

# codex alimentarius commission

FOOD AND AGRICULTURE  
ORGANIZATION  
OF THE UNITED NATIONS

WORLD HEALTH  
ORGANIZATION

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**Agenda Item 13**

**CX/FFP 00/13**

## **JOINT FAO/WHO FOOD STANDARDS PROGRAMME**

### **CODEX COMMITTEE ON FISH AND FISHERY PRODUCTS**

Twenty-fourth Session  
Ålesund, Norway, 5-9 June 2000

#### **DISCUSSION PAPER ON THE USE OF CHLORINATED WATER <sup>1</sup>**

##### **The use of chlorine in fish processing**

##### **1. Summary**

Concerns have been raised regarding the production of hazardous by-products when chlorine is used for disinfection in the fish processing industry. The principal concerns are associated with the uptake of chlorine from wash water by fishery products and the uptake or formation of disinfection byproducts in fish resulting from the use of chlorinated water. Current guidelines of the Codex Alimentarius allow a maximum concentration of 10 mg/l chlorine in water in contact with fish. A survey of regulatory standards or guidelines in several countries showed that no country permitted more than this level and in most, the standard or guideline was lower. Much higher concentrations are used in some other sectors of the food processing industry when compared to the fishery sector. There is only very sparse literature, generally involving laboratory model systems, on the possible formation of hazardous by-products resulting from the use of chlorine disinfection in fish processing. However, there is considerable literature on the formation of hazardous chlorine byproducts when drinking water is chlorinated. Considering the short contact times involved in washing of fish, the risk of contamination from the use of chlorinated potable water supplies, even after further chlorination in the processing plant, is considered to be very low. Chlorine is principally used as an aid to hygienic fish processing rather than as a decontamination treatment. Model system studies on chlorinated water used for washing fish have shown that mutagens are not present at levels up to 20 mg/l free chlorine. The current scientific evidence does not warrant changing the recommended Codex levels of 10 mg/l for water in direct contact with fishery products. In many instances, chlorination of water used in fish processing and maintenance of distribution systems are essential controls for the prevention of contamination by waterborne pathogens and in reducing the incidence of cross contamination.

##### **1. Introduction**

At the meeting of the Codex Fish and Fishery Products Committee (CCFFP), Bergen, Norway, in June 1998 the issue of using chlorine as a disinfectant to reduce the microbial load of raw fishery products such as prawns and shrimps was discussed. Views expressed at the Bergen meeting were that the use of chlorinated water was common practice in the fish processing sector, but that significant differences exist between countries. Concerns were expressed about toxic residues and possible risks to public health that may result from chlorine by-products arising from the use of elevated levels of chlorine in water used for washing fish and fishery products. Concerns were also expressed about gaps in knowledge with respect to current practices at industry level in different countries and there was a broad consensus that additional information was needed. The current Codex recommendations allows up to 10 mg/l chlorine in water that comes in contact with fishery products and up to 100 mg/l in water for cleaning equipment and facilities. In

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view of the fact that the CCFFP is in the process of revising all Codes of Practice for Fish and Fishery Products, do the recommendations for chlorine use need to be revised ?

These issues were previously referred to the Codex Committee on Food Hygiene (CCFH) which concluded that a technical paper should be prepared on residual levels of chlorine in products such as frozen prawns and shrimps when washed with chlorinated water and on recommended levels used in processing. The CCFH requested that such a paper be developed by the CCFFP (ALINORM 97/13A). FAO and WHO agreed to undertake this task.

## **2. Background**

The use of chlorine as a water disinfectant has been one of the most important public health interventions for the prevention of waterborne diseases over the past 100 years. Chlorination is generally regarded as an essential public health measure for ensuring that drinking water is microbiologically safe. As a result of disinfection, waterborne infectious diseases such as typhoid, dysentery and cholera, are largely under control in industrialized countries. The same is not true however, for the poorest countries of the world where inadequate and unsafe water supplies are major causes of morbidity and mortality.

The advantages of chlorine-based disinfectants are that they are cheap, readily available in most countries of the world, effective against most bacterial waterborne pathogens and provide lasting protection of the water supply as residual levels of chlorine can be maintained throughout the distribution system. Some disadvantages have come to light over the past 20 years however, with the discovery of chlorine byproducts which result from the reaction between chlorine and organic or inorganic matter in water and also, the emergence of waterborne pathogens such as *Cryptosporidium* and *Giardia*, which are more resistant to traditional disinfection practices.

