Proceedings of 3rd AFSA Conference on Food Safety and Food Security
September 15-17, 2016, India
Asian Food Safety And Food Security Association
ISSN: 2306-2150

SEASONAL VARIATIONS OF FORMALDEHYDE AND RISK ASSESSMENT OF MARKETED FISH CONTAMINATED WITH FORMALDEHYDE: FISH AND FOOD SAFETY ISSUE

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Abstract

The study was undertaken to determine the formaldehyde (FA) content in marketed fish and analyze risk assessment of consumers. Five species of fish (*Stromateus chinensis, Ompok pabda, Labeo rohita, Tenualosa ilisha* and *Amblypharyngodon mola*) from Kawran Bazaar of Dhaka city were analyzed under different conditions: fresh, dipped in plain water, dipped in 5% brine, fried in oil, boiled in water and cooked as curry. Dipping treatments in all cases were done for 1 hour. Boiling water where the fish is cooked and the gravy in the fish curry were also tested for FA. The FA contents, determined by spectrophotometric method, were found to be 9.42±2.68 to 19.23±4.32 mg kg^{-1} in fresh fish (October to March), 13.67±6.59 to 24.53±7.17 mg kg^{-1} in fresh fish (April to September), 5.26±1.41 to 12.67±4.06 mg kg^{-1} in fish dipped in water, 3.76±0.98 to 10.1±2.20 mg kg^{-1} in 5% brine water, 0.87±0.25 to 2.59±0.61 mg kg^{-1} in fried fish, 0.67±0.27 to 2.29±0.18 mg kg^{-1} in cooked fish, 0.57±0.10 to 1.53±0.22 mg kg^{-1} in boiled fish, 0.61±0.14 to 1.66±0.10 mg kg^{-1} in boiled fish water and 0.77±0.14 to 2.47±0.12 mg kg^{-1} in the gravy from fish curry. High priced commercial fishes (*Stromateus chinensis*) contained more FA than low price small fishes (*Labeo rohita*). FA contents in all fishes and conditions were still very low compared to oral reference value (0.2 mg kg^{-1}), as assigned by United States Environmental Protection Agency. The effects of dipping in water and 5% brine, or frying, boiling or cooking showed a significant ($p<0.05$) reduction of FA contents in all the samples. Study indicates that collected fish species obtained from wet market were still found to be safe for human consumption.

Keywords*:* Marketed fish, Formaldehyde, Seasonal variation and Risk assessment

INTRODUCTION

Fishes are one of the major sources of food and protein to human being. About 60% of the total animal protein intake is coming from fish (Department of Fisheries, 2015). In Bangladesh, different food items are reported to be adulterated by unsafe chemicals at different marketing steps from farms to consumers. Recently, there have been complaints from the consumers that many food items including fresh fish, fruits, vegetables and even milk available in the domestic markets are contaminated with formaldehyde; which might have been used intentionally to improve their appearance and extend shelf life (Reza et al., 2009, Yeasmin et al., 2010). Consumable fishes are being contaminated by formaldehyde by some evil traders. The fresh fish are sprayed with or dipped into formaldehyde by the fish traders while transporting through domestic market chain (Nowsad, 2010).

Formaldehyde is a natural component of a variety of foodstuffs (International Agency for Research on Cancer, 1995). Recently, International Agency for Research on Cancer (IARC) has classified formaldehyde as a Group 1 carcinogenic to humans (World Health Organization, 2002; International Agency for Research on Cancer, 2012). Formaldehyde develops postmortem in marine fish and crustaceans, from the enzymatic reduction of trimethylamine oxide to formaldehyde and dimethylamine (Sotelo et al., 1995; Badii & Howell, 2002). The highest concentrations of formaldehyde naturally occurring in foods (i.e., up to 60 mg kg^{-1}) are in some fruits (Tsuchiya et al., 1975) and marine fish (Tsuda et al., 1988). Formaldehyde concentrations in fish show higher extreme values: 220–290 mg kg^{-1}; however, averages are between 2 and 50 mg kg^{-1} (Bianchi et al., 2007; Weng et al., 2009). However, formaldehyde accumulates during the frozen storage of some fish species, including cod, pollack, and haddock (Sotelo et al., 1995).

