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Seasonal Variation in Composition, Quality and Heavy Metal Safety of Giant Tiger Prawn (*Penaeus monodon*) of the Bay of Bengal along the Bangladesh Coast

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Abstract

This research was conducted to investigate the seasonal variation in composition, quality and heavy metal safety of Giant Tiger Prawn (Penaeus monodon) of the Bay of Bengal along the Cox's Bazar Coast in the southeast part of Bangladesh. The parameters of composition study were protein, lipid, ash, moisture. Parameters for overall quality study were TVB-N and TMA-N, and the heavy metals investigated during this research were Cadmium (Cd), Chromium (Cr), Lead (Pb), Copper (Cu), Zinc (Zn). Seasons selected for this research were autumn, winter, spring, summer and rainy season. Result of the present research shows that the composition, (protein, lipid, ash, moisture), quality (TVB-N and TMA-N) and heavy metal content of Penaeus monodon vary in different seasons. Compositional difference i.e. nutrient content protein, lipid, ash and moisture is significantly different in autumn and rainy season. Protein content in autumn and rainy season was 18.5% and 13.4%, similarly lipid content was 2.15% and 1.72% respectively. The quality in terms of TVB-N and TMA-N of market sample was significantly different in different seasons but all remained within the maximum allowable limit (TVB-N > 30 mg/100g; and TMA-N > 10 mg/100g). But the heavy metal content of Penaeus monodon differed significantly in various seasons. In general, during the rainy season most heavy metals were lowest in concentration, during winter season most of the heavy metals were highest in concentration. Some heavy metals were above the maximum allowable limit in winter and summer.

Keywords: *Penaeus monodon*; Composition; Quality; Heavy metal; Seasonal variation; Bay of Bengal

Introduction

Prawn and shrimp of Bangladesh water is famous for delicious taste and large size. Prawn and shrimp make a great contribution in export earnings as well as for domestic consumption. The contribution of prawn and shrimp in export earning of Bangladesh is praiseworthy. It is nearly 75-85% of Fisheries export earnings. Penaeus monodon is an exportable species. At present Bangladesh export prawn and shrimp to the UK, EU, USA, Japan, Saudi Arabia, UAE and the Gulf States. The proximate composition, quality and safety of prawn and shrimp is influenced by many factors among which seasonal variation is most important. Such aspects are important and need consideration for export and domestic consumption as well as to produce a nutritious and safe product. Composition e.g., protein, lipid, ash, moisture of prawn and shrimp varies in different seasons i.e., autumn, winter, spring, summer, rainy season. Average percentage of these components varies with season. Such variation depends on species, size, maturity and spawning, water temperature, geographical variation etc. Prawn and shrimp quality and safety also vary in different seasons of the year. Because quality deterioration and rate of spoilage in prawn, shrimp and fish is accelerated by ambient temperature, sunlight, time elapsed between catch and consumption, bacteria, muscle enzymes, water pollution etc. Connell [1] stated in all species of fish seasonal changes in certain bodily characteristics occur although less noticeably in shellfish. Seasonal, cyclical changes in composition are observed in many species though less noticeable in some shellfish. In Bangladesh data on seasonal variation in nutritional composition, quality, heavy metal concentration of prawn and shrimp are not sufficient. Some research studies

