Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

Available online at www.jcbsc.org

Section D: Environmental Sciences

CODEN (USA): JCBPAT Research Article

Assessment of Heavy Metals Accumulation in Washed and Unwashed Leafy Vegetables Sector-26 Vashi, Navi Mumbai, Maharashtra.

R.D.Mohite[1]* N. Basavaiah[2], P.U. Singare[3], A.V.R. Reddy[4], R.K.Singhal[4], U. Blaha[5]

[1] Department of Chemistry, K.B.P.College, Vashi, Navi Mumbai, India

[2] Indian institute of Geomagnetism, New Panvel, Navi Mumbai 410 218, India

[3]Department of Chemistry, Bhavan's College, Munshi Nagar, Andheri (West), Mumbai 400 058,

[4]Babha Atomic Research Centre Mumbai, Trombay, Mumbai, India

[5]ERDS-tec Environmental Solutions, P.O. Box 1404, 72004 Tübingen, Germany

Received: 30 July 2016**; Revised:** 12 August 2016**; Accepted:** 15 August 2016

Abstract: The accumulation of Pb, Cu, Zn, Fe, Cr, Ni and Mn in vegetables near to industrial area sector-26 Vashi Navi Mumbai were investigated using X-ray fluorescence spectroscopy(XRF).The four leafy vegetables washed and unwashed studied include Kardai*(Carthamustinctorius L.)*,Red Mat*(Amaranthus dubius)*, Spinach*(Spinaciaoleracea L)*, Mayalu*(Basellaalba.L)*. The metal concentrations in the unwashed vegetables was high as compare to washed vegetable sample which suggests anthropogenic sources contamination. The levels of Pb, Fe, Cr was observed above the WHO-ML in both washed and unwashed samples. Elevated concentrations of heavy metals were recorded in washed and unwashed sample. The results revealed that heavy metal values in the washed sample ranged from 3.35 mg kg^{-1}- 4.7 mg kg^{-1}(Pb), 12.5 mg kg^{-1}-17.9 mg kg^{-1}(Cu), 52.1 mg kg^{-1}- 65.9 9 mg kg^{-1} (Zn), 391 mg kg^{-1}-737.6 mg kg^{-1}(Fe), 1.0 mg kg^{-1}-5.9 mg kg^{-1} (Cr),6.5 mg kg^{-1} -7.9 mg kg^{-1} (Ni), 67.3 mg kg^{-1}- 276.2 mg kg^{-1} (Mn) while those of unwashed were found to be 4.4 mg kg^{-1}-6.8 mg kg^{-1} (Pb), 15.8 mg kg^{-1}- 20.0 mg kg^{-1}(Cu), 66.0 mg kg^{-1}- 75.8 mg kg^{-1} (Zn), 1893.0 mg kg^{-1}- 2049.0 mg kg^{-1} (Fe), 9.0 mg kg^{-1}-

23.8 mg kg^{-1} (Cr), 8.0 mg kg^{-1}- 10.4 mg kg^{-1}(Ni), 92.3 mg kg^{-1}- 337.2 mg kg^{-1}(Mn).The levels of Cu,Zn,Ni, Mn in washed and unwashed vegetable samples were below the WHO-ML.

Keywords: Heavy Metals, Washed and unwashed Vegetables, XRF Spectroscopy.

INTRODUCTION

Vegetables are part of daily diets in many households forming an important source of vitamins and minerals required for human health. They are made up of chiefly cellulose, hemi-cellulose and pectin substances that give them their texture and firmness.[1] large quantities of pollutants have continuously been introduced into ecosystems as a consequence of urbanization and industrial processes. Metals are persistent pollutants that can be biomagnified in the food chains, becoming increasingly dangerous to human and wildlife. Heavy metals contamination is a major problem of our environment .They are also one of the major contaminating agents of our food supply [2, 3]. The uptake and accumulation of heavy metals in vegetables are influenced by many factors such as climate, nature of soil, water and the degree of maturity of plants [4, 5]. Determination of the chemical composition of plants is one of the most frequently used methods of monitoring environmental pollution. Various plants have been used as bio indicators [6]. Heavy metals ranks high amongst the chief contaminants of leafy vegetables [7]. Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments [8]. Emissions of heavy metals from the industries and vehicles may be deposited on the vegetable surfaces during their production, transport and marketing. [9]

