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Occurrence of Heavy Metal in Green Coconut Water and Surface Seawater of the Sea Beach Areas of Bangladesh

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ABSTRACT

Background: Green coconut water is a most popular functional drink in all tropical countries. The presence of toxic heavy metals in surface seawater is a major problem globally, with a large share in developing countries like Bangladesh. The objective of the study was to assess the concentration of heavy metals like Pb, Cr, Ni, Cu, and Cd in green coconut water and surface seawater around sea beach areas of Bangladesh. **Methods:** Green coconut water and surface seawater samples were collected from six sea beach areas and transferred to the laboratory. Then, they were allowed for digestion, and finally, the concentration of heavy metal was assessed by the atomic absorption spectrophotometer (AAS). **Results:** In green coconut water, the concentrations of heavy metal exist bellowing the safe limit with the following order: Pb > Cr > Cu > Ni > Cd. But, Pb, and Cr were prevalent in surface seawater and found to decrease in a sequence of Pb > Cr > Ni > Cd, Cu. Besides, Human health risks associated with the intake of these metals were evaluated in terms of metal pollution index (MPI), daily intake of metals (DIM), health risk index (HRI), and hazard index (HI). However, most of the index values were found to be bellowing the reference value. **Conclusion:** The concentration of green coconut water is almost proportional to surface seawater in sea beach areas. The high prevalence of Pb and Cr in surface seawater is alarming, and this impact is already seen in green coconut water. So, it is necessary to take action on seawater pollution in Bangladesh.

Keywords: Green coconut; Heavy metal; Health risk; AAS; Reference value

1. INTRODUCTION

Green coconut water (Cocos nucifera) is the liquid endosperm that fills the central cavity enclosed by a solid endosperm protected by the hard sell and the husk.(1) Documented health benefits related to the green coconut water include nutritious, wholesome beverage, rehydration fluid, gastroenteritis, anticholera and traditional medicine. It's a rich source of carbohydrates, and electrolytes like- sodium, potassium and magnesium. Because of electrolytic and refreshing properties coconut water is considered as a natural functional drink and a lot of interest in using it to treat and prevent dehydration.(2) Green coconut water also used as a solution for treating diarrhoea and high blood pressure. By offering these benefits, coconut water occupies apex position in our daily life.(3)

Plants uptake and bio transfer these nutrients from the soil, which are beneficial, sometimes hazardous or have no known biological function.[4a] Heavy metals are a major hazard which contaminates the food chain drastically and this is also an unrequested problem in green coconut water. Unfortunately, prolonged consumption of toxic heavy metals leads to the disruption of numerous physiological and biochemical processes in the human body.[5]

Heavy metal contamination in the aquatic environment has attracted global attention owing to its abundance, persistence, and environmental toxicity.[6a,7] The metal pollution of aquatic ecosystems has been increasing due to the effects of urbanization and industrialization.[8,9,10,11] Their concentrations elevated promptly through tanneries, sugar, fertilizer, pharmaceutical waste metal, and chemical industries wastes, which are located in and around the major cities in Bangladesh.[12,13] Some of these are also located on the banks of major rivers and lakes.[14] Due to the direct inflow of contaminated water by the river and channel to the sea and finally, marine water is polluting drastically. Heavy metal discharge into aquatic environments can change both ecosystems and diversity of soil quality because of their accumulative behaviour and toxicity and finally transfer to the food chain.[15,16] All of the sea beach areas are located on the coast of Bay of Bengal where the pollution problem is acute due to the stress caused by domestic and industrial effluents. Heavy metal contamination is one of the immerging issues which drastically transferred from one ecosystem to another. This effect is more evident from the abnormal values of a set of physical and chemical parameters. Moreover, fruits and vegetables which are cultivated around the sea beach areas are contaminating by hazardous contaminants. Green coconut water which is found around the sea beach areas not out of this problem. So far, there is limited, or no, work focused on heavy metals investigation in green coconut water near this coastal area.

Soil-to-plant transfer of heavy metals is the major pathway of human exposure of heavy metal.[17] So, it is necessary to determine the concentration of heavy metals in green coconut water. No systematic study has previously been attempted to investigation heavy metals in green coconut water, which could pose new threats to public health. In this study, heavy metals like- Pb, Cr, Ni, Cd, and Cu in green coconut water found in sea-beach areas were analyzed spectrophotometrically and at the same time surface, seawater of Bay of Bengal around sea beach areas was also analyzed. Finally, heavy metal profiles were compared with green coconut water and surface seawater collected from the same places and the same times, and the impact of contaminated seawater on green coconut water was analyzed.

