Mineral and Heavy Metal Contents of Some Vegetable Available In Local Market of Dhaka City in Bangladesh

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Abstract: Vegetables are an excellent source of most of nutrients and essential source of vitamins and minerals that play a vital role in ameliorating food deficit and overcoming nutritional problem. The present study was carried out to assess minerals and heavy metals content of some non-conventional wild vegetables, commonly edible vegetables from fresh water cultivated unknown sources and waste water irrigated vegetables available in Dhaka city, Bangladesh. In total of 16 vegetables samples were analyzed by using standard analytical methods of AOAC (2005), atomic absorption spectrophotometer, UV spectrophotometer and flame emission spectrophotometer. Vegetable samples were collected from three sites and analyzed for their minerals and metals concentrations. Results reveal that the essential mineral Ca, Na, K, Mg andessential trace element Fe, Znfound were ranged from 171.01-932.69, 91.26-655.62, 107.50-864.28, 56.49-920.67 and 3.5-74.92, 0.84-29.45mg/100grespectively in three types of vegetables. In case of heavy metals Cu, Crand Ni were foundin all samples ranged from0.284-7.55, 0.034-1.10, 0.25-1.506 and 0.25-1.506 mg/100g respectively.Cd was found in waste water irrigated and fresh water cultivated vegetables ranged from 0.005-0.009 and 0.01-0.015mg/100g respectively. Pb was found in wild vegetables and the range was 0.12-0.96 mg/100g. A significant increase (p<0.05) in Cu, Cr, Ni, Cd and Pb were found when compared to WHO/ FAO permissible value.Hg and Co were absent in all kind of vegetables.

Key words: Heavy metals, Health, Minerals, Waste water, Wild Vegetables.

I. Introduction

Vegetables are part of daily diets in many households forming an important source of vitamins and minerals required for human health. They also act as neutralizing agents for acidic substances formed during digestion (Thomson and Kelly, 1990). Along with other food alternatives, vegetables are considered the cheap source of energy. Vegetables are very rich sources of essential nutrients such as carotene, protein, vitamins, calcium, iron, ascorbic acid and palpable concentration of minerals (Jimoh and Oladiji, 2005). Minerals are inorganic substances, present in all body tissues and fluids and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life (Hays and Swenson, 1985). Minerals may be broadly classified as macro (major) or micro (trace) elements. The macro-minerals include calcium, phosphorus, sodium and chloride, while the micro-elements include iron, copper, cobalt, potassium, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium and sulfur (Eruvbetine, 2003). The macro-minerals are required in amounts greater than 100 mg/dl and the micro-minerals in vegetables may vary depending on the inherent (varieties, maturity, genetics, and age) and environmental (soils, geographical locations, season, water source and use of fertilizers) conditions of plants and animals and on methods of handling and processing (Pennington and Calloway, 1973).

But pollution and contamination of vegetables with heavy metals such as Cadmium (Cd), Mercurry (Hg), Cobalt (Co), Nickel (Ni), lead (Pb) etc are a serious threat because of their toxicity, bioaccumulation and bio magnifications in the food chain (Eisler, 1988).Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in different body parts. Most of the heavy metals are extremely toxic because of their solubility in water. Even low concentrations of heavy metals have damaging effects to man and animals because there is no good mechanism for their elimination from the body. Nowadays heavy metals are ubiquitous because of their excessive use in industrial applications. Wastewater contains substantial amounts of toxic heavy metals, which create problems (Chen et al., 2005).

Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination, but also affect food quality and safety (Muchuweti et al., 2006). Food and water are the main sources of our essential metals; these are also the media through which we are exposed to various toxic metals. Heavy metals are easily accumulated in the edible parts of leafy vegetables, as compared to grain or fruit crops (Mapanda et al., 2005). Vegetables take up heavy metals and accumulate them in their edible and inedible parts in quantities high enough to cause clinical problems both to animals and human beings consuming these metal-rich plants (Alam et al., 2003).Generally, humans are exposed to these metals by ingestion (drinking or eating) or inhalation (breathing). Metals like iron, copper, zinc and manganese are required for metabolic activities in organisms, whereas arsenic, cadmium, chromium, mercury, nickel and lead are cumulative poisons. They have been reported to be exceptionally toxic (Ellen et al., 1990). Lead has been associated with intoxications leading to problems in the kidney and liver, the central nervous system, reproductive organs and anemia (IOCCC, 1996). So, these metals have been included in the regulations for hazardous metals.