The potential of chlorine to react with organic matter in drinking water and form hazardous chlorinated compounds, referred to as disinfection by-products has come under scrutiny in recent years. One of the major determinants of disinfection by-products is the level of organic matter in the source water. Water drawn from surface sources (rivers and lakes) usually has a higher concentration of organic matter than ground water sources (wells and springs). The principal disinfection by-products are the trihalomethanes and trihaloacetic acids but others have been identified (WHO, 1998). Recent reports have identified possible associations between these and different forms of cancer, however, much of the evidence is inconclusive and public health gains from reduced waterborne diseases far outweighs the risks from cancer (WHO, 1998). The cholera epidemic in Latin America that began in 1991, was fostered, at least in part, by the misconception that disinfection by-products pose a greater risk to public health than waterborne pathogens (Otterstetter and Craun, 1997).

There is a possibility of hazardous products being formed by contact of chlorine with foods of animal origin, although this has not been demonstrated for fishery products. Chlorination of amino acids present in solution can give rise to mutagens and studies on chlorinated water used to wash poultry under laboratory conditions have shown mutagenic activity in the wash waters. Conditions for washing of poultry, where super-chlorinated water is circulated, with extended exposure time, are not the same as washing practices in fish processing, and studies on poultry wash waters might not be applicable to the situation in fish processing.

## **3. Forms of chlorine used in fish processing**

The chemistry of aqueous chlorine has been previously reviewed (Fukayama et al 1986; WHO, 1996; WHO, 1998). Hypochlorous acid (HOCl) is the primary bactericidal agent in aqueous chlorine solutions that will kill most microorganisms given a sufficient dose and contact time. Inhibitory or lethal activity depends on the amount of free available chlorine (as HOCl) that comes in contact with microbial cells. The dissociation of HOCl is pH and temperature dependant, for instance at pH 6, HOCl is the predominant species, representing more than 90% of chlorine in solution at 25°C. Chlorine is rapidly consumed and loses its antimicrobial activity on contact with organic matter. This will also occur on exposure to air, light or metals.

Chlorine is used in the fish processing sector as a water disinfectant and is probably the most widespread disinfectant in use. Its uses include washing fishery products, addition to water for making ice for chilling fish, and in water for thawing frozen products. It is also used in water to cool canned fish after retorting to prevent “leaker” spoilage. Chlorine is commercially available in several forms, the most common being a granular or powdered form as calcium hypochlorite or in liquid form as sodium hypochlorite (NaOCl) or bleach (Table 1). In any of these forms it acts as a powerful oxidizing agent and reacts with a wide variety of compounds. Chlorine is a gas under normal pressure and temperature. It can be compressed into a liquid and distributed in cylinders and fed automatically into water supplies of fish processing plants or on-board fishing vessels.

The use of chlorine dioxide is less common in fish processing, probably because of its instability and the hazards involved in handling and transportation. However, it is used and has been shown to be effective in killing a large number of microorganisms, including some that are resistant to treatment with chlorine and to extend the storage time of many foods, including fishery products (Richardson *et al.*, 1998). Some of the reported advantages of chlorine dioxide over aqueous chlorine as a disinfection agent are that it is seven times more potent than aqueous chlorine in killing bacteria, the bactericidal activity of chlorine dioxide is not affected by alkaline conditions and/or the presence of high levels of organic matter (Lin *et al.*, 1996). For these reasons, it is under investigation by many authorities for use in the fish processing sector.

#### 4. Concentrations of chlorine used in fish processing

During the preparation of this review, many countries provided data on the use of chlorine in the fish processing sector at national level. These data are summarized in Table 1. In general, specific national standards or recommendations for residual levels of chlorine in water that comes in contact with fish or fishery products during processing and preparation do not exist. In most instances, the recommendations of the WHO Drinking Water Guidelines are usually followed - residual levels of between 0.2 and 0.5 mg/l in the water distribution system (WHO, 1996). Levels of chlorine in water used for washing equipment and facilities (floors, walls, etc.) vary according to the level of surface contamination. Where high levels of chlorine are used, a final rinse with potable water is the usual industrial practice. It is very unlikely that consumers of fishery products will be exposed to any risk from the use of chlorine in cleaning and washing equipment and facilities provided good manufacturing practices are followed.

