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Impact of Gypsum and Potash Fertilizers on Heavy Metals and Nutrients Levels in Some Selected Leafy Vegetables and Assessment of Potential Health Risk

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Abstract

Field experiment was conducted in absence and presence of potash and gypsum fertilizers, to compare and investigate the quantity levels of heavy metals and nutrients in leafy vegetables with growth stage and plant species variations, respectively. Seeds of *Spinacia oleracia* (Spinach), *Colocasia esculenta* (Taro), *Ipoma aquatica* (Water spinach), *Cucurbita maxima* (Pumpkin leaves), *Basella alba* (Indian spinach), *Amaranthus gangeticus* (Red amaranth), *Coccinia grandis* (Ivy gourd), *Corchorus olitorius* (Jute leaves), *Basella rubra* (Malabar Spinach), *Coriandum sativum* (Coriander leaves), *Amaranthus lividus* (Amaranth) were sown in the experimental filed in Joypurhat district of Bangladesh. The quantity of heavy metals [cadmium (Cd), lead (Pb), nickel (Ni), and zinc (Zn)] and nutrients [sodium (Na), potassium (K) and calcium (Ca)] in vegetables were determined by atomic absorption spectrometer and flame photometer, after the microwave digestion of these vegetables with 70% concentrated HNO_3. The quantities of heavy metals were increased with the age of the plant, but the increases were not linear. Moreover, the order of heavy metals level in different vegetables was Zn >Ni >Cd >Pb. The Hazard Quotient (HQ) for Zn, Ni, Cd and Pb were as 0.143, 0.085, 0.1029 and 0.806, respectively. The sequence of HQ for the heavy metals followed the decreasing order Pb >Zn >Cd >Ni. The HQ value for all the heavy metals, Zn, Cd Ni and Pb were less than 1, which is considered safe or indicates no adverse effect on human health.

Key words: Fertilizer, leaf extracts, heavy metals, nutrients.

Introduction

Bangladesh has made significant progress in vegetable production and its export. More than 60 types of vegetables of indigenous and exotic origin are grown in the country. Based on the growing season, vegetables are categorized as summer/rainy season vegetables, winter season vegetables and all-season vegetables. Currently about 162 thousand farmers are involved with vegetable production in the country. Many university-graduates have now joined this profession, some of whom have already made significant contributions in the production of pesticides-free vegetables. According to FAO, vegetable production has increased five times in the past 40 years. Bangladesh has scored 3rd in global vegetable production. Literate youths are coming up with this venture. They are achieving their target with the use of improved technology and their talents. Vegetable and fruits are now exported to about 50 countries of the world (Web-1). As per the Export Promotion Bureau (EPB), every year vegetables worth more than Tk. 6.50 million (650 crore 41 lakh and 20 thousands) are exported. Most of the vegetables are from Narsingdi, Kishoreganj, Jashore, Bogura, Rajshahi, Magura, Moulovibazar, Dinajpur, Cox's bazar, Sylhet and Gazipur. The exported

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vegetables includes yard-long bean, cowpea, cucumber, snake gourd, bitter gourd, tomatoes, papaya, eggplant, pumpkin, lady's finger, pumpkin, amaranth, spinach, Indian spinach, cauliflower, cabbage, green chili, taro, coco yam, green papaya, plantain, jute leaves, pumpkin leaves, arum leaves, water lily, mustard green, bean seed, jackfruit seed, aroid, etc. Although vegetable production has increased remarkably but it is much lower than that of our requirement. As per the nutritionists, one should take at least 220-225 g of vegetable per day. But we get only 80-90 g i.e. less than half of the requirement. Moreover, the level of nutrient in cultivated vegetables also depends on cultivated area (non-polluted area, industrial area, mining area, arsenic contaminated area), even causal fertilizer also.