A big portion of our population is deprived from the knowledge of including vegetables in the daily meal. Though the vegetables are comparatively cheap form the foods of animal origin and affordable by the much population, the lack of knowledge about its importance in meeting the daily micronutrients requirement is one of the principle reason behind the wide spread prevalence of malnutrition. On the other hand, lack of scientific knowledge and cultivation land, some people using abundant places, waste water, pesticides, fertilizers etc. which are significant source of heavy metals and thus contaminating vegetables grown in that condition.

Now a day, people are searching alternative safe food source. So that, they tend to consume wild vegetables because, wild vegetables grow plenty naturally, need not require land to cultivate and labor. Another is they strongly believe that, wild vegetables have medicinal property and without any confusion they are consuming locally available wild plant as vegetable though nutrient content of many of which are still unknown, and people do not have adequate knowledge either those are beneficial or not, have any toxic effect on body or not.Focusing on malnutrition, food safety aspect, heavy metal contamination, nutrient composition providing and adequate nutritional information it should be a logical task to carry out a study on wild, waste water cultivated and common vegetables because it shows a great importance on broad term.So in the present study, an attempt has been taken to determine the minerals and heavy metal contents of some wild, waste water cultivated and fresh water cultivated vegetables from unknown sources available in Dhaka city.

II. Materials And Methods

2.1 Place of experiment and sample collection: The present study was carried out at Cereal Technology section, Institute of Food Science and Technology (IFST), Bangladesh council of Scientific and Industrial Research (BCSIR), Dhanmondi, Dhaka-1205. Samples were collected from several local markets (market sites; in around 1-15 km from the city center) and from Hazaribagh, Jhowchar, Kamrangirchar of Dhaka city near the Buriganga river. The tannery industries in the Hazaribag area discharge their waste water into the Buriganga River. The locations, namely Hazaribagh, Jhowchar, and Kamrangirchar were selected basing on the anticipated contamination. People of Jhowchar, Kamrangirchar are using waste water of Buriganga River for irrigation passing by metallurgical factory, wastewater treatment area of a leather and textile industrial estate and textile industry.

2.2 Sampling: Sample of fresh raw wild vegetables and fresh water cultivated vegetables were purchased from several local market (1kg of each sample from each market) inside in Dhaka city; waste water irrigated fresh raw vegetables were purchased from Hazaribagh, Jhowchar, Kamrangirchar (5kg of each sample from each area) area of Dhaka city. Then sub-sample (3kg each) were taken at random from the composite sample and were processed for analysis.

2.3 Sample preparation for analysis: The freshly collected raw vegetables are initially washed up with tap water thoroughly until the attached dust particles, soil, unicellular algae etc. were removed. Then they were washed with distilled water and finally with deionized water. The washed materials were dried with blotting paper followed by filter paper at room temperature to remove surface water. These were immediately kept in desiccators to avoid further evaporation of moisture from the materials. After that, uneatable portions of the vegetables were removed and the edible portion was chopped into small pieces. The samples were then oven dried at 55° C and then crushed using a stainless steel blender and passed through a 2 mm sieve. The resulting fine powder was kept in air tight packet at room temperature before analysis.