The current Codex Recommended International Code of Practice for Shrimps and Prawns (CAC/RCP/17-1978 Codex Alimentarius Volume B, 2nd Edition, FAO/WHO, 1984) and the Codex Recommended International Code of Practice for Fresh Fish CAC/RCP/9-1976 (FAO/WHO, 1983) include the following statements under the sections that cover handling of fish at sea:

*It has been established in the fish processing industry that the injection of chlorine into a supply of cold water used for general wash-up helps to control microbial contamination. The fishing vessels involved in handling or processing large quantities of fish or shrimp might gain considerably in hygiene by having chlorine introduced into water lines. Chlorine dosage should be around 10 ppm during the normal use and 100 ppm of residual concentration during the clean-up.*

Some national authorities have adopted this Codex value and recognize that up to 10 mg/l active chlorine in fish processing water and ice that contacts seafood to be generally recognized as safe (GRAS). The use of chlorine up to this concentration is based on a history of safe use and accepted industry practice over many years. During the preparation of this review no data or evidence was found that suggests that there are public health problems associated with this practice.

Recent studies in the UK have found that chlorination is the only practicable and effective method of providing clean seawater for use in the inshore shrimp industry where shrimp are cooked on board fishing vessels. An on-line hypochlorite injection system is recommended for seawater treatment at a dosage of 20 ppm. This system, together with improved handling and storage of cooked shrimp, has been found to double the chilled storage life while improving both the eating and microbiological quality of products (Watson and Prout, 1996). Concentrations of 20-30 mg/l in running water have been used to reduce the numbers of *Listeria monocytogenes* while thawing frozen salmon (Eklund *et al.*, 1997). The removal of this pathogen

from the surface of fish destined for cold smoking is a major health gain for the industry as the temperature of the cold smoking process are insufficient to kill *L. monocytogenes*. Other work has shown that exposure of gilled and gutted salmon to 200 mg/l free chlorine reduced the aerobic plate counts by up to 99.2% in industrial-scale trials (Bremner and Osborne, 1998). Chlorine at levels of 20-25 mg/l were shown to be effective in killing strains of both *Escherichia coli* and *L. monocytogenes* is a fish model system under laboratory conditions (Lin *et al.*, 1996).

#### 4.1 Concentrations of chlorine used elsewhere in the food industry

In other sectors of the food industry, aqueous chlorine is also widely used as a disinfectant and sanitiser (Wei *et al.*, 1985). The reported concentrations used that come into contact with foods are, in some instances, far higher than those used in the fish processing sector. For disinfection of fruit and vegetables levels of 50-200 mg/l, with contact times of 1-2 minutes, are regularly used (WHO, 1998a). Levels up to 2000 mg/l are approved as the maximum concentration of hypochlorite for commercial washing of fruit and vegetables (Beuchat *et al.*, 1998). Chlorine is also widely used in the flour industry as a bleaching agent to improve its baking quality at levels up to 2500 mg/l.

Intensive poultry processing has relied on chlorinated water to reduce the amount of spoilage and pathogenic bacteria on carcasses for many years. In comparison to the fish processing sector, higher levels of chlorine are used and contact times are longer. Studies have demonstrated the beneficial effects of adding chlorine to poultry chiller water (25-30 mg/l in chill water and 4-9 mg/l residual chlorine in overflow water) as a means of reducing carcass cross-contamination by *Salmonella* (James *et al.*, 1992). In addition, the chlorination of poultry chiller water has been shown to be especially effective in minimizing levels of *Salmonella typhimurium*, *Campylobacter jejunei* and other bacterial pathogens (NRC, 1988). Based on these and other data, a level of 30 mg/l are approved for direct contact with poultry carcasses in the United States.

Since the early 1970's, chilling red meat carcasses with chlorinated water has been widely practised. More recently spray treatments of beef carcasses with chlorinated water have been demonstrated to be effective in reducing both spoilage and pathogenic bacteria (Cutter and Siragusta, 1995). In other studies spray treatments with chlorine dioxide were no more effective than water for reducing the faecal contamination on beef (Cutter and Dorsa, 1995). Authors claim that the observed reductions in microbial load were due to the physical removal of bacteria that occurs during spray treatments rather than any bactericidal action of chlorine dioxide.

### 5. Reactions of aqueous chlorine with fishery products

There is only a very sparse literature on the uptake of chlorine from wash water by fishery products, and there are no published data on the formation of disinfection by-products in fish resulting from the use of chlorinated water. Johnston *et al.*, (1982) studied the uptake of radioactive chlorine, ( $^{36}\text{Cl}$ ), by headed, shell-on, shrimp soaked for 30 minutes in a solution containing 150 mg/l HOCl, equivalent to 87 mg/l free chlorine. They found that 2% of the chlorine was incorporated into the shrimp. Of this, 75% was in the edible portion. Of the chlorine in the edible portion, approximately 22% was in the trichloroacetic acid fraction, 73% in the aqueous fraction following deproteination, and 3% in the lipid fraction. No attempt was made to identify the chlorinated by-products.