In Joypurhat district of Bangladesh, field experiment was conducted in absence and presence of potash and gypsum fertilizers, to compare and investigate the levels of heavy metals and nutrients in leafy vegetables with growth stage and plant species variations, respectively. Vegetables and soil samples were collected at different time intervals, before and after the addition of potash and gypsum fertilizers. Potash is some of various mined and manufactured salts that contain potassium in water-soluble form (USGS, 2008; Web-2). Gypsum is a soft sulfate mineral composed of calcium sulfate dihydrate, with the chemical formula $CaSO_4 \cdot 2H_2O$ (Web-3, Klein and Hurlbut, 1985). Seeds of *Spinacia oleracia* (Spinach), *Colocasia esculenta* (Taro), *Ipoma aquatica* (Water spinach), *Cucurbita maxima* (Pumpkin leaves), *Basella alba* (Indian spinach), *Amaranthus gangeticus* (Red amaranth), *Coccinia grandis* (Ivy gourd), *Coriandum sativum* (Coriander leaves), *Amaranthus lividus* (Amaranth), *Corchorus olitorius* (Jute leaves), *Basella rubra* (Malabar Spinach) were sown in the experimental filed.

The present study focuses on the impact of fertilizers on heavy metals and nutrients levels in variation of using fertilizers in cultivation of vegetables. The quantity of heavy metals [cadmium (Cd), lead (Pb), nickel (Ni), and zinc (Zn)] and nutrients [sodium (Na), potassium (K) and calcium (Ca)] in vegetables were determined by Atomic Absorption Spectrometer (AAS) and Flame Photometer and justified according to Hazard Quotient (HQ).

Materials and Methods

Experimental area: Experimental fields were set up at Panchbibi, one of the largest vegetable growing areas of Joypurhat district in Bangladesh during November, 2016. Experimental fields consisted of 10 replicate rectangular areas (2 m × 1 m) for each leafy vegetable and each replicate was separated by 20 cm buffer area which was left as barren. Seeds of 9 types of vegetables were sown on 8th November, 2016. After 20 days latter fertilizers were applied at the rate of 50 and 60 kg/ha from the source of gypsum and muriate of potash (MoP), respectively.

Vegetables and soil sample collection and preservation: Plant and soil (top soils, 0-15 cm) samples were collected at four growth stages of vegetables, before the addition of fertilizers (20 days after sowing) and then after the addition of fertilizers at 1, 3 and 7 days after sowing. The leaves of all vegetable samples were collected carefully. Plant samples were dried at room temperature and then kept in separate polythene bags and properly labeled. Soil samples were collected at the same time of sample collection. The plant and soil samples were analyzed in the laboratory.

Digestion and determination: Amount 0.5 g of each vegetable sample was weighed and then each of them was placed in Teflon tube. For predigestion 10 ml of 70% concentrated nitric acid was added to each tube and then it was kept under room temperature for 30 minutes. After that all the Teflon tube containing samples were placed in the digestion rotor in a particular sequence. Then it was taken for microwave digestion. The condition of the microwave digester was 800 W and 180ºC (Thompson and Walsh, 1989). The total time of digestion was 30 minutes and cooling time was also 30 minutes.

After completing the digestion all the sample were filtered and placed each of them into volumetric flask and were diluted to 25 ml with deionized water. Then all of them were kept in room temperature and then were taken for determination of different elements by Atomic Absorption Spectrometer (AAS) and Flame photometer.

Results and Discussion

Estimation of heavy metals (Zn, Cd, Ni and Pb) and nutrients (Ca, K, and Na) in leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals was carried out by AAS and Flame photometer, respectively. The total quantity of nutrients and heavy metals before addition and after addition of potash and gypsum fertilizers (after 1, 3 and 7 days) were in increasing order: without addition>addition of fertilizer after 1 day > after 3 days > after 7 days (Tables 1-7).

Determination of calcium (Ca)

Table 1. Determination of Ca of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	849.16	850.66	898.10	1015.00
Taro	106.66	110.83	141.01	232.51
Jute leaves	3391.70	3393.91	3465.21	3607.59
Water spinach	197.82	200.83	234.01	327.58
Pumpkin leaves	247.52	249.67	289.92	397.50
Malabar Spinach	932.52	940.89	1024.11	1232.55
Red amaranth	337.16	349.16	398.87	452.52
Ivy gourd leaves	435.71	436.33	462.59	537.24
Coriander leaves	527.83	531.66	571.50	693.02
Amaranth	599.10	601.16	635.15	712.59