According to the United State Environmental Protection Agency (EPA), maximum daily oral reference dose (R_fD_0) for formaldehyde is 0.2 mg\kg body weight\day (Wang et al., 2007) and 0.15 mg kg^{-1} body $weight^{-1}$ day^{-1} (Xuang et al., 2009). In 1985, Italian Ministry of Health has proposed formaldehyde values of 60 mg kg^{-1} and 10 mg kg^{-1} for *Gadidae* and crustaceans, respectively (Bianchi et al., 2007). Taking into account that fish and fish products fulfill an important role in human nutrition, the aim of our study was to determine the formaldehyde content of different wet marketed fish and risk assessment of consumers.

2. Materials and Methods

2.1 Quantitative estimation of formaldehyde

2.1.1 Sample size

Five types of commercial fish were selected as target sample. Fish species were analyzed under different circumstances; dipped in water for 1 h, dipped in 5% brine for 1 h, fresh, fried, boiled, cooked, water used in boil and fish gravy.

2.1.2 Determination of formaldehyde

The fish samples were cut into small pieces and 30 g of the sample was homogenized with 60 ml of 6% w/w TCA. The mixture was filtered and the pH of the filtrate was adjusted to 7.0 with 30% w/w KOH and stored in ice for 1 h. The test was performed by mixing 5 ml of the standard solution, TCA, fish extract; 2 ml of Nash's Reagent and then heated in the water bath at 60˚C for 30 min. The absorbance at 415 nm was measured immediately by UV/vis spectrophotometer (Shimadzu, UV-1800). Triplicate of the absorbance was prepared for each sample and recorded for further calculation. The sample reading was placed on the standard curve for the calculation of formaldehyde content of the sample.

2.2 Risk assessment

2.2.1 Exposure analysis

Available national data of average fish consumption (g day^{-1} $person^{-1}$) and primary data of residual formaldehyde concentration in fish (mg kg^{-1}) was used for exposure analysis. In case of body weight based on national data of different age group subpopulation such as children, adolescent and adult, were used for the distribution of body weight. Exposure was calculated as per following equation.

Exposure or Daily Intake Rate (DIR) = Concentration of contaminant (mg kg^{-1}) x Consumption (kg day^{-1}) / Body weight (kg)

2.2.2 Hazardous quotient (HQ)

Hazardous quotient (HQ) for the consumers through the consumption of formaldehyde treated fish was assessed by the ratio of daily intake rate (DIR) to the oral reference dose (R_fD_0) for each fish (US-EPA 2013). If the value of HQ is less than 1, then the exposed population is said to be safe, if HQ is equal to or higher than 1, is considered as not safe for human health, therefore potential health risk occurred, and related interventions and protective measurements should be taken (US-EPA, 2013). An estimate of risk to human health (HQ) through consumption of formaldehyde treated fish was calculated by the following equation:

$$\mathbf{HQ = DIR / R_fD_0}$$

R_fD_0 is an estimate of a daily oral exposure for the human population, which does not cause deleterious effects during a lifetime (US-EPA, 2009).

2.3 Data analysis

Probable risk was assessed based on the available fish consumption and formaldehyde concentration data. Initially available consumption and concentration data was fit into descriptive analyses using Microsoft Office Excel 2007 and XL-stat version 16 for DMRT to understand the differences of the variables. Estimated formaldehyde intake (maximum, minimum, median, mean, and SD) was determined per different scenarios separately.

3. Results and Discussion

3.1 Seasonal variation of formaldehyde

Seasonal variation of formaldehyde content in selected fish species in Kawran bazaar was found significantly difference ($p<0.05$) in table 1. The ideal ice to fish ratio should be at least 2:1 in summer and 1:1 in winter (Clucas and Ward, 1996). This indicates that in summer fish are more susceptible to spoilage than winter. This is because of most of wholesalers, retailers and vendors use formaldehyde in high amount on marketed fish in summer than winter. So, formaldehyde content was low in fish in October to March than April to September.