2.4 Determination of mineral and heavy metal content: It is usually necessary to destroy the organic matter in plant substances (raw powdered sample) before total constituent of inorganic material in it could be determined. The methods to bring about the destruction of organic matter fall into two main groups, which may be described as "Wet Oxidation" and "Dry Ashing". In this study wet oxidation method is used for sample

preparation. Approximately 0.5 gm. plant materials (raw powdered sample) were taken in a 50 ml Pyrex beaker and added 10 ml of conc. nitric acid (65%) and digested the sample on a hot plate in low temperature ($55-70^{\circ}c$) for about 30 minutes. Cooled the sample at room temperature and 5ml perchloric acid (70 to 72%) was added and again digested until the contents become colorless. Cooled and diluted the sample with deionized water and filtered (if necessary) to a 100ml volumetric flask and made the volume up to the mark. Diluted and filtered sample prepared by digestion was used for the estimation of Ca, Mg, Cu, Zn, Ni, Cr, Co, Cd, Pb, and Hg by Atomic Absorption Spectrophotometer (Model: Shiamdzu-AA7000) directly following calibration method and estimation procedure of the equipment. Further dilution was done where necessary. Measurement of sodium (Na), potassium (K) were done by Flame Emission Spectrophotometer (Model: JENWAY, PFP7) and iron (Fe) by UV Spectrophotometer (Analytikjena, SPECORD 205).

2.5 Data analysis: An elaborate and constructive analysis was made to each of the table that represents information about selected eighteen vegetables. Possible cross table analysis between different variables have also been done by MS Word, MS Excel and SPSS16 program.

III. Results & Discussion

"Table 1" shows the edible vegetable plants and their part used for cooking.

Table 1: Vegetables used in experiment								
Code	Origin of Plants	Local Name	Botanical Name	Family	Parts used for cooking (Parts analyzed)			
DF		Dhekishak	Dryopteris filix-mas	Polypodiaceae	Stems and leaves			
EF	es	Helencha	Enhydra fluctuans	Compositeae	Leaves, young plant parts			
PO	Jur	Gimashak	Portulaca oleracea	Portulacaceae	Leaves and tender stems			
NSF	1 so	Shapla	Nymphaea stellata	Nymphaceae	flower			
NSS	Vild	Shapla	Nymphaea stellata	Nymphaceae	Stems			
BC	٨	Sarisa shak	Brassica campestris	Cruciferae	Leaves and tender stems			
AGW		Lalshak	Amaranthus gangeticus	Amaranthaceae	Leaves and tender stems			
SOW	d	Palonggshak	Spinacia oleracea	Chenopodiaceae	Leaves and tender stems			
LSW	wa	Laushak	Lagenaria siceraria	Cucurbitaceae	Leaves and tender stems			
BOW	nig	Phulkopi	Brassica oleracea var botrytis	Cruciferae	Flower heads			
RSW	vas ir	Mula	Raphanus sativus	Cruciferae	Taproot			
RSLW	٨	Mulashak	Raphanus sativus	Cruciferae	Leaves, young plant parts			
AGC	-73	Lalshak	Amaranthus gangeticus	Amaranthaceae	Leaves and tender stems			
SOC	lly ateo	Palonggshak	Spinacia oleracea	Chenopodiaceae	Leaves and tender stems			
BOC	liva	Phulkopi	Brassica oleracea var botrytis	Cruciferae	Flower heads			
RSC	Natı Culı	Mula	Raphanus sativus	Cruciferae	Taproot			

In this study, biochemical analysis of the edible part of six wild vegetable, six waste water irrigated vegetable and four fresh water cultivated vegetables were done. Biochemical analysis includes major mineral (Calcium, Sodium, Potassium, Magnesium), essential trace mineral (Iron, Zinc) and non-essential trace mineral (toxic or heavy metals- Copper, Chromium Nickel, Lead, Mercury, Cadmium, Cobalt) specifically. The analysis shows variant concentration/ proportions of biochemical and other contents. The concentration levels of mineral found in 16 vegetables are summarized in "Table 2".