The highest quantity of Ca was found as 3607.59 mg/kg in Jute leaves after the addition of potash and gypsum fertilizers among the ten (10) vegetables. In Jute leaves, Ca was also found higher amount (3391.70 mg/kg) before addition of potash and gypsum fertilizers (Table 1). The second highest quantity of Ca was found in malabar spinach as 932.52 mg/kg and 1232.55 mg/kg before and after the addition of potash and gypsum fertilizers (7 days), respectively. The third highest was in Spinach and that was 849.16 mg/kg and 1015.00 mg/kg before and after the addition of potash and gypsum fertilizers (7 days), respectively. Ca was found in water spinach, pumpkin leaves, red amaranth, ivy gourd, coriander leaves and amaranth vegetables in the quantity of 327.58, 397.50, 452.52, 537.24, 693.02 and 712.59 mg/kg, respectively (Table 1). The increasing trend of Ca after the addition of potash and gypsum fertilizers at 1, 3 and 7 days were found infinitesimal and very small.

It is also shown that the highest quantity of Ca was in Jute leaves (3607.59 mg/kg) and the lowest was in Taro (232.51 mg/kg) and the quantity of Ca found in different vegetables followed the increasing order as taro <water spinach < pumpkin leaves < red amaranth < ivy gourd < coriander leaves < amaranth < spinach < malabar spinach < jute leaves.

Determination of potassium (K)

Table 2. Determination of K in various kinds of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	5400.57	5408.72	5512.52	5671.87
Taro	4608.63	4611.26	4698.75	4898.75
Jute leaves	4357.45	4368.82	4515.42	4625.62
Water spinach	3513.33	3545.29	3628.75	3838.75
Pumpkin leaves	1324.56	1329.48	1381.92	1510.01
Malabar Spinach	4934.92	4935.11	5011.87	5146.87
Red amaranth	1638.30	1653.41	1720.62	1875.62
Ivy gourd leaves	1071.11	1079.87	1112.57	1212.52
Coriander leaves	5003.27	5009.85	5092.75	5213.12
Amaranth	1550.01	1558.29	1616.25	1723.87

In Spinach, K was also found higher quantity (5400.57 mg/kg) before addition of potash and gypsum fertilizers. The highest quantity of K was also found as 5671.87 mg/kg in the same vegetable (spinach) after the addition of potash and gypsum fertilizers among the ten (10) vegetables (Table 2). The second highest quantity of K was found in Coriander leaves as 5003.27 mg/kg and 5213.12 mg/kg before and after the addition of potash and gypsum fertilizers (7 days), respectively. The third highest was Malabar Spinach as 4934.92 mg/kg and 5146.87 mg/kg before and after the addition of potash and gypsum fertilizers (7 days), respectively. Moreover, K was found in taro, jute leaves, water spinach, red amaranth, amaranth, pumpkin leaves, ivy gourd leaves in the quantity of 4608.63, 4357.45, 3513.33, 1638.30, 1550.01, 1324.56 and 1071.11 mg/kg and 4898.75, 4625.62, 3838.75, 1875.62, 1723.87, 1510.01 and 1212.52 mg/kg before and after addition of 7 days of potash and gypsum fertilizers, respectively (Table 2). The increasing trend of K after the addition of potash and gypsum fertilizers at 1, 3 and 7 days were found infinitesimal, very small and small change, respectively.

It is shown that the highest quantity of K was in Spinach (5400.57 mg/kg) and the lowest was in Ivy gourd leaves (1212.52 mg/kg) and the quantity of K found in different vegetables followed the increasing order as spinach > coriander leaves > malabar spinach > taro > jute leaves > water spinach > red amaranth > amaranth > pumpkin leaves > ivy gourd leave.

The highest quantity of Na was found as 838.95 mg/kg in spinach after the addition of potash and gypsum fertilizers among the ten (10) vegetables (Table 3). In spinach Na was also found higher quantity (722.31 mg/kg) before addition of potash and gypsum fertilizers. The second highest quantity of Na was found in water spinach as 590.12 mg/kg and 717.59 mg/kg before and after the addition of potash and gypsum fertilizers (7 days), respectively. The third highest was coriander leaves as 374.72 mg/kg and 493.75 mg/kg before and after the addition of potash and gypsum fertilizers (7 days), respectively. Moreover, Na was found in malabar spinach, red amaranth, ivy gourd, taro, jute leaves, amaranth, pumpkin leaves in the quantity of 176.11, 170.76, 161.32, 71.64, 45.06, 20.76, 26.19 mg/kg and 292.70, 288.75, 267.29, 178.95, 138.12, 115.62, 89.20 mg/kg before and after addition of 7 days of potash and gypsum fertilizers, respectively (Table 3). The increasing trend of Na after the addition of potash and gypsum fertilizers at 1, 3 and 7 days were found no change or very little change, very small and small change, respectively.