have been conducted in the Department of Fisheries Technology, Bangladesh Agricultural University, Mymensingh on proximate composition of shrimp but research on seasonal variation of composition, quality and safety of prawn and shrimp is very less in Bangladesh. Enough correct and reliable data on seasonal variation in composition, quality and safety are necessary for quality control, quality assurance and safety measures, also for new product development (value added product). Such information is important for consumers' health and nutrition, taste, dietary satisfaction and safety. The broad objective of this research was to study the seasonal variation in composition, quality and safety aspect of Giant Tiger Prawn *(Penaeus monodon)* of Bangladesh in different seasons of the year. Specific objective of this research was to estimate the composition e.g. protein, lipid, ash and moisture of Penaeus monodon in autumn, winter, summer, rainy season to check the level of TVB-N and TMA-N of Penaeus monodon in autumn, winter, summer and in rainy season; and monitoring the level of heavy metals e.g. cadmium (Cd), chromium (Cr), lead (Pb), copper (Cu), zinc (Zn) in the muscle of Penaeus monodon in autumn, winter, summer, rainy season. Such research is important to select the best prawn as food to find nutrition, taste, dietary satisfaction. It is also important to know the season in which prawn is of the best quality. Such research is also important to know the safety in terms of heavy metal concentration in different seasons of the year. Seasonal variation in composition, quality, and safety is very important for consumers' nutrition, taste, dietary satisfaction, and safety. Such information is important because consumers have less chance to assess the composition, quality and safety of prawns in the marketplace. Since the aquatic environment is getting polluted day by day considerable attention has been paid to the quality and safety aspect of prawns by the regulatory agencies in developed nations. People of Bangladesh are not much aware of risk related to quality and safety aspect. For a better awareness of people, a thorough investigation is necessary. The reliable data will be helpful to grow people's awareness. At the same time the authority will be able to take necessary action. This is important for local consumers as well as for the export of Giant Tiger Prawn *(Penaeus monodon)* for foreign consumers. Such research is important for product development too. Because safe and better-quality products can only be prepared from safe and best quality raw material. Some research studies [2-4] have conducted in the Department of Fisheries Technology, Bangladesh Agricultural University, Mymensingh, Bangladesh. That research was in a specific season of the year. Season was selected randomly, and prawn species was also selected randomly. But more extensive research was necessary to achieve the objectives stated in this article. Because enough data on seasonal variation in nutrition composition, quality and safety are necessary for planning and effective quality control activities for nutritional benefit, taste, dietary satisfaction of the consumers at home and abroad.

Materials and Method

Sample collection and temporary storage

Giant Tiger Prawn *(Penaeus monodon)* was purchased from a supplier of Cox's Bazar. Prawn samples were packed in a Styrofoam box with sufficient ice (1:1), cover of the box was tightly closed by tap to make the box airtight. Then the samples (chilled) were transported to the laboratory of the Department of Fisheries Technology, Bangladesh Agricultural University, Mymensingh-2202. On arrival at the laboratory a part of the samples was subjected to laboratory analysis and the rest was stored in a deep freeze for subsequent analysis. Giant Tiger Prawn *(Penaeus monodon)* sample was purchased from the same supplier harvested from same zone in autumn, winter, spring, summer and rainy season.

Laboratory analysis

Proximate composition (protein, lipid, ash and moisture) was conducted according to A. O. A. C [5], TVB-N and TMA-N level were checked by chemical test according to A M C [6].

Heavy metal (Cd, Cr, Pb, Cu, Zn) of prawn muscle was estimated by Spectrophotometric analysis. Sample preparation was done according to our previous experiment [7]. Sample digestion was done according to the method of Eboh et. al. [8]. The digested sample was filtered and subjected to analysis by Atomic Absorption Spectrophotometer (HG-AAS, PG-990, PG Instruments, UK) according to Clesceri et. al. [9]. The method is briefly described below:

Sample preparation

In the case of prawn and shrimp the shell, appendage, head are removed. Only the muscle is taken. Approximately 5g homogenized sample is taken in a crucible and dried at 105°C for 24 hours in an electric oven. This dried sample is used for heavy metal analysis.

Sample digestion

An accurately weighed 0.5–1.0 g oven dried sample is taken in a Micro Kjeldahl flask. A volume of 10 ml Nitric acid is added to the flask. Then 5 ml per-chloric acid is added to this flask. The Micro Kjeldahl flask containing sample and acid mixture in placed in an Electro-thermal heater and heated at 30°C - 80°C temperature. Heating starts at 30°C and gradually increased to 80°C. During heating the colour of the liquid in flask (sample + acid) is turned into red colour., which is turned into white colour afterwards. Then the flask with the content is cooled. Then 6 ml 6N HCl is added to the flask. The Kjeldahl flask with its content is placed in the Electro-thermal heater and heated at 30°C - 80°C. Heating temperature gradually rises from 30°C to 80°C. This time the colour of the liquid (sample + acid) in the flask is first

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yellow colour which is turned into white colour afterwards. Then the flask with its contents is cooled. The contents of the flask are taken in a 50ml volumetric flask. The volume is made 50 ml with distilled water. This solution is filtered by ash less filter paper (Whatman No.1).

