ISSN-1996-918X



Pak. J. Anal. Environ. Chem. Vol. 20, No. 1 (2019) 82 - 87



http://doi.org/10.21743/pjaec/2019.06.11

Assessment of Heavy Metals in Vegetables, Sewage and Soil, Grown Near Babu Sabu Toll Plaza Lahore, Pakistan

Naveed Ahmad^{*1}, Muhammad Saeed Akhtar¹, Ramna Zafar¹, Rida Ahmed¹, Sabir Hussain¹, Muhammad Ishaqe² and Muhammad Naeem³

¹Department of Physics, Division of Science and Technology, University of Education, Lahore, Pakistan. ²Provincial Pesticide Reference Laboratory Kala Shah Kaku Lahore, Pakistan. ³Department of Applied Chemistry Research Center P.C.S.I R, Lahore, Pakistan.

> *Corresponding Author Email: dr.naveedahmadsammar@ue.edu.pk Received 13 August 2018, Revised 08 April 2019, Accepted 30 June 2019

Abstract

The regular monitoring of toxic metals in sewage, effluents and vegetables is quite essential to avoid their excessive absorption/consumption in the food chain. The quantification of heavy metals in wastewater (sewage/industrial water), soil and vegetables grown in suburb area (Babu Sabu Toll Plaza) Lahore, Pakistan during 2015-16 have been investigated. These heavy metals include; Pb, Hg, Zn, Cu and Cd. For brief survey, 20, 20 and 90 samples of sewage water, soil and vegetable, respectively were collected for study. In wastewater, the concentration of heavy metals is observed as Zn > Cu > Cd > Pb, however, Hg was under detection limits. The measured values when compared with WHO standards, these were slightly higher than the safe limits. In soil samples, concentration was observed as Zn > Cu > Pb > Hg > Cd and is in the safe limits. The vegetables were found contaminated with heavy metals exhibiting concentration little higher than permissible limits of WHO/FAO.

Keywords: Atomic absorption spectroscopy; Heavy metals; Quantification; Environment

Introduction

Water is essentially required for the existence of living beings on the planet and for survival. The use of total available water is 6% for the domestic purposes, 3% for industrial usage and nearly 90% water is consumed for the irrigation purposes [1]. Literature suggests that there are several contributions on investigation of heavy metals in soil, plant samples and fish species in rivers and sea of Turkey have been reported [2-5]. In Pakistan the shortage of the water supply system results in irrigation of crops with the waste water system. The industrial effluents contain heavy metals (Pb, Cd, Ni, Zn, Mg, Co, Fe, As, and Cr, Cu) that transfer to the food chain and causes harmful effect on the health of consumer [1]. The collection levels of heavy metals particularly Pb in the vegetables is relatively higher in the locations near major roads [6]. The pronounced concentration of

lead in the vegetable species is because of power stations, coal in the brickfields and industrial waste results in particulate matter. The extreme toxicity of heavy metals have significant impact on the health of animals and human consumers because there is no particular process to eliminate accumulated metals from the body and this is all due to anthropogenic activities [7]. The of heavy consumption metals through contaminated intake can cause various diseases like cancer, dermatitis and thalassemia in the human body [8]. Some body's systems directly induces impairment due to these toxic elements such as cardiovascular and blood circulation system, nervous (central and peripheral), reproductive, detoxification pathways (kidneys, liver, skin, colon, liver), energy production pathways, endocrine (hormonal), gastrointestinal,

immune, enzymatic, and urinary system [1]. The pronounced concentration of pb in the vegetable species is because of power stations, coal in the brickfields and industrial waste and results in particulate matter deposition on the vegetable surface and then penetrates into the leaves and plant tissues [9].

Water gets polluted with runoff of rainwater, urban areas, the water of industrial areas, and agricultural water that flows directly from the storm water without any treatment. The disposal water causes major issues due to inadequate sanitation and viruses and bacteria in water sources cause diseases. The issues are linked with the municipal wastes and disposal of sewage water that are crucial aspects of water pollution [10].