Determination of sodium (Na)

Table 3. Determination of Na in various kinds of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	722.31	724.20	766.25	838.95
Taro	71.64	75.97	117.29	178.95
Jute leaves	45.06	48.92	96.45	138.12
Water spinach	590.12	598.79	632.08	717.59
Pumpkin leaves	26.19	29.65	34.37	89.20
Malabar Spinach	176.11	180.27	230.62	292.70
Red amaranth	170.76	174.18	191.24	288.75
Ivy gourd leaves	161.32	166.11	180.20	267.29
Coriander leaves	374.72	385.39	412.08	493.75
Amaranth	20.76	26.19	54.37	115.62

It is shown that the highest quantity of Na was in spinach (722.31 mg/kg and 838.95 mg/kg) and the lowest was in pumpkin leaves (26.19 mg/kg and 89.20 mg/kg) before and after addition (7 days) of potash and gypsum fertilizers, respectively. The quantity of Na found in different vegetables followed the increasing order as spinach > water spinach > coriander leaves > malabar spinach > red amaranth > ivy gourd > taro > jute leaves > amaranth > pumpkin leaves. This sequence is also found in all selected vegetables before and after addition of potash and gypsum fertilizers.

To estimate the quantity of heavy metals (Zn, Cd, Ni and Pb) in leafy vegetables before and after the addition of gypsum and potash fertilizers (1, 3 and 7 days interval), atomic absorption spectrometer (AAS) was used. The total quantities of heavy metals before addition and after addition of gypsum and potash fertilizers are shown in Tables 4-7.

Among the vegetables, spinach, water spinach, coriander leaves, malabar spinach, red amaranth, ivy gourd leaves, taro, jute leaves, amaranth and pumpkin leaves the highest quantity of trace element Zn was found as 9.859 mg/kg in malabar spinach before the addition of gypsum and potash fertilizers (Table 4). In malabar spinach Zn was also found higher quantity as 10.074 mg/kg after 7 days from the addition of gypsum and potash fertilizers. The changes of trace element Zn quantity before and after 1 day and 3 days from the addition of gypsum and potash fertilizers were very negligible and this trend was noticed in all cultivated vegetables. The second highest quantity of Zn was found in Taro 9.127 mg/kg and 9.399 mg/kg before and after the addition of gypsum and potash fertilizers (7 days), respectively. The third highest was spinach as 8.459 mg/kg and 8.512 mg/kg before and after the addition of gypsum and potash fertilizers (7 days), respectively. Moreover, Zn was found in amaranth, red amaranth, ivy gourd leaves, pumpkin leaves, jute leaves, coriander leaves and water spinach in the quantity of 7.561, 6.549, 6.341, 6.249, 5.235, 5.191, 5.010 mg/kg and 7.609, 7.12, 6.577, 6.390, 5.299, 5.293, 5.057 mg/kg before and after addition of 7 days of gypsum and potash fertilizers respectively (Table 4). The increasing trend of Zn after 1, 3 and 7 days from the addition of gypsum and potash fertilizers were found no change, very negligible change and small change respectively (Table 4).

Determination of zinc (Zn)

Table 4. Determination of Zn in various kinds of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	8.459	8.459	8.463	8.512
Taro	9.127	9.126	9.141	9.399
Jute leaves	5.235	5.235	5.252	5.299
Water spinach	5.010	5.010	5.013	5.057
Pumpkin leaves	6.249	6.251	6.299	6.390
Malabar spinach	9.859	9.860	9.871	10.074
Red amaranth	6.549	6.549	6.581	7.12
Ivy gourd leaves	6.341	6.342	6.347	6.577
Coriander leaves	5.191	5.194	5.200	5.293
Amaranth	7.561	7.561	7.577	7.609

It is found that the highest quantity of Zn was in malabar spinach (9.859 mg/kg and 10.074 mg/kg) and the lowest was in Water Spinach (5.010 mg/kg and 5.057 mg/kg) before and after addition (7 days) of gypsum and potash fertilizers, respectively. The quantity Zn found in different vegetables followed the increasing order; malabar spinach > taro > spinach > amaranth > red amaranth > ivy gourd leaves > pumpkin leaves > jute leaves > coriander leaves > water spinach.

