

3. CHEMICAL HAZARDS IN SEAFOOD HANDLING AND PROCESSING

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Introduction:

The potential hazards likely to occur in food items can be categorised into three classes: Biological, Chemical and Physical. A hazard may cause a food to become unsafe for consumption. For the purpose of implementation of HACCP, the conditions or contaminants that can cause illness or injury to people are referred to as hazards. Hazards include pathogenic bacteria, viruses, parasites, harmful chemicals and objects like pieces of metal, glass, stones, sand, mud etc. Chemical contamination can occur at any stage in food production and processing. The mere presence of a chemical may not always represent a hazard. The quantity of the chemical determines whether it is a hazard or not. Regulatory limits are set for some of these contaminants. Chemical hazards can be classified in to three major groups.

1. Naturally occurring chemical

Allergens

Mycotoxins (e.g. Aflatoxin)

Scombrototoxin (Histamine), Putrescine, Cadaverine, Tyramine, Tryptamine etc.

Ciguatera poison

Puffer fish poison

Pyrrrolizidine alkaloids

Shellfish toxins - (PSP, DSP, NSP, ASP, etc.)

2. Unintentionally or incidentally added chemicals

Agricultural chemicals such as: i. Pesticides, ii. Fungicides, iii. Fertilizers, pollutants like toxic elements and compounds, toxic metals and radicals like Lead, Cadmium, Zinc, Mercury, Arsenic, Cyanide and their compounds, all constitute hazards, if they are present in significant quantities.

3. Intentionally added chemicals and Food Additives

They are purposefully added to food at some point during the growth of the food material, preparation or processing. They can be either food preservatives, food additives, vitamins & minerals, or even contaminants; for example, antibiotics used in aquaculture, sulfites used to control melanosis in shrimp and also as a preservative, nitrites as preservatives, colouring

agents, detergents present in food at high levels.

Some of these chemicals can cause allergic reactions in sensitive persons and hence regarded as hazards.

1.1 Histamine in Fish (Scombroid Toxin)

Histamine poisoning or scombroid fish poisoning is very frequent in many fish eating countries. High levels of histamine in the fish muscle is the reason for poisoning and is usually associated with Scombroid fishes and other dark meat fishes. Over 50 species, including popular species such as tunas, bonitos, mackerels, blue fish, dolphin (*Mahi mahi*), carangids, herring, sardine and anchovies have been shown to be potential threats of histamine poisoning. These fishes have high contents of free histidine which during spoilage are converted to histamine by bacteria. Histamine production increases with temperature and 37°C is the optimum for microbial activity. The main histamine producing bacteria are *Morganella morganii*, *Klebsiella pneumoniae* and *Hafnia alvei*. Low temperature storage right from catch reduces histamine production.

Histamine is very resistant to heat and so, even if the fish is cooked, canned or heat treated otherwise, histamine is not destroyed. The human body will tolerate a certain amount of histamine without any reaction. The presence of other biogenic amines such as cadaverine and putrescine will act as potentiators for histamine toxicity.

Symptoms of Histamine poisoning:

The most common symptoms are facial flushing, urticaria, oedema and gastrointestinal problems such as nausea, vomiting and diarrhoea. Neurological symptoms like, headache, tingling, burning sensation in the mouth etc., are also common.

Toxin	Animals/organ involved
Tetrado	Puffer fish, mostly in fish ovaries, liver and intestine
Ciguatera	Coral reef associated fishes
Paralytic shellfish poison (PSP)	Bivalves, Filter feeding shellfish mostly digestive glands & gonads
Diarrhetic Shellfish Poison (DSP)	Bivalves, Filter feeding shellfish mostly digestive glands & gonads

Control of formation of biogenic amines

Low temperature storage or holding fish at 0°C at all times is the most effective preventive measure. All studies seem to agree that storage at 0°C or very near to it, limits histamine formation in fish. Frequent increase in product temperature during storage can result in more histamine production. Sensory analysis is an effective screening method to avoid histamine containing fish. Standards vary from country to country but range from 10 to 50mg per 100g.