 Table 2: Mineral contents in vegetables (mg/100g dry wt)

Samples	Ca	Na	K	Mg	Fe	Zn	
DF	274.25	91.26	107.50	153.30	14.17	2.22	
EF	932.69	131.82	126.48	56.49	21.15	4.14	
PO	678.21	527.28	119.10	920.67	26.90	15.55	
NSF	507.00	152.10	442.68	366.25	4.23	8.96	
NSS	382.54	648.96	864.28	143.62	3.50	3.52	
BC	255.84	608.40	716.72	195.83	27.40	0.84	
AGW	354.77	309.11	637.64	634.35	43.85	13.28	
SOW	171.01	655.62	459.44	600.95	60.62	24.38	
LSW	436.52	111.89	182.48	544.24	58.84	11.23	
BOW	730.38	429.11	171.48	240.95	31.52	18.37	
RSW	716.88	361.38	174.26	379.82	23.87	16.89	
RSLW	417.25	431.36	163.68	455.10	61.40	16.86	
AGC	356.93	634.19	184.25	323.99	65.38	15.51	
SOC	229.17	485.57	157.52	631.02	74.92	29.45	
BOC	687.32	165.73	142.63	360.91	31.83	12.28	
RSC	860.36	109.50	149.44	321.37	19.85	11.76	

3.1 Major and trace minerals

3.1.1 Calcium

Calcium content of vegetables is difficult to compare with other country because the amount of calcium always depends on the nature of soil. Calcium is rich in alkaline soil and poor in acidic soil. The result exposed that Calcium was present in variable concentration and found highest 932.69 mg/100g in wild vegetable Enhydra fluctuans and lowest 171.01mg/100g in waste water irrigated Spinacia oleracea. Fresh water cultivated Raphanus sativus (860.36) and waste water irrigated vegetable Brassica oleracea var botrytis (730.38) also contained higher amount of calcium. Ca is important because of its role in bones, teeth, muscles system and heart functions (Brody, 1994).

3.1.2 Sodium and Potassium

Sodium content in waste water irrigated Spinacia oleracea was higher and lowest amount was found in Dryopteris filix-mas. Other vegetable also contained considerable amount. Wild vegetables Nymphaea stellata steam contained highest 864.28mg/100g potassium and lowest amount was found in Dryopteris filix-mas about 107.50 mg/100g. The amount of potassium in waste water irrigated was found higher than two other sources. Concentration of potassium varies in vegetables collected from different sources. An increased level of potassium in blood causes the reduced renal function and abnormal breakdown of protein and severs infection and gastrointestinal damage. Na plays an important role in the transport of metabolites. The ration of K/Na in any food is an important factor in prevention of hypertension arteriosclerosis, with K depresses and Na enhances blood pressure (Saupi et al., 2009).

3.1.3 Magnesium

Magnesium was found highest (920.67) in wild vegetable Portulaca oleracea and lowest 56.49 mg/100g in wild vegetable Enhydra fluctuans. In humans, Mg is required in the plasma and extra cellular fluid, where it helps in maintaining osmotic equilibrium. It is required in many enzyme –catalysed reactions, especially those in which nucleotide participate where the reactive species is the magnesium salt, e.g., Mg ATP²⁻. Lack of Mg is associated with abnormal irritability of muscle and convulsions and excess Mg with depression of the central nervous system (Somnath et al., 2012). Magnesium are essential for making good of worn out cells, building of red blood cells and maintaining body mechanisms (WHO, 1996). Absence of calcium, magnesium in diet might result in weak, stunted growth and poor bone development (Effiong and Udo, 2010).

3.1.4 Iron

Iron content was ranged between 3-75 mg/100gm. The highest amount was found in fresh water irrigated Spinacia oleracea about 74.92 and lowest in Nymphaea stellata Stem. The amount of iron was found in wild vegetables is lower than two other sources comparatively. Iron is an essential trace element for hemoglobin formation, normal functioning of the central nervous system and in the oxidation of carbohydrates, proteins and fats (Odhav et al., 2007). Fe is necessary for the formation of haemoglobin and also plays an important role in oxygen and electron transfer in human body (Kaya and Incekara, 2000) and normal functioning of the central nervous system and fats (Adeyeye and Otokiti, 1999).