2. METHODS

2.1 Study area and sample collection

This study was conducted on sea beach areas of Bangladesh, which passes through the Bay of Bengal. At first, six districts like Chattogram, Cox's Bazar, Noakhali, Bhola, Khulna, and Bagerhat were purposefully selected for this study, which covers the majority of the sea beach sites. Then for each district, 06 samples of green coconut water and surface seawater of Bengal cast were collected from individual locations. Both coconut water and seawater samples were filtered (0.45 m filters, cellulose nitrate, Millipore) into prewashed polypropylene tubes using a plastic syringe (BD Plastipak, 50mL). Samples were acidified to 0.30 M with HNO_3 (65% pure, Oxoid) and kept at 40 ℃ in the dark until analysis.

2.2 Sample preparation and digestion

To prepare the samples for analysis, both seawater and green coconut samples were filtrated through Whatman filter paper (0.45 μm pore size). For green coconut water, a 50 mL sample was mixed with 10 mL 65% HNO_3, 4 mL of 30% H_2O_2 and 4 mL HCl solution in a 100 mL round bottle flask and allowed for two hours with mixing for complete digestion. After digestion, the mixture was passed through Whatman no. 41 filter paper and made up to 100 mL volume with deionized water in a round bottle flux. For seawater 50 mL filtrated sample was mixed with 5 mL of 65% HNO_3 and boiled at 130 ℃ on a hot plate until the volume came to about 25-30 mL and light color. The addition of HNO_3 and boiling were repeated till the solution becomes light-colored or clear. The final volume was made to the desired level with deionized water passing through the Whatman no. 41 filter paper. Then 12 mL sample was transferred to the falcon tube and used for evaluation by Atomic Absorption Spectrometry (ZEEnit 700P).

2.3 Analytical techniques and accuracy check

All the samples were analyzed for Pb, Cr, Ni, Cd, and Cu by atomic absorption spectrophotometer (Model ZEEnit 700P# 150Z7P0110, AnalytikJena, Germany)

using GF-AAS system. The instrument calibration standards were made by diluting standard (1000 mg/L) supplied by Sigma-Aldrich, Switzerland. The results were expressed as ppm for seawater and green coconut water samples. Prior to use, all glassware and containers were cleaned by 20% nitric acid, finally rinsed with deionized ultrapure water several times, and allowed for drying. The standard deviations of the means observed for the certified materials were between 0.55–7%, and the percentage recovery was between 88 and 99%. The results indicated a good agreement between the certified and observed values.

2.4 Description of summary indices

2.4.1. Metal pollution index

The metal pollution index (MPI) was calculated to determine the overall concentration of heavy metal detected in green coconut water by the following equation. It is an effective tool to assess the green coconut water quality with respect to heavy metals. This is obtained by calculating the geometric mean of the total heavy metal concentration.[18a] The heavy metals used for calculating the MPI were Pb, Cr, Ni, Cd, and Cu.

$$MPI\ (mg/L) = (Cf_1 \times Cf_2 \times Cf_3 \ldots\ldots Cf_n)^{1/n}$$

Where, Cf_n is the concentration of metal in the sample.

2.4.2 Daily intake of metals (DIM)

Accumulation of heavy metal in the human body depends on the daily consumption by a person with specific body weight. The DIM does not account for the possible metabolic excretion of the metal but only considers the possible ingestion rate. The DIM was calculated based on the following equation.[19]

$$DIM = \frac{C_{metal} \times D_{green\ coconut\ water\ intake}}{B_{average\ body\ weight}}$$

Where, C_{metal} = Metal concentration in green coconut water (mg/L), $D_{green\ coconut\ water\ intake}$ = Daily intake of green coconut water (250 mL for an adult), and $B_{average\ body\ weight}$ = Average body weight (70 kg for an adult).

Mean consumption value of 25 mL and 50 mL d-1 of green coconut water was used for children and adult persons in the study. For children and adults, one cup and one glass were considered during DIM calculation.