1.2 Biotoxins in seafoods:

Marine biotoxins are responsible for a number of seafood borne diseases. Two main types of poisoning by marine animals are recognised. Fish poisoning is caused by consuming fish containing poisonous tissues and shellfish poisoning results from ingestion of shellfish that have accumulated toxins from the plankton they have consumed. Biotoxins are severe hazards in seafoods. The important biotoxins are given below.

a) Tetrodotoxin (Puffer fish poison)

This is the most widely known and studied type of fish poisoning. Tetrodotoxin is probably the most lethal of all fish poisons. The toxin is not produced by algae. Apparently, it is produced by quite commonly occurring symbiotic bacteria. The toxin is mainly found in the liver, ovaries and intestine in various species of puffer fish, octopus and two Japanese shellfishes. Puffer fish is a delicacy in Japan. The muscle of the fish is normally free of toxin.

Symptoms of Poisoning

Puffer fish poisoning causes neurological symptoms that develop 10-45 minutes after ingestion. Symptoms are tingling sensation in face and extremities, paralysis, respiratory problems and cardiovascular collapse.

b) Ciguatera

Ciguatera poisoning is the most common form of fish poisoning. Ciguatera poisoning is caused by ingestion of fish that have become toxic by feeding on toxic dinoflagellates (marine algae). This form of toxicity is associated with the food chain of the fish. The toxic agent apparently originates in blue green algae and is then passed directly to herbivorous fish and indirectly to carnivorous species. The principal source is the benthic species *Gambierdiscus toxicus* which lives around coral reefs. Distinct zones of toxicity are well known to local fishermen. More than 400 tropical and subtropical food fishes are involved in this. Fish species such as red snapper (*Lutjanus bohar*), grouper (*Variola louti*) and moray eel have been recorded as ciguateric. Among the organs, liver is the most toxic followed by viscera and muscle.

Symptoms and characteristics of Ciguatoxin poisoning

Symptoms include nausea and neurological deficits similar to PSP but more severe and enduring. Mouse bio-assay and gas chromatographic methods are adopted for estimation of the toxin.

c) Paralytic Shelf fish Poisoning (PSP)

PSP has been associated with dinoflagellate blooms (>106cells/litre) which may cause a reddish or yellow discolouration of the water. Mussels, clams, oysters, scallops etc. which feed on toxic dinoflagellates retain the toxin for a long time and become toxic. Some clear the toxin very quickly and are toxic during the actual bloom. The toxin is found in their syphon. A greater number of human deaths occurs from the consumption of contaminated **shellfish**. The dinoflagellates identified are *Alexandrium catenella* and *Gonyaulax tamarensis*. The toxin is known as saxitoxin and is stable to heat and not destroyed by cooking. It is highly toxic and 1g of the toxic shellfish meat can kill 5 people. Estimated lethal dose for humans is 1 to 4mg. Symptoms of poisoning include tingling & burning sensations and numbness of lips and finger tips, drowsiness etc. The toxin depresses respiratory and cardiovascular regulatory centres and death usually occurs from respiratory failure. Information on the occurrence of these toxins in tropical waters is scarce. After a number of mouse bioassay tests, the US-FDA has set up a limit of 80 µg of poison per 100 g shellfish meat as marketable for human consumption.

A mouse unit (MU) was defined as the minimum amount of poison that would kill a 20 gram mouse in 15 minutes when 1 ml of an extract of shellfish was injected intraperitoneally. Higher amounts than the minimum can kill in a shorter time.

d) Diarrhetic Shellfish Poisoning (DSP)

The DSP toxins are normally accumulated by shellfish from the dinoflagellate, *Dinophysis fortii*. The most widely distributed toxin is okadaic acid and its derivatives. The primary symptom is acute diarrhoea. Thousands of cases of DSP have been reported from Europe, Japan and Chile.

Monitoring of Biotoxins

Mouse bioassay and HPLC are the important methods of monitoring biotoxins. Reliable sampling plans are required for effective monitoring.

Toxin	Tolerance	Method of Analysis
Ciguatera	Control not possible	No reliable method
PSP	80ug/100g	Mouse bio-assay /HPLC
DSP	0-60ug/100g	Mouse bio-assay/HPLC

Control of biotoxins

The control of marine biotoxin is difficult; they are all non-protein in nature and extremely stable. Cooking, smoking, drying and salting do not destroy the toxin. The major preventive measure is inspection and sampling from fishing areas and shellfish beds and analysis for toxin (using mouse bioassay). The phytoplankton blooms in the water will give some warning. Environment is monitored for plankton and toxin. Removal of toxin through the depuration process has some potential. Organo-metallic compounds like methyl mercury, demethylmercury, organo-arsenicals and other similar organic compounds also are of concern.