Analysis by Atomic Absorption Spectrophotometer

The digested and diluted sample is then subjected to analysis by Atomic Absorption Spectrophotometer. That means the absorbance of colour of solutions is measured by Atomic Absorption Spectrophotometer at a specific wavelength. The wavelength for such measurement is for As, Cr and Cd is 193.7nm, 127nm and 217nm respectively. The absorbance and corresponding concentration of heavy metal is observed or estimated from a standard graph which is previously prepared by standard compound of heavy metal.

Calculation

The actual concentration of heavy metal is calculated by the following formula:

$$Heavy\ metal\ (ppm) = \frac{ppm\ conc.\ Observed\ \times\ Final\ volume\ of\ sample\ (ml)}{Weight\ of\ sample\ in\ g}$$

Result and Discussion

Seasonal variation in major components of Giant Tiger Prawn *(Penaeus monodon)* is shown in table 1. The components studied in this research were protein, lipid, ash and moisture. Seasonal variation in the most important nutritional component, i.e., protein shows a distinct pattern. Protein percentage was 18.2% in autumn, 17.71% in winter, 16.85% in summer and only 13.40% in the rainy season. The lipid percentage of this species also shows a distinct pattern of seasonal variation. Lipid was 6% in autumn, 5.1% in winter, 0.62% in summer and 1.72% in the rainy season. Ash (total minerals) content also showed slight variation indifferent seasons. Ash percentage was 2.10% in autumn, 1.67% in winter, 1.19% in summer and 1.73% in the rainy season. A similar pattern in seasonal variation in moisture content (%) of *Penaeus monodon* was observed. Moisture content was 74.93% in autumn, 77.92% in winter, 82.65% in summer and 77.65% in the rainy season. Such compositional difference in various seasons i.e., seasonal variation was detected in freshwater fishes as well as in marine fishes of Bangladesh which we have reported in our previous publications [10-12].

Seasonal variation in chemical composition of fish has been studied by many researchers around the world. Most of the researchers and authors stated that the factors affecting chemical composition of fish are numerous, being either of an intrinsic nature bearing upon genetics, morphology, physiology or environmental relating to the living conditions particularly feeding. Among the factors the difference between species, individual variation, anatomical difference, physiological difference, sex difference, and the most important one is seasonal change affect the chemical composition of fish and shellfish including prawn and shrimp. The significance of seasonal variation is complex, and it is almost impossible to distinguish surely between the effects of the many factors which play a part. The principal ones are the stage of sexual development and feeding conditions. Appreciable variations are sometimes encountered. The Atlantic sardine contains 2% lipid in the spring and 8.6% in the fall. This species protein content varies between 16% in March and 20.6% in July. Similar variations are found in many pelagic deep-sea fishes that get their nourishment from plankton the abundance and composition of which vary greatly. Mansur (1995) studied the biochemical composition of British coast herring *(Clupea harengus)*, in this species pre-spawning herring contain 17% fat and post-spawning herring contain 9% fat, pre-spawning herring contain 63% moisture and post-spawning herring contain 69% moisture. Investigations on the cultivated carp have brought into evidence the decisive effect of feed composition on its value. By improving dietary conditions, the percentage of edible parts increased from 55 to 67%, the lipid content increased from 0.4 to 4.9% and that of protein from 14.0% to 19.5%. The sexual development stage of development influences the composition of fish and shellfish including prawn and shrimp. During the first two years of life, when the sardine is immature, its fat content remains around 3%, while at the end of the third year, when it spawns, it oscillates between 5 and 15% depending upon the season. In the female of horse mackerel, the protein content falls regularly from 18 to 16% during the sexual cycle. It is not encountered in the male fish of that species. Connell (1980) explained the cause of seasonal variation in body constitutes of fish and shellfish in most understandable way. He stated that in all species of fish, seasonal changes in certain bodily characteristics occur. At certain times ordinary fish appear thinner, flabbier and less likely than at others, the flesh being more watery and softer and containing less protein and fat. Fish in this condition is called in 'poor condition' or 'out of season'; usually such fish have poor appeal and gives lower yield. Poor condition occurs at the period after the fish have spawned. For instance, in the case of many species in temperate or Arctic waters this is the spring. Just before spawning and during it energy reserved in the flesh, and in some species in the liver, is transformed for the development of the gonads (eggs and spawn). During spawning and for some period afterwards most fish do not feed. As a consequence of both effects the flesh after spawning becomes severely depleted of protein, carbohydrate and fat. Similar poor conditions can arise, however, when for some reason the fish are not feeding or are feeding at an abnormally low level. Once fish start feeding again, they normally recover their good condition. Seasonal, cyclical changes in flesh composition are observed in all species of fish though less noticeably in some shellfish. In white fish, fatty pelagic fish, prawn and shrimp, shellfish such changes in flesh composition have influence on sensory quality of fish, prawn and shrimp after cooking. Fish, prawn and shrimp in poor condition is not desirable for the processors or industries because they are not fit for the production of best quality product with excellent appearance, succulence and flavor. In our present research the protein, lipid,