3.1.5 Zinc

The amount of zinc was ranged between 0.8-29.5. The maximum amount of zinc was detected in fresh water irrigated Spinacia oleracea about 29.45 and minimum in wild vegetable Brassica campestris. One of the most important metals for normal growth and development in human beings is Zinc. Its deficiency may be due to inadequate dietary intake, impaired absorption, excessive excretion or inherited defects in zinc metabolism. According to FAO's food balance data, it has been calculated that about 20% of the world's population could be at risk of zinc deficiency.Zn is an essential metal for the normal functioning of various enzyme systems. Its deficiency, particularly in children, can lead to loss of appetite, growth retardation, weakness, and even stagnation of sexual growth (Saracoglu et al., 2009).

3.2 Heavy Metals (Toxic Metal): Heavy metals are of great significance in Eco chemistry and ecotoxicology because of their toxicity at low levels and tendency to accumulate in human organs. For bioaccumulation of heavy metals in different vegetables various mechanisms like binding metal with organic acids, proteins or other ligands can be speculated. The concentration of heavy metals found in analyzed samples are shown in "Table 3"

Table 3: Heavy metal contents in vegetables (mg/100g dry wt)								
Samples	Cr	Cu	Ni	Pb	Hg	Cd	Co	
DF	0.60^{*}	3.38*	0.42^{*}	0.089^{*}	ND	ND	ND	
EF	0.79^{*}	1.38^{*}	0.33^{*}	0.096^{*}	ND	ND	ND	
PO	0.88^{*}	1.48^{*}	0.46^{*}	0.086^{*}	ND	ND	ND	

Mineral and I	Heavy Metal	Contents of Some	Vegetable	Available In .	Local Market of	^c Dhaka City
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NSF	1.10^{*}	1.15*	0.26*	0.012^{*}	ND	ND	ND
NSS	0.54^{*}	1.81^{*}	0.25^{*}	0.065^{*}	ND	ND	ND
BC	0.99^{*}	1.12^{*}	0.52^{*}	ND	ND	ND	ND
AGW	0.43^{*}	1.013^{*}	0.837^{*}	ND	ND	0.041^{*}	ND
SOW	0.258^{*}	3.016*	1.219^{*}	ND	ND	0.105^{*}	ND
LSW	0.117	1.107^{*}	1.506^{*}	ND	ND	0.063*	ND
BOW	0.088	0.597^{*}	1.404^{*}	ND	ND	0.01	ND
RSW	0.034	0.284^{*}	0.846^{*}	ND	ND	0.013	ND
RSLW	0.167	7.034*	1.26^{*}	ND	ND	0.044^{*}	ND
AGC	0.336	4.085^{*}	0.854^{*}	ND	ND	0.005^{*}	ND
SOC	0.599^{*}	7.55^{*}	0.973^{*}	ND	ND	0.009^{*}	ND
BOC	0.316	2.67^{*}	0.558^{*}	ND	ND	0.007^{*}	ND
RSC	ND	2.90^{*}	0.711^{*}	ND	ND	0.005^{*}	ND

ND- Not Detectable, *(p<0.05)

3.2.1 Chromium: Results of the present study shows that, among the three groups of vegetables minimum quantity of chromium was found in Fresh water cultivated vegetable Raphanus sativus (0.038 mg/100g) and maximum in Nymphaea stellata flower (1.102 mg/100gm) indicated a significance increase (p<0.05) compared to WHO/ FAO permissible value. Cr concentration was in the order of Fresh water cultivated vegetables > Waste water irrigated vegetables > Wild vegetables in all sample. This meant that the source of irrigation in market-bought samples was probably wastewater because of the scarcity of fresh water. The waste water generally led to changes in the physicochemical characteristics of soil and consequently heavy metal uptake by vegetables.Chronic exposure to Cr may result in liver, kidney and lung damage (Zayed and Terry, 2003).

