

**ANALYSIS OF HEAVY METALS IN DIFFERENT
WINTER VEGETABLES COLLECTED FROM
DIFFERENT SUPER SHOPS LOCATED IN DHAKA CITY**

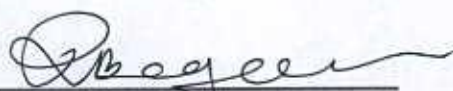
By

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A Thesis
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*DEDICATED TO
MY
BELOVED PARENTS*



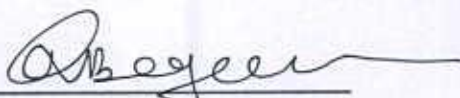
CERTIFICATE

This is to certify that the thesis entitled "ANALYSIS OF HEAVY METALS IN DIFFERENT WINTER VEGETABLES COLLECTED FROM DIFFERENT SUPER SHOPS LOCATED IN DHAKA CITY" submitted to the Faculty of Agriculture, Sher-e-Bangla Agricultural University, Dhaka, in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE (M.S.) in AGRICULTURAL CHEMISTRY, embodies the results of a piece of bona fide research work carried out by MD. REFATUL ISLAM, Registration. No. 07- 02508 under my supervision and guidance. No part of this thesis has been submitted for any other degree or diploma.

I further certify that such help or source of information as has been availed of during the course of this investigation has duly been acknowledged.

Dated:

Dhaka, Bangladesh


(Prof. Dr. Rokeya Begum)

Supervisor

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For any errors or inadequacies that may remain in this work, of course, the responsibilities are entirely on the Author.

The Author

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MD. REFATUL ISLAM

ABSTRACT

The experiment was conducted to measure the content of heavy metals such as Arsenic (As), Cadmium (Cd), and Lead (Pb) in different winter vegetables collected from different outlets of four super shops (Aagora, Nandan, Swapno and Meena Bazaar) located in Dhaka city using atomic absorption spectrophotometer. The result of this study showed that, there was a common sequence in heavy metal content was found in different vegetables of different outlets. In case of As content in different outlets, the descending order of the vegetables were Red Spinach > Radish > Brinjal > Cauliflower > Bean > Bottle Gourd > Carrot. For Cd the order was, Bottle Gourd > Brinjal > Radish > Bitter Gourd > Cabbage. For Pb the order was, Bottle Gourd > Brinjal > Radish > Bean. Among the four outlets the range of As, Cd and Pb concentration in the vegetables were $0.41-1.37 \mu\text{g g}^{-1}$, $0.21-0.59 \mu\text{g g}^{-1}$, $0.07-0.81 \mu\text{g g}^{-1}$ respectively. Among the concentrations of As Cd and Pb in different vegetables from different outlets, highest As content ($1.37 \mu\text{g g}^{-1}$) was found below the maximum permissible limit ($2.6 \mu\text{g g}^{-1}$) of various international authorities except Cd ($0.59 \mu\text{g g}^{-1}$) and Pb ($0.81 \mu\text{g g}^{-1}$) that exceeded the recommended limit ($0.2, 0.3 \mu\text{g g}^{-1}$, respectively) in vegetable. The result also noticed that the highest content of As and Pb were found in leafy vegetables and the highest Cd was found in fruity vegetables.

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LIST OF ABBREVIATIONS

Abbreviations

Full word

%	Percent
$\mu\text{g g}^{-1}$	Micro Gram per Gram
AAS	Atomic Absorption Spectrophotometer
As	Arsenic
Cd	Cadmium
cm	Centi-meter
Cu	Copper
<i>et al.</i>	<i>and others</i>
FAO	Food and Agricultural Organization
g	Gram
j.	Journal
kg	Kilogram
mg	Milligram
No.	Number
Pb	Lead
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

INTRODUCTION

Consumption of food contaminated with heavy metals is a major source of health problems for man and animals. These metals can pose a significant health risk to humans, particularly in elevated concentrations above the very low body requirements (Gupta and Gupta, 1998). Trace quantities of certain heavy elements, such as chromium, nickel, copper; iron and zinc are essential micronutrients for higher animals and for plant growth. Lead (Pb), cadmium (Cd), and Arsenic (As) are significant environmental pollutants that are capable of interfering in the physiological process of aquatic organisms. Anthropogenic activities, such as agriculture, industry and urban life increase the Pb, Cd, and As contents of soils and waters and, therefore, have an effect on the metal contents of vegetables (Naser, 2009). Dietary exposure to heavy metals, namely Cd, Pb,As has been identified as a risk to human health through the consumption of vegetable crops (Kachenko and Singh, 2006). Heavy metals have toxic and mutagenic effects even at very low concentration. Several cases of human disease, disorders, malfunction and malformation of organs due to metal toxicity have been reported (Avena J.M. 1979). Along with the human beings, animals and plants are also affected by toxic levels of heavy metals. Toxicological significance of heavy metals has been recognized several decades ago in developed countries. (Hansen H. 1982).

Fruits and vegetables are an important component of diet after cereals. It is known that systematic health problems can develop as a result of excessive accumulation of dietary heavy metals such as Cd, As, Pb, in human body (Oliver M.A. 1997). Heavy metals are extremely persistent in the

environment. They are no biodegradable and thermo stable and thus readily accumulate to toxic levels (Sharma R. K. *et al.* 2007).

The vegetables are important food crops of Bangladesh and are rich in vitamins and minerals, which are very essential for maintaining good health. Most of the vegetables contain more than 80 percent water. Dietary plants also contain hundreds of antioxidants. But vegetables that are grown in arsenic contaminated soil, people unknowingly consume such arsenic contaminated crops and become exposed to arsenic toxicity. Bangladesh is primarily based on agriculture. However, widespread uses of ground water for irrigation suggested that ingestion of irrigated crops and vegetables could be a major exposure route for arsenic (WHO, 2001; Duxbury *et al.*, 2003)

Based on persistent nature and cumulative behavior as well as the probability of potential toxicity effects of heavy metals as a result of consumption of leafy vegetables and fruits, there is need to test and analyze these food items to ensure that the levels of these trace elements meet the agreed international requirements. This is particularly important for chain shop vegetables product from the part of the country where only limited data on heavy metal contents of such highly consumed agricultural materials are available.

There are several kinds of chain shop in Dhaka city. Apparently they collect their vegetables from different parts of Bangladesh. As for example most of their vegetable product comes from Bagura, Dhaka, Dinajpur, Gazipur, Narayanganj, Narsingdi, Rajshahi, Rangpur, Tangail and some other districts of Bangladesh. All the districts are Arsenic affected (Diponkor 2001).

We know very little about the presence of arsenic in the food chain due to limited data. To assess the health risks of arsenic in foods we need reliable and representative data on arsenic concentrations and food consumption patterns, which are not yet robust enough for Bangladesh. However, we cannot exclude what will be the known As concentrations in crops, which will ultimately affect human exposure level via foods because of the prolonged input of arsenic-contaminated irrigation water.

This study therefore, presents data on the concentration of some specific heavy metals (As, Cd, Pb,) found in some selected winter vegetables from different outlets of the chain shops of Dhaka city.

The present research work is undertaken with the following objectives:

- This investigation was carried out to monitor the levels of heavy metals (As, Cd, Pb) in some selected winter vegetables from 4 outlets in Dhaka city.
- To estimate the highest and lowest concentration of heavy metals (As, Cd, Pb) in different type of vegetables for comparing with safe value recommended by WHO/CEC.
- Comparing the different types of vegetables in according to heavy metals content.



CHAPTER 2

REVIEW OF LITERATURE

REVIEW OF LITERATURE

Warren and Delavult (1962) found that the range of lead level in some vegetables was 0.30-45 $\mu\text{g g}^{-1}$.

Smiled *et al.* (1982) carried out field experiments to determine the yield and As accumulation by radish, lettuce, carrot, potato and wheat on soils having As concentration between 35 and 108 mg kg^{-1} on dredged soil of the river Rhine and Meuse, UK. The highest level of As accumulation was found in Radish (concentration ranging from 0.8 to 21 mg As kg^{-1}). The order of decreasing arsenic accumulation was Radish > Lettuce > Carrot > Potato > Spring Wheat grain.

Hibben *et al.* (1984) reported that a mean Pb concentration of 15.20 $\mu\text{g g}^{-1}$ was found in some vegetables of Spain and 4.61 $\mu\text{g g}^{-1}$, 3.80 $\mu\text{g g}^{-1}$ and 1.24 $\mu\text{g g}^{-1}$ in some vegetables of USA, Egypt and Netherlands, respectively.

Fritaz and Venter (1988) conducted a pot experiment and grown the vegetables of lettuce, spinach, carrot, raddish, bush bean and tomato. They found that heavy metal (Pb, Cu, Zn and Ni) concentration were generally the highest in the leaves and the lowest in the roots and fruits. Among the heavy metal, a high Cu level was found in roots carrots.

Low and Lee (1992) reported that the As content of the edible parts of vegetables (onions, lettuces, tomatoes, spinach and various *Brassica* Sp.) was analyzed for As concentration. The highest arsenic concentration (2.0 $\mu\text{g g}^{-1}$) was found in bean sprouts (*Phaseolus radiatus*) and the lowest (0.20 $\mu\text{g g}^{-1}$) in *Pachyrhizus erosus*.

Miaz and Wilke (1997) conducted a pot trial experiment on the influence of irrigated sewage affected soil and heavy metal uptake by plant. They found that contents of Cd, Cu, Pb and Zn increased in crop with increasing soil pollution, but Cd and Zn uptake increased relatively more than that of Cu and Pb. The Cd in leaves ranged from 0.1-8.2 mg kg⁻¹, dry matter respectively.

Venter (1993) conducted an experiment in five locations in Germany. They found that the lettuce and kohlrabi had higher contents of heavy metals (Pb, Cd, Zn, Cu, Cr and Ni) than the spinach. Limits for toxic substances exceeded in some samples of lettuce and kohlrabi.

Barman and Lal (1994) conducted an experiment at industrially polluted field in Kalipur, West Bengal. They reported that the average levels (and ranges) of metal bioaccumulation, respective of vegetable species were 259.20 (40.0-530.0); 58.20 (9.0-93.0); 3.2 (1.0-8.0); 90.0 (27-245) µgg⁻¹ in dry weight for Zn, Cu, Cd and Pb respectively.

Carbonell-Barrachina *et al.* (1995) carried out a pot experiment by supplying different concentrations of As (0-10 mg L⁻¹) through irrigation water and found that the concentration of arsenic in tomato remained within 0.5 mg As kg⁻¹.

O'Neill (1992) reported that the accumulation of arsenic in the edible parts of most plants was generally low. Organic arsenicals and As (III) were the most phototoxic for grass species in relation to plant growth. Arsenic uptake and translocation was species-specific and the photo-availability of Arsenic concentration followed the trend of As (V) < As (III). Arsenic concentration

in root and shoot was significantly increased with increasing As application rate regardless of the As chemical forms (Carbonell *et al.*).

Thomas *et al.* (1972) reported that the cadmium and lead content in some vegetables (potato, tomato, lettuce and cabbage) foodstuffs were in the range of 0.01-0.22 and 0.01-3.85 $\mu\text{g g}^{-1}$ respectively.

Zupan *et al.* (1997) conducted an experiment in heavy metal contaminated soil in Slovenia. They reported that the highest concentrations of heavy metals (Cd, Pb and Zn) were observed in edible green parts of vegetables (spinach, lettuce) and roots (carrot and radish) whereas in leguminous vegetables (pods and seeds) was very low.

Helgesen *et al.* (1998) reported that the soil to carrot uptake rate (bio availability) of arsenic was $0.47 \pm 0.06\%$ of the arsenic content of soils having As concentrations of 6.5-338 mg kg^{-1} .

Moslehuddin *et al.* (1998) carried out 4 pot and 2 field experiments to evaluate the vegetables uptake of heavy metals from the application of zinc oxysulphate containing 20% Zn, 4.17% Cd as Zn sources in red amaranth, sorghum, tomato and cabbage. Zinc was applied at the rate of 0, 2, 4 and 6 kg ha^{-1} in all cases. They reported that the edible portion take up more of Zn and lesser uptake of Cd and Pb. The highest uptake of Cd was found as 0.02, 0.016, 0.028 and 0.019, that of Pb were 0.40, 0.25, 2.80 and 2.10 mg kg^{-1} in all case of red amaranth, sorghum, tomato and cabbage respectively.

Wiersma *et al.* (1998) collected and analysed the cereals, fruits, fodder crops and vegetables from major growing areas in the Netherlands together with their corresponding soils. The Cd and Pb levels of cereals were high with high respect to the proposed maximum acceptable concentrations. In lettuce

and spinach relatively high Cd levels occurred and fruits such as tomatoes, cucumbers and apples Cd level were low. The Pb level in curly kale was high. The soils had median values for As, Cd, Pb, Hg of 11.0, 0.4, 23.0 and 0.07 mg kg⁻¹ respectively.

Li *et al.* (1996) conducted an experiment in greenhouse on cabbage to determine the accumulation of heavy metal from metal enriched sewage sludge compost. They found that the accumulation of Cu, Cd, Zn, Ni, and Pb were higher, where the higher rates of compost application.

Mitev and Peycheva (1999) carried out an experiment to know the accumulation rate of arsenic in leaves of green beans and tomatoes from the soil having 0.0 to 50.0 mg kg⁻¹. They found that the concentration of arsenic in green bean were higher than tomatoes.