Table 1: Seasonal variation of formaldehyde in fish

Type of fish	Formaldehyde content (mg kg^{-1})	
	October to March	April to September
Rup Chanda (*Stromateus chinensis*)	19.23(±4.32)^{e}	24.53(±7.17)^{d}
Pabda (*Ompok pabda*)	12.17(±5.11)^{d}	17.39(±4.55)^{a}
Rui (*Labeo rohita*)	10.18(±3.06)^{c}	13.67(±2.91)^{b}
Hilsa (*Tenualosa ilisha*)	9.42(±2.68)^{a}	20.91(±8.19)^{c}
Mola (*Amblypharyngodon mola*)	10.21(±3.71)^{b}	21.17(±6.59)^{e}

*****The values in the same column having similar superscripts do not differ significantly ($p<0.05$)

3.2 Water dipped, 5% brine water dipped and different cooking practiced to decreased the formaldehyde concentration

Formaldehyde concentration gradually decreased by dipping treatment in water and 5% brine (Table 2, 3). In case of 1 h dipping water 49-57% formaldehyde decreased from fish body. On the other hand, dipping 5% brine reduced 59-66% from fish body. It was found that formaldehyde in the fish body was removed within 1 h by washing with tap water or when kept in melting ice and the time were directly proportional to the concentration of formaldehyde used (Yeasmin et al., 2013). Formalin degraded more quickly at high temperature than at low temperature in water. It took 72 hr for formalin to degrade completely at 30 and 35^{0}C. No effect of salinity on formalin degradation was found in water. After 72 hours' formalin was almost completely degraded in water with different salinities at 25^{0}C (XU et al., 1995). On the other hand, in the present study selected fish were dipped for 1 hr in plain water and 5% brine. However, formaldehyde concentration decreased more by dipping 5% brine than dipping in plain water.

Different cooking methods were used to reduce the formaldehyde concentration from fish muscle. The formaldehyde content generally decreased in all of the fish species analyzed after cooking. Formaldehyde content was in the range of 10.40 to 27.80 mg kg^{-1}in fresh fish, 2.15 to 5.75 mg kg^{-1} in fried fish, 1.98 to 5.30 mg kg^{-1} in fish gravy, 1.94 to 5.19 mg kg^{-1} in cooked fish and 1.36 to 3.64 mg kg^{-1} in boiled fish water and 1.25 to 3.33 mg kg^{-1} in boiled fish. The decrease in levels occurred when the samples were cooked in open pots, thus allowing the evaporation of formaldehyde during the cooking process since the formaldehyde is soluble in water at 20^{0}C. In addition, the boiling point for formaldehyde is 101^{0}C, so the evaporation of formaldehyde maybe occurred due to its low volatility (Leslie, 1994). Thus, the present results were in agreement that exposure to formaldehyde would decrease if the fish was cooked (Benchman, 1996). Decrement of formaldehyde concentration was also observed for the shrimps and cuttle-fish by using canning, cooking, boiling and roasting methods (Bianchi et al., 2007).

Table 2: Formaldehyde content in fish dipped in plain water

Type of fish	Formaldehyde content (mg kg^{-1})						
	Fresh fish	Dipped fish	Fried fish	Boiled fish	Boiled fish water	Cooked fish	Fish gravy
Mola	28.46(±11.42)^{e}	12.67(±4.06)^{e}	2.59(±.61)^{e}	1.53(±.22)^{e}	1.66(±.10)^{e}	2.29(±.18)^{e}	2.47(±.12)^{e}
Rup chanda	23.73(±4.47)^{d}	10.43(±5.11)^{d}	2.11(±.37)^{d}	1.27(±.36)^{d}	1.36(±.31)^{d}	1.91(±.41)^{d}	1.98(±.22)^{d}
Hilsa	19.98(±7.81)^{c}	8.96(±1.54)^{c}	1.87(±.13)^{c}	1.08(±.21)^{c}	1.18(±.13)^{c}	1.69(±.11)^{c}	1.73(±.34)^{c}
Rui	11.74(±3.85)^{b}	5.50(±3.22)^{b}	1.14(±.21)^{b}	0.66(±.17)^{b}	0.72(±.26)^{b}	1.03(±.21)^{b}	1.05(±.29)^{b}
Pabda	11.66(±2.93)^{a}	5.26(±1.41)^{a}	1.11(±.16)^{a}	0.64(±.11)^{a}	0.70(±.12)^{a}	0.97(±.16)^{a}	1.01(±.05)^{a}