For irrigation purposes, the application of wastewater have been increased from past few years and application of wastewater results in contamination soils with toxic heavy metals that threats the residents about consuming these vegetables and crops grown in the polluted areas regarding the effect of food quality and safety [11]. The contaminated wastewaters contain a higher content of trace elements and heavy metals such as As, Cd, Ni, Pb, Co and Cr [10]. Toxic level of Pb hinder transpiration, germination, reduces rate of gas exchange, photosynthesis in leaves and chlorophyll. The wastewater can be suitable for the irrigation if the content of all the toxic metals can be reduced considerably [12]. The application of contaminated water for irrigation purpose to growing crops results in deterioration of soil [13].

Vegetables constitute the major part of the daily intake of human beings, and toxic heavy metal contamination of vegetables is because of contamination of atmosphere and soil that causes a threat to the safety and quality of life [14]. The toxic heavy metals in the consumable part of the vegetable transfers through the soil and causes a harmful impact on the health of human beings even in case of lower proportions. Lahore is the second largest city of Pakistan. In this area, leakage in the sewage pipes is the main reason of pollution of water, as it allows sewage water to mix into drinking water pipes, causing an add to in waterborne diseases. The samples collected for wastewater measurement contains high quantity of heavy metals and trace elements and accumulates the salts in sewage irrigated soil [15].

Considering the above mentioned facts, the present study was designed to quantify the heavy metals (Zn, Pb, Cu, Hg, and Cd) in sewage water, and evaluation of the impact of sewage water irrigation on soil and vegetables like beet, ladyfinger, spinach, cauliflower, pumpkin, brinjal and zucchini cultivated in suburb area of Lahore named as Babu Sabu Toll Plazas around Lahore District.

The purpose of study was to assess status of heavy metal in sewage water, soil and vegetables grown in the vicinity of Babu Sabu Toll Plaza, Lahore situated at (31.5387° N, 74.2629° E) during the years 2015-2016. Wherein, farmers mostly used wastewater to raise vegetables.

Materials and Methods

Collection of soil, water and vegetable samples

Twenty soil samples were randomly collected in zipped polythene bags with spiral auger having a diameter of 2.5 cm wide in width from 0-10 and 10-20 cm depths, bulked to make a composite sample. The processing of samples included air-dried, passed through 2-mm sieve and preserved in plastic bottles for chemical analyses. Ninety (90) random samples of vegetable (Beet, Spinach, Cauliflower, Pumpkin, Ladyfinger, Brinjal, Zucchini) were collected from the same fields of the selected region. The methodology for collecting samples was similar to previous researchers [1]. In the laboratory, the edible vegetable parts were washed with distilled water to remove soil particles, and then crushed, sun-dried and ground controlled manner), (in for determination of heavy metals. Twenty (20) samples of sewage water were collected in plastic bottles cleaned with 2 mL concentrated nitric acid to avoid any sort of microbial activities during the process of storage of samples. All the samples of soil, wastewater and vegetable were handled carefully and then analysis was carried out.

Pre-treatment of soil, water and vegetable samples

In order to determine concentration of toxic heavy metals in soil, 20 g of dried soil sample from each collected sample was taken and mixed with 40 mL of Diethylene Triamine Penta acetic acid (DTPA) extracting solution at pH 7.3. Samples were agitated in reciprocal shaker at 180 rpm for two hours. Heavy metals concentration in vegetables was estimated by digesting it with 1 mL EDTA, tri-acid mixture 6 mL HNO₃ and 2 mL H_2O_2 per 15 g of vegetable sample (HNO₃ + EDTA + H_2O_2 + sample; 6:1:2:15). All the digested samples were then cooled down and the mixture was filtered through the filter paper (Whatman No. 42). The volume of the mixture was measured as 15 mL by using distilled water. The analysis of soil, water and vegetable were carried out following the procedure described by AOAC [16]. The concentration of heavy metals (Pb, Zn, Cu, Cd, and Hg) in soil, waste water and vegetables were estimated by using the technique of Atomic Absorption Spectrophotometry (Shimadzu-7000, Japan) using respective hollow cathode lamps [17].