Carbonell-Barrachina *et al.* (1999) found inner root and outer skin concentration of more than 1 mg As kg⁻¹ (above permissible limit) in turnip (*Brassica napas L.*)

Cobb *et al.* (2000) conducted an experiment in mine wastes and in waste amended soils and found that tomato and beans contained As, Cd, Pb, and Zn mainly in the roots and little was translocated in fruits. Radish roots accumulated fewer metals compared with leaves, whereas lettuce roots and leaves accumulated similar concentrations of four metals. Lettuce leaves and radish roots accumulates significantly more than bean and tomato fruits.

Alamgir and Chakrabarty (2000) reported that the mean concentrations of Pb in cabbage, cauliflower, tomato, potato, radish, lady's finger. Brinjal and bottle gourd were 0.53, 1, 1.3, 3.0, 0.38, 0.09, 0.23, 0.08 and 0.23 µgg⁻¹

respectively. They are also reported that the mean concentrations of Pb in Spinach, Red Spinach were 0.99, 1.02 $\mu\text{g g}^{-1}$ respectively.

Bunzl *et al.* (2001) reported that the plant uptake of metals from slag-contaminated soils and studied the soil to plant transfer of arsenic, copper, lead, thallium and zinc by the bean (*Phaseolus vulgaris* L.), Knolkhol (*Brassica oleracea* var. *gongylodes* L.), lettuce (*Lactuca sativa*), carrot (*Daucus carota* L.) from a control soil (Entisol) and from a contaminated soil (1:1 soil-slag mixture). As, Pb, Cu, Cu and Zn for all vegetables were significantly smaller than the corresponding plant-soil concentration ratios for uncontaminated soil. The ability of a plant to accumulate a given metal as observe for a control soil might not exist for a soil slag mixture and vice versa.

Zubillaga and Lavado (2002) applied bio solid compost with soil and then grew lettuce. They reported that Zn concentration in leaves increases as compost proportion decreases, ranging from 56.20 to 80.40 mg kg^{-1} when composted bio solids application increased than the concentration of Cu and Ni in lettuce increased from 5.10 to 9.80 mg Cu kg^{-1} and 2.30 to 3.70 mg Ni kg^{-1} respectively.

Thustos *et al.* (1998) have grown radish, carrot, spinach and green bean on unpolluted Fluvisols, Luvisols with elevated content of As and Chernozem with high content of Cd. They reported that the highest content of As was accumulated in spinach grown in Luvisols. The highest Cd content was always found in vegetables grown on contaminated Chernozem soil. Among the vegetables the highest accumulations of As and Cd was found in leaves and roots of spinach. They observed that highest accumulation of As was

found in spinach roots mainly in secondary roots. Radish, carrot and green beans accumulated higher amount of As in roots than in above ground portion.

Chowdhury *et al.* (2002) conducted that an experiment in As effected area of West Bengal, India. They reported that the shallow, large diameter tube wells installed for agricultural irrigation contain and appreciable amount of As (Mean 0.58 mg L^{-1}). They also found that individual food composites and group food contained the highest As levels (μgg^{-1}) were potato skin (0.293 and 0.104), leaf of vegetables (0.212 and 0.294) arum leaf (0.33 and 0.34) papaya (0.196 and 0.373) rice (0.226 and 0.245) wheat (0.007 and 0.362) cumin (0.478 and 0.209) turmeric powder (0.297 and 0.280) cereals and bakery goods (0.136 and 0.294), other vegetables (0.092 and 0.123) species (0.092 and 0.207) for the Jalangi and Domki blocks respectively.

Farid *et al.* (2003) conducted an experiment in both As free and As contaminated irrigation plots, were analyzed for Arsenic. As concentration (ppm) of different vegetables grown in As containing irrigation water found in the descending order of amaranth (0.572) > china shak (0.539) > red amaranth (0.321) > katua data (0.284) > Indian spinach (0.189) > chilli (0.112) > potato (0.103) > bitter gourd (0.049) > cabbage (0.072) > brinjal (0.049) > okra (0.04) > tomato (0.03) > cauliflower (0.011) and that for As free irrigation water were much lower and in the order of china shak (0.278) > red amaranth (0.163) > amaranth (0.139) > katua data (0.114) > chilli (0.103) > Indian spinach (0.1) > potato (0.063) > cabbage (0.055) > okra (0.031) > tomato (0.011) > cauliflower (0.001). Relationship between As in irrigation water and the descending order of tomato ($R^2 = 0.986$) > potato ($R^2=0.889$) > red amaranth ($R^2=0.887$) > katua data ($R^2=0.682$).

Alam (2003) conducted an experiment in Samta village in Jessore district of Bangladesh to see As level of various vegetables. They reported that the highest As concentrations of snake gourd, ghotkol, taro, green papaya, elephant foot and bottle gourd leaf were 0.489, 0.440, 0.446, 0.389, 0.338 and 0.306 $\mu\text{g g}^{-1}$ respectively. Some vegetables such as bottle guard leaf, ghotkol, taro and elephant foot had much higher concentration of Pb. Other leafy vegetables contained higher concentration of Zn and Cu.

Demirezen and Aksoy (2006) have investigated the concentrations of some heavy metals in different vegetables grown in various parts of Turkey. The levels of heavy metals (lead, cadmium, copper, and zinc) have been examined in selected fruits and vegetables sold in local Egyptian markets.

Fytianos *et al.* (2001) studied the contents of heavy metals in vegetables grown in an industrial area of Northern Greece, and Sobukola *et al.* (2010) investigated the concentrations of some heavy metals in fruits and leafy vegetables from selected markets in Lagos, Nigeria.

Jahanara (2007) Collected 400 vegetable samples of 20 varieties of three categories from a local market of Dhaka city for speciation of arsenic (Inorganic arsenic, MMA and DMM) and estimated the amount of inorganic phosphate. The study reported that significant variation in the concentrations of arsenic in leafy vegetables.

Dahal B.M. *et al.* (2008) did an experiment on Arsenic contamination of soils and agricultural plants through irrigation water in Nepal. In that study they monitored the influence of arsenic-contaminated irrigation water on alkaline soils and arsenic uptake in agricultural plants at field level. The arsenic concentrations in irrigation water ranges from <0.005 to

1.014 mg L⁻¹ where the arsenic concentrations in the soils were measured from 6.1 to 16.7 mg As kg⁻¹. The arsenic content in different parts of plants are found in the order of roots > shoots > leaves > edible parts. The mean arsenic content of edible plant material (dry weight) were found in the order of onion leaves (0.55 mg As kg⁻¹) > onion bulb (0.45 mg As kg⁻¹) > cauliflower (0.33 mg As kg⁻¹) > rice (0.18 mg As kg⁻¹) > brinjal (0.09 mg As kg⁻¹) > potato (<0.01 mg As kg⁻¹).

Ismail *et al.* (2009) reported that only heavy metals of Cu, Mn, and Zn were found in tomatoes and brinjals. Zn had the highest while Cu was the lowest mean concentration for both types of brinjals and tomatoes. The concentration of copper is higher in oval brinjal than in long brinjal. The concentration of manganese and zinc were higher in long brinjal compared to oval brinjal. The concentration of copper, manganese and zinc were higher in cherry tomato than in beefsteak tomato. The concentrations of Cd, Cu and Pb in both types of tomatoes and brinjals were lower than those detected in Pakistan. The Zn level was higher than that found in Pakistan tomatoes and brinjals. Although, the concentration of Zn was higher than that reported studies in Pakistan for both tomatoes and brinjals, it was below than Provisional Tolerable Daily Intakes (PTDI) value.

Bhattacharya P. *et al.* (1998) reported that Ganga-Meghna-Bramhaputra basin is one of the major arsenic-contaminated hotspot in the world. Arsenic-contaminated irrigation water (0.318–0.643 mg l⁻¹) and soil (5.70–9.71 mg kg⁻¹) considerably influenced in the accumulation of arsenic in rice, pulses, and vegetables in the study area. The total arsenic concentrations in the studied samples ranged from <0.0003 to 1.02 mg kg⁻¹. The highest and lowest mean arsenic concentrations (milligrams per kilogram) were found in

potato (0.654) and in turmeric (0.003), respectively. Higher mean arsenic concentrations (milligrams per kilogram) were observed in Boro rice grain (0.451), arum (0.407), amaranth (0.372), radish (0.344), Aman rice grain (0.334), lady's finger (0.301), cauliflower (0.293), and Brinjal (0.279).

Anawar H.M. *et al.* (2002) studied to evaluate of Health Risk and Arsenic Levels in Vegetables Sold in Markets of Dhaka (Bangladesh) and Salamanca (Spain) by Hydride Generation Atomic Absorption Spectroscopy. The mean and range of the total As concentration in the vegetables from the markets of Dhaka, Bangladesh were 114 and 1.0–293 $\mu\text{g}/\text{kg}$, respectively. Total As concentration in 77 % of Bangladesh vegetables measured was higher than that recommended by the standard. The mean and range of As concentrations for vegetables grown in Spain were 65 and bdl–130 $\mu\text{g}/\text{kg}$, respectively, for Salamanca, 102 and bdl–423 $\mu\text{g}/\text{kg}$, respectively, for Almeria. The As content of the Bangladesh vegetables was approximately two fold to threefold higher than those observed for the vegetables from Almeria and Salamanca (Spain).

Bhatti S.M. *et al.* (2013) showed As uptake of four vegetable species (carrot, radish, spinach and tomato) with As irrigation levels ranging from 50 to 1000 $\mu\text{g L}^{-1}$ and two irrigation techniques, non-flooded (70% field capacity for all studied vegetables), and flooded (110% field capacity initially followed by aerobic till next irrigation) for carrot and spinach only. Only the 1000 $\mu\text{g As L}^{-1}$ treatment showed a significant increase of As concentration in the vegetables over all other treatments ($P < 0.05$). The distribution of As in vegetable tissues was species dependent; As was mainly found in the roots of tomato and spinach, but accumulated in the leaves and

skin of root crops. The trend of As bioaccumulation was spinach > tomato > radish > carrot.

Lin M.L. *et al.* (2013) studied inductively coupled plasma mass spectrometry coupled with ultrasonic slurry sampling electro thermal vaporization (USS-ETV-ICP-MS) has been applied to determine As, Cd, Hg and Pb in 0.5% m/v slurries of several herb samples. This method has been applied to the determination of As, Cd, Hg and Pb in NIST SRM 1547 peach leaves and SRM 1573a tomato leaves reference materials and three herb samples purchased from the local market and ground to 150 μ m. The analysis results of the standard reference materials agreed with the certified values which are at sub μ g g⁻¹ levels. The method detection limits estimated from standard addition curves were about 0.3, 0.1, 0.1 and 0.2 ng g⁻¹ for As, Cd, Hg and Pb, respectively, in original herb samples.

Carbonell-Barrachina A.A. *et al.* (1999) investigated The response of tomato (*Lycopersicon esculentum* Mill, cultivar Marmande) plants to different levels of arsenic (As) in nutrient solution the processes of uptake, distribution and accumulation of As, and the effect of arsenite on yield and plant growth. The experiment was performed at three levels of As: 2, 5 and 10 mg/L [added as sodium arsenite (NaAsO₂)] in a nutrient solution, together with the corresponding control plants. Arsenic uptake depended on the As concentration in solution and As content in the roots increased as the time of treatment increased. Although the As level of 10 mg/L damaged the root membranes, resulting in a significant decrease in the upward transport of As. Arsenic exposure resulted in a drastic decrease in plant growth parameters (e.g. maximum decrease of 76.8% in leaf fresh weight) and in tomato fruit yield (maximum reduction of 79.6%). However, it is important

to note that the As concentration in the fruits was not toxic or harmful for human consumption.

Burló F. *et al.* (1999) showed that the uptake of arsenic (As) species by *Lycopersicon esculentum*, growing under soilless culture conditions, was studied. A 4×3×2 factorial experiment was conducted with four As species (arsenite, arsenate, methylarsonate, and dimethylarsinate), three As concentrations (1, 2, and 5 mg L⁻¹) and two tomato cultivars (Marmande and Muchamiel). The phytoavailability and phytotoxicity were primarily determined by the As species. Both MA and DMA showed a higher upward translocation than arsenite and arsenate, and treatments with MA and DMA clearly reduced plant growth and fruit yield. The As concentration in tomatoes treated with arsenite or arsenate were within the range considered normal in food crops; however, the As concentration in tomatoes treated with MA and DMA were close to or even above the maximum limit.

Saraswati *et al.* (1994) determined the arsenic and selenium in spinach and tomato leaves reference materials using flow injection and atomic absorption spectrometry which was developed for the determination of trace amounts of arsenic and selenium in proposed spinach and tomato leaves standard reference materials (SRM 1570a and SRM 1573a). The method has detection limits of 0.15 ng As/ml and 0.17 ng Se/ml. Standard Reference Materials (SRM 1571 and 1547) were analyzed and the results agreed well with the certified values.

McBride M. B. (2012) studies in Arsenic and Lead Uptake by Vegetable Crops Grown on Historically Contaminated Orchard Soils. Here Transfer of Pb and As into vegetables grown on orchard soils historically contaminated

by Pb arsenate pesticides was measured in the greenhouse. Lettuce, carrots, green beans, and tomatoes were grown on soils containing a range of total Pb (16.5–915 mg/kg) and As (6.9–211 mg/kg) concentrations. Arsenic concentrations were the highest in lettuce and green beans, lower in carrots, and much lower in tomato fruit. Transfer of Pb into lettuce and beans was generally lower than that of As, and Pb and As were strongly excluded from tomato fruit.