*****The values in the same column having similar superscripts do not differ significantly ($p<0.05$)

Table 3: Formaldehyde content in fish dipped in 5% brine water

Type of fish	Formaldehyde content (mg kg^{-1})						
	Fresh fish	5% brine dipped fish	Fried fish	Boiled fish	Boiled fish water	Cooked fish	Fish gravy
Mola	32.57(±13.13)^{e}	10.19(±2.20)^{e}	2.36(±.73)^{e}	1.37(±.17)^{e}	1.49(±.39)^{e}	2.12(±.12)^{e}	2.16(±.28)^{e}
Rup chanda	23.54(±11.09)^{d}	8.70(±3.72)^{d}	1.93(±.44)^{d}	1.07(±.62)^{d}	1.21(±.31)^{d}	1.67(±.33)^{d}	1.71(±.39)^{d}
Hilsa	21.31(±9.64)^{c}	8.31(±2.17)^{c}	1.71(±.37)^{c}	0.98(±.11)^{c}	1.09(±.16)^{c}	1.54(±.58)^{c}	1.61(±.04)^{c}
Rui	12.44(±3.18)^{b}	4.84(±1.01)^{b}	1.13(±.71)^{b}	0.61(±.29)^{b}	0.68(±.22)^{b}	0.91(±.63)^{b}	0.93(±.47)^{b}
Pabda	10.37(±4.16)^{a}	3.76(±.98)^{a}	0.87(±.25)^{a}	0.57(±.10)^{a}	0.61(±.14)^{a}	0.67(±.27)^{a}	0.77(±.14)^{a}

*****The values in the same column having similar superscripts do not differ significantly ($p<0.05$)

3.3 Formaldehyde content in marketed fish

Formaldehyde contents in marketed fish in October to March and April to September were found 9.42 to 19.23 mg kg^{-1} and 13.67 to 24.53 mg kg^{-1} respectively (Table 4). Formaldehyde increased from 0.50 to 1.4 mg kg^{-1} during frozen storage of rake-gill mackerel at -20^{0}C; whilst in lizard fish it increased from 16.8 to 42.5 mg kg^{-1} after six months (Tunham et al., 2010). Formaldehyde content in haddock and mullet were 1.47-4.87 mg kg^{-1} and average values in cod was around 100 mg kg^{-1} (Bianchi et al., 2007). Formaldehyde naturally formed from the post-mortem of enzymatic reduction of TMAO to equimolar amounts of formaldehyde and dimethylamine (DMA) (Bianchi et al., 2005). Formaldehyde content was in the range of 0.38 to 15.75 mg kg^{-1} in fresh fish (Noordiana et al., 2011) and 3.95 to 13.40 mg kg^{-1} in fish markets (Hossain et al., 2008).

Table 4: Formaldehyde content in marketed fish

	Formaldehyde content (mg kg^{-1})	
	October to March	April to September
Max.	19.23	24.53
Min.	9.42	13.67
Median	13.68	19.42
Mean	12.54	18.16
Stdev.	3.78	5.88

3.4 Risk assessment from consuming marketed fish

The average daily intake rate in October to March and April to September were used for human health risk assessment (Table 5). The daily intake of formaldehyde from food consumption is dependent on the fish and amount of fish consumed. Assessment of human health risk from ingestion of fish treated with formaldehyde required information on the quantities of fish consumed. National data showed that, on an average, population consumed 58.65 g day^{-1} of fish. Protein sources in the diet were mainly obtained from fish. The risks were computed as an exposure analysis and hazard quotient (HQ) in case of children; adolescent and adult people were found to be less than 0.2 mg kg^{-1} and 1 respectively (Fig. 1). In case of the value of HQ is less than 1; the concentration of formaldehyde in fish is unlikely to cause adverse effects on human when the fish are consumed. In fact, the average daily intake rate (0.2 mg kg^{-1} day^{-1}) is sufficient to guarantee the consumer safety (Xuang et al., 2009). It was assumed that oral exposure to formaldehyde in humans from dietary sources would not exceed 100 mg formaldehyde per day corresponding to 1.7 and 1.4 mg kg^{-1} body weight per day for 60 kg and 70 kg respectively (European Food Safety Authority, 2014). However, the study showed that the consumption of commercial fish could influence the risk of formaldehyde.