MATERIALS AND METHODS

Study area: Navi Mumbai, formerly known as New Bombay, is a city on the west coast of the Indian state of Maharashtra. It was developed in 1972 as a twin city of Mumbai, and is one of the largest planned cities in the world, with a total area of 344 km^2 and 163 km^2. Navi Mumbai lies on the mainland on the eastern seaboard of Thane Creek and spreads over parts of two districts of Maharashtra; Thane, and Raigad. The region is hilly in some parts, and certain areas of the region are protected wetlands. Navi Mumbai is a part of South Konkan coast line. This coastal line joins Sahyadri mountain ranges to the south and 50 to 100 m high hills to the east. Thus the Navi Mumbai area lies between mountain ranges and a coast line. The most developed areas of Navi Mumbai are Vashi is the queen of Navi Mumbai. Has been selected for the case study since numerous sources emit trace metals including several major and minor industries located near the city. Majority of industries such as refineries, chemicals fertilizers are located in MIDC.the vegetables are cultivated in a close proximity to the emission sources of trace metals.

Sample Collection: Vegetable Samples were collected from sector 26 Vashi Navi Mumbai in the year 2013, this farmland were chosen for this study mainly because the vegetables harvested from the selected farmland are supplied to the residents in these areas and also marketed to the nearby markets for public consumption. Vegetable samples including Kardai, Red Mat, Spinach, and Mayalu were collected from plots and samples were harvested in a 1mx1m quadrant. Vegetables were handpicked using vinyl gloves and carefully packed into polyethylene bags. Only the edible parts of each vegetable were used for analysis. In addition, soil samples were collected from the sites form where the vegetables were taken. Vegetable samples were divided into two sub-samples; one sub-sample was thoroughly washed several times with tap water followed by distilled water to remove dust particles and the second sub-sample was left untreated. All vegetable samples were oven dried at 80°C for 24 hrs.

Site location Map Sector 26 Vashi, Navi Mumbai

X-ray Fluorescence Analysis: Analysis for metal determination was performed on 8 bulk samples; 4 washed and 4 unwashed using XRF techniques. For sample preparation 20 g of dried vegetable material was ground for 20 minutes to ensure the uniform distribution of metals in a planetary mono mill (Fritsch Pulverisette 6). Two grams of ground material were taken for analysis. Measurement was performed with a Spectro XEPOS XRF spectrometer (AMETEK) using the Turbo Quant-Powders method. Samples were analyzed for Cr, Mn, Fe, Ni, Co, Zn, and Pb. Analysis was carried out in the environmental magnetic laboratory at IIG.

RESULT

The distribution of Chromium (Cr), Manganese (Mn), iron (Fe), Nickel (Ni), copper (Cu), Zinc (Zn) Lead (Pb) with their maximum limits in waste water irrigated vegetables are presented in Table 1. The concentrations of Cr, Mn, Fe, Ni, Cu, Zn, Pb, in different vegetable samples from irrigated sites of sector 26 vashi Navi Mumbai are listed in Tables 1. According to the data presented in Table 1, washing the vegetables resulted in lowering the metal contamination in the samples, which indicates the source of contamination had been the air-born particles. As it can be seen, the amount of reduction in all plants was not the same, and since the same washing method was applied to all the vegetables, it can be concluded that the differences may be a result of morphologic nature of the plants surface, plant tissues being even or uneven, and the amount of fluff and absorbents on the outer surface of the plants.