Calatayud M. *et al.* (2013) studied about Transformation of arsenic species during in vitro gastrointestinal digestion of vegetables. This study evaluates the effect of in vitro gastrointestinal digestion on pentavalent arsenic forms [As(V), MMA(V), DMA(V)] present in various vegetables (garlic, broccoli, asparagus, spinach) after soaking or boiling in aqueous solutions of these species. Results showed transformation of up to 22% to As(III), 35% to MMA(III)/MMAS, and 26% to DMA(III)/DMAS.

Carbonell-Barrachina A.A. *et al.* (1995) studied in influence of arsenite concentration on arsenic accumulation in tomato and bean plants. Tomato and bean plants were grown in nutrient solution containing four levels of arsenite: 0, 2, 5, and 10 mg As l⁻¹. Arsenite was phytotoxic to both plant species; tomato plants, however, were more tolerant to As pollution than bean plants. Arsenic in tomato root tissue seemed to be so effectively compartmentalized that its impact in plant growth and metabolism was minimal. However, in bean plants upon uptake, As was readily transported to shoots and accumulated to high concentrations in leaf tissue. The observed differential absorption and translocation of arsenite or its metabolized species by tomato and bean plants were probably responsible for the different plant tolerance to As pollution.

Melo E.E. *et al.* (2009) in his study of Accumulation of arsenic and nutrients by castor bean plants grown on an As-enriched nutrient solution under greenhouse conditions in pots containing a nutrient solution with increasing doses of As (0, 10, 50, 100, 250, 500 and 5000 $\mu\text{g L}^{-1}$) in a completely randomized design with four replications, showed that increasing As concentration in nutrient solution caused a decrease in shoot and root biomass but did not result in severe toxicity symptoms in castor bean growing under a range of As concentration from 0 to 5000 $\mu\text{g g}^{-1}$. The As doses tested did not affect the accumulation of nutrients by castor bean.

Paloma M. *et al.* (2013) showed in their study Uptake and Accumulation of Arsenic in Different Organs of Carrot Irrigated with As-Rich Water that the translocation of As from root to shoot and leaves in carrot plant. Both roots and leaves demonstrated a higher accumulation rate of As at an As concentration of 41 than 131 $\mu\text{g L}^{-1}$ in the soil solution. The ratios of $\text{As}_{\text{root}}/\text{As}_{\text{leaves}}$ showed no statistically significant differences for the different irrigation treatments, and had an average value of 0.36 indicating the high magnitude of As translocation from roots to leaves in carrot plants. The leaves of carrots had a higher affinity for As than roots did.

Codling E. E. *et al.* (2012) in their study Accumulation of Lead and Arsenic by Carrots Grown on Lead-Arsenate Contaminated Orchard Soils showed that Total concentrations of arsenic and lead in these soils ranged from 93 to 291 and from 350 to 961 mg kg^{-1} for arsenic and lead, respectively. Arsenic in peeled carrot ranged from 0.38 to 1.64 mg kg^{-1} , while lead ranged from 2.67 to 7.3 mg kg^{-1} dry weight. This study demonstrated that carrots will accumulate arsenic and lead in the root, which may become a human health risk when consumed.



Sharma R.K. *et al.* (2009) tested vegetables (*Beta vulgaris* L., *Abelmoschus esculentus* L. and *Brassica oleracea* L.) from the production and market sites of India for Cu, Cd, Zn and Pb. At market sites, the mean concentration of Cu in cauliflower and of Zn and Cd in both palak and cauliflower had exceeded the PFA standard. Zn at the production sites also exceeded the PFA standard in cauliflower. Cd concentration in vegetables tested from both production and market sites was many folds higher than the EU standard. The contributions of these vegetables to dietary intake of Cu, Zn, Cd and Pb were 13%, 1%, 47% and 9% of provisional tolerable daily intake, respectively.



CHAPTER 3

MATERIALS AND METHODS

MATERIALS AND METHODS

This chapter includes the details of the materials and methods of this research work. The experimental materials, site, experimental design, collection of vegetables samples etc are described under their headings below. This study was undertaken during the season 2013-14 to determine the status of arsenic and other heavy metals in vegetables from Four Outlets of different Four Super Shops of Dhaka city.

3.1. Experimental site:

Primarily the raw sample were washed and cut in the Botany department laboratory of Jahangirnagar University. Then they were dried in oven in the Lab. Of Dept. of Microbiology in Jahangirnagar University. The samples were grinded and digested in the Heavy Metal Analysis Laboratory of Soil Recourses Development Institute (SRDI).

3.2. Sampling site and location:

Samples were collected from four super shops located in Dhaka city. They were:

S.N.	Super Shop Name	Outlets Location
1	Aagora	Zhigatola Outlet
2	Nandan	Dhanmondi 27 Outlet
3	Meena Bazaar	Dhanmondi 15 Outlet
4	Shwapno	Mirpur Outlet

3.3. Collection of vegetables sample:

Samples were collected from 04 (Four) outlets of Dhaka city randomly. They were arranged in shelves in wet condition under light. 11 samples were collected from respected outlets, thus the total $11 \times 4 = 44$ samples from each outlet in different amount as below:

The amount of vegetables is given below:

Kinds of vegetables	SL No.	English Name	Amount
Leafy Vegetables	1	Spinach	1000 g
	2	Red Spinach	1000 g
	3	Cabbage	1 pc
Fruity Vegetables	1	Tomato	1000 g
	2	Brinjal	1000 g
	3	Bottle gourd	1000 g
	4	Bitter gourd	1000 g
	5	Bean	1000 g
	6	Cauliflower	1 pc
Roots and tubers	1	Carrot	1000 g
	2	Radish	1000 g

The amount of vegetables samples was more or less same. The vegetable samples were put into the individual polythene bag with definite marking and tagging and kept in fridge at temperature of around 0° C as the sample collection was not possible at a time. After collecting all the samples from all the outlets roots, rotten parts and other extraneous materials were removed. Then they were washed in cool water and then kept in air tight polythene bag by tagging in fridge again until preparing for drying.

3.4. Types of vegetables:

Type of Vegetables	SL No.	English Name	Scientific Name	Family Name
Leafy Vegetables	1	Spinach	<i>Spinacia oleraceae</i>	Chenopodiaceae
	2	Red Spinach	<i>Amaranthus tricolor</i>	Amaranthaceae
	3	Cabbage	<i>Brassica oleraceus var. capitata</i>	Cruciferae
Fruity Vegetables	1	Tomato	<i>Lycopersicon esculentum</i>	Solanaceae
	2	Brinjal	<i>Solanum melongena</i>	Solanaceae
	3	Bottle gourd	<i>Lagenaria</i>	Cucurbitaceae
	4	Bitter gourd	<i>Momordica charantia</i>	Cucurbitaceae
	5	Bean	<i>Lablab niger var. sativum</i>	Fabaceae
	6	Cauliflower	<i>Brassica oleraceae var. botrytis sub. Var. cauliflower</i>	Cruciferae
Roots and tubers	1	Carrot	<i>Daucus carota subsp. sativus</i>	Apiaceae
	2	Radish	<i>Raphanus sativus</i>	Cruciferae

3.5. Experimental Design:

Subsamples were taken at random. Collected Samples were prepared for experiment in this way:

3.5.1. Sample Chopping:

Samples stored in freeze firstly kept in normal temperature for sometimes. Then they were kept in chopping board and chopped by a sharp knife. The chopped sample pieces were near about 0.5 inch.

3.5.2. Sun Drying:

The chopped sample pieces were kept under sun light for 7 days. It was done for partial drying. When the samples lost their wet condition they were packed by aluminum foil.

3.5.3. Oven drying:

The partial by sun dried samples were kept in racks of the Drying Oven. Then the Oven was set at 45 ° C for 24 hours and 30 ° C for next 24 hours. As all of the samples could not be to dry at a time so the sun dried samples were kept in air tight poly bags.

3.5.4. Sample Grinding:

All the samples were powdered manually in a grinder individually. The grinded samples were kept in air tight poly bags.

3.6. Vegetables analysis

3.6.1. Sample Digestion:

The vegetable sample weighing 0.5 g was transferred into a dry clean digestion vessel. 10 mL Nitric Acid (HNO_3) was added to the vessel and allowed it for 30 minutes to heat at 95-105°C. Then the sample allowed standing it for overnight with covering the vessel to vapor recovery device. The following day, the digestion vessel was placed on a heating block and was heated at a temperature slowly raised to 115-120 °C until the digestion became clear. After cooling, 2 mL of Hydrogen Per oxide (H_2O_2) was added and kept for few minutes. Again the vessel was heated at 120-125 °C. Heating was stopped when the liquid sample was clear after which the volume was reduced to 5 mL. The digest was cooled, diluted to 50 mL with deionized water and filtered through Whatman No. 42 filter paper into plastic bottle.(Haque 2003)

3.6.2. Analysis:

Concentration of heavy metals in the acidic solution was estimated using Atomic absorption spectrophotometer, (Chemito Technologies Pvt. Ltd., India, Model No – AA – 203, Slit width 0.5 nm). Estimations were carried out using the hollow cathode lamps depending upon the element to be tested. The results were expressed as $\mu\text{g g}^{-1}$ (on a dry weight basis).

3.7. Standards:

Standard solutions of the heavy metals namely Arsenic (As), Lead (Pb), Cadmium (Cd) was provided by Merck (Darmstadt, Germany). The standards were prepared from the individual 1000 mg/L standards (Merck) supplied in 0.1 N HNO₃.

3.8. Quality Assurance:

Appropriate quality assurance procedures and precautions were taken to ensure the reliability of the results. Samples were carefully handled to avoid cross contamination.

Glassware was properly cleaned, and reagents used were of analytical grades. Deionized water was used throughout the study. Reagent blank determinations were used to apply corrections to the instrument readings.

CHAPTER 4

RESULTS AND DISCUSSION

RESULTS AND DISCUSSIONS

The result on different amount of As and other heavy metals concentration in the different type of vegetables collected from different outlets are presented in this chapter.

4.1. Aagora Super Shop:

Table 1: Heavy metals concentration in different vegetables

Type of Vegetables	S.N.	Name of Vegetables	Heavy Metals amount in $\mu\text{g g}^{-1}$		
			As	Cd	Pb
Leafy Vegetables	1	Spinach	1.31	0.29	0.85
	2	Red Spinach	1.19	0.39	0.63
	3	Cabbage	0.98	0.26	0.81
Fruity Vegetables	4	Tomato	0.95	0.42	0.46
	5	Brinjal	0.96	0.41	0.47
	6	Bottle gourd	0.62	0.47	0.53
	7	Bitter gourd	1.07	0.31	0.59
	8	Bean	0.78	0.36	0.11
	9	Cauliflower	0.82	0.32	0.31
Root Vegetables	10	Radish	0.97	0.38	0.41
	11	Carrot	0.47	0.27	0.32

The results were expressed a wide variation of heavy metals of different types of vegetables.

Arsenic (As)

The As concentrations of the vegetables ranged from 0.47 $\mu\text{g g}^{-1}$ in Carrot to 1.31 $\mu\text{g g}^{-1}$ in Spinach. In case of Leafy vegetables the range was 0.98 $\mu\text{g g}^{-1}$ in Cabbage to 1.31 $\mu\text{g g}^{-1}$ in Spinach. For Fruity vegetables the range was from 0.62 $\mu\text{g g}^{-1}$ in Bottle gourd to 1.07 $\mu\text{g g}^{-1}$ in Bitter gourd. In case of root vegetable As found in Radish and Carrot was 0.97 $\mu\text{g g}^{-1}$ and 0.47 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order As concentrations ($\mu\text{g g}^{-1}$) Spinach (1.31) > Red Spinach (1.19) > Bitter Gourd (1.07) > Cabbage (0.98) > Radish (0.97) > Brinjal > (0.96) > Tomato (0.95) > Cauliflower (0.82) > Bean (0.78) > Bottle Gourd (0.62) > Carrot (0.47).

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Cadmium (Cd)

The Cd concentrations of the vegetables ranged from 0.26 $\mu\text{g g}^{-1}$ in Cabbage to 0.47 $\mu\text{g g}^{-1}$ in Bottle Gourd. In case of Leafy vegetables the range was 0.26 $\mu\text{g g}^{-1}$ in Cabbage to 0.39 $\mu\text{g g}^{-1}$ in Red Spinach. For Fruity vegetables the range was from 0.31 $\mu\text{g g}^{-1}$ in Bitter gourd to 0.47 $\mu\text{g g}^{-1}$ in Bottle gourd. In case of root vegetable Cd found in Radish and Carrot was 0.38 $\mu\text{g g}^{-1}$ and 0.27 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Cd concentrations ($\mu\text{g g}^{-1}$) Bottle Gourd (0.47) > Tomato (0.42) > Brinjal (0.41) > Red Spinach (0.39) > Radish (0.38) > Bean (0.36) > Cauliflower (0.32) > Bitter Gourd (0.31) > Spinach (0.29) > Carrot (0.27) > Cabbage (0.26).

Lead (Pb)

The Pb concentrations of the vegetables ranged from $0.11 \mu\text{g g}^{-1}$ in Bean to $0.85 \mu\text{g g}^{-1}$ in Spinach. In case of Leafy vegetables the range was $0.63 \mu\text{g g}^{-1}$ in Red Spinach to $0.85 \mu\text{g g}^{-1}$ in Spinach. For Fruity vegetables the range was from $0.11 \mu\text{g g}^{-1}$ in Bean to $0.59 \mu\text{g g}^{-1}$ in Bitter gourd. In case of root vegetable Pb found in Radish and Carrot was $0.41 \mu\text{g g}^{-1}$ and $0.32 \mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Pb concentrations ($\mu\text{g g}^{-1}$) Spinach (0.85) > Cabbage (0.81) > Red Spinach (0.63) > Bitter Gourd (0.59) > Bottle Gourd (0.53) > Brinjal (0.47) > Tomato (0.46) > Radish (0.41) > carrot (0.32) > Cauliflower (0.31) > Bean (0.11).