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ash, moisture of *Penaeus monodon* varied significantly in autumn, winter, summer and rainy season. Certainly, the cause of such variation/change in protein, lipid, ash, moisture in *Penaeus monodon* of present research is seasonal variation. It may be related to the availability of natural feed in sea the plankton (both phytoplankton and zooplankton) the concentration of which is changed in different season. The second reason behind such marked variation in protein, lipid, ash, moisture in the flesh of *Penaeus monodon* is the influence of spawning.

Information on major components of chemical composition of aquatic animals, particularly fish and prawn, is important for many reasons. Major components e.g., protein, lipid, ash and moisture are considered bio-factors for the consumers. Protein from seafood, e.g., fish and prawn have many biological functions in human health notably source of energy, antioxidant property, anti-mutagenicity, anti-aging, anti-carcinogenicity. Lipid from seafood also supplies energy in human cells, DHA and EPA are essential human cells, DHA and EPA has anti-stress effect and increase learning capacity and memory capacity in children. Seafood which possesses low quantity ash (total minerals) are recommended for people with heart trouble, therefore minerals present in the edible parts of prawn and fish are of interest [13]. At the same time information and knowledge on the variation in quantity of these major components in various seasons is also important. It is well established fact that prawn and shrimp of Bangladesh water is famous in the international market because of their delicious taste and flavor, large size, good nutritional composition and safety. Information derived from the present research is important for international buyers, consumers as well as for domestic consumers.