Table 1: Concentrations (mg/kg) of heavy metals in vegetables from sector-26 vashi Navi Mumbai

	Vegetable Name	Pb	Cu	Zn	Fe	Cr	Ni	Mn
Washed Vegetables	Kardai	3.35	12.5	52.15	391	1	6.55	67.35
	Red Mat	3.75	12.8	62.35	574.15	4.6	7.3	94.45
	Spinach	3.35	17.95	54.7	546.95	1.5	7.9	276.25
	Mayalu	4.7	13.5	65.95	737.65	5.95	7.7	67.7
Unwashed Vegetables	Kardai	6.85	20.05	75.85	2049	9.05	10	108.5
	Red Mat	5.55	15.85	64.05	1905.5	18.35	8	123.35
	Spinach	4.45	20.9	66	1893	9.55	8.9	337.25
	Mayalu	4.85	16.25	69.25	2094	23.85	10.4	92.3
WHO-ML*	----------	0.3	73	100	425	0.05	67	500

***Values refer to maximum limit of World Health Organization (CODEX, 2001)**

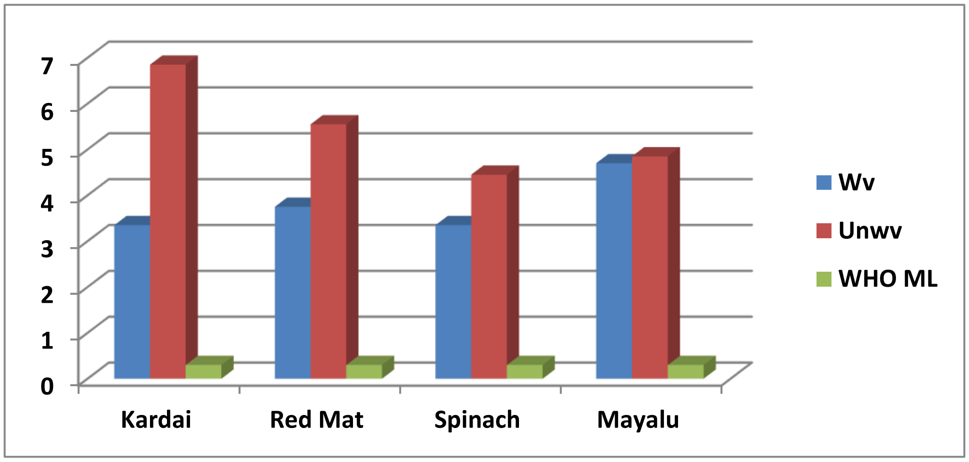

Figure 1: Lead distribution in the vegetables

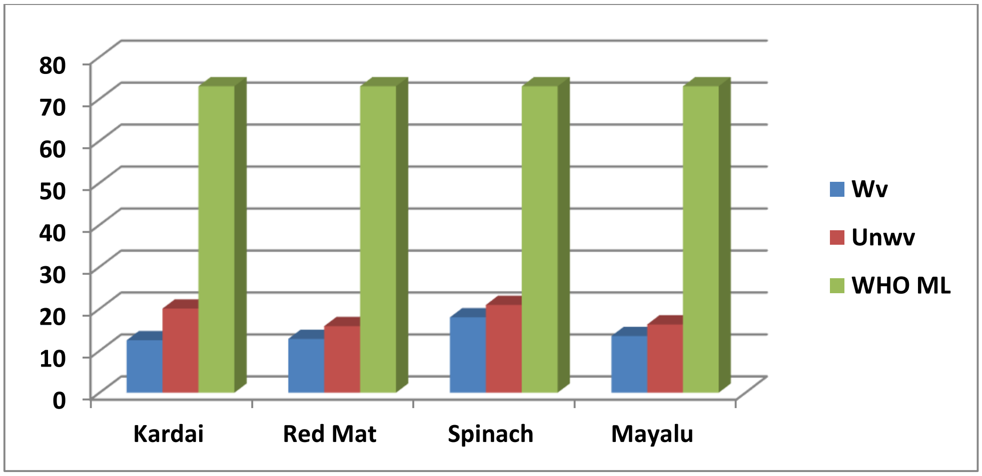

Figure 2: Copper distribution in the vegetables

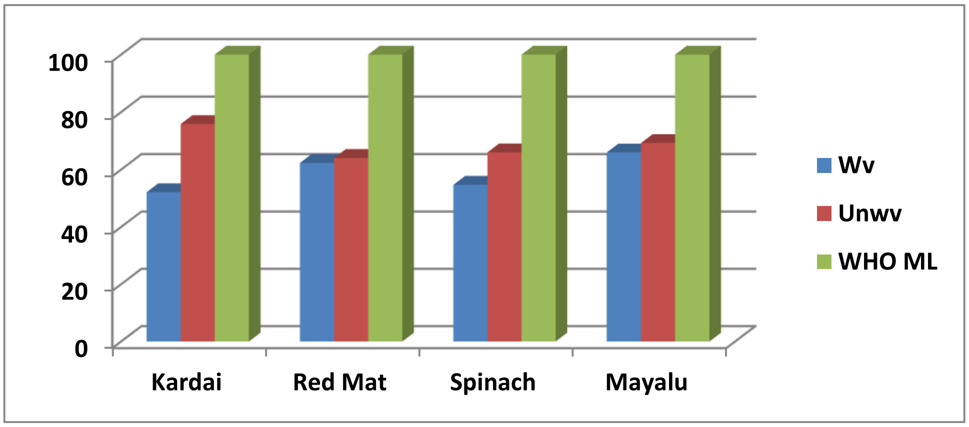

Figure 3: Zinc distribution in the vegetables

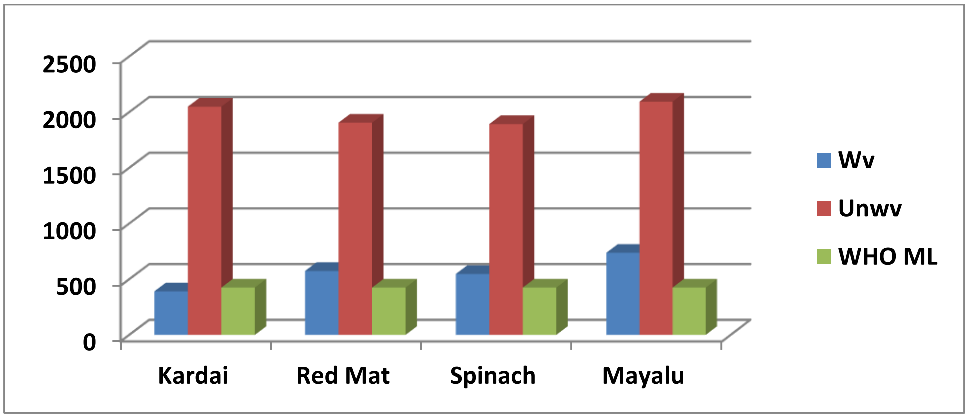

Figure 4: Iron distribution in the vegetables

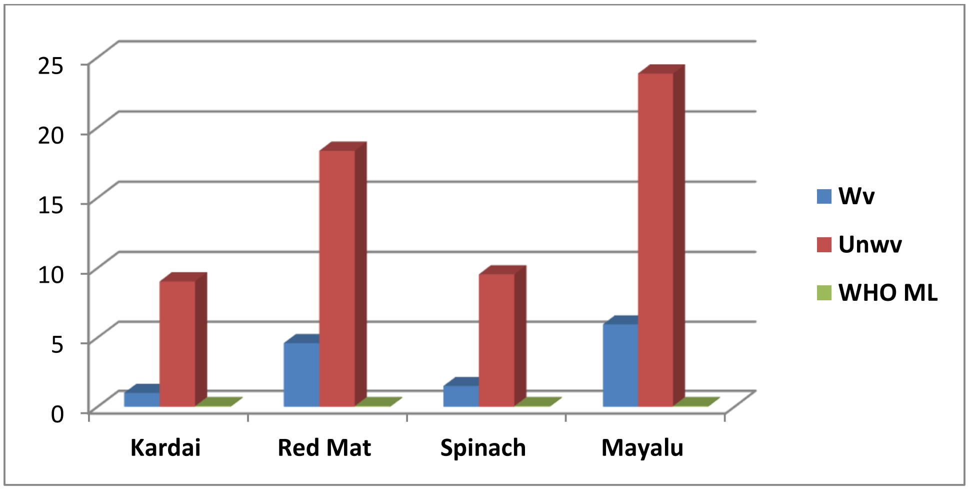

Figure 5: Chromium distribution in the vegetables

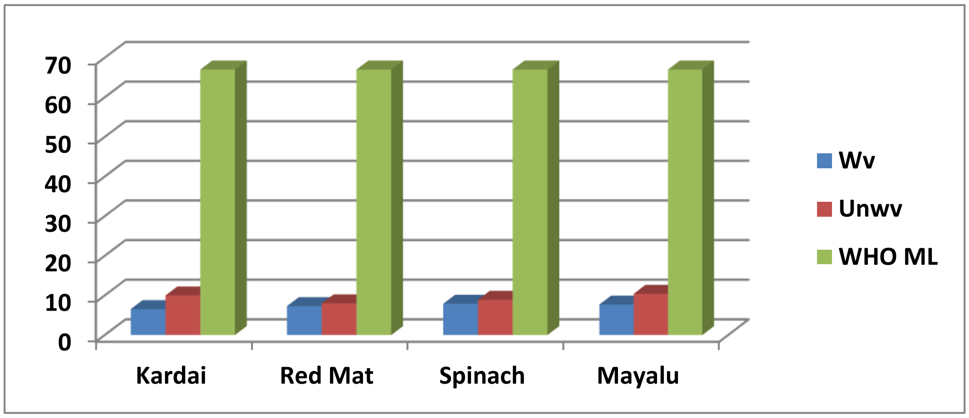

Figure 6: Nickel distribution in the vegetables

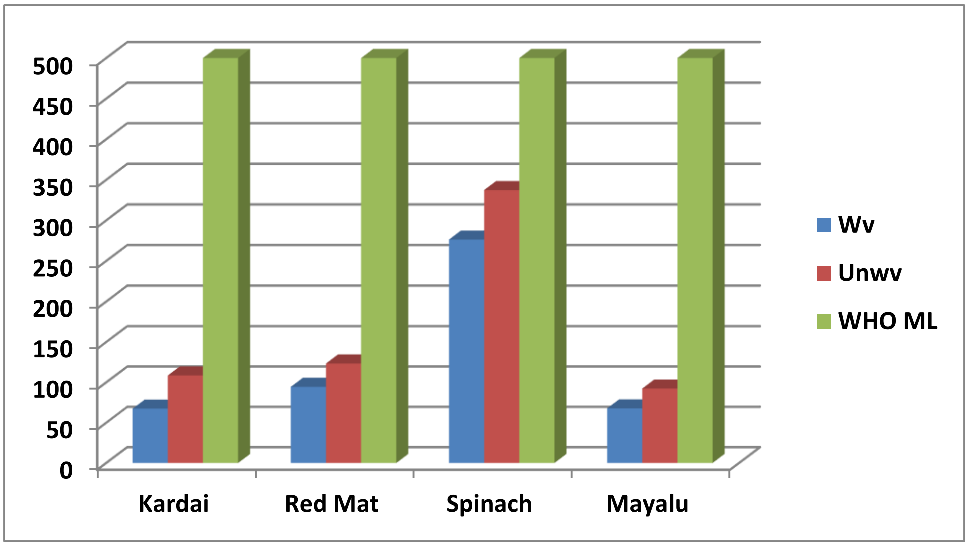

Figure 7: Manganese distribution in the vegetables

DISCUSSION

1. Lead: Lead (Pb), with atomic number 82, atomic weight 207.19, and a specific gravity of 11.34, is a bluish or silvery-grey metal with a melting point of 327.5°C and a boiling point at atmospheric pressure of 1740°C. It has four naturally occurring isotopes