4.2. Nandan Super Shop:

Table 2: Heavy metals concentration in different vegetables

Type of Vegetables	S.N.	Name of Vegetables	Heavy Metals amount in $\mu\text{g g}^{-1}$		
			As	Cd	Pb
Leafy Vegetables	1	Spinach	1.09	0.36	0.35
	2	Red Spinach	1.13	0.21	0.42
	3	Cabbage	0.91	0.23	0.61
Fruity Vegetables	4	Tomato	1.23	0.52	0.52
	5	Brinjal	0.92	0.49	0.47
	6	Bottle gourd	0.52	0.51	0.51
	7	Bitter gourd	0.72	0.26	0.57
	8	Bean	0.71	0.39	0.28
	9	Cauliflower	0.89	0.22	0.40
Root Vegetables	10	Radish	0.99	0.29	0.36
	11	Carrot	0.41	0.37	0.21

The results were expressed a wide variation of heavy metals of different types of vegetables.

Arsenic (As)

The As concentrations of the vegetables ranged from 0.41 $\mu\text{g g}^{-1}$ in Carrot to 1.23 $\mu\text{g g}^{-1}$ in Tomato. In case of Leafy vegetables the range was 0.91 $\mu\text{g g}^{-1}$ in Cabbage to 1.13 $\mu\text{g g}^{-1}$ in Red Spinach. For Fruity vegetables the range was from 0.52 $\mu\text{g g}^{-1}$ in Bottle gourd to 1.23 $\mu\text{g g}^{-1}$ in Tomato. In case of root vegetable As found in Radish and Carrot was 0.99 $\mu\text{g g}^{-1}$ and 0.41 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order As concentrations ($\mu\text{g g}^{-1}$) Tomato (1.23) > Red Spinach (1.13) > Spinach (1.09) > Radish (0.23) > Brinjal (0.92) > Cabbage (0.89) > Cauliflower (0.89) > Bitter Gourd (0.72) > Bean (0.71) > Bottle Gourd (0.52) > Carrot (0.41).

Cadmium (Cd)

The Cd concentrations of the vegetables ranged from 0.21 $\mu\text{g g}^{-1}$ in Red Spinach to 0.52 $\mu\text{g g}^{-1}$ in Tomato. In case of Leafy vegetables the range was 0.21 $\mu\text{g g}^{-1}$ in Red Spinach to 0.36 $\mu\text{g g}^{-1}$ in Spinach. For Fruity vegetables the range was from 0.26 $\mu\text{g g}^{-1}$ in Bitter gourd to 0.52 $\mu\text{g g}^{-1}$ in Tomato. In case of root vegetable Cd found in Radish and Carrot was 0.29 $\mu\text{g g}^{-1}$ and 0.37 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Cd concentrations ($\mu\text{g g}^{-1}$) Tomato (0.52) > Bottle Gourd (0.51) > Brinjal (0.49) > Bean (0.39) > Carrot (0.37) > Spinach (0.36) > Radish (0.29) > Bitter Gourd (0.26) > Cabbage (0.23) > Cauliflower (0.22) > Red Spinach (0.21).

Lead (Pb)

The Pb concentrations of the vegetables ranged from 0.21 $\mu\text{g g}^{-1}$ in Carrot to 0.61 $\mu\text{g g}^{-1}$ in Cabbage. In case of Leafy vegetables the range was 0.35 $\mu\text{g g}^{-1}$ in Spinach to 0.61 $\mu\text{g g}^{-1}$ in Cabbage. For Fruity vegetables the range was from 0.28 $\mu\text{g g}^{-1}$ in Bean to 0.57 $\mu\text{g g}^{-1}$ in Bitter Gourd. In case of root vegetable Pb found in Radish and Carrot was 0.36 $\mu\text{g g}^{-1}$ and 0.21 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Pb concentrations ($\mu\text{g g}^{-1}$) Cabbage (0.61) > Bitter Gourd (0.57) > Tomato (0.52) > Bottle Gourd (0.51) > Brinjal (0.47) > Red Spinach (0.42) > Cauliflower (0.40) > Radish (0.36) > Spinach (0.35) > Bean (0.28) > carrot (0.21).

4.3. Swapno Super Shop:

Table 3: Heavy metals concentration in different vegetables

Type of Vegetables	S.N.	Name of Vegetables	Heavy Metals amount in $\mu\text{g g}^{-1}$		
			As	Cd	Pb
Leafy Vegetables	1	Spinach	1.33	0.27	0.81
	2	Red Spinach	1.11	0.34	0.60
	3	Cabbage	0.99	0.24	0.77
Fruity Vegetables	4	Tomato	0.94	0.38	0.41
	5	Brinjal	0.95	0.36	0.42
	6	Bottle gourd	0.60	0.42	0.50
	7	Bitter gourd	1.00	0.29	0.55
	8	Bean	0.75	0.31	0.07
	9	Cauliflower	0.81	0.30	0.29
Root Vegetables	10	Radish	0.98	0.33	0.38
	11	Carrot	0.41	0.26	0.30

The results were expressed a wide variation of heavy metals of different types of vegetables.



Arsenic (As)

The As concentrations of the vegetables ranged from 0.41 $\mu\text{g g}^{-1}$ in Carrot to 1.03 $\mu\text{g g}^{-1}$ in Spinach. In case of Leafy vegetables the range was 0.99 $\mu\text{g g}^{-1}$ in Cabbage to 1.33 $\mu\text{g g}^{-1}$ in Spinach. For Fruity vegetables the range was from 0.60 $\mu\text{g g}^{-1}$ in Bottle gourd to 1.00 $\mu\text{g g}^{-1}$ in Bitter gourd. In case of root vegetable As found in Radish and Carrot was 0.98 $\mu\text{g g}^{-1}$ and 0.41 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order As concentrations ($\mu\text{g g}^{-1}$) Spinach (1.33) > Red Spinach (1.11) > Bitter Gourd (1.00) > Cabbage (0.99) > Radish (0.98) > Brinjal > (0.95) > Tomato (0.94) > Cauliflower (0.81) > Bean (0.75) > Bottle Gourd (0.60) > Carrot (0.41).

Cadmium (Cd)

The Cd concentrations of the vegetables ranged from 0.24 $\mu\text{g g}^{-1}$ in Cabbage to 0.42 $\mu\text{g g}^{-1}$ in Bottle Gourd. In case of Leafy vegetables the range was 0.24 $\mu\text{g g}^{-1}$ in Cabbage to 0.34 $\mu\text{g g}^{-1}$ in Red Spinach. For Fruity vegetables the range was from 0.29 $\mu\text{g g}^{-1}$ in Bitter gourd to 0.42 $\mu\text{g g}^{-1}$ in Bottle gourd. In case of root vegetable Cd found in Radish and Carrot was 0.33 $\mu\text{g g}^{-1}$ and 0.26 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Cd concentrations ($\mu\text{g g}^{-1}$) Bottle Gourd (0.42) > Tomato (0.38) > Brinjal (0.36) > Red Spinach (0.34) > Radish (0.33) > Bean (0.31) > Cauliflower (0.30) > Bitter Gourd (0.29) > Spinach (0.27) > Carrot (0.26) > Cabbage (0.24).

Lead (Pb)

The Pb concentrations of the vegetables ranged from $0.07 \mu\text{g g}^{-1}$ in Bean to $0.81 \mu\text{g g}^{-1}$ in Spinach. In case of Leafy vegetables the range was $0.60 \mu\text{g g}^{-1}$ in Red Spinach to $0.81 \mu\text{g g}^{-1}$ in Spinach. For Fruity vegetables the range was from $0.07 \mu\text{g g}^{-1}$ in Bean to $0.55 \mu\text{g g}^{-1}$ in Bitter gourd. In case of root vegetable Pb found in Radish and Carrot was $0.38 \mu\text{g g}^{-1}$ and $0.30 \mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Pb concentrations ($\mu\text{g g}^{-1}$) Spinach (0.81) > Cabbage (0.77) > Red Spinach (0.60) > Bitter Gourd (0.55) > Bottle Gourd (0.50) > Brinjal (0.42) > Tomato (0.41) > Radish (0.38) > carrot (0.30) > Cauliflower (0.29) > Bean (0.07).



4.4. Meena Bazaar Super Shop:

Table 4: Heavy metals concentration in different vegetables

Type of Vegetables	S.N.	Name of Vegetables	Heavy Metals amount in $\mu\text{g g}^{-1}$		
			As	Cd	Pb
Leafy Vegetables	1	Spinach	1.22	0.38	0.37
	2	Red Spinach	1.37	0.25	0.45
	3	Cabbage	0.95	0.28	0.65
Fruity Vegetables	4	Tomato	1.24	0.59	0.55
	5	Brinjal	0.98	0.51	0.49
	6	Bottle gourd	0.55	0.55	0.54
	7	Bitter gourd	0.78	0.29	0.59
	8	Bean	0.72	0.41	0.30
	9	Cauliflower	0.91	0.27	0.43
Root Vegetables	10	Radish	1.04	0.33	0.39
	11	Carrot	0.48	0.39	0.23

The results were expressed a wide variation of heavy metals of different types of vegetables.

Arsenic (As)

The As concentrations of the vegetables ranged from 0.48 $\mu\text{g g}^{-1}$ in Carrot to 1.49 $\mu\text{g g}^{-1}$ in Tomato. In case of Leafy vegetables the range was 0.95 $\mu\text{g g}^{-1}$ in Cabbage to 1.37 $\mu\text{g g}^{-1}$ in Red Spinach. For Fruity vegetables the range was from 0.55 $\mu\text{g g}^{-1}$ in Bottle gourd to 1.49 $\mu\text{g g}^{-1}$ in Tomato. In case of root vegetable Arsenic found in Radish and Carrot was 1.04 $\mu\text{g g}^{-1}$ and 0.48 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order As concentrations ($\mu\text{g g}^{-1}$) Tomato (1.24) > Red Spinach (1.22) > Spinach (1.20) > Radish (1.04) > Brinjal (0.98) > Cabbage (0.95) > Cauliflower (0.91) > Bitter Gourd (0.78) > Bean (0.72) > Bottle Gourd (0.55) > Carrot (0.48).

Cadmium (Cd)

The Cd concentrations of the vegetables ranged from 0.25 $\mu\text{g g}^{-1}$ in Red Spinach to 0.59 $\mu\text{g g}^{-1}$ in Tomato. In case of Leafy vegetables the range was 0.25 $\mu\text{g g}^{-1}$ in Red Spinach to 0.38 $\mu\text{g g}^{-1}$ in Spinach. For Fruity vegetables the range was from 0.28 $\mu\text{g g}^{-1}$ in Bitter gourd to 0.59 $\mu\text{g g}^{-1}$ in Tomato. In case of root vegetable Cd found in Radish and Carrot was 0.23 $\mu\text{g g}^{-1}$ and 0.39 $\mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Cd concentrations ($\mu\text{g g}^{-1}$) Tomato (0.59) > Bottle Gourd (0.55) > Brinjal (0.51) > Bean (0.41) > Carrot (0.39) > Spinach (0.38) > Radish (0.33) > Bitter Gourd (0.29) > Cabbage (0.28) > Cauliflower (0.27) > Red Spinach (0.25).

Lead (Pb)

The Pb concentrations of the vegetables ranged from $0.23 \mu\text{g g}^{-1}$ in Carrot to $0.65 \mu\text{g g}^{-1}$ in Cabbage. In case of Leafy vegetables the range was $0.37 \mu\text{g g}^{-1}$ in Spinach to $0.65 \mu\text{g g}^{-1}$ in Cabbage. For Fruity vegetables the range was from $0.30 \mu\text{g g}^{-1}$ in Bean to $0.59 \mu\text{g g}^{-1}$ in Bitter Gourd. In case of root vegetable Pb found in Radish and Carrot was $0.39 \mu\text{g g}^{-1}$ and $0.23 \mu\text{g g}^{-1}$ respectively. The vegetable can be arranged in the descending order Pb concentrations ($\mu\text{g g}^{-1}$) Cabbage (0.65) > Bitter Gourd (0.59) > Tomato (0.55) > Bottle Gourd (0.54) > Brinjal (0.49) > Red Spinach (0.45) > Cauliflower (0.43) > Radish (0.39) > Spinach (0.37) > Bean (0.30) > carrot (0.23).

These study showed the differences in the As, Cd, and Pb concentrations ($\mu\text{g/g}$) of different vegetable species in different locations. In all these vegetables regardless of four outlets, a similar trend in metal contents was observed i.e.

In case of As , the descending order of the vegetables according to the content of As was Red Spinach > Radish > Brinjal > Cauliflower > Bean > Bottle Gourd > Carrot.

Wherever Haque, M.E. (2004) observed in experiment with arsenic content on various types of vegetables that Arsenic concentration of different vegetables in the descending order of Cabbage > Bitter Gourd > Tomato > Cauliflower > Spinach > Brinjal > Bean > Bottle Gourd.

Smiled *et al.* (1982) carried out the order of decreasing arsenic accumulation was Radish> Lettuce> Carrot> Potato> Spring Wheat grain.

Bhatti SM *et al.* (2013) showed the trend of As bio accumulation was spinach > tomato > radish > carrot.

The trend in Cd content , the order was Bottle Gourd > Brinjal > Radish > Bitter Gourd > Cabbage> Red spinach.

Haque, M.E. (2004) reported that, Bitter Gourd > Bottle Gourd > Tomato > Cabbage > Bean > Brinjal.

In findings of Alamgir and Chakrabarty (2000) according to mean concentration of As in vegetables the descending order was Bottle Gourd > Brinjal > Carrot > Cabbage > Radish > Tomato.

For Pb , the descending order of the vegetables analyzed was Spinach > Bottle Gourd > Brinjal > Radish > Bean.

Haque, M.E. (2004) found that the Pb concentration as Spinach > Radish > Bitter Gourd > Bottle Gourd > Tomato > Bean.

Alamgir and Chakrabarti (2000) showed that in Pb content the order was Tomato > Radish > Cauliflower > Bottle Gourd > Brinjal.



4.5. The range of (As) concentration of vegetables from four outlets:

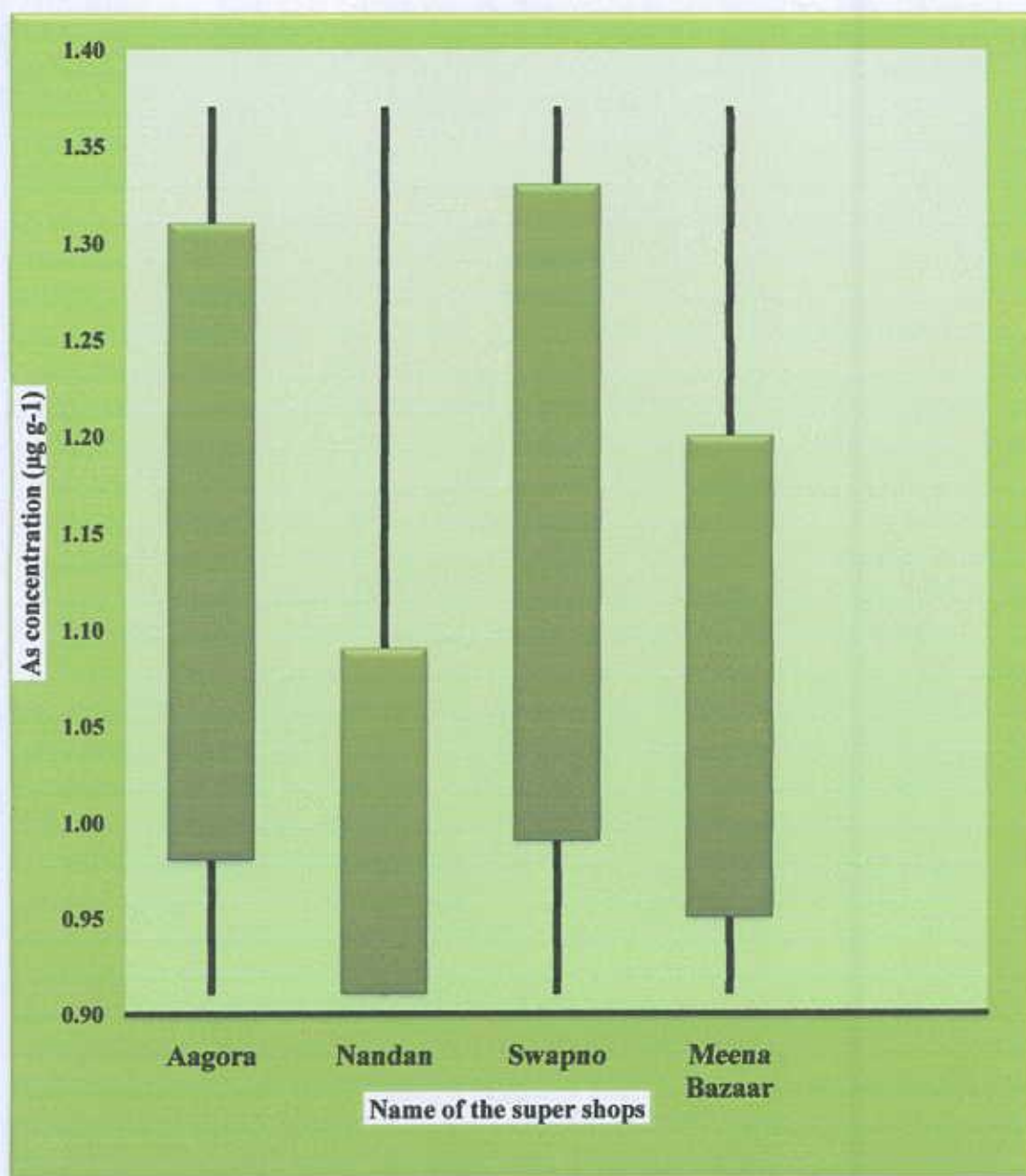


Figure: 01- The highest and lowest range of As concentration ($\mu\text{g g}^{-1}$) of Leafy vegetables

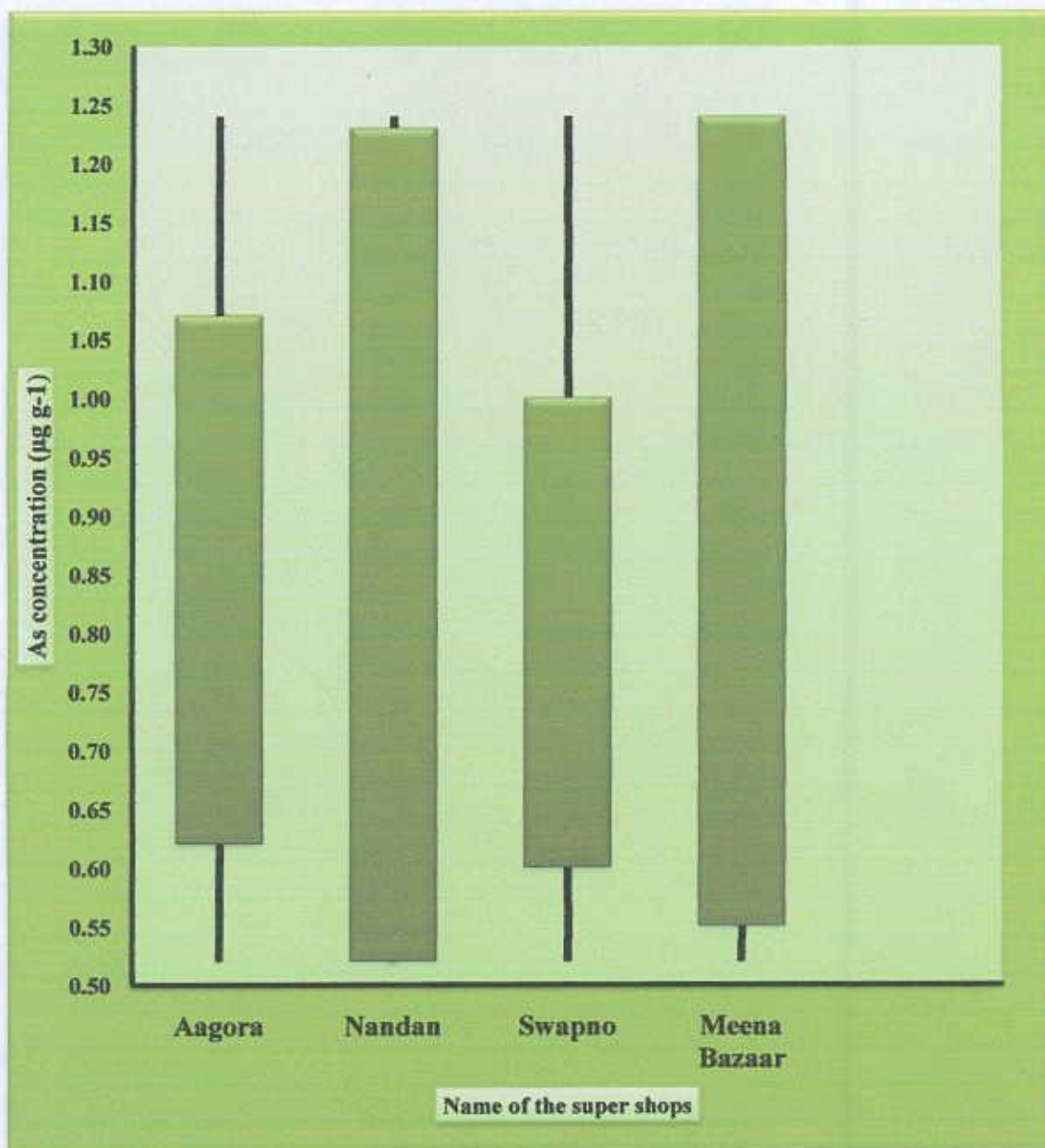


Figure: 02- The highest and lowest range of As concentration ($\mu\text{g g}^{-1}$) of Fruity vegetables

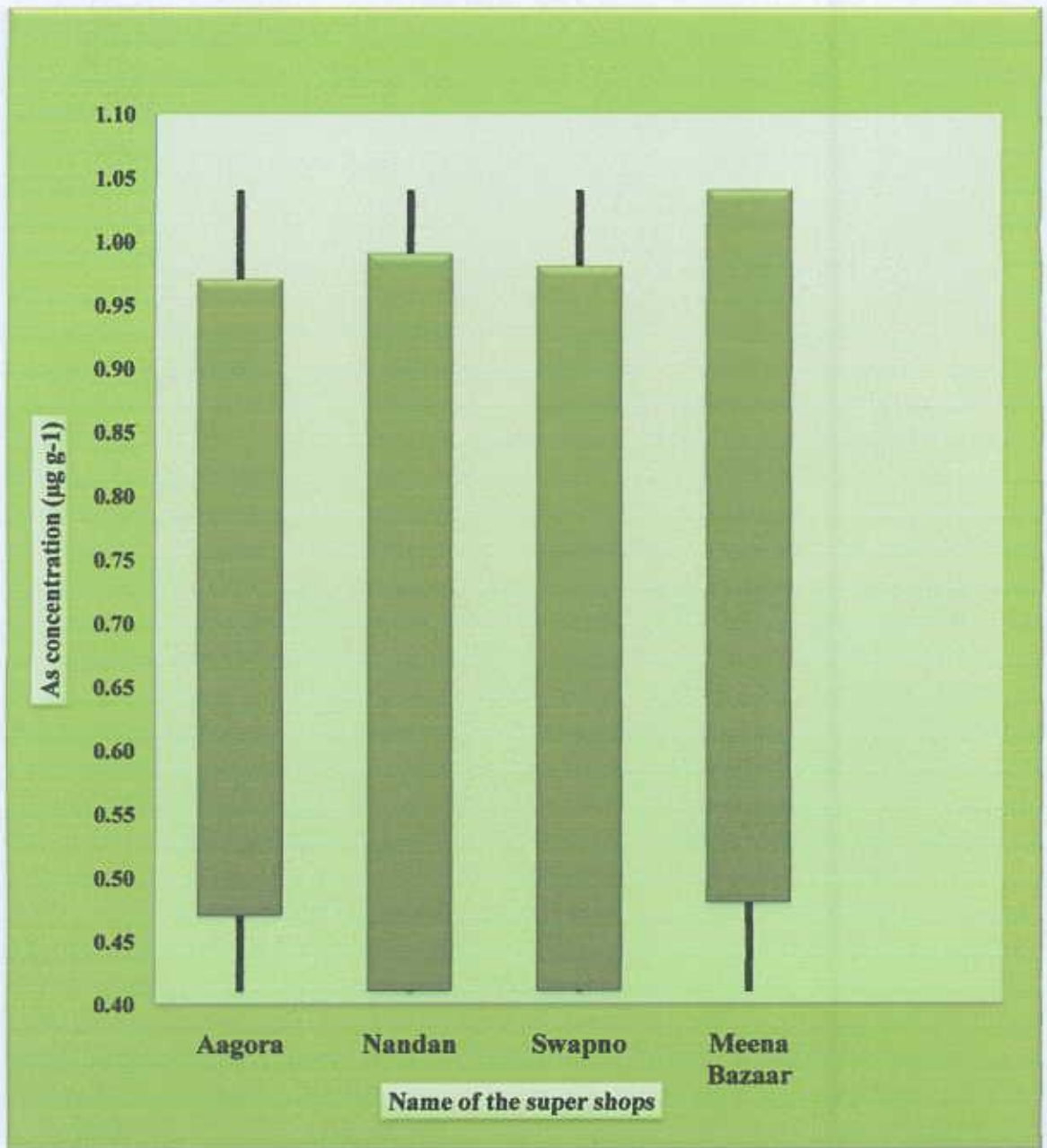


Figure: 03- The highest and lowest range of As concentration ($\mu\text{g g}^{-1}$) of root vegetables