The overall quality of chilled Penaeus monodon in different seasons has been stated in table 2. Two universal and widely used parameters TVB-N and TMA-N were studied during the present research. Connell et. al. [14] and Connell [1] stated that TVB-N and TMA-N tests are useful for measuring spoilage in fish and fishery products including prawn and shrimp caused by autolytic enzymes and putrefactive bacteria. These two parameters are applicable to chilled, frozen, dried, salted, canned prawn and fish. Connell [1] also mentioned the normal range of TVB-N and TMA-N in the chilled, frozen, salted, dried fish and prawn. A range of not more than 30mg TVB-N/100 g fish or prawn is specified for chilled fish and prawn. On the other hand, a range of not more than 10mg TMA-N/100 g fish or prawn is specified for chilled fish and prawns. The maximum allowable limit of TVB-N and TMA-N is different among the countries and regulatory agencies. Raw fish to be used for canning, chilled fish and prawn, frozen fish and prawn, dried fish, salted fish, fermented fish, European pickled herring, canned fish all such products has maximum allowable limit of TVB-N and TMA-N. Considering the usefulness of TVB-N and TMA-N to assess the quality of prawn, fish and fishery products these two parameters have been accepted for quality assessment of fish and fishery products under health control and monitoring of production condition in European Union [15]. Considerable attention has been paid to TVB-N and TMA-N of prawns and fish throughout the world and a maximum allowable limit is set. This maximum allowable limit determines the acceptability and safety of prawns, fish, fishery products on the basis of quality [14,16-19]. Results obtained in the present research are stated in table 2. In table 2 the TVB-N and TMA-N content are within the acceptable level even much below the Maximum Allowable Limit in autumn, winter, summer, rainy season. But TVB-N and TMA-N content were different in different seasons. TVB-N content was highest (18.40 mg/100g) in summer season and lowest (2.75 mg/100g) in autumn. It indicates that very little deterioration took place in chilled Penaeus monodon by autolytic enzymes. The reason behind the difference in TVB-N content in different seasons is that the rate of autolytic enzyme activity is different in various seasons depending on ambient temperature. The TMA-N content of the chilled *Penaeus monodon* was highest (3.8 mg/100g) in rainy season and was lowest (1.00 mg/100 g) in winter. TMA-N content was also slightly varied in different seasons. It also indicates that very little spoilage took place by putrefactive bacteria. Both TVB-N and TMA-N content of chilled *Penaeus monodon* were within the normal range i.e. within Maximum Allowable Limit. The Penaeus monodon of the present research was caught from the Bay of Bengal along the Cox's Bazar coast of Bangladesh and immediately chilled with sufficient ice in a Styrofoam box with sufficient ice (1:1), cover of the box was tightly closed by tap to make the box airtight. Then the chilled Penaeus monodon samples were transported to the laboratory of the Department of Fisheries Technology, Bangladesh Agricultural University, Mymensingh-2202 by bus which took nearly 14 hours journey. So, time elapsed between catch and laboratory analysis was minimum and there was no chance of deterioration during transportation. The overall quality of chilled *Penaeus monodon* was in excellent condition during autumn, winter, summer and rainy season.

Heavy metal (metal and elements) concentration in the flesh of *Penaeus monodon* in different seasons have been presented in table 3. Five metal and elements cadmium (Cd), Chromium (Cr), Lead (Pb), Copper (Cu) and Zinc (Zn) were detected and estimated in the flesh of Giant Tiger Prawn *(Penaeus monodon)* caught in autumn, winter, summer and in rainy season. Cd concentration was above maximum allowable limit in winter (4.02 ppm) and summer (1.50 ppm). Cr concentration was above maximum allowable limit in all four seasons i.e., autumn (7.47 ppm), winter 4.02 (ppm), summer (1.3 ppm) and in rainy season (0.33 ppm). Similarly, Pb concentration was also above maximum allowable limit in autumn (4.507 ppm), summer (5.76 ppm), rainy season (4.9 ppm) but in winter season Pb concentration was 0.67 ppm which is within the maximum acceptable level. Cu concentration was above maximum allowable limit in autumn (33.17 ppm), in

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winter (44.80 ppm) but it was below the maximum allowable limit in summer (5.76 ppm) and in rainy season (9.11 ppm). Zn concentration was within the maximum acceptable level in all four seasons i.e., autumn (94.89 ppm), winter (81.72 ppm), summer (90.9 ppm), rainy season (64.98 ppm). The variation in heavy metal concentration in the flesh of *Penaeus monodon* in different seasons may be due to the extent of pollution. Heavy metal present in the source usually contaminates water. Fish, prawn and other aquatic animals are capable of absorbing heavy metal and accumulate in the flesh by a process known as bioaccumulation. Apparently, it may appear that the concentration of heavy metal in sea water is very low. But accumulation of repeated small amounts can exceed the maximum allowable limit in prawn and shrimp. It has been proved that aquatic animals, particularly prawns, shrimp, fish can gradually accumulate heavy metal throughout life. Connell [1] stated that aquatic life, including food fishes, is capable of absorbing and concentrating pollutants. In some isolated instances severe injury to health or death have occurred from eating such contaminated fish. Some harmful substances occur, naturally and inevitably, but in background concentrations so very low as to present no foreseeable hazard to man. On the other hand, man-made pollution of the aquatic (marine and freshwater) environment has in recent years increased considerably both in extent and in respect of the number of substances involved. There is therefore growing concern throughout the world about the impact of pollutants on the quality and safety of the food we get from aquatic sources.