Determination of cadmium (Cd)

Table 5. Determination of Cd in various kinds of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	0.081	0.081	0.084	0.093
Taro	0.119	0.119	0.128	0.135
Jute leaves	0.041	0.041	0.043	0.063
Water spinach	0.029	0.035	0.039	0.056
Pumpkin leaves	0.044	0.042	0.046	0.069
Malabar spinach	0.089	0.089	0.110	0.121
Red amaranth	0.057	0.060	0.063	0.089
Ivy gourd leaves	0.049	0.048	0.055	0.073
Coriander leaves	0.034	0.033	0.041	0.052
Amaranth	0.059	0.062	0.069	0.091

The highest quantity of Cd was found in Taro (0.119 mg/kg and 0.135 mg/kg) and the lowest was in Coriander leaves (0.034 mg/kg and 0.052 mg/kg) before and after (7 days) addition of gypsum and potash fertilizers, respectively.

The second and third highest quantity of Cd were found malabar spinach (0.089 mg/kg and 0.121 mg/kg) and spinach (0.081 mg/kg and 0.093 mg/kg) before and after addition of gypsum and potash fertilizers, respectively (Table 5). The quantity of Cd was found in amaranth, red amaranth, ivy gourd leaves, jute leaves, pumpkin leaves and water spinach were as 0.059 and 0.091 mg/kg, 0.057 and 0.089 mg/kg, 0.049 and 0.073 mg/kg, 0.041 and 0.063 mg/kg, 0.034 and 0.052 mg/kg before and after addition of 7 days of gypsum and potash fertilizers, respectively. The change of Cd after 1, 3 and 7 days were as 0.119, 0.119, 0.128, and 0.135 mg/kg in Taro before and after 1, 3, and 7 days from the addition of gypsum and potash fertilizers, respectively (Table 5). This negligible change in quantity of Cd was found in another 9 vegetables (Table 5). The quantity of Zn found in different vegetables followed the increasing order as taro > malabar spinach > spinach > amaranth > red amaranth > ivy gourd leaves >jute leaves > pumpkin leaves > water spinach> coriander leaves.

Determination of nickel (Ni)

Table 6. Determination of Ni in various kinds of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	0.413	0.413	0.421	0.511
Taro	0.624	0.624	0.633	0.713
Jute leaves	0.141	0.142	0.157	0.197
Water spinach	0.096	0.101	0.122	0.149
Pumpkin leaves	0.190	0.199	0.208	0.242
Malabar spinach	0.549	0.550	0.567	0.621
Red amaranth	0.345	0.351	0.410	0.571
Ivy gourd leaves	0.228	0.232	0.239	0.253
Coriander leaves	0.134	0.134	0.138	0.144
Amaranth	0.401	0.401	0.421	0.574

The highest quantity of Ni was found in taro as 0.713 mg/kg after 7 days from the addition of gypsum and potash fertilizers among the vegetables. In taro Ni was also found higher quantity (0.624 mg/kg) before addition of gypsum and potash fertilizers (Table 6). The second highest quantity of Ni was found in malabar spinach as 0.549 mg/kg and 0.621 mg/kg before and after (7 days) the addition of gypsum and potash fertilizers, respectively. The third highest quantity of Ni was found in amaranth as 0.401 mg/kg and 0.574 mg/kg before and after (7 days) the addition of gypsum and potash fertilizers, respectively. Moreover, Ni was found in red amaranth, spinach, ivy gourd leaves, pumpkin leaves, jute leaves, coriander leaves, water spinach in the quantity of 0.345 and 0.571 mg/kg, 0.413 and 0.511 mg/kg, 0.228 and 0.253 mg/kg, 0.190 and 0.242 mg/kg, 0.141 and 0.197 mg/kg, 0.134 and 0.144 mg/kg, 0.096 and 0.149 mg/kg before and after addition of 7 days of gypsum and potash fertilizers, respectively (Table 6). The increasing trend of Ni after the addition of gypsum and potash fertilizers at

1, 3 and 7 days were found no change or very little change.