4.6. The range of Cadmium (Cd) concentration of vegetables in four outlets:

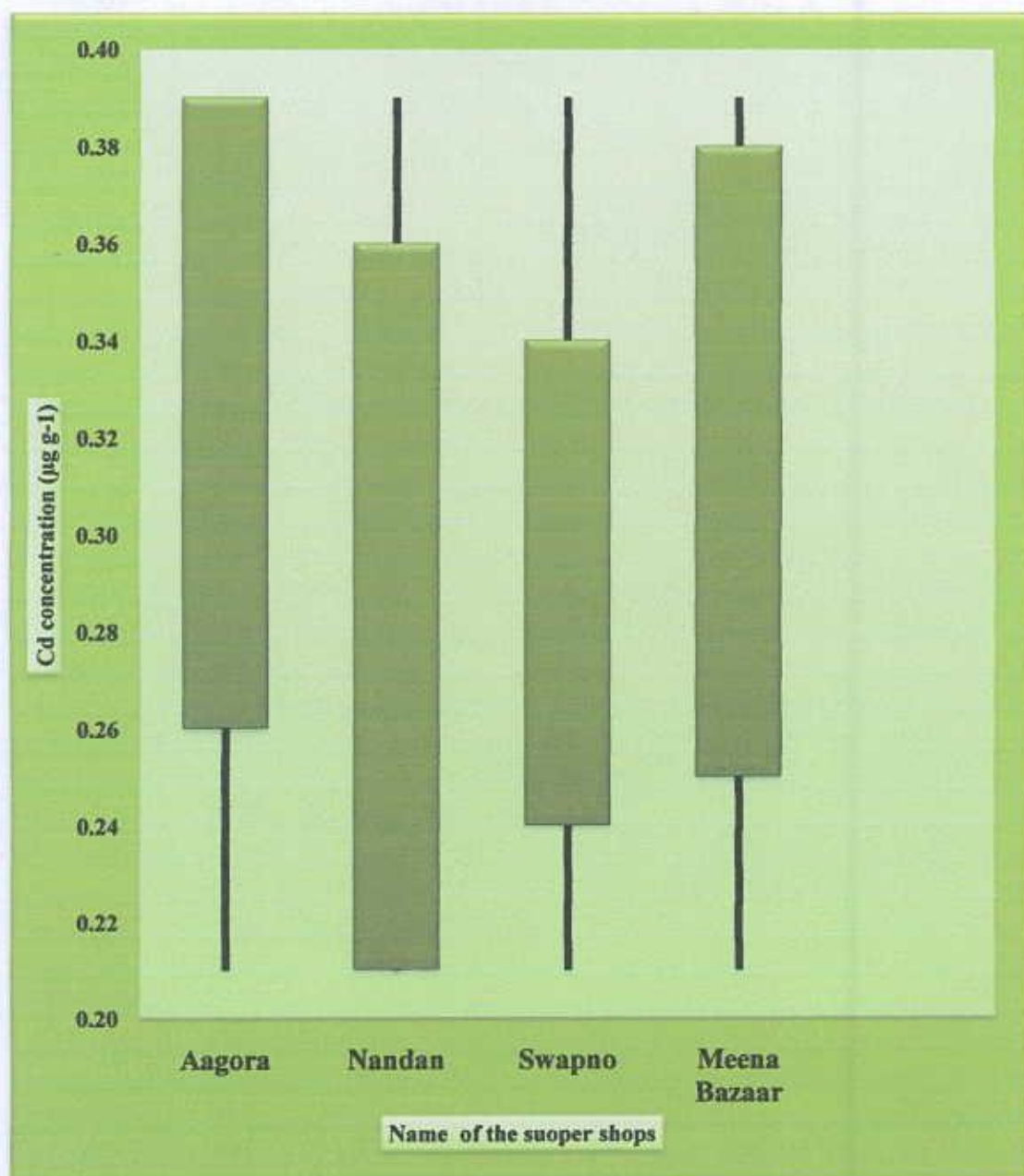


Figure: 04- The highest and lowest range of Cd concentration ($\mu\text{g g}^{-1}$) of Leafy vegetables

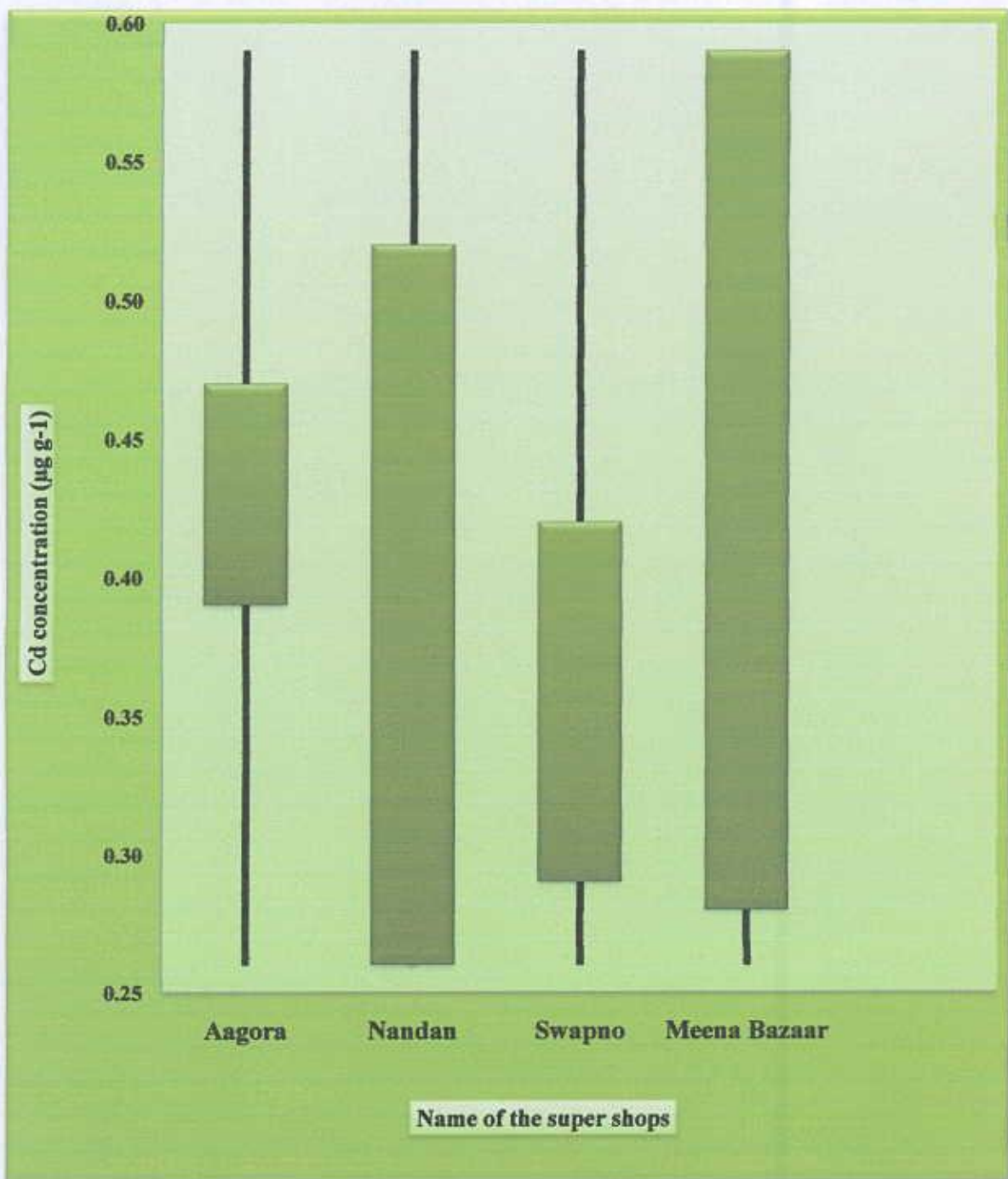


Figure: 05- The highest and lowest range of Cd concentration ($\mu\text{g g}^{-1}$) of Fruity vegetables

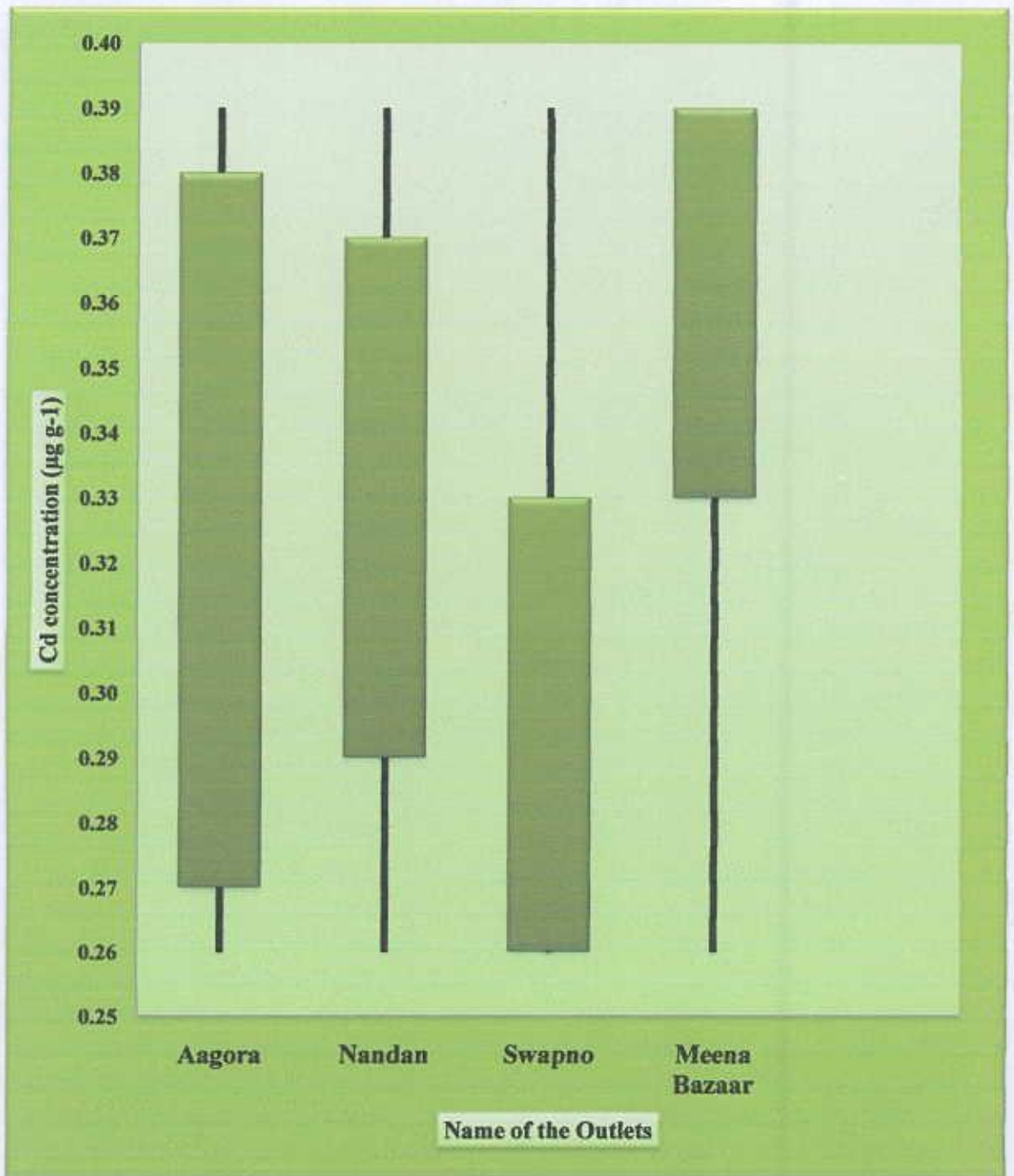


Figure: 06- The highest and lowest range of Cd concentration ($\mu\text{g g}^{-1}$) of Root vegetables

4.7. The range of Lead (Pb) concentration of vegetables in four outlets:

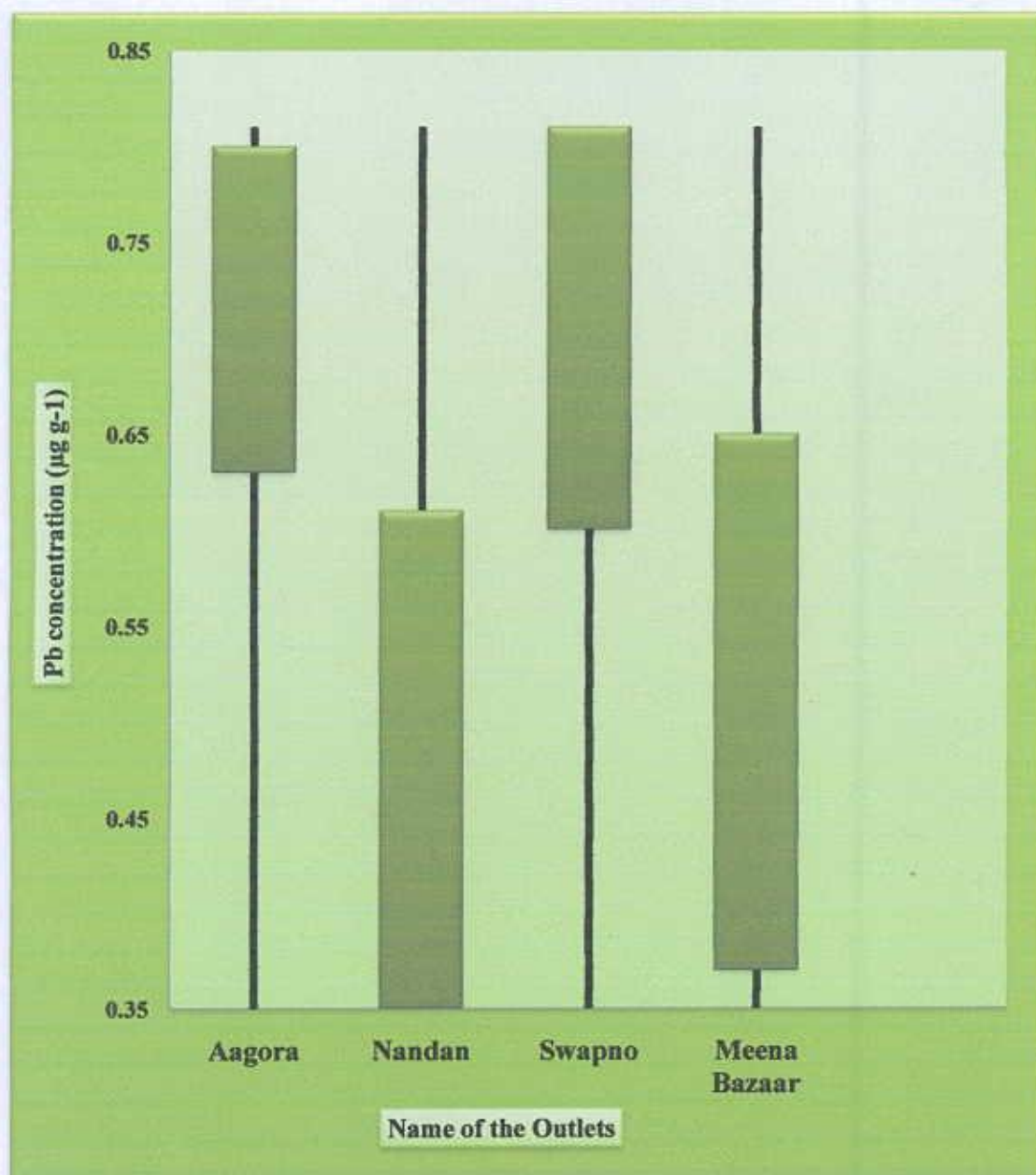


Figure: 07- The highest and lowest range of Pb concentration ($\mu\text{g g}^{-1}$) of Leafy vegetables