2.4.3 Health risk index (HRI)

Regular exposure to heavy metal is hazardous for human and animal health with a minimum dose. Health risk caused by a metal or a group of metal is calculated by health risk index (HRI). If HRI is greater than one for any foodstuff that indicates, the population is at a potential health risk. This value depends on the DIM value and oral reference dose (Rf_D). Rf_D is a numerical estimate of the daily oral exposure to humans that is not likely to cause harmful effects during the lifetime, and it also includes the sensitive subgroups such as children.[20] The HRI for heavy metal exposure due to green coconut water consumption was calculated using the following equation. The oral reference doses for Pb, Cr, Ni, Cd, and Cu are 0.0035, 1.5, 0.02, 0.003 and 0.0035 (mg/kg/day) respectively.[21a]

$$HRI = DIM/Rf_D$$

2.4.4 Hazard index

Toxic effects of heavy metal by more than one heavy metal are expressed as the hazard index (HI). It is the sum of hazard quantities derived from green coconut water, according to the following equation.

$$HI = \sum THQ = THQ\ metal\ 1 + THQ\ metal\ 2 + \ldots\ldots\ldots + THQ\ metal\ n.$$

Target hazard quotient (THQ) and total target hazard quotient (TTHQ) can be calculated to establish a hazard index.[22]

Here,

$$THQ = (Efr \times ED \times FIR \times C)/ (Rf_D \times BW \times AT) \times 10^{-3}$$

Where, Efr is the exposure frequency (365 days/year), ED is the exposure duration (70 years), FIR is the drinking rate of green coconut water (mL/person/day), C is the metal concentration in green coconut water (mL/kg), Rf_D is the oral reference dose (mL/kg/day), BW is average body weight and AT is the averaging time for noncarcinogens (365 days/year number of exposure years).

3. RESULTS AND DISCUSSION

If needed, this section can be separate to some sub sections. Please use table in center position, sentences position: left, title position: top. Figures in left position, title position: bottom. (This section must be written with the single line spacing, first line indentation: 1 cm, fonts: Palatino Linotype, size 10, justified).

3.1 Presence of heavy metal in surface water of Bay of Bengal

Heavy metal concentration was prevalent in all surface seawater samples of the sea beach areas (Table 1). The order of metal concentration in the seawater samples was as follows: Pb > Cr > Ni > Cd, Cu, and they exceed maximum permissible limits of marine water quality

standard.[23] The obtained data are comparable with the other available literatures.[24,25] The prevalence of these heavy metals in the water of the Bay of Bengal was higher than the past studies in the Straits of Malacca, Malaysia but lower than seawater of Northwest Spain.[6b,26]

The high concentration of Pb might be due to the high concentration Pb in Kharnaphuli river water (46.09 μg/L) and Buriganga river (58.17 μg/L) that flow directly into the sea and contaminate the seawater of Bay of Bengal.[27] It was also due to point and non-point sources like leaded gasoline, petroleum, municipal runoffs, and atmospheric deposition.[28] The concentration of Pb in these samples was greater than that found in the past studies in the same places, but Ni and Cd levels were the same. Cr naturally exists in soil and rocks of some extend. Besides, anthropogenic activities like tannery waste, waste from the chemical laboratory, and textile waste are the main sources of Cr in seawater. In Bangladesh, chromium solutions are used in tannery industries for leather processing purposes. Liquid wastages from the tanneries are poured into the drain without any type of treatment and then they mixed with seawater of the Bay of Bengal by direct riverine inflow.[29] Ni found in nature as several oxidation states. Among them the divalent state is found to be predominant, while the trivalent state may be formed by redox reactions in the cell.[30] In this research, Ni was higher than the standard level, and that concentration was 0.02 mg/L whereas its world seawater average concentration is 0.0066 mg/L.[31a] Cd naturally exists in seawater from rocks, steel industry, nonferrous alloys, superalloys electroplating industry, Ni-Cd batteries, agricultural fertilizer, industrial activities, and waste treatment plant.[32] The average concentration of Cd in the research area was found to be 0.01 mg/L. Although it is at low level, yet it is contaminated. Chromium present in all samples with considerable levels but it was also higher than the maximum permissible limit.[31b]