Lin *et al.*, (1996) in a study of the bactericidal activity of chlorine and chlorine dioxide soaked 2.5 cm cubes of fish muscle in 40, 100, 200 and 400 mg/l chlorine solutions for 5 minutes. The study showed that the fish cubes contained free chlorine in amounts depending on the initial concentration of the soaking solution, but the authors did not attempt to determine the amounts or natures of any chlorination by-products.

## 5.1 Reactions of chlorine in drinking water

There is a wealth of information in the scientific literature on the formation of disinfection by-products from chlorination of drinking water and on issues relating to chemical and microbial risks to human health (ILSI, 1993; WHO 1998; Carlson and Hardy, 1998). One of the major determinants of disinfection by-products is the level and nature of organic matter in the source water. The major organic materials in surface waters are the complex polysaccharides humic and fulvic acids arising from the degradation of plant materials. Studies of chlorination of water and of model compounds show that chlorination of these compounds produces a variety of mutagenic compounds including halocarbons, such as chloroform.

Public water supplies to fish processing plants could contain these chlorination by-products, and they could also be formed in the plant by further chlorination of the public water supply, or by chlorination of raw waters in the plant. Fishery products would be exposed to these contaminants if present in the process water.

## 5.2 Reaction of chlorine with poultry wash water

Chlorine is used in the disinfection of poultry chiller water and there are some published studies on chlorination by-products present in these waters. Schade *et al.*, (1990) sampled recirculated chilled wash water from a poultry processing, chlorinated the sample to various levels up to 400 mg/l chlorine with a contact time of 17-19 hours at 3-4°C, and examined extracts for mutagenicity using the Ames test. They found that the extracts were mutagenic and the degree of mutagenicity was proportional to the chlorine dose. However, samples chlorinated at 20 mg/l were not different from the control. Tsai *et al.*, (1997) also treated samples of recirculated poultry chilled water at 400 mg/l with a contact time of 4 hours at 21°C and found extracts to be mutagenic in the Ames test. Haddon *et al.*, (1996) chlorinated suspensions of chicken muscle with high concentrations of chlorine - equal weights of chlorine and chicken solids - overnight at room temperature and isolated and identified various mutagens. These data suggest that chlorine at concentrations of 20 mg/l or less will not give rise to mutagenic compounds.

## 5.3 Reaction of chlorine with compounds present in fish

Chlorination of compounds present in surface waters have been shown to induce mutagenicity, but these compounds, mainly complex polysaccharides, are not present in fish. The precursors of the compounds responsible for the mutagenic compounds in poultry chilled wash water were not identified, but could possibly be the non-protein, low molecular weight compounds present in foods of animal origin.

Horth *et al.*, (1987) treated solutions of amino acids, purines and pyrimidines, and nucleosides and nucleotides at 1 mg/l for 24 hours at room temperature. They did not find mutagenicity in the purine and pyrimidines nor in the nucleosides and nucleotides. They found mutagenicity following chlorination of some of the amino acids, principally the sulphur-containing acids, tyrosine, and the heterocyclic ring acids, and they identified some of the chlorination byproducts. Sen *et al.*, (1989) reacted 7 mM tryptophan solution (1482 mg/l) with 7mM chlorine solution (245 mg/l) for 4 hours at 25°C and found the reaction products were mutagenic in the Ames test. Owosu-Yaw *et al.*, (1990) chlorinated 14 mM solutions of tryptophan at even higher ratios of chlorine, 3:1 and 7:1 and identified some of the mutagenic byproducts.

## 6. Risk assessment of the use of chlorine in fish processing

Assessing risks to human health resulting from the consumption of fishery products containing residual levels of chlorine or chlorine by-products will involve hazard identification, hazard characterization, exposure assessment and risk characterization (WHO, 1995). The Committee on Evaluation of the Safety of Fishery Products, Institute of Medicine, Food and Nutrition Board, USA, concluded in their 1991 Seafood Safety Report that “the extent of contamination of seafood with products resulting from the use of chlorine and other halogen compounds does not appear to be assessed, and there are not relevant appraisals of the associated risks in the available literature” (Ahmed, 1991). No published

data exists regarding the formation of disinfection by-products and their uptake by fishery products under commercial processing conditions, and any risk assessment of the use of chlorine in fish processing will have to be based on information from other fields.