with atomic weights 208, 206, 207 and 204 (in decreasing order of abundance). Despite the fact that lead has four electrons on its valence shell, its typical oxidation state is +2 rather than +4, since only two of the four electrons ionize easily. Apart from nitrate, chlorate, and chloride, most of the inorganic salts of Pb^{2+} have poor solubility in water [10]. Lead (Pb) exists in many forms in the natural sources throughout the world and is now one of the most widely and evenly distributed trace metals. Soil and plants can be contaminated by lead from car exhaust, dust, and gases from various industrial sources.Pb^{2+} were found to be acute toxic to human beings when present in high amounts. Since Pb^{2+} is not biodegradable, once soil has become contaminated, it remains a long-term source of Pb^{2+} exposure. Metal pollution has a harmful effect on biological systems and does not undergo biodegradation [11].In the environment, lead is known to be toxic to plants, animals, and microorganisms. Although a maximum Pb limit by WHO standards is 0.3 mg /kg [12]. Data showed that in all vegetables, lead concentration is more than permitted level, so they are not suitable for consumption. [Fig.7]

2. Copper: Copper is essential trace element to plants and the amount of copper present in plants varies with the copper content of soil on which it is grown. The copper concentration in food stuffs reported in the range of 1.75 to 9.26 µg/g. [13].In the present study the copper content in the range of 12.5 to 17.95 mg/kg in the washed sample