Table 1. The concentration of heavy metal in surface seawater of sea beach areas

Districts	Heavy metals (mg/L)				
	Pb	**Cr**	**Ni**	**Cd**	**Cu**
Chattogram	0.55±0.03	0.49±0.04	0.017±0.01	0.014±0.03	0.015±0.07
Cox's Bazar	0.45±0.04	0.44±0.04	0.014±0.01	0.013±0.03	0.015±0.04
Noakhali	0.41±0.01	0.14±0.04	0.016±0.02	0.012±0.03	0.011±0.01
Bhola	0.38±0.06	0.13±0.01	0.016±0.01	0.013±0.08	0.011±0.01
Khulna	0.35±0.02	0.31±0.03	0.015±0.01	0.011±0.01	0.012±0.02
Bagerhat	0.33±0.05	0.32±0.07	0.011±0.01	0.012±0.01	0.013±0.02
Average	0.41±0.05	0.31±0.04	0.02±0.01	0.01±0.03	0.01±0.03
Safe limit[a]	0.05	0.05	0.1	0.005	0.0009

Results are shown as mean ± SD; Where sample size n = 06; Safe limit[a]: Marine water quality standards by EQR (Malaysian Environmental Quality Report).[23]

3.2 Prevalence of heavy metal in green coconut water

Toxic heavy metal concentrations in green coconut water collected from sea beach areas of six districts are listed in Table 2. The average concentrations of studied metals in green coconut water were followed the decreasing order of Pb>Cr>Cu>Ni>Cd. Though coconut water has no heavy metal standards and no previous studies and guidelines on the permissible levels, but considering with drinking water, all metals exist in green coconut water were bellowing the safe limits.[33a,21b] But the concentrations of Pb and Cr exist around the borderline comparing with drinking water. The considerably higher concentrations of Pb and Cr might be due to the heavy metal contaminated soil and water in sample collection areas because the plant absorbs a number of elements from soil.[4b] Pb and Cr levels in the water, soil, and sediments of the Bay of Bengal generally exceed the criteria of international marine water quality .[34]

In contrast to the uniformity, high level of Pb was found in samples obtained from Chattogram, which is similar with a maximum permissible limit of drinking water and this high concentration is might be due to the contaminated soil and seawater in Chattogram sea beach area.[35] Chattogram is a port city, and also a coastal city of the country and its pollution problem is acute due to the stress caused by domestic and industrial effluents, gas production plants, shipbreaking yard, port activities, and untreated urban from metropolitan.[36a] The average level of Cr was higher in all coastal regions and it is due to a higher concentration of Cr in soil (1to 3000 mg/kg)

and seawater (5 to 3000 mg/L) in Bangladesh. It is also due to the disposal of tannery waste without any treatment to the Buriganga river. The tanning industries of Hazaribagh are processing 220 metric tons of hiding a day with an associated release of 600 - 1000 kg of solid waste for each ton of processed hide.[37] These wastes are directly mixed with seawater by direct inflow. Mean Ni, Cd, and Cu concentrations in green coconut water samples were lower than the safe limit which, is represented in Table 2.[33b]

Table 2. The concentration of heavy metal in green coconut water

Districts	Heavy metals (mg/L)				
	Pb	Cr	Ni	Cd	Cu
Chattogram	0.013± 0.004	0.014± 0.009	0.0014 ± 0.0001	0.0019±0.0001	0.0051±0.0004
Cox's Bazar	0.006± 0.001	0.013± 0.008	0.0074 ± 0.0001	0.0017±0.0001	0.0062±0.0004
Noakhali	0.009± 0.001	0.004± 0.003	0.0056 ± 0.0004	0.0011±0.0002	0.0087±0.0001
Bhola	0.006± 0.001	0.004± 0.001	0.0009 ± 0.0007	0.0011±0.0002	0.0043±0.0001
Khulna	0.006± 0.005	0.004± 0.009	0.0012 ± 0.0009	0.0014±0.0007	0.0022±0.0003
Bagerhat	0.005± 0.002	0.005± 0.002	0.0023 ± 0.0008	0.0016±0.0001	0.0023±0.0001
Average	0.008±0.002	0.007±0.005	0.003±0.0005	0.0015±0.0002	0.0048±0.0002
Safe limit[b]	0.01	0.05	0.07	0.003	2
Safe limit[c]	0.02	0.1	-	0.005	1.3

Results are shown as mean ± SD;Where sample size n = 06.Safe limit[b]: Maximum level of heavy metals in drinking water by WHO (WorldHealth Organization), FourthEdition[33]; Safe limit[c]: Maximum level of heavy metal in drinking water by US EPA (United States Environmental Protection Agency), 2012 Edition.[21]

3.3 Summary indexes

3.3.1 Metal pollution index (MPI)

MPI is a reliable and precise method of metal pollution monitoring in the environment and in food safety and a higher MPI value indicates greater aggregation of metal accumulation in the sample.[36a,18b] Here heavy metal accumulation in green coconut water is proportional to seawater (Figure 1). This index suggests that metal pollution in green coconut water is below the risk level and all selected locations have almost uniform metal pollution index.