It is shown that the highest quantity of Ni was in taro (0.624 mg/kg and 0.713 mg/kg) and the lowest was in water spinach (0.096 mg/kg and 0.149 mg/kg) before and after addition (7 days) of gypsum and potash fertilizers respectively. The quantity of Ni found in different vegetables followed the increasing order as water spinach < coriander leaves < jute leaves <pumpkin leaves < ivy gourd leaves < spinach <red amaranth<amaranth<malabar spinach < taro.

The highest quantity of Pb was reported in taro as 1.98 mg/kg and this result was constant before and after the addition of gypsum and potash fertilizers (Table 7). The second highest quantity of Pb was found in malabar spinach 0.188 mg/kg and 0.191 mg/kg before and after addition of gypsum and potash fertilizers, respectively. The third and fourth highest quantity of Pb were reported in Amaranth (0.182 and 0.182 mg/kg) and Red Amaranth (0.181 and 0.181 mg/kg) before and after the addition of gypsum and potash fertilizers, respectively. It may be mentioned that the cultivation work has been done in non-polluted field and the detection limit of Pb in AAS was as 0.180 mg/kg. Therefore, the finding of Pb quantity is reasonable. Moreover, it is also found that the quantity of Pb in ivy gourd leaves, jute leaves, pumpkin leaves, coriander leaves, spinach, water spinach were in below detection limit (Table 7).

Determination of lead (Pb)

Table 7. Determination of Pb in various kinds of leafy vegetables before and after the addition of potash and gypsum fertilizers in different time intervals.

Name of the vegetables	Before the addition of fertilizers (mg/kg)	After the addition of fertilizers (1 day later) (mg/kg)	After the addition of fertilizers (3 days later) (mg/kg)	After the addition of fertilizers (7 days later) (mg/kg)
Spinach	BDL	BDL	BDL	BDL
Taro	0.197	0.197	0.197	0.197
Jute leaves	BDL	BDL	BDL	BDL
Water spinach	BDL	BDL	BDL	BDL
Pumpkin leaves	BDL	BDL	BDL	BDL
Malabar spinach	0.188	0.188	0.191	0.191
Red amaranth	0.181	BDL	0.181	0.181
Ivy gourd leaves	BDL	BDL	BDL	BDL
Coriander leaves	BDL	BDL	BDL	BDL
Amaranth	0.182	0.182	0.182	0.182

Note: BDL= Below Detection Level.

Area comparison: For acquiring knowledge about heavy metals and the present condition of soil, a comparison with previous work and the present study was carried out involving industrial area, arsenic contaminated area, near mine area and urban area of abroad and in Bangladesh as shown in Table 8.

In present study, the quantity of heavy metals (Zn, Ni, Cd and Pb) were estimated from ten (10) leafy vegetables which were cultivated at non-polluted soil, near village area in Joypurhat district, Bangladesh. The results showed that the quantity of Zn, Ni, Cd and Pb were average as 7.133, 0.398, 0.084 and 0.188 mg/kg, respectively in these ten (10) vegetables (Table 8) where Ahmad and Goni 2010 reported that the quantity of Ni and Pb were average as 2.97 and 3.89 mg/kg, respectively in the vegetables cultivated in industrial area in Dhaka, Bangladesh. Islam and Hoque 2014 also reported the quantity of Ni and Pb in vegetables was average of 5.34 and 0.76 mg/kg, respectively cultivated in industrial area in Dhaka, Bangladesh. The highest quantity of Ni and Pb were reported by Rahman *et al.* 2013 and those are 1.44 and 3.7 mg/kg, respectively, cultivated in arsenic contaminated area Noakhali. According to Zhuang *et al.* 2009 reported that the quantity of Pb in near mine area at Dabaoshan (China) was average 0.17 mg/kg in vegetables where Sharma *et al.* 2007 found higher quantity of Pb 1.42 mg/kg in vegetables cultivated in urban area at Voranashi (India).

Table 8. Comparison of studies of metal Quantity (mg/kg) in vegetables at different places.