2.1 Toxic metals

Toxic metals such as cadmium, mercury, arsenic, selenium, lead etc. above the normal level impair the quality, safety and marketability of seafoods. Organo metallics like methyl mercury, demethylmercury, organo-arsenicals and organo-tin compounds are also of concern. Many fish importing countries have stringent standards for some of these metals and other toxic contaminants. Increasing amounts of chemicals may be found in predatory species as a result of bio-magnification or they may be there as a result of bio-accumulation when these pollutants are accumulated over the life span. In this case, an older species will have a higher level of contaminant than younger fish of the same species. High levels of mercury in tuna and sword fish had caused worries both among the importing and producing countries for some time. The regulatory and health authorities of many countries have introduced permissible limits in seafoods. The presence of higher levels of cadmium in the economically important class, cephalopods, caused concern during the last decade and has caused several instances of detention and rejection in the European market. Cephalopods, universally, are predators themselves, feeding on a wide range of other marine animals particularly of bio-accumulating types. Other bivalve molluscs are also found to contain higher levels of some of the toxic metals. Monitoring of metals can be performed by Atomic Absorption Spectrophotometer.

Control: Increased environmental monitoring should be introduced. Depuration of molluscs will remove some of the contaminants.

2.2 Organochlorine pesticides and PCBs:

Organochlorine pesticides and polychlorinated biphenyls now occur in all organisms in all environments. The compounds of concern are DDT and its derivatives [DDE (Dichloro diphenyl dichloro ethane), DDD or TDE], aldrin, dieldrin, benzene hexachloride (BHC - isomer is known as gamaxane) and PCBs. These compounds pose special problems in environmental toxicology in that they are extremely persistent and are lipophilic in nature. Filter feeders such as oysters, mussels and clams are good integrators of these chemicals. Their presence in farmed shrimp is also very significant. Oysters concentrate these pesticides even at a concentration of 0.01µg/L in the environmental water. Concentration factor for DDT group of chemicals was found to be 15000. The discovery in 1966 of PCB in fish attracted attention amongst the scientific community. Subsequent research revealed that they are, in fact, widespread environmental contaminants representing a potential hazard to human health. The organo-phosphorous pesticides include malathion, parathion, diazinon, dimethoate, quinolphos etc. Carbamate pesticides include carbaryl, carbofuran, aldicarb etc.

Control: Reduce chemical and biological contamination of the aquatic environment. Increased environmental monitoring should be initiated.

3.1 Antibiotics used in Aquaculture

Antibiotics are used in aquaculture as prophylactics, as growth promoters and in the treatment of diseases. Prophylactic use of antibiotics is the process of administration of antibiotics in the advance of disease occurrence and this is a common practice in shrimp hatcheries in Asia to reduce the incidence of diseases. A recent review (2001) reports wide spread prophylactic use of antibiotics in both shrimp hatcheries and in shrimp ponds in Southeast Asia. Antibiotics are usually administered in aquatic feeds and most commercial shrimp feeds contain antibiotics.

Some of the commonly used antibiotics in aquaculture

Group	Compounds	Field of application
Sulphonamides	Sulphamerazine sulphaimidine	Broad-spectrum bacteriostatic agents with activity against furunculosis in salmonids sulphadimethoxine (trout and salmon)
Potentiated sulphonamide	Combination of trimethoprim and sulphadiazine	Used for treating salmon and trout. (furunculosis, vibriosis and enteric red mouth)
Tetracyclines	Chlortetracycline Oxytetracycline-1:2:3:4	Widely used in Aqua culture. Effective against several fish pathogens and is relatively cheap. Used in salmon, trout, turbot & shrimp farming. In Canada, these antibiotics are approved for treatment against "red tail" in lobsters.
Penicillines (Beta lactams)	Ampicillin Amoxycillin-2:4 Benzyl penicillin-3	Used to treat furunculosis in salmon & rainbow trout fry syndrome.
Quinolones	Ciprofloxacin Enrofloxacin Norfloxacin Oxolinic acid Perfloxacin Flumiquinone Sarafloxacin	EU MRL is 150µg/kg of fish muscle.
Nitrofurans	Furazolidone	Broad spectrum antimicrobial agent used in shrimp farms in Asia.
Macrolides	Erythromycin* Spiramycin	*Use permitted in Japan
Other antibiotics	Chloramphenicol Florafenicol-1:3:4 Thiamphenicol-4 Nalidixic acid Milozacin	Residues in foods may cause aplastic anaemia in man. Use banned in E.U. Used to treat RTFS and furunculosis in salmon.

The MRL accepted by some of the countries are given in Annexure I.