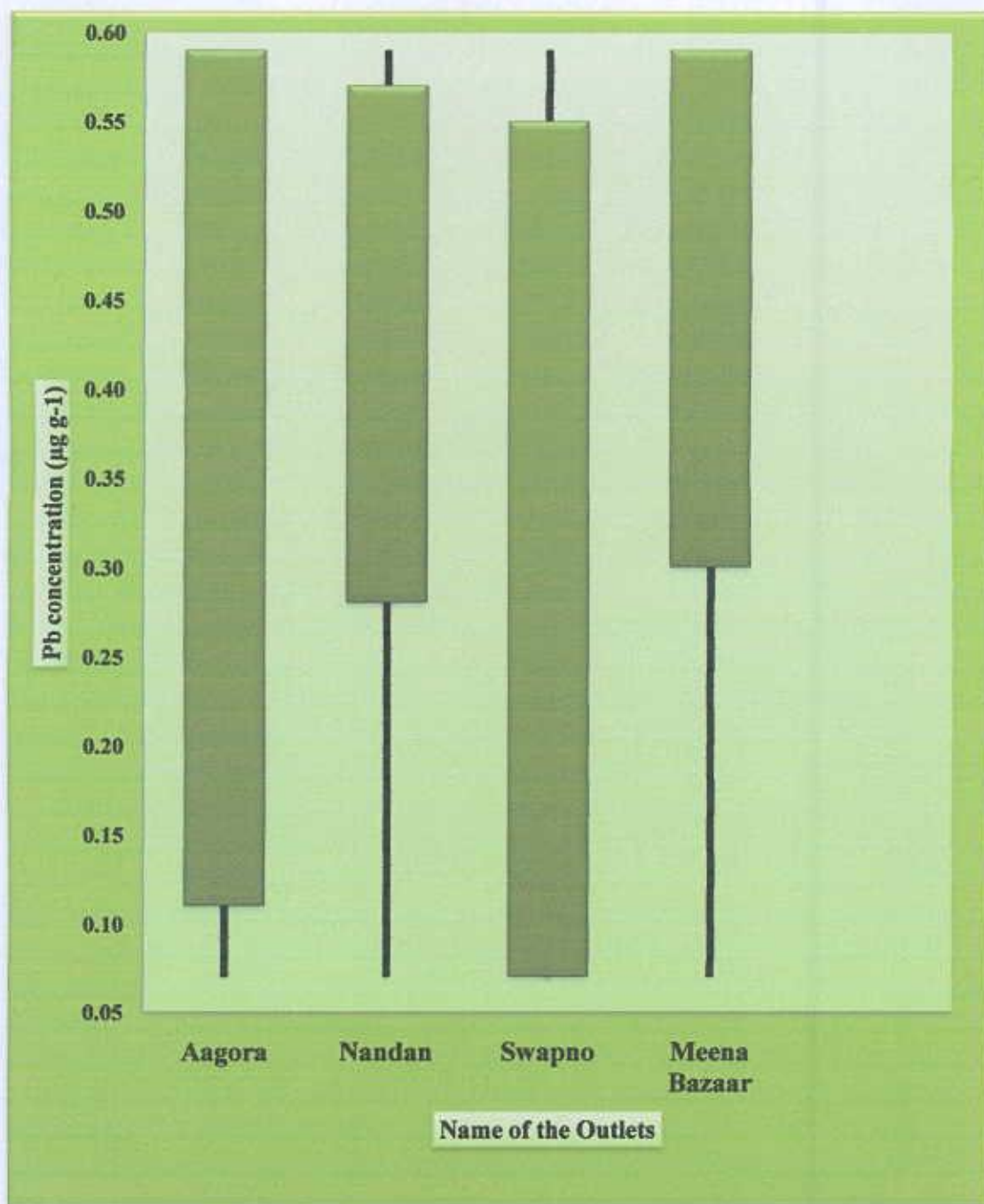


Figure: 08- The highest and lowest range of Pb concentration ($\mu\text{g g}^{-1}$) of Fruity vegetables

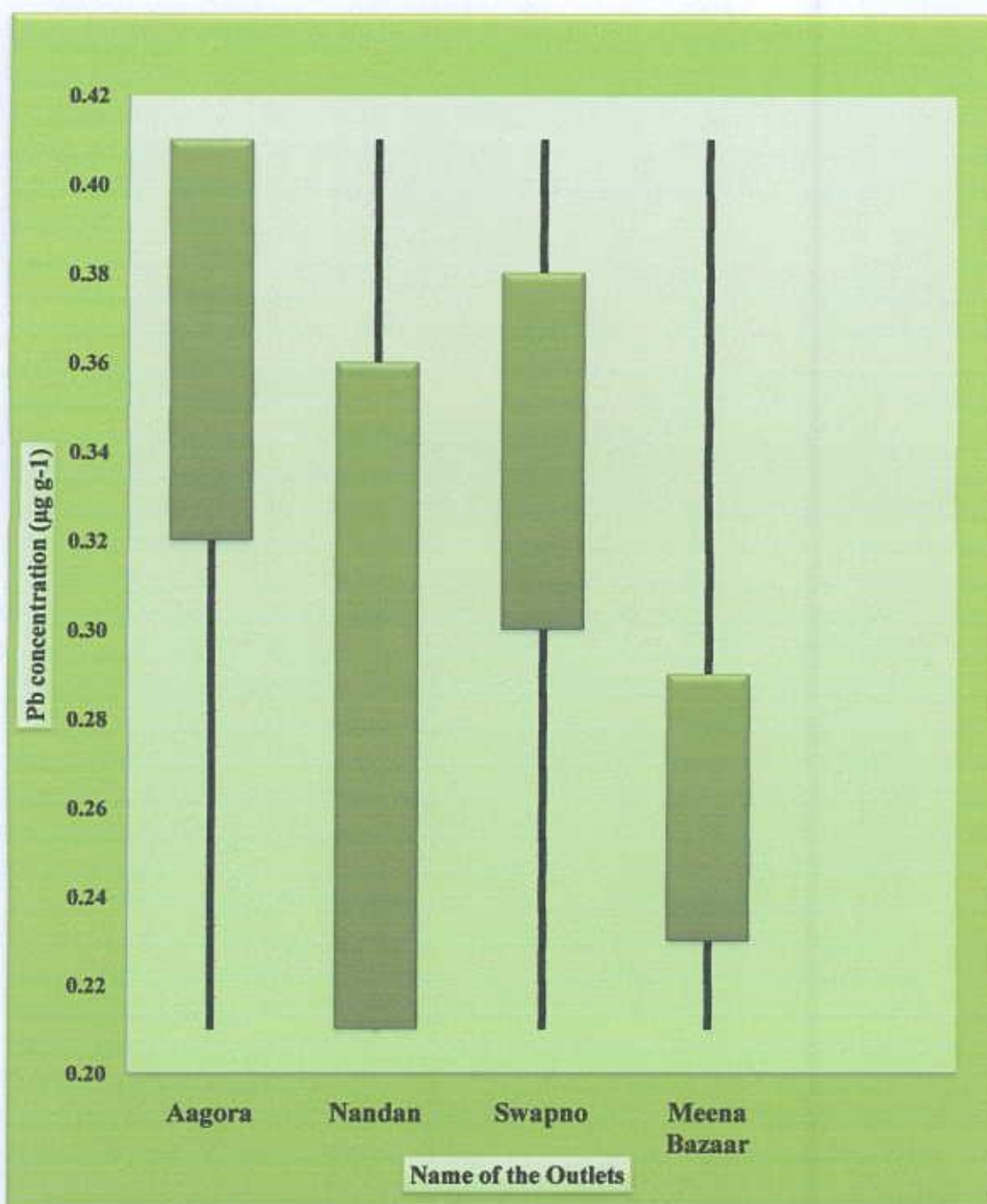


Figure: 09- The highest and lowest range of Pb concentration ($\mu\text{g g}^{-1}$) of Root vegetables

According to table (1-3) the As content of Leafy vegetables ranged from $0.91 \mu\text{g g}^{-1}$ - $1.37 \mu\text{g g}^{-1}$, fruity vegetables was $0.52 \mu\text{g g}^{-1}$ - $1.24 \mu\text{g g}^{-1}$ and for root vegetables was $0.41 \mu\text{g g}^{-1}$ - $1.04 \mu\text{g g}^{-1}$. As highest level ($1.37 \mu\text{g g}^{-1}$) measured in vegetables in this study were lower than the reported values of Anawar, H.M. *et al.* (2002) who evaluate the range of the total As concentration in the vegetables from the markets of Dhaka, Bangladesh was $1.0 \mu\text{g g}^{-1}$ - $2.93 \mu\text{g g}^{-1}$.

The results showed that (Table 3-6), Cd content ($\mu\text{g g}^{-1}$) of different kind of vegetables ranged from 0.21 - 0.39 in leafy vegetable, 0.26 - 0.59 in fruity and 0.26 - 0.39 in root vegetables which was not dependent to any specific source or outlets. Namely Cd level ($0.59 \mu\text{g g}^{-1}$) measured in vegetables in this study were higher than the reported values of Thomas *et al.* (1992) but lower than Miaz and Wilke (1997). Thomas *et al.* (1992) reported that the Cd in some vegetables (potato, tomato, lettuce and cabbage) foodstuffs were in the range of 0.01 - $0.22 \mu\text{g g}^{-1}$ and Miaz and Wilke (1997) reported that the Cd in leaves ranged from 0.1 - $8.2 \mu\text{g g}^{-1}$.

In order to Table (7-9) , it showed that ,the (Pb) content was not varying from source to source. The analyzed range of Pb concentration ($\mu\text{g g}^{-1}$) of different type of vegetables was 0.35 -0.81 in case of leafy vegetables. It was $0.07 \mu\text{g g}^{-1}$ - $0.59 \mu\text{g g}^{-1}$ in fruity vegetables and $0.21 \mu\text{g g}^{-1}$ - $0.41 \mu\text{g g}^{-1}$ in case of root vegetables. Where this study showed the highest level of Pb content was 0.81 there Warren and Delavult (1962) found the range of lead level in some vegetables was 0.30 - $45 \mu\text{g g}^{-1}$.