with an average of 15.2 mg/kg. Whereas in unwashed sample the average Cu concentration reported as 15.85 to 20.9 mg/kg respectively. The concentration of Cu in plants varied much with dependent nearby factors like proximity industries and use of fertilizers and Cu based fungicides. The maximum permissible limit for Cu in vegetables is 73 mg/kg WHO and in the present study the concentration of Cu will within the limits in all the four vegetables.

3. Zinc: Maximum permitted level for Zinc in vegetables is 100mg /kg. WHO[12] by this way, the concentration of Zn in washed vegetables was as fallows Mayalu> Red mat >Spinach >Kardai whereas in unwashed sample Kardai>Mayalu>Spinach>Red Mat [Fig.6] shows that there were not any pollution in selected vegetables compare to WHO standard level. Knowledge of Zn toxicity in humans is minimal. The most important information reported is its interference with Cu metabolism [14-15] the symptoms that an acute oral Zn dose may include: tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhea, pancreatic is and damage of hepatic parenchyma [16].

4. **Iron:** Iron is a most essential mineral that is required for human and plants life for their growth. The iron content in the body is found in red blood cells and carries oxygen to every cell in the body. Iron also is involved in producing ATP (adenosine triphosphate, the body's energy source). Extra iron is stored in the liver, bone marrow, spleen & muscles. In the industrial fields, iron is major elemental component for all the purposes made by industries. In the present study iron was found be higher in both washed and unwashed sample compare with WHO limits.