Chlorination reaction products will be present in the process water used in fish processing plants if they are present in the public water supplies. These reaction products could also be generated by chlorination of water used in the plants. The mutagenic products are formed in waters, predominately surface waters, containing organic matter; water from boreholes are usually low in organic matter, and the risk of mutagens being present after chlorination is much less. Standards for residual chlorine or chlorine by-products in fish and fishery products have not been developed at national level (Table 1). These compounds are controlled by limiting product exposure during handling and processing. For instance, current UK legislation demands that drinking water does not contain more than 0.1 mg/l of trihalomethanes. The standard set by the United States Environmental Protection Agency (USEPA) for total trihalomethanes in drinking water is 80 µg/l. When water containing such levels comes in contact with products, it is likely that only trace amounts would be taken up by products. Contact times between water and fish are short during typical washing operations, though some operations, such as thawing might involve longer contact times. Even with longer contact times the amount of chlorination by-products taken up will be limited to what can diffuse into the product in that time.

Some of these chlorinated by products, the halocarbons, will be lost when products are cooked. Entz *et al.*, (1982) studied residues of halocarbons in a variety of foods, including composites of meat, fish and poultry. They report on losses of analytes due to preparation and handling of foods and found that cooking removed most of the volatile halocarbons. In a study on ready-to-eat foods, 53% were found to be chloroform positive, including fried breaded shrimp (24 µg/kg), cheddar cheese (80 µg/kg), butter (670 µg/kg) and peanut butter (29 µg/kg) (Heikes, 1987). Levels of 1 to 10 µg/kg chloroform have been detected in flour products, cod liver oil, fish, mussels and milk, and much higher levels in coffee (up to 80 µg/kg) and 90 µg/kg in sausages (WHO, 1994). Mean levels of chloroform in the skin, fat and muscle of chicken carcasses when treated with 5 mg/l chlorine for 20 minutes were 3, 14 and 3 µg/kg respectively (Robinson, Mead and Barnes, 1981). Human exposure to chloroform is principally from food, drinking-water and indoor air in approximately equivalent amounts (WHO, 1994). The total estimated mean intake is approximately 2 µg/kg body weight per day.

Wash water in fish processing will contain high levels of organic matter, especially water used to wash products such as peeled and deveined prawns and shrimps or skinless fish fillets. No published data exists regarding the formation of disinfection by-products and their uptake by fishery products under commercial processing conditions. In addition, little data has been published about the nature of the reactions of chlorine with organic constituents of seafoods and the likely risks to public health associated with chlorine residues. Sections 5.2 and 5.3 above briefly review the mutagenicity of poultry chiller water and of model compounds. The results of these studies might bring some bearing on the issue of use of chlorine in fish processing, but it is questionable to what extent these results can be extrapolated to fish processing.

In the case of the studies on poultry chiller water, the wash waters were chlorinated to very much higher levels of free chlorine than are used in the fish processing industry or appear in regulatory guidelines for the use of chlorine in fish processing. Also contact times, many hours, were much longer than typical contact times in fish processing. The samples for chlorination were taken from recirculated waters with high solids contents or were model preparations with high solids contents. These concentrations would not be reached in fish processing except in unusual circumstances, for example, soaking of shrimp or fillets in still water for many hours.

A wide variety of organic materials in foods are subject to oxidation and chlorination reactions in aqueous chlorine solutions (Wei *et al.*, 1985). In a review of reactions of aqueous chlorine with model food compounds, Fukayama *et al.*, (1986) concluded that the primary reactions of chlorine with carbohydrates generally result in oxidation products, although low levels of volatile halocarbons may be produced. The toxicological significance of chlorine-modified carbohydrates is not known. In view of the high levels of chlorine used for treating flour, considerable work has been done to determine if chlorinated flour is toxic.

All evidence has indicated that chlorination of flour at the levels used commercially does not pose a significant human health risk (Fukayama *et al.*, 1986).

The work of Horth *et al.*, (1987) could be more relevant because they used low concentrations of chlorine with nitrogen-containing compounds that are present in muscle foods. They used a long contact time of 24 hours, and the experimental conditions used a homogeneous solution of reactants. In the case of fish processing, contact times are much shorter than this, and the chlorine could act only with compounds near the surface of the product into which the chlorine would diffuse. Some recent work indicates that extracts of water chlorinated at 200 mg/l (chlorine water used to wash red grouper and salmon fillets) were weakly mutagenic to *Salmonella typhimurium* TA 100 but the mutagenic reaction products were not identified. However, extracts of water chlorinated at 20 mg/l and extracts of the tested fish samples, did not show such mutagenic activity (Cheng-I Wei, personal communication).