Mechanism of uptake of heavy metals from soil & sewage to the different parts of plants of vegetable

The absorption of heavy metals in vegetables and plants can be understood by absorption via leaves *i.e.* foliar absorption. This absorption take place when concentration of heavy metal contents is higher in plant nutrients through two basic steps (a) penetration of metal in plant through stomatal pores and (b) internalization and adsorption of metal content through cuticle [18]. Physical, biological and chemical mechanisms are involved in vegetation of heavy metals in plants. Vegetables and plants can physically absorb the heavy metals through their leaves as described by Kinnersley and Scott [19]. The biological and chemical factors [20, 21] for the heavy metal adsorption depend on size of heavy metal particulates e.g. Copper, Manganese and Cobalt can pass through plant cuticle of aerial organs or damaged surfaces [22, 23]. Xiong et al. [24] proposed diffusion mechanism for the small sized particles in the plant leaf through cuticular and stomatal and pathways. Stomatal pathway

penetration is easy process because of comparatively smaller size of sub-stomatal cells as compared to the external cells. The penetration of hydrophilic substances in cuticle is through active pores and stomata while lipophilic substances diffuses from cuticle [25, 26]. For instance, Ag-NPs coating in cuticular wax enhances the lipophilicity and heavy metal transfer in cuticle [26]. Both pathways for cuticle penetration are particularly for fine particles [27].

Results and Discussion

Heavy metal concentration in waste water

The farmers mostly use sewage or industrial water for irrigation of vegetables around Lahore. The heavy metal content in the soil and sewage water industrial water are shown in Table 1. The ranges of concentrations of Zn, Cu, Cd and Pb are 25.3-32.37, 7.86-12.14, 0.98-9.41, and 0.96-2.34 mgL⁻¹ with average values of 31.31 ± 4.25 , 9.33 ± 2.32 , 3.57 ± 3.15 and 1.42 ± 0.59 mgL⁻¹, respectively in the sewage/industrial water. In the previous study, wastewater samples were collected from Peshawar and Rawalpindi and found higher concentration of Pb, Ni, Cr, Zn, Cu, and Cd [10, 28]. The researchers measured concentration of heavy metals in industrial water in Faisalabad and Attock area and found similar result [20].

Heavy metal concentration in soil

The heavy metals concentration in soil sample is mentioned in Table 1. The Zn, Cu, Cd, Pb and Hg concentrations in the upper layer of soil ranged from 37.9-66.29, 8.32-1640, 0.42-1.92, 0.98-4.42 and 0.84-1.84 mg kg⁻¹, respectively. The heavy metals concentration in soil samples was within safe limits as mentioned in WHO (1996) and FAO (1985) [29, 30]. Khan et al. and Fernández reported similar results in Faisalabad city [1, 27]. Jawahar and Javed [31] reported heavy metals concentration level measured in Sheikhupura and Muredke zone while Mian and Ahmad [32] described the same tendency in Rawalpindi sector. A significant quantity of heavy metals was measured in a study conducted in Sargodha [33]. An interesting thing is observed that higher quantity of heavy metals is present in water as compared to soil. High pH of soil might be cause of non-solubility of metals in soil.

Heavy metal concentration in vegetables

The concentrations of heavy metals in different vegetables are listed in Table 2. The concentration ranges of Pb , Cd, Cu, Zn and Hg are 0.37 - 22.12 , 0.36 - 2.37, 2.86 - 10.12, 10.96 - 30.12 and 0.009 - 0.032 mgkg⁻¹ and the average concentration for these metals is 4.59 ± 5.75 , 1.194 \pm 1.93, 5.13 \pm 1.94, 20.40 \pm 5.52 and 0.016 \pm 0.009 mgkg⁻¹, respectively.

The heavy metal concentration levels in the study was found higher than the permissible limits except Hg which was in the safe limit described by WHO (1996) [29]. The analysis showed that it is independent of the effect of heavy metal concentration by plant species and physