production of organically bound chlorine in the U.S. (Smith, 1993).

**TABLE 1**  
**Production of Organically Bound Chlorine in the United States**

<u>Source*</u>	<u>Kilotons/year</u>	<u>Percent</u>
End Products		
Polymers and plastics	3147	78.1
Solvents	543	13.5
Other <sup>b</sup>	137	3.4
By-products		
Pulp and paper production	161	4.0
Pulp and paper products	20	0.5
Public water treatment	9	0.22
Municipal wastewater	3.9	0.10
Pools and spas	2.4	0.06
Household laundry and cleaning	2.2	0.05
Industrial and institutional		
laundry and cleaning	0.8	0.02
Cooling towers	0.7	0.02
Textile manufacturing	0.2	0.005
Total	4027	

\* Does not include chlorofluorocarbons, chemical intermediates, manufacturing by-products, combustion and natural sources

<sup>b</sup> Pharmaceuticals, agrichemicals, flame retardants and chloroparaffins

The estimated production of chlorinated organics produced in the U.S. shown in Table 1 includes both intentional production (end uses) and unintentional production (by-products). The table shows that household use of hypochlorite is a very small source of chlorinated organics.

Unlike some chlorinated organic compounds that are directly applied or released into the environment, chlorinated by-products from household use of sodium hypochlorite are primarily released into sewer or septic tank systems where they are effectively treated. Chlorinated organic compounds are known to undergo both biologic (aerobic and anaerobic) and non-biologic dehalogenating mechanisms (Omori and Alexander, 1978; Lackmann, Maier and Shamat, 1981; U.S. EPA, 1986b; U.S. EPA, 1981). The biodegradability of chlorinated compounds depends mainly on the degree of halogenation, the position(s) of the chlorine and the molecular weight.

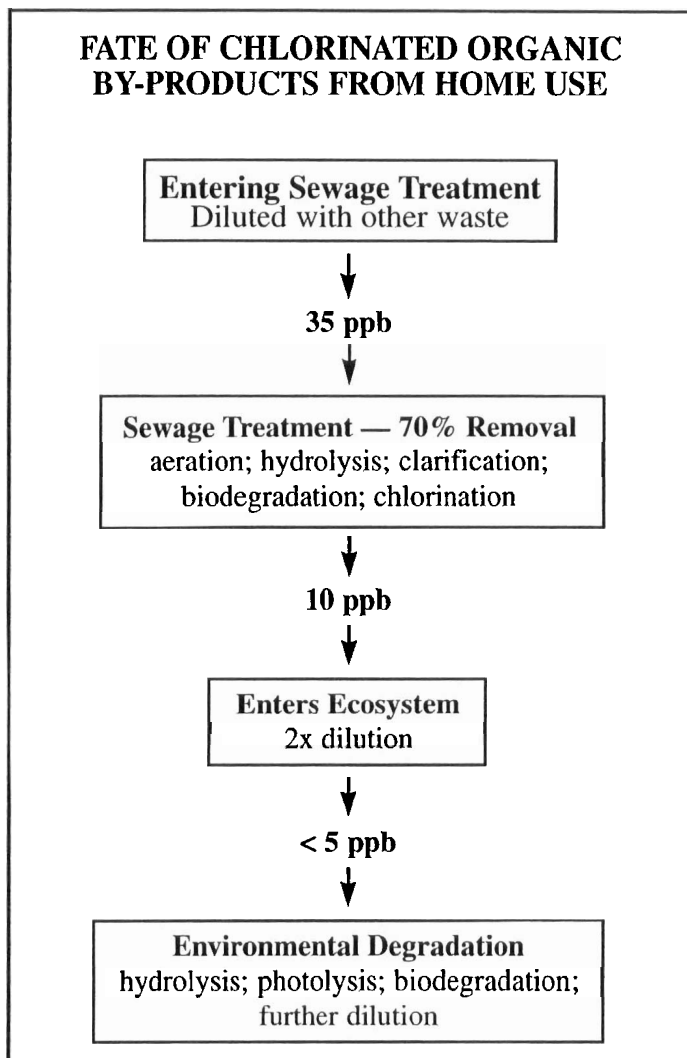
An EPA study (U.S. EPA, 1986b) examined 40 activated sludge wastewater treatment plants and identified 32 chlorinated organic compounds that were commonly present. The average removal efficiency from the wastewater for these chemicals was generally greater than 90%. Other studies (The Clorox Company, 1992; Ong *et al.*, 1996) have shown that the chlorinated by-products formed during laundry bleaching are no less biodegradable than the starting soil, and that 65-75% biodegrade under simulated activated sludge treatment conditions. Additional research suggests that further degradation is possible (Henkel, 1991).

Approximately 12% of the chlorinated organic compounds formed from household laundry use are volatile (Ong *et al.*, 1996). Chloroform accounts for about 80% of the volatiles. Approximately 28% of the chloroform that reaches an activated sludge treatment plant is biodegraded (U.S. EPA, 1986b). The remaining chloroform is primarily air stripped. The principal removal mechanism of tropospheric chloroform is hydroxyl radical oxidation (California Air Resources Board, 1990). Chloroform is not involved in stratospheric ozone depletion.

### Treatability

As sodium hypochlorite rapidly and almost completely degrades to chloride, the risk assessment addresses the small amounts of chlorinated organic compounds formed during household use. Further, the assessment includes chlorinated by-products formed from the use of household cleaning and laundering products which produce hypochlorite species. This assessment addresses the fate of chlorinated organics entering an activated sludge treatment plant. Approximately 75% of all U.S. wastewater receives activated sludge treatment (Rappaport, 1988).

Household disposal of sodium hypochlorite-containing cleaning products provides an opportunity for a majority of the chlorinated by-products to be removed prior to the wastewater returning to the environment. The chlorinated organic concentration entering a secondary activated sludge treatment plant that originated from household use of a cleaning or laundering product containing the hypochlorite specie is approximately 35 ppb (see Appendix for calculations). The fate of these by-products in an activated sludge treatment plant and in the environment is summarized in Figure 1.



**Figure 1.** Fate of sodium hypochlorite by-products

Following dilution with other household and industrial wastewater, the chlorinated organic by-products will enter a wastewater treatment plant. Various removal mechanisms during activated sludge treatment, including biodegradation, volatilization and adsorption, will reduce the concentration to 10 ppb. The median organic halide concentration observed in U.S. secondary wastewater effluents is approximately 245 ppb (Hull and Reckhow, 1993).

### Exposure

The wastewater effluent will undergo further dilution at the outfall. Under worst case conditions, either mean or critical low flow, greater than 90% of U.S. sewage flow originating from activated sludge treatment plants will be diluted at least two-fold upon discharge to receiving waters (Rappaport, 1988). Greater than 50% of the activated sludge flow will be diluted at least 27 fold (Rappaport, 1988). Using the more conservative dilution factor of 2, the initial environmental concentration of chlorinated by-products formed from household use entering the environment is expected to be around 5 ppb.

Continued mixing of the wastewater effluent with surface waters will further reduce the chlorinated organic concentration. It is expected that biodegradation will continue and that ultimately 90% of the chlorinated organic by-products will biodegrade (Henkel, 1991). It is further anticipated that other removal mechanisms, such as photolysis, hydrolysis, adsorption, as well as continued dilution, will reduce the chlorinated organic concentration to undetectable and insignificant levels.

## ENVIRONMENTAL EFFECTS

### Sodium Hypochlorite

Sodium hypochlorite is low in toxicity to avian wildlife, but highly toxic to freshwater fish and invertebrates (U.S. EPA, 1991). Thirty-three freshwater species in 28 genera have been exposed to sodium hypochlorite, and the acute LC<sub>50</sub> values for total residual chlorine (sum of the free and combined chlorine) range from 28 µg/L for *Daphnia magna* to 710 µg/L for three spine stickleback (U.S. EPA, 1986a). Necrosis, chlorosis and leaf abscission have been noted when sodium hypochlorite is applied directly to plants (Chase and Osborne, 1984).

### Sodium Hypochlorite By-products

Short-term chronic aquatic toxicity tests with fish and invertebrates were conducted to determine the potential toxicity of chlorinated organic by-products formed in household laundry wash water that were not removed by the activated sludge reactor (Ong *et al.*, 1996). In order to account for the toxicity attributed to laundry, laundry wash water which contained chlorinated by-products from the use of sodium hypochlorite bleach was diluted to 20% and then treated in a simulated activated sludge treatment plant. At the highest concentrations tested, fathead minnows at 400 ppb chlorinated organic compounds (150 ppb background + 250 ppb from laundry) and *Ceriodaphnia dubia* at 194 ppb chlorinated organic compounds (51 ppb background + 143 ppb from laundry), no toxicity attributable to treated laundry wash water was

observed. *Ceriodaphnia dubia* reproduction was also monitored and no adverse effects were noted.

A bioaccumulation study (Ong *et al.*, 1996) was conducted with concentrated laundry wash water which had been biologically treated. In accordance with EPA's effluent bioconcentration protocol, no bioconcentratable compounds were identified at the detection limit of 10 ng/L.

The biodegradation studies conducted with laundry wash water indicate that the chlorinated organic by-products formed from the household use of sodium hypochlorite are effectively treated using conventional wastewater treatment practices, and that any remaining by-products may continue to degrade following release into the environment. Biological testing indicates that the chlorinated organic products that enter the environment from household use of hypochlorite are unlikely to pose a toxicological, reproductive or bioaccumulative hazard to aquatic life.

## RISK ASSESSMENT

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### *Sodium Hypochlorite*

It is anticipated that consumer quantities of sodium hypochlorite accidentally or intentionally applied to surface waters will present an acute hazard to those aquatic organisms in the immediate vicinity and that rapid dilution and degradation will occur. In fresh water, sodium hypochlorite breaks down rapidly into non-toxic compounds when exposed to sunlight (U.S. EPA, 1991). In addition, sodium hypochlorite is a strong oxidizing agent. It reacts very rapidly with oxidizable inorganic compounds and more slowly with organic compounds. Sunlight, pH, temperature, salinity and reactant concentrations will affect the degradation rate of sodium hypochlorite in the environment. Based on wastewater treatment and laboratory studies, the half-life of sodium hypochlorite, in both freshwater and marine environments, can be seconds to hours (Jolley *et al.*, 1981). The high reactivity of sodium hypochlorite precludes it from being environmentally persistent or bioaccumulative.

### *Sodium Hypochlorite By-products*

The short-term chronic toxicity studies conducted with fathead minnow and *Ceriodaphnia dubia* were performed at laundry chlorinated organic concentrations approximately 30 to 50 times higher (143/5 and 250/5) than the predicted environmental concentration, and resulted in no observed toxicity attributable to the laundry chlorinated organic compounds. Based on the premise that the median organic halide concentration observed in U.S. wastewater effluents is approximately 245 ppb and these are conservatively assumed to be diluted two-fold, organic halide concentrations in the receiving waters attributable

to all municipal sources is estimated to be 123 ppb. This level is also less than the concentration of laundry chlorinated organic concentrations shown to have no effect. A greater disparity between exposure and effect concentrations may exist, since the no-observed effect concentration is the highest concentration that could be tested, due to test constraints. Based on these comparisons, the current level of sodium hypochlorite use is acceptable from an environmental standpoint.

## CONCLUSION

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Sodium hypochlorite is an important ingredient for household, institutional and industrial cleaning, bleaching and disinfection. It is effective against a broad array of bacteria, spores, viruses and fungi. It cleans, sanitizes and disinfects hard surfaces as well as towels and clothes; and it performs under hot, cold and hard water conditions.

Sodium hypochlorite itself will not reach the environment except through misuse or spills. The chlorinated by-products formed during use of hypochlorite-containing products have been shown to be biodegradable and effectively treated at activated sludge plants. The small portion of by-products not removed by wastewater treatment does not increase the toxicity of treated wastewater and the by-products are not expected to bioaccumulate. Thus, use of hypochlorite is not likely to adversely impact the environment.

## APPENDIX

To predict the environmental concentration and fate of chlorinated organics attributed to household use of sodium hypochlorite:

- 2,200 metric tons of chlorinated organics formed from household use (includes all hypochlorite species) (Smith, 1993).
- 26.9% U.S. population use a septic system (van der Leeden, Troise and Todd, 1990). The assumption is the remaining population's wastewater will be treated by activated sludge treatment in municipal system.
- $4.56 \times 10^{13}$  L/yr national wastewater treatment flow (van der Leeden *et al.*, 1990) (estimated for 1991 U.S. population).

70% removal efficiency of chlorinated organics by activated sludge treatment (Ong *et al.*, 1996).

### **Concentration entering a wastewater treatment plant:**

$$\frac{2,200 \times 1000 \text{ kg/metric ton} \times 0.731 \times 0.026 \times 10^9 \text{ } \mu\text{g/Kg}}{4.56 \times 10^{13} \text{ L/yr}} = 35 \text{ } \mu\text{g/L}$$

### **Concentration following activated sludge treatment:**

$$35 \text{ } \mu\text{g/L} \times (1 - 0.70) = 10 \text{ } \mu\text{g/L (pbb)}$$

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