Chlorine incorporation into proteins in a variety of foods has been demonstrated but little is known about the toxicity of the chlorinated derivatives (Fukayama *et al.*, 1986). These are generally formed at microgram per kg (ppb) levels and usually require concentration to obtain adequate levels for mutagenicity testing. Extrapolation of these data for meaningful risk assessment on commercial processing conditions for fish and fishery products is not possible.

Johnston *et al.*, (1983) concluded that exposure of shrimp (headed, shell-on) to 87 mg/l chlorine for 30 minutes resulted in the incorporation of 12.2  $\mu$ moles of chlorine per 25 g of edible tissue. In the absence of other data, if it is assumed that all the chlorine was present in the shrimp as chloroform, a “worse case scenario” for the level of chloroform ingested as a result of eating shrimp exposed to these levels may be calculated as follows.

*Exposure Assessment of Chlorinated By-Products (expressed as chloroform) in Shrimps (as the result of treatment of shell-on, headed shrimps with 150 mg/l HOCl for 30 minutes at ambient temperature; Ghanbari et al., 1981).*

Global Shrimp Consumption in grams per person per day (WHO, 1998c)

|                      | Middle East | Far East | Africa | Latin America | Europe |
|----------------------|-------------|----------|--------|---------------|--------|
| Ave                  | 0.3         | 2.3      | 0      | 1.5           | 3.0    |
| 90 <sup>th</sup> per | 0.6         | 4.6      | 0      | 3.6           | 6.0    |

(assume 90<sup>th</sup> percentile = 2 x average)

LADD (Lifetime Average Daily Dose) =  $\frac{W \times C}{BW}$

|    |   |  |
|----|---|--|
| W  | = | Global shrimp consumption (g/person/day) |
| C  | = | concentration of chloroform (mg/kg)      |
| BW | = | 60 kg (JECFA default value)              |

Calculated LADD's ( $\mu$ g/kg bw/day) based on Global Shrimp Consumption

|                  | Middle East | Far East | Africa | Latin America | Europe |
|------------------|-------------|----------|--------|---------------|--------|
| Ave              | 0.1         | 0.8      | 0      | 0.5           | 1.0    |
| 90 <sup>th</sup> | 0.2         | 1.5      | 0      | 1.0           | 2.0    |

Based on these calculations and assumptions, the level of chloroform exposure from ingesting shrimp, which is exposed to chlorine levels of about 10 times higher than the Codex recommended level of 10 mg/l, is extremely low. The USEPA Reference Dose (RfD) for chloroform is 10  $\mu$ g/kg bw/day. The effects of cooking are not taken into these calculations and these would likely lead to very much lower concentrations in the final product.

In 1994, the Food Safety and Inspection Service (FSIS) of the US Department of Agriculture carried out a risk assessment to evaluate the potential human health effects from the presence of chloroform in chicken fat and skin. FSIS allows the use of compounds in concentrations contributing to 30 mg/l available chlorine on poultry carcasses, which is used in immersion chilling where carcasses contact chlorine water for extended periods. The study estimated that the additional lifetime cancer risk in the population from the consumption of chloroform residues in chicken ranged from two in one billion to five in one hundred million for fat, and from two in one billion to four in 100 million for skin. The overall conclusion was that the risk estimates are several orders of magnitude below the level of one in one million additional lifetime cancer risk considered negligible by the USEPA and FDA in their regulation of pesticides and other chemicals. From a risk management perspective, the FSIS concluded that the minimal risk of developing cancer from chloroform in poultry is far outweighed by the reduction in bacterial numbers that could translate into tens of thousands of prevented foodborne disease cases. Mast *et al.*, (1997) concluded that chlorine reaction products in poultry processing are mainly confined to the skin, unless contact is prolonged, and most of the chlorine is likely to be present in the form of organic salts.

## **7. Sensory changes due to the use of chlorine**

Studies in the UK on chlorine taints in shrimp evaluated different chlorine dips and detectable sensory changes (Watson and Prout, 1996). Defrosted raw shrimp were cooked and dipped in water dosed with NaOCl to levels of 500, 100, 50 and 20 ppm chlorine for five minutes. Results showed that shrimp dipped in 500 ppm dosed water were strongly tainted in both odour and taste, whilst those dipped in 100 ppm dosed water displayed only some odour taint and at 50 ppm and below there was no apparent effects. Most individuals are able to taste chlorine or its byproducts in drinking water at concentrations below 5 mg/litre, and some at levels as low as 0.3 mg/litre (WHO, 1996).

## **8. Chlorine and microbiological control**

While chlorine is widely used in the food industry for reducing microbial contamination, a key issue is that it cannot be relied on to effectively kill bacterial pathogens on the surface of fish and fishery products. It is widely recognised that it is used principally as a hygienic processing aid rather than a decontamination treatment. When fishery products such as prawns and shrimp are dipped/washed in chlorinated water, the numbers of bacteria are usually reduced. However, washing with only potable water can reduce bacterial loads by as much as 90%. When chlorinated water is used, it is not clear how much of the ensuing reduction in microbial numbers is due to the physical removal effect of washing or the disinfecting effect of chlorine. There will be a certain amount of protection from chlorine for bacteria attached to the surfaces of fish and fishery products. For instance, the inaccessibility of HOCl to microbial cells in crevices, under shrimp shells or fish scales and pockets in the skin undoubtedly contributes to chlorine's overall lack of effectiveness.

Many examples of beneficial effects resulting from the use of chlorinated water to reduce microbial loads of foods exist in the literature. Chlorine at levels of 100-200 mg/l have been recommended to control *L. monocytogenes* (El-Kest and Marth, 1988), however, experimental results have shown that these levels are ineffective in eliminating this pathogen when it is attached to the exoskeleton of shrimp (McCarthy, 1992).

The very high level of organic matter in water resulting from washing fish and shrimp, particularly peeled or deheaded shrimp and fish fillets, may neutralize chlorine before its lethality can be manifested. McCarthy (1996) demonstrated the reduced effectiveness of chlorine in inactivating *Listeria monocytogenes* attached to latex gloves in the presence of organic nutrients in water that had been used to boil crabs. To build in safety factors, higher disinfection doses and longer contact times may be used in order to overcome the protective effect of particulate organic matter.

The ability of microorganisms to attach to surfaces of fish processing equipment as biofilms and thus become more resistant to antimicrobial agents is well established. When pathogens such as *L. monocytogenes* exists on working surfaces in the form of a biofilm it is more resistant to chlorine (Krysinski *et al.*, 1992; Frank and Koffi, 1990).

## Conclusions

The extent of contamination of seafoods with products resulting from the use of chlorine compounds has not been assessed and there are no relevant appraisals of the associated risks in the literature. Risks can arise either from the contaminating fishery products from chlorine by-products present in process water, or from chlorine reaction products which may be formed when chlorine reacts edible fish tissues.

It is very unlikely that consumers of fishery products will be exposed to any risk from the use of chlorine in cleaning and washing equipment and facilities provided good manufacturing practices are followed (i.e. contact surfaces are thoroughly rinsed after application of chlorine solutions).

Consumer exposure to chlorine by-products from the consumption of fish that has been exposed to water treated with up to 10 mg/l chlorine is likely to be very low. This is based on the worst case risk assessment assumptions on chloroform exposure from poultry treated with 30 mg/l chlorine which indicated minimal, if any, additional cancer risk from this source; and on the exposure assessment calculations based on the results of exposing shrimp to 150 mg/l chlorine for 30 minutes and chlorine uptake. Consumer exposure to chlorine by-products primarily results from chlorinated process water and even if low levels are present in raw fishery products, most of these will be lost on cooking.

The organic material present in the edible tissues of fish and fishery products is subject to oxidation and chlorination reactions when exposed to aqueous chlorine solutions. Limited data is available regarding the toxicity of such chlororganic compounds. Soon to be published experimental results show no mutagenic activity in extracts of fish filets treated with water containing 20 mg/l chlorine.

While additional work in this area is recommended, the current scientific evidence does not warrant changing the recommended Codex levels of 10 mg/l for water in direct contact with fishery products. Chlorination of water used in fish processing and maintenance of distribution systems are critical points in preventing contamination by waterborne pathogens and in reducing the incidence of cross contamination.

More information is needed on the levels and reactivity of chlorine used in the seafood industry, the identity and toxicity of reaction products, and the level of these compounds to which consumers are exposed before coming to a conclusion about the risks of using chlorine in fish processing.

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**Table 1 Recommendations for chlorine used in fish processing**

| <b>COUNTRY</b> | <b>National recommendations regarding concentration of chlorine in water that comes in contact with fish and fish products. (mg/l residual chlorine)</b> | <b>Levels used for cleaning operations of equipment and premises (mg/l)</b> | <b>Type of chlorine compounds used, recommended or permitted</b>              | <b>National standards for chlorine or chlorine by-product residues in fish/fishery products</b> |
|----------------|--|---|---|---|
| Belgium        | As Codex guidelines  | As Codex guidelines   | Chlorine gas, hypochlorite  | None  |
| Canada         | Maximum 7.0  | No limits in cleaning but must be well rinsed after application             | Chlorine gas, sodium hypochlorite, calcium hypochlorite and chlorine dioxide. | None  |
| China          | 0.05 to 0.3  | Not specified   | Sodium hypochlorite   | None  |
| Denmark        | As low as possible.  | Approximately 200   | Hypochlorite for disinfection; Chlorine gas for water                         | None  |
| Finland        | 0.1  | Not specified   | Many different compounds  | Drinking water standards  |
| France         | 0.1  | Potable water standards   | Chlorine, gaseous chlorine and sodium hypochlorite                            | None  |
| Iceland        | 1.0  | Not specified - rinse with potable water required after application         | Not specified   | None  |
| Japan          | 1.0  | Not specified   | Sodium hypochlorite, High-test hypochlorite                                   | None  |
| Lithuania      | 0.3  | Potable water standards   | Sodium hypochlorite, chloramine, Commercial products                          | None  |
| Morocco        | 0.25 to 0.5  | 100 to 200  | Not specified   |   |
| New Zealand    | 0.3  | up to 200; Difficult equipment to clean up to 400; Canning operations 5.0   | Chlorine dioxide; high-test hypochlorite; hypochlorite based compounds.       | None.   |

Table 1 (continued)

| <b>COUNTRY</b>     | <b>National standards regarding concentration of chlorine in water that comes in contact with fish and fish products (mg/l residue chlorine)</b> | <b>Levels used for cleaning operations of equipment and premises (mg/l)</b>   | <b>Type of chlorine compounds used, recommended or permitted</b>                                 | <b>National standards for chlorine or chlorine by-product residues in fish/fishery products?</b> |
|--------------------|--|---|--|--|
| South Africa       | 0.5 or less  | 100-200   | Chlorine gas, sodium hypochlorite, calcium hypochlorite, chlor-bromide gas and chlorine dioxide. | None   |
| Switzerland        | 0.1  | Potable water standards   | Chlorine gas, sodium hypochlorite, chlorine dioxide  | None   |
| Thailand           | 2 – 10   | Gloves dip                    50 -<br>100<br>Utensil                            50 -<br>300<br>Equipment                    300 -<br>500<br>Floors and walls            1000-<br>5000 | Sodium/calcium hypochlorite,<br>chlorine gas   | None   |
| USA                | Up to 10   | Regulated according to chlorine compound in use   | Chlorine gas, Sodium and potassium Hypochlorite, chlorine dioxide                                | None   |
| Codex              | up to 10   | Up to 100   | Not specified  | None   |
| ASEAN <sup>1</sup> | 2 or equivalent level of other permitted agents  |   |  |  |

<sup>1</sup> ASEAN-Canada Fisheries Post-Harvest Technology Project, 1977.

**Table 2. Regional Per Capita Food Consumption.**  
**(Based on GEMS/FOOD DATA, WHO, 1998)**

(in grams per person per day)

| <b>Regional Diets</b>      |                       |                    |                |                       |                 |
|----------------------------|-----------------------|--------------------|----------------|-----------------------|-----------------|
| <b>Commodity</b>           | <b>Middle Eastern</b> | <b>Far Eastern</b> | <b>African</b> | <b>Latin American</b> | <b>European</b> |
| <b>Chicken Meat</b>        | 30.5                  | 11.5               | 5.5            | 25.3                  | 44.0            |
| Pelagic Marine Fish Fresh  | 4.3                   | 5.8                | 12.9           | 7.0                   | 3.8             |
| Crustaceans fresh/frozen   | 0.3                   | 2.3                | 0.0            | 1.5                   | 3.0             |
| Diadromous Fresh           | 1.3                   | 5.3                | 4.7            | 1.3                   | 1.5             |
| Demersal Marine Fish Fresh | 2.0                   | 3.0                | 2.4            | 0.0                   | 9.0             |
| Marine Fish fresh/Frozen*  | 2.8                   | 5.2                | 5.1            | 18.3                  | 2.8             |
| <b>Total Vegetables</b>    | <b>233.0</b>          | <b>178.9</b>       | <b>77.0</b>    | <b>150.4</b>          | <b>371.6</b>    |
| <b>Total Fruits</b>        | <b>204.4</b>          | <b>85.4</b>        | <b>94.7</b>    | <b>271.3</b>          | <b>212.4</b>    |

\*NES = Not Specified Elsewhere