3.3.2 Daily intake of meal (DIM)

The DIM value was calculated for an adult on the basis of age and consumed volume (Table 3). Average daily intake of green coconut as drinks was also considered. The DIM value was somewhat higher for Pb and Cr and Ni but lower Cd and Cu.

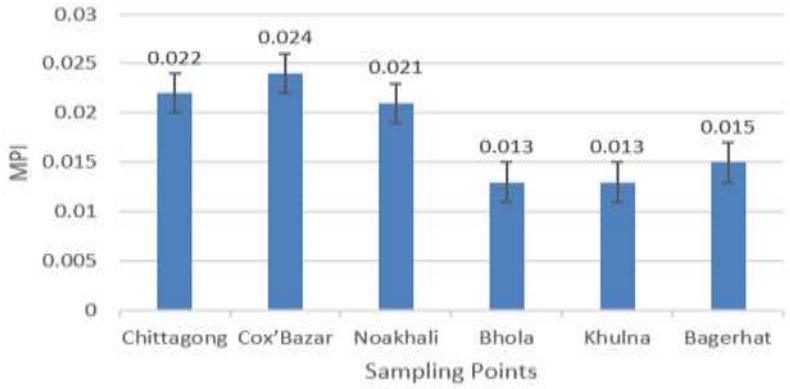

Figure 1. Metal pollution index (MPI) of green coconut water

3.3.3 Health risk index (HRI)

HRI was highest for Pb and lowest for Cr (Table 4). The health risk associated with Pb and Cu due to consumption alone was calculated to be < 1 for all six regions and exceeded the safe limit. But the index of other metals was bellowed the safe limit. High levels of Cu exposure are associated with a wide array of systemic effects, including cardiovascular, hematological, neurological, endocrine, and reproductive toxicity.[38,39]

3.3.4 Hazard index (HI)

The noncarcinogenic effects of multiple heavy metals are express by HI value. HI is presented in Table 3. HI <1 for each district. Highest HI (0.172) was observed in Chattogram, and the lower value was observed for Khulna and Bagerhat for adults. So excessive drinking of green coconut water is not safe for health.

Table 3. Daily intake of heavy metals (DIM) in mg/L Kg-1 body weight from green coconut water consumption

Metals	Chattogram	Cox's Bazar	Noakhali	Bhola	Khulna	Bagerhat
Pb	0.05	0.05	0.05	0.02	0.02	0.02
Cr	0.05	0.05	0.002	0.002	0.002	0.002
Ni	0.05	0.03	0.02	0.003	0.004	0.008
Cd	0.002	0.006	0.004	0.004	0.005	0.006
Cu	0.02	0.02	0.03	0.02	0.009	0.008
HI[a]	0.172	0.156	0.106	0.05	0.04	0.04

HI[a] is the hazard index for adult

Table 4. Health risk index (HRI) of green coconut water sample

Metals	Chattogram	Cox's Bazar	Noakhali	Bhola	Khulna	Bagerhat	Average
Pb	3.71	1.71	2.57	1.71	1.71	1.43	1.86
Cr	0.009	0.009	0.003	0.003	0.004	0.003	0.005
Ni	0.07	0.37	0.28	0.045	0.06	0.12	0.16
Cd	0.63	0.57	0.37	0.37	0.47	0.53	0.49
Cu	1.46	1.77	2.49	1.23	0.63	0.66	1.37

4. CONCLUSION

Green coconut water is a popular drink in Bangladesh and around the world. Heavy metal pollution is also a burning issue because of its accumulation effects in all foods. However, the maximum amount of heavy metals in green coconut water is not established by national and international organizations. Safety limits of heavy metals in green coconut water need to be placed with exigency. In the present study, concentration of lead and chromium was higher than the maximum tolerable limit, and it is due to the contaminated water and soil in coastal areas. So, this study suggested that point sources of heavy metal should be closely monitored, industrial effluent and domestic sewage discharge in seawater should be reduced.

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Conflict of Interest

The authors declare no conflict of interest.

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