[Fig.4] The range of iron in washed sample shows 391 to737.65 mg/kg whereas in unwashed sample 425 to 2094 mg/kg respectively. The accumulation of Fe in washed vegetable samples are order of Mayalu> Red Mat> Spinach> Kardai whereas in unwashed vegetable samples are order of Mayalu > Kardai> Red Mat> Spinach respectively.

5. Chromium: Human exposure to chromium occurs from both natural and anthropogenic sources. Chromium is present in the Earth's crust, with the main natural source of exposure being continental dust present in the environment, Exposure to Chromium may occur through breathing air, drinking water, or eating food containing Cr or even through skin contact. In human beings and animals, it is considered to be an essential metal for carbohydrates and lipid metabolism within a certain range of concentrations (up to 200µg/day). However exceeding normal concentrations leads to accumulation and toxicity that can result in hepatitis, gastritis, ulcers and lung cancer [17] in the present study the concentration of chromium in washed sample range (1.0 to 5.95 mg/kg) and unwashed sample range (9.05 to 23.85 mg/kg) respectively. Observed values are high as Compared with WHO-ML (0.05mk/kg) [Fig.5]. In the present study the accumulation order of Cr in washed samples Mayalu> Red Mat> Spinach> Kardai and in unwashed samples Mayalu> Red Mat> Spinach> Kardai respectively. The accumulation trend in both washed and unwashed samples is same.

6 Nickel: Nickel is one of many trace metals widely distributed in the environment, being released from both natural sources and anthropogenic activity, with input from both stationary and mobile sources. It is present in the air, water, soil and biological material. Natural sources of atmospheric nickel levels include wind-blown dust, derived from the weathering of rocks and soils, volcanic emissions, forest fires and vegetation. Nickel finds its way into the ambient air as result of the combustion of coal, diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources [18, 19-23.]

Many harmful effects of nickel are due to the interference with the metabolism of essential metals, such as Fe (II), Mn (II), Ca (II), Zn (II), Cu (II) or Mg (II), which can suppress or modify the toxic and carcinogenic effects of nickel. The toxic functions of nickel probably result primarily from its ability to replace other metal ions in enzymes and proteins or to bind to cellular compounds containing o-, s-, and N-atoms, such as enzymes and nucleic acids, which are then inhibited.

Nickel has been shown to be immunologic, altering the activity of all specific types involved in the immunological response, resulting in contact dermatitis or asthma [24, 25].In the present study the concentration of Ni in both washed and unwashed vegetable sample are below the permissible limits as compare to the WHO-ML (67 mg/kg) [Fig.6].the accumulation trend of Ni in washed samples Spinach> Mayalu> Red Mat> Kardai whereas in unwashed samples Mayalu> Kardai> Spinach> Red Mat respectively.

7 Manganese: Manganese is a very common compound that can be found everywhere on earth. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic at high concentrations. Manganese effects occur mainly in the respiratory tract and in the brain. Manganese compounds exist naturally in the environment as solids in the soils and small particles in the water. Manganese particles in air are present in dust particles. These usually settle to earth within a few days. Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter surface water, groundwater and sewage water. Through the application of manganese pesticides, manganese will enter soils. For animals manganese is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism. In plants manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil this causes disturbances in plant mechanisms. Manganese can cause both toxicity and deficiency symptoms in plants. When the pH of the soil is low manganese deficiencies are more common. In the present study the conc. of Mn in both washed and unwashed vegetable samples are below the WHO- ML (500mg/kg). The accumulation order in washed samples order of Spinach> Red Mat> Mayalu> > Kardai whereas in unwashed samples Spinach> Red Mat> Kardai> Mayalu respectively.

CONCLUSION

The results of study revealed that washed and unwashed vegetables accumulated Pb, Fe, and Cr above the WHO-ML whereas level of Cu, Zn, Ni, and Mn in washed and unwashed vegetables was within the acceptable limit of WHO-ML. These vegetables are in high demand in local market and other areas within the locality because they are part of daily staple food. Continuous consumption of these vegetables will inevitably result to health consequences. There is a need for regular evaluation of trace metals in these vegetables. The study can be used for environmental monitoring based on metals.

ACKNOWLEDGEMENTS

Authors are thankful to Dr.N. Basavaiah Indian Institute of Geomagnetism Navi Mumbai for providing all the facilities for permitting heavy metal measurement.