District (Country)	Sampling site description	Average metal quantity of vegetables				References
		Zn	Ni	Cd	Pb	
Panchbibi, Joypurhat (Bangladesh)	Non-polluted area	7.133	0.398	0.084	0.188	Present study, Agricultural area
Dhaka (Bangladesh)	Industrial area	ND	5.34 (1.61-11.7)	ND	0.76 (0.06-3.45)	(Islam and Hoque, 2014)
Dhaka (Bangladesh)	Industrial area	ND	2.97	ND	3.89	(Ahmad and Goni, 2010)
Noakhali (Bangladesh)	Arsenic contaminated area	ND	1.44 (0.32-4.67)	ND	3.7 (0.67-16.5)	(Rahman *et al.*, 2013)
Dabaoshan (China)	Near mine area	ND	ND	ND	0.17 (0.01-0.39)	(Zhuang *et al.*, 2009)
Voranashi (India)	Urban area	ND	ND	ND	1.42 (0.9-2.2)	(Sharma *et al.*, 2007)

Note: ND= Not detected

Assessment of potential health risk

Human health risk assessment: To assess the human health risk by consumption of vegetables containing heavy metals some parameters needs to calculate according to Environmental Protection Agency (US EPA, 2010), World Health Organization (WHO, 1993), World Health Organization (WHO, 1989), World Health Organization (WHO, 2004).

According to US EPA, human health risk assessment is defined as the process to estimate the nature and probability of adverse health effects in humans exposed to chemicals in contaminated environmental media, now or in the future. The parameters for risk assessment were introduced by US EPA for the estimation of potential health risk caused by any chemical contaminant over prolonged exposure (US EPA, 1989). The estimation of daily intake and the oral reference dose (R_fD) for the metal (mg/kg body weight/day) are given below.

Health risk due to consumption of contaminated vegetables with heavy metal was evaluated through calculation of the ratio between exposure and the reference oral dose (R_fD). According to Khan *et al.* 2009, if HQ < 1, the exposed population will be experienced with no adverse effects, and for HQ < 1 indicates a chance of non-carcinogenic effects and its probability will be increased with increasing the values of the HQ (Khan *et al*,. 2009; Ahemad and Kibret, 2014). Moreover, the health can also be evaluated through comparing the values of HQ with R_fD. According to New York State Department of Health (NYSDOH, 2007), the health risk will be minimum for HQ ≤ R_fD, if HQ is 1-5 times of R_fD, the risk will be lower, if HQ is 5-10 times of R_fD, the risk will be moderate. The risk will be higher if the HQ is 10 times of R_fD (Javed and Usmani, 2016).

Human health risk, determined by 'Health Hazard Quotient (HQ)': In the present study, the Hazard Quotient (HQ) for Zn, Ni, Cd and Pb were as 0.143, 0.085, 0.1029 and 0.806 respectively (Table 10). The sequence of HQ for the heavy metals followed the decreasing order Pb > Zn > Cd > Ni. The HQ value for all the heavy metals Zn, Cd Ni and Pb were less than 1, which is considered safe for human health or indicates no adverse effect on human health (Table 10). Islam and Hoque (2014) reported that the HQ values of heavy metal, Ni and Pb were as 1.144 and 3.257, respectively for the vegetables cultivated at industrial area in Dhaka, Bangladesh (Islam and Hoque, 2014) which were both more than 1, indicates low health risk for consumption (Table 10) . While Ahmad and Goni 2010 found HQ values as 0.636 and 16.671 for Ni and Pb in the cultivated vegetables at industrial area in Dhaka, Bangladesh. According to New York State Department of Health (NYSDOH, 2007), the HQ values for Ni was in safe but the values of HQ for Pb

Table 9. Estimated Daily Intake of Metal (DIM) through vegetables.

Sampling site description	Name of the heavy metals	Average conc. of vegetables (mg/kg)	Daily intake metal by human being (mg/g)	R_fD (mg/day)	References for R_fD (mg/day)
Agricultural area, Panchbibi (Joypurhat)	Zn	7.133	2.140	15.00	WHO 1993
	Ni	0.398	0.119	1.400	US EPA 2010
	Cd	0.084	0.0252	0.245	WHO 1992
	Pb	0.188	0.0564	0.070	US EPA 2010
Industrial area (Dhaka), (Islam and Hoque, 2014)	Ni	5.34	1.602	1.400	US EPA 2010
	Pb	0.76	0.228	0.070	
Industrial area (Dhaka), (Ahmad and Goni, 2010)	Ni	2.97	0.891	1.400	US EPA 2010
	Pb	3.89	1.167	0.070	
Arsenic contaminated area (Noakhali), (Rahman *et al*., 2013)	Ni	1.44	0.432	1.400	US EPA 2010
	Pb	3.70	1.110	0.070	
Near mine area (Dabaoshan-China), (Zhuang *et al*., 2009)	Pb	0.17	0.051	0.070	US EPA 2010
Urban area (Voranashi, India), (Sharma *et al.*, 2007)	Pb	1.42	0.426	0.070	

Table 10. Health risk index for metal contamination of vegetables measured by Hazard Quotient (HQ).