4.8. Comparison of heavy metal content of vegetables with safe levels:

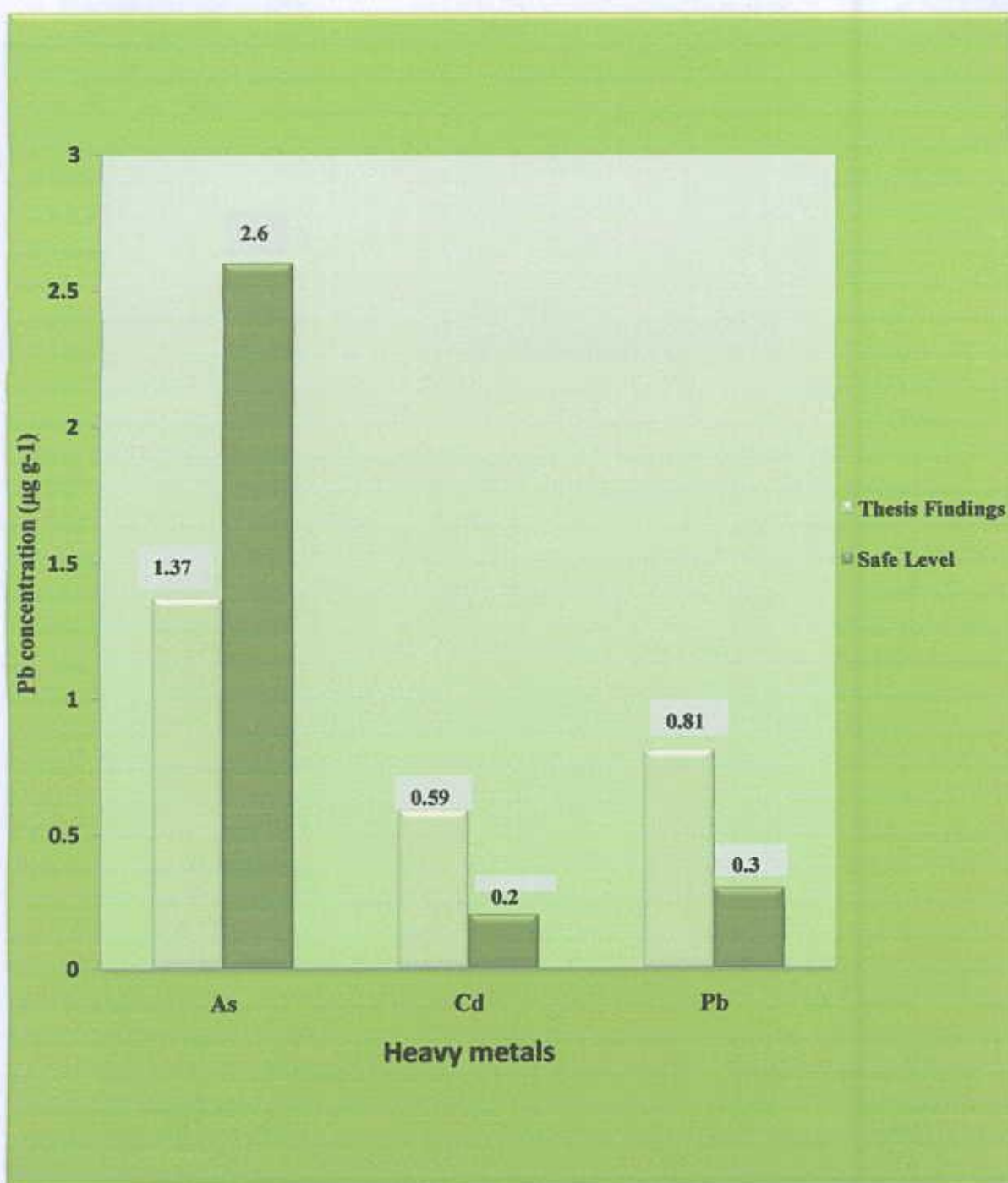


Figure: 10- Comparison of heavy metal content in vegetables with safe level

Among the concentration levels of As , Pb and Cd in this study ,the As content was lower than and the Pb and Cd content were higher than the allowable levels set by the Commission of the European Communities (CEC) and World Health Organization (WHO). Safe values for As in vegetables recommended by the WHO is $2.6 \mu\text{g g}^{-1}$ (FAO/WHO, 1996). Pb limit set by the CEC was 0.3 mg/g and the allowable level of Cd was 0.2 mg/g (Jamali *et al.*, 2007).



4.9. Comparison of heavy metals in different types of vegetables:

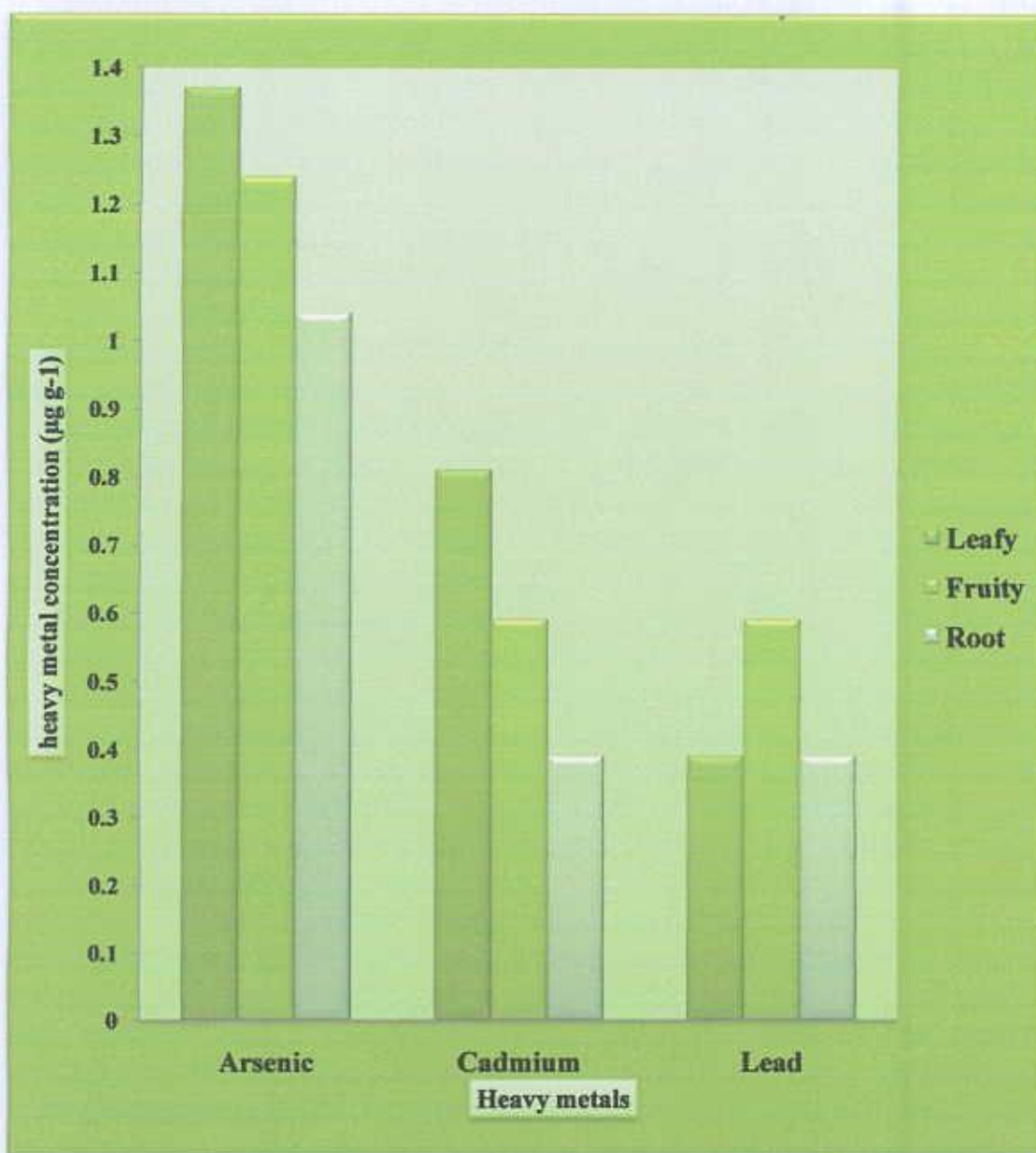


Figure: 11- Comparison of heavy metals concentration ($\mu\text{g g}^{-1}$) in various types of vegetables

Though the source was different but considering the four outlets, on the basis of table 10, the highest amount of Arsenic (As) was found in leafy vegetables ($1.37 \mu\text{g g}^{-1}$) whereas the highest concentration of arsenic of fruity and root vegetable was $1.24 \mu\text{g g}^{-1}$ and $1.04 \mu\text{g g}^{-1}$ respectively lower than the highest content of Leafy vegetables which was anti reported by Low and Lee (1992) but corroborated by Tlustos *et al* (2002).

Low and Lee (1992) reported that the highest arsenic content among the edible parts of different vegetables, was $2.0 \mu\text{g g}^{-1}$ found in bean (fruity vegetable) and lowest ($0.20 \mu\text{g g}^{-1}$) in spinac (leafy vegetable).

Tlustos *et al* (1998) reported that the highest content of As among the different vegetables, the highest accumulations of As was found in leaves (spinach).

On the basis of this study, the highest amount of Cd was found in leafy type vegetables ($0.81 \mu\text{g g}^{-1}$) which was higher than fruity ($0.59 \mu\text{g g}^{-1}$) and root ($0.39 \mu\text{g g}^{-1}$) type vegetables though the outlets were different (table 10). These findings corroborated with the findings of Zupan *et al.* (1997) and Wiersma *et al.* (1998).

Zupan *et al.* (1997) reported that the highest concentrations of heavy metals (Cd) were observed in edible green parts of vegetables (spinach, lettuce) and roots (carrot and raddish) whereas in fruity vegetables (tomato) was very low .

Wiersma *et al.* (1998) analyzed that in lettuce and spinach relatively high Cd levels occurred and fruits such as tomatoes, cucumbers and apples Cd level were low.

It also described in these paper the Pb concentration of fruity vegetables was ($0.59 \mu\text{g g}^{-1}$) was greater than that of leafy ($0.39 \mu\text{g g}^{-1}$) and root ($0.39 \mu\text{g g}^{-1}$) type vegetables though the collection sources of vegetables samples were different (table 10) .Which was not supported by the investigation of Fritaz and Venter (1988) who found that heavy metal (Pb) concentration were generally highest in the leaves and lowest the roots and fruits. Among the heavy metal, a high Cu level was found carrots in root.

CHAPTER 5

SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

The study was undertaken to determine the status of As, Cd, and Pb content in different vegetables sold in different outlets of super shops located in Dhaka city which were grown in different location of Bangladesh. 44 vegetable samples were collected during season of 2013-2014. The randomly selected outlets were of Aagora, Nondon, Meena Bazaar and Swapno. After collecting the samples they were washed in clean water. Roots and other extraneous parts were removed. Cutting only the edible parts of the vegetables into small pieces they were air dried and finally oven dried. The samples were then ground in grinding mill. The metal concentration was determined by Atomic Absorption Spectrophotometer (AAS).

Though there was wide variation in As, Cd, and Pb concentration of different types of vegetables collected from four different outlets of four different chain shops it was observed that there was a common sequence in heavy metal contents for the vegetables of different outlets.

For all of the outlets, the descending order of the vegetables according to the content of As was Red Spinach > Radish > Brinjal > Cauliflower > Bean > Bottle Gourd > Carrot. In Cadmium (Cd) content the order was Bottle Gourd > Brinjal > Radish > Bitter Gourd > Cabbage. For Lead (Pb) the descending order of the vegetables analyzed was Bottle Gourd > Brinjal > Radish > Bean.

The experiment also reports that whether the content of heavy metals of the vegetables are within the safe limit for human consumption or not. It was found that Arsenic (As) content of leafy vegetables ranged from 0.91-1.37 $\mu\text{g g}^{-1}$, for fruity vegetables it was 0.52-1.24 $\mu\text{g g}^{-1}$ and for root vegetables that was 0.41-1.04 $\mu\text{g g}^{-1}$, Cadmium (Cd) content ranged from 0.21 to 0.39 $\mu\text{g g}^{-1}$ in leafy vegetable, 0.26 to 0.59 $\mu\text{g g}^{-1}$ in fruity and 0.26 to 0.39 $\mu\text{g g}^{-1}$ in root vegetables and the Pb concentration was 0.35- 0.81 $\mu\text{g g}^{-1}$ in case of leafy vegetables, 0.07-0.59 $\mu\text{g g}^{-1}$ in fruity vegetables and 0.21- 0.41 $\mu\text{g g}^{-1}$ in case of root vegetables. Among the highest concentration of As Cd and Pb in different vegetables , As content was found to be below the maximum permissible limits of various international authorities except Cd and Pb that exceeded the recommended limit in vegetable .

Another finding of this research work is that the highest amount of Arsenic (As) was found in leafy vegetables (1.37 $\mu\text{g g}^{-1}$) whereas the highest concentration of arsenic of fruity and root vegetable was 1.24 $\mu\text{g g}^{-1}$ and 1.04 $\mu\text{g g}^{-1}$ respectively lower than the highest content of leafy vegetables. The highest amount of lead (Pb) was found in leafy vegetables (0.81 $\mu\text{g g}^{-1}$) which was higher than fruity (0.59 $\mu\text{g g}^{-1}$) and root (0.39 $\mu\text{g g}^{-1}$) types and the cadmium concentration of fruity vegetables (0.59 $\mu\text{g g}^{-1}$) was greater than that of leafy (0.39 $\mu\text{g g}^{-1}$) and root (0.39 $\mu\text{g g}^{-1}$) type vegetables though the collection sources of vegetables samples were different.

Consumption of foodstuffs with elevated levels of heavy metals may lead to high level of accumulation in the body causing related health disorder. The biomonitoring of trace elements in vegetables needs to be continued , at least Cd and Pb in most of the food commodities , because this can help us in

choosing health giving vegetables comprising one of the main kinds of food for humans in our country.

The super chain shops don't grow their own items or they have no contact grower specifically. They just collect their vegetables from different part of country. The As is accumulate only from underground water whereas the Cd and Pb content were found higher may be due to high quantity of chemical fertilizers and pesticides from farmers side.

Recommendation may vary from shop to shop. Super shop collectors should be more conscious in collecting their vegetables from farmer's level. Farmers should reduce their level of using pesticide and chemical fertilizer. Along with the govt. department of the businessmen are sincere in testing the preservatives and ripening chemicals used in foods and in raw vegetables. But they were not concerned about the heavy metal contents of those products. The study was conducted only in four outlets. It should include more outlets of different chain shops. However, to reach a specific conclusion and recommendation more research on analysis of heavy metals should be done by the authority in collecting their vegetable products from different parts of the country.

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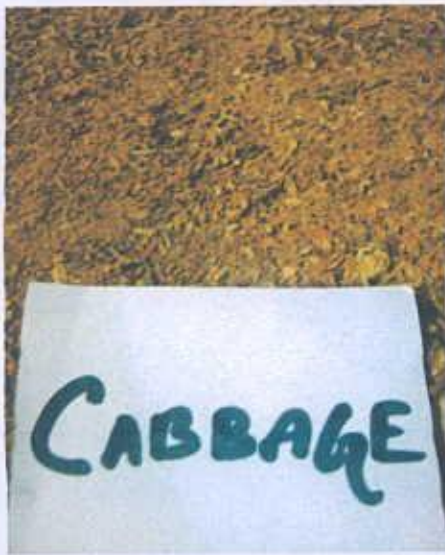
PLATES

PLATES









CABBAGE



BRINTAL



SPINACH



RED
AMARANTH



CAULIFLOWER



TOMATO



BEAN



BITTER
GOURD



CARROT