Table 5: The daily intake rate and hazard quotient for individual's formaldehyde via dietary intake of marketed fish

Individuals		Exposure rate (mg kg^{-1})		Hazard quotient (HQ)	
		October to March	April to September	October to March	April to September
Max.	Adult	0.0211	0.0305	0.1054	0.1526
	Adolescent	0.0232	0.0335	0.1158	0.1677
	Children	0.1048	0.1517	0.5238	0.7585
Min.	Adult	0.0136	0.0196	0.0678	0.0982
	Adolescent	0.0166	0.0239	0.0829	0.1199
	Children	0.0222	0.0322	0.1110	0.1607
Median	Adult	0.0166	0.0241	0.0831	0.1203
	Adolescent	0.0192	0.0278	0.0961	0.1392
	Children	0.0359	0.0521	0.1798	0.2605
Mean	Adult	0.0168	0.0244	0.0841	0.1219
	Adolescent	0.0196	0.0283	0.0979	0.1417
	Children	0.0436	0.0632	0.2181	0.3158
Stdev.	Adult	0.0023	0.0033	0.0113	0.0164
	Adolescent	0.0021	0.0031	0.0107	0.0155
	Children	0.0214	0.0309	0.1070	0.1549

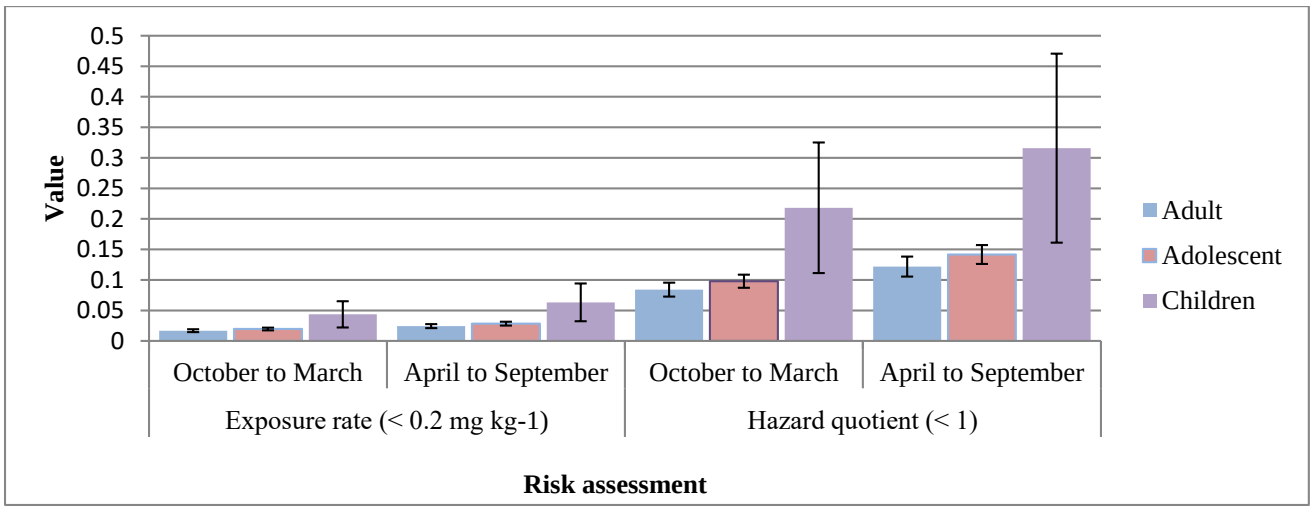

Fig. 1. Exposure rate and hazard quotient of consuming marketed fish

4. CONCLUSION

There were no adverse health effects on human due to the formaldehyde contaminated fish consumption in the whole year based on the risk assessment. Thus, the fish from wet market can be taken for consumption with caution that formaldehyde content might be kept in control. However, all fishes taken from the market should be washed thoroughly by dipping at least 1 h before cooking and cooking must be done under sufficient heat treatment to remove residual formaldehyde in fish.

5. Acknowledgement

Author expresses his sincere acknowledge to Fish Technology Research Section, Institute of Food Science and Technology (IFST), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka for their institutional support.

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