3.2.2 Copper: In this study, the amount of Cu in all the tested samples varied between 0.2 and 7.6 mg/100g; with waste water irrigated Raphanus sativus contained the lowest; 0.248 mg/100gm and Fresh water cultivated Spinacia oleracea contained the highest; 7.55 mg/100g. A trend was observed Cu, i.e., maximum accumulation in Fresh water cultivated vegetables and minimum in waste water irrigated samples. But all sample indicated a significance increase (p<0.05) compared to WHO/ FAO permissible value. The differences of the metal contents in these vegetables depend on the physical and chemical nature of the soil and absorption capacity of each metal by the plant, which is altered by various factors like environmental and human interference, and the nature of the plant (Zurera et al., 1989).

3.2.3 Nickel: The nickel levels in the samples varied between 0.25 and 1.5 mg/100g with the lowest observed in Nymphaea stellata stem and highest observed in waste water irrigated Lagenaria siceraria with range contents of 0.254 and 1.506 mg/100g respectively. However, results obtained from this study indicates that significantly excess quantity of nickel is present in all vegetables; compared to the permissible level of nickel 0.1 mg/100g in vegetables recommended by WHO and FAO (FAO/WHO, 2001).

3.2.4 Cadmium: Cadmium is a non-essential element in foods and natural waters and it accumulates principally in the kidneys and liver (Divrikli et al., 2003). The dietary limit in food and food stuff for cadmium is 0.02 mg/100gm. High concentration of cadmium causes severe diseases such as tubular growth, kidney damage, cancer, diarrhea and incurable vomiting. Results of the study shows that among the three groups of vegetables maximum amount of cadmium was found in waste water irrigated Spinacia oleracea (0.105 mg/100g). The range of cadmium was higher in waste water irrigated leafy vegetables compared to the permissible level of cadmium 0.02 mg/100g in vegetables recommended by WHO and FAO (FAO/WHO, 2001).

3.2.5 Lead: Lead being a serious cumulative body poison enters into the body system through air, water and food and cannot be removed by washing fruits and vegetables (Divrikli et al., 2003). The concentration of lead if exceeding the maximum permissible limits 0.03 mg/100gm (FAO/WHO, 2001) in human, affect nervous system, bones, liver, pancreases, teeth and gum & causes blood diseases. Results of the study showed that among the three groups of vegetables maximum quantity of lead was found in wild vegetable Enhydra fluctuans about 0.096 mg/100gm and minimum in Nymphaea stellata flower about 0.012 mg/100gm. Among the three groups of vegetables only wild vegetable contained lead and in other two groups no lead has found in detectable level.Farooq M. has reported lowest levels of Cu, Cd, Cr, and Pb (0.823, 0.073, 0.546 and 1.893) in the leaves of spinach, cabbage, cauliflower, radish (Farooq M, Anwar F and Rashid U, 2008). Pb causes both acute and chronic poisoning, and poses adverse effects on kidney, liver, vascular and immune system (Heyes, 1997).

3.2.6 Mercury and Cobalt: Mercury is more toxic than Cd and Pb. The concentration of mercury exceeding the maximum permissible limit $(0.03 - 1 \ \mu g)$ in food and food stuff cause serious health problems such as loss of vision, hearing and mental retardation and finally death occurs. In this study no mercury and cobalt has found in detectable level in any groups of vegetable.

IV. Conclusion

Vegetables play a significant role in human nutrition. Levels of essential minerals, trace elements and heavy metals of some wild, waste water irrigated and commonly edible vegetables available in Dhaka city were studied. The findings of the present study concluded that from the analysis in various constituents it showed that vegetable is a good source of minerals and trace elements. Wild vegetable contained appreciable amount of minerals that could be included in diets to support our daily allowance needed by the body because of low cost and wide availability. Common edible vegetable available in local market contained heavy metals that might be incorporated via contaminated soil, irrigated waste water or others. Heavy metals found in all kinds of vegetables that were above the WHO/FAO recommended safe permissible level. Awareness of people and regular monitoring of levels of these metals in vegetables is essential to prevent the incorporation in the food chain. Consumers are purchasing these heavy metals contaminated vegetables, which is a great concern of our health risk. So, it is strongly recommended to avoid the consumption of these vegetables. Finally, it is recommended that emergency initiatives should be taken by the government and its related organizations or authority to develop specific awareness on heavy metals contain of vegetables.

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