Table 1: Changes in composition of *Penaeus monodon* in different seasons of the year.

Parameter	Autumn	Winter	Spring	Summer	Rainy
Protein (%)	18.2	17.71	15.98	16.85	13.40
Lipid (%)	6.00	5.1	2.23	0.62	1.72
Ash (%)	2.10	1.67	0.64	1.19	1.73
Moisture (%)	74.93	77.92	79.82	82.65	77.65

Table 2: Overall quality of chilled *Penaeus monodon* in terms of TVB-N and TMA-N value.

Parameter (mg/100g)	Autumn	Winter	Spring	Summer	Rainy	MAL (mg/100g)
TVB-N	2.75	8.00	2.73	18.40	17.72	30
TMA-N	2.11	1.00	2.09	3.03	3.8	10

Table 3: Heavy metal concentration in *Penaeus monodon* in different seasons of the year.

Heavy metal (ppm)	Autumn	Winter	Spring	Summer	Rainy	MAL (ppm)
Cd	0.587	4.02	0.1	1.50	0.3	1.0
Cr	7.472	4.69	2.6	1.3	0.33	0.05
Pb	4.507	0.67	0.01	5.76	4.9	2.0
Cu	33.178	44.80	12.50	8.3	9.11	10.00
Zn	84.894	81.72	74.2	90.9	64.98	100.00

Heavy metal pollution in food, particularly aquatic food like prawn and fish is a major concern throughout the world. Aquatic environmental pollution from different sources causes heavy metal contamination in prawn and fish. Potential sources of heavy metal pollution in water are waste dump and dumping stations, industrial effluents, sewerage disposal and lagoon, low-grade feed ingredients in farmed prawn and shrimp etc. Different heavy metals (metal and element) accumulate from water to flesh of prawn and fish by a process called 'bioaccumulation' during the feeding and straining. Continuous accumulation in the flesh of prawn and shrimp once exceeds the maximum allowable limit is injurious to human health. Almost all heavy metals are harmful to human health. Therefore, there is a growing concern throughout the world about the impact of pollutants, particularly heavy metal, on the quality and safety of prawn and fish i.e., the food from aquatic sources. Heavy metal polluted aquatic food particularly prawn and fish if eaten continuously, consumers are affected by different health injury e.g., renal problem, irreversible problem in stomach, retarded growth in children, cancer, breakdown of central nervous system etc. Food regulatory agencies in different countries and health authorities have taken necessary steps e.g., imposed a statutory limit on heavy metal present in prawn and fish. The statutory limit for different heavy metals also varies according to species. Many countries are now taking voluntary or mandatory action to reduce the pollution of aquatic environment with heavy metal.

Apart from the actions stated previously some countries are also taking alternate measures to control heavy metal pollution in aquatic food. Analysis and finding out a safe level of heavy metal in a particular season is one of these alternate measures. Some

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countries are detecting the suspected area of aquatic environment that cause heavy metal pollution in prawn and fish. Spot checks on specific elements on fish, prawn and shrimp caught in suspect areas, for example near effluent discharges or waste dumps. Connell [1] stated that the elements of most concern are cumulative poisons, that is those that cause injury to health through progressive and irreversible accumulation in the body as result of ingestion of repeated small amounts. In some countries importance is given to the weekly consumption of fish, prawn and shellfish and such aquatic food.

In the present research we tried to calculate/estimate the level of heavy metal in Penaeus monodon in different seasons of the year. Among the heavy metals (metals and elements) Cd, Cr, Cu, Zn were lowest in rainy season, but lead was lowest in winter season. Heavy metal concentration in Penaeus monodon was significantly different in different seasons of the year of the Bay of Bengal along the Bangladesh coast. Some heavy metals were above maximum allowable level in the flesh of Penaeus monodon in winter season but within acceptable level in another season.

Conclusion

On the basis of the results of present research we can conclude that the proximate composition, quality and heavy metal concentration of Giant Tiger Prawn *(Penaeus monodon)* of the Bay of Bengal along the Bangladesh coast vary significantly in different seasons.

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