Sampling site description	Name of the heavy metals	Daily intake of vegetables (kg/day)	R_fD (mg/kg body weight/day)	$HQ = \frac{(Div) \times (Cmetal}{RfD \times Bo}$
Present study Agricultural area, Panchbibi (Joypurhat)	Zn	2.140	15.00	0.143
	Ni	0.119	1.400	0.085
	Cd	0.0252	0.245	0.1029
	Pb	0.0564	0.070	0.806
Industrial area (Dhaka) (Islam and Hoque, 2014)	Ni	1.602	1.400	1.144
	Pb	0.228	0.070	3.257
Industrial area (Dhaka) (Ahmad and Goni, 2010)	Ni	0.891	1.400	0.636
	Pb	1.167	0.070	16.671
Arsenic contaminated area (Noakhali) (Rahman *et al*., 2013)	Ni	0.432	1.400	0.309
	Pb	1.110	0.070	15.857
Near mine area (Dabaoshan-China) (Zhuang *et al.*, 2009)	Pb	0.051	0.070	0.743
Urban area (Voranashi, India) (Sharma *et al.*, 2007)	Pb	0.426	0.070	6.086

is much higher than 1 (HQ > 10 times), indicates high health risk. Vegetables cultivated in arsenic contaminated area, Noakhali (Bangladesh) have been studied and the results showed that the values of HQ for Ni (0.309) and Pb (15.857) were no risk and high risk, respectively. The HQ value for Pb was found less than 1 (0.743) for the cultivation of vegetable near mine area Dabaoshan (China) which indicates the health risk for the consumption of vegetables was lower. While HQ values for Pb were found 6.086 in cultivated vegetables at urban area Voranashi (India) which was greater than 1 and indicates the health risk is moderate (Table 10).

Conclusion

Metal contamination in soil is received increasing attention all over the world. Principally there are two major pathways for human exposure to soil contamination: soil-plant-human (food chain pathway) and soil-human (incidental soil ingestion). The present study focused on food chain pathway. Quantity of different elements in vegetables depends upon the relative level of exposure of plants to the contaminated soil. In the present study it was found that quantity of K, Ca, Na, Zn, Ni, Pb and Cd in vegetables samples were not higher than the World Average value (Pendias and Pendias, 2000) and these are within the permissible limit (Codex General Standard for Contaminants and Toxins in Food and Feed, 1995). Macronutrients (K, Ca and Na) are abundant in all type of vegetables. Lokeshappa *et al.* studied the elemental quantity in different agricultural products and the results obtained are comparable with the present study (Lokeshappa *et al.*, 2012). Since, there was no industrial unit near the study area, so the presence of Ni, Cd and Pb in smaller quantity indicates that they may have been come from atmospheric deposition by air or other anthropogenic sources. The elemental quantity of the studied vegetables varied in different samples and hence variations in elemental quantity among different varieties reflect the difference in uptake capabilities and their further translocation to the edible portion of the plants. Soil-to-plant transfer is one of the key components of human exposure to metals through food chain. In this study, the daily intake of heavy metals (Zn, Cd, Ni and Pb) for human with an average body weight 70 kg has been calculated (Table 9) and found that intake of toxic metals from vegetables is not high and within the suggestive values. Furthermore, the quantity of Pb in most of the vegetables is found below the detection level except in taro, malabar spinach, red amaranth and amaranth. The daily intake of Pb was as estimated as 0.0564 mg/g and HQ value for Pb calculated was as 0.806 which is lower than the risk value. Pb is very toxic element, its long term exposure to lower level leads to build up possible kidney disease, lung damage and fragile bones, hypertension, arthritis, diabetes, anemia, cancer, cardiovascular disease, strokes etc (UNEP/FAO/ WHO/WMO/IAEA/IOC, 1981). The calculated Hazard Quotient (HQ) for the elements Zn, Ni, and Cd is also found below 1 which indicates safe with no risk to human health. It is therefore suggested to consume those vegetables in highest amount in the diet to bear no health risk.

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