REFERENCES

1. O.P.Sobukola, O.U.Dairo, Modeling drying kinetics of fever leaves (Ocimum viride) in a convective hot air dryer. *Niger. Food J,* 2007, **25(1):**145-153.
2. M.I.Zaidi, A.Asrar, A. Mansoor And M.A. Farooqui, The heavy metals concentration along roadside trees of Quetta and its effects on public health. *J. Appl. Sci,* 2005, 5(4): 708-711.
3. M.H.Khair,. **T**oxicity and accumulation of copper in Nannochloropsis oculata (Eustigmatophycea, Heterokonta). *World App. Sci.J.* 2009, **6(3):** 378-384.
4. D.Scott, J. M.Keoghan, and B. Allen, Native and low input grasses-a new elahigh country persopective.J.res,1996,39:499-512,
5. D.Voutsa, A. Griminess, And Samara, C, Trace elements in vegetables grown in industrial areas in relation to the soil and air particulate matter, *Environ.Pollut*. 1996,94:325-335,
6. P.Kasanen , F.T.VenetVaara Comparison of biological collection of airborne heavy metals near ferrochrome and steelwork. *Water Air Soil Pollut,* 1991, 60: 337-359.
7. F.Mapanda, E.N.Mangwayana, J. Nyamangara, K.E.Giller , The effect of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. Agric. *Ecosys. Environ,*2005, 107: 151-165
8. O.P.Sobukola , O.M. Adeniran, A.A. Odedairo ,O.E. Kajihausa ,Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria. *African Journal of Food Science,*2010, 4(2): 389 -3 93
9. M.S.Jassir, A.Shaker, M.A.Khaliq, Deposition of heavy metals on green leafy vegetables sold on roadsides of Riyadh city, Saudi Arabia. Bull. *Environ. Contam. Toxicol,*2005,75, 1020–102
10. WHO Regional Office for Europe, Air Quality Guidelines, chapter 6.7, Lead, Copenhagen, Denmark, 2nd edition, 2001, *http://www.euro. who.int/ document /aiq/6_7lead.pdf*
11. E. Pehlivan, A. M. Özkan, S. Dinç, and S. Parlayici, "Adsorption of Cu_{2+} and Pb_{2+} ion on dolomite powder," *Journal of Hazardous Materials, vol. 167,* no. 1–3, pp. 1044–1049, 2009. View at Publisher · View at Google Scholar · View at Pub Med
12. Codex Alimentarius Commission (FAO/WHO). Food additives and contaminants. *Joint FAO/WHO Food Standards Program 2001, ALINORM* 01/12A:1-289.
13. R.Nath, V.Lyall, R.Chopra, R.Prasad, V.Paliwal, Gulati, N.Sharma, R.Chanadan, Assessment of Environmental Pollution of Cadmium in North India. – *Bull. Post. Grad. Instt,* 1982, 16: 202-208.
14. A.O.Barone, Ebesh and R.G. Harper, Placental copper transport in rats: Effects of elevated dietary zinc on fetal copper, iron and metallothionien. *J. Nutr.* 1998, 128(6): 1037-1041.

15. E.J.Gyorffy and H. Chan, Copper deficiency and mycrocytic anemia resulting from prolonged ingestion of over-the-counter zinc. *Am. J. Gastroenterol*, 1992, 87: 1054-1055. [PubMed].

16. M,Salgueiro, J. Zubillaga, M. Lysionek, A. Sarabia, M.I.Caro And R. Paoli, 2000. J. Zinc as an essential micronutrient: *A review. Nutr. Res.*, 20(5): 737-755.

17. E.C.Garcia,M.L. Cabrera, Lorenzo, J.Sanchez, andC. Lopez, "Daily dietary intake of chromium in Southern Spain measured with duplicate diet sampling", *Br. J. Nutr.*, 2001, 86:391-396.

18. G.D.Clayton, F.E.Clayton, Patty's Industrial Hy-giene Toxicology, 4 th ed.; *A Wiley-Interscience publication: New York*, pp 1994, 2157-2173.

19. P.GRANDJEAN Human exposure to nickel. IARC sci. Publ, 1984, 53, 469

20. T.W.Clarksonn, Biological Monitoring of Toxic Metals; plenum press: New york, pp 265-282, Environmental Health CRITERIA 108. Nickel. WHO, Genewa, 1981, 1991.

21. R.Von Burg Toxicology update. *J. Appl. Toxicol*, 1997, 17, 425.

22. SPECTRUM. Chemical Fact sheet. Nickel, 1998, *web. site:http://www.speclab. com/ elements/ nickel.htm* (accessed 03.03.2005)

23. J.J. Scott-Fordsmand, Toxicity of nickel to soil organ-isms in Denmark. Rev. Environ. Contam, Toxicol 1997, 148, 1.

24. T.P.Coogan D.M.Latta, E.T.Snow, M.Cost. Toxicity and carcinogenicity of nickel compounds. *Crit. Rev. Toxicol*, 1989, 19 (4), 341.

Corresponding author: R.D.Mohite,

Department of Chemistry, K.B.P.College, Vashi, Navi Mumbai, India