3.2. Food Additives and Allergens

Allergens are not present in all foods. They are some ingredients which cause the food sensitivity.

Allergens are proteins derived from allergenic foods. They may find access to a food

material as a result of cross contamination during handling and processing. Cross contamination means the inadvertent introduction of an allergen in to a product that would not intentionally contain an allergen as an ingredient.

Eight major food groups – milk, eggs, fish/crustacean/fresh shellfish, tree nuts, peanuts, wheat and soybeans account for 90% of food allergens.

Cleaning and sanitizing chemicals are used widely in food production, particularly in dairy industry. These products should be used in accordance with the manufacturer’s instruction and recommendations. These chemicals must be used with care and at proper concentrations for effective application and sanitizers for their no rinse properties.

Food additives, including colouring materials are used in many fish and fishery products. Before using a food additive the processor should become familiar with the applicable level of the additive and the allergic type reactions that may occur if not properly used.

The council Directive No.95/2/EC on Food Additives says that only additives which satisfy the requirements laid down by the scientific committee for food may be used in food stuffs. The Directive has listed various food additives.

Food Stuff	Additive	Max-level
<p>CITRATES</p> <p>Unprocessed fish crustaceans, molluscs including such products</p>	<p>E 331. Sodium citrates E 332. Potassium citrate E 333. Calcium citrate</p>	
<p>SORBATES & BENZOATES (Sa + Ba)</p> <p>Semi preserved fish products including fish roe products Salted, dried fish Shrimps, cooked Crangon cragon</p>	<p>Sorbates & Benzoates</p>	<p>2000 mg/kg</p> <p>200</p> <p>2000</p> <p>6000</p>
<p>SULPHITES</p> <p>Crustaceans and cephalopods- Fresh frozen and deep frozen crustaceans, penaeidae family -upto 80 units between 50 and 120 units -over 120 units -cooked</p>	<p>Sulphiting agents</p>	<p>150 SO₂ mg/kg</p> <p>150 mg/kg</p> <p>200 mg/kg</p> <p>300 mg/kg</p> <p>50 mg/kg</p>

<u>SODIUM & POT. NITRATE</u>		
Pickled herring and sprat	Nitrates	200 mg/kg
<u>POLYPHOSPHATE</u>		
Surimi	Polyphosphates	1 g/kg
Fish and crustacean paste		5g/kg
Filletts of unprocessed fish, frozen, deep frozen		5g/kg
Frozen and deep frozen crustacean products		5g/kg
<u>CALCIUM DISODIUM EDTA</u>		
Canned and bottled crustaceans/ molluscs	EDTA Salts	75 mg/kg
Canned and bottled fish		75 mg/kg
Frozen and deep frozen crustaceans		75 mg/kg

CONTROLLING CHEMICAL HAZARDS

- Source Control i.e. specifications of raw materials, ingredients and vendor certification.
- Process Control i.e. formulation control and the proper use and control of food additives.
- Control of incidental contamination with chemicals.

APPENDIX – 1

(a) Maximum Residue Levels of some of the contaminants in Seafood

Heavy metals	Residual limits (ppm)		
	EU	U.S.A	Japan
1. Mercury	0.5	1.0	0.4
2. Cadmium	2.0	3.0	Nil
3. Arsenic	1.0	76.0	Nil
4. Lead	1.0	1.5	Nil
5. Tin	250.0	Nil	Nil
6. Nickel	Nil	80.0	Nil
7. Chromium	Nil	12.0	Nil

(b) Pesticide limits as per Council Directive No.86/363/EEC (Col.No.3)

Pesticides	Residual limits (ppm)		
	EU	U.S.A	Japan
1. BHC	0.2	0.3	Nil
2. Aldrin	0.2	0.3	Nil
3. Dieldrin	0.2	0.3	Nil
4. Endrin	0.05	0.3	Nil
5. DDT	1.0	5.0	5.0

(c) Antibiotics: Maximum Residual Limits in Seafoods

Name of antibiotic	Residual limits (ppb)		
	EU	U.S.A	Japan
Chloramphenicol	Nil	Nil	Nil
Furazolidone	Nil	Nil	Nil
Neomycin	Nil	Nil	Nil
Tetracycline	100	Nil	Nil
Oxytetracycline	100	100	100
Trimethoprim	50	Nil	Nil
Oxolinic acid	300	Nil	Nil
Nalidixic acid	Nil	Nil	Nil
Sulphamethoxazol	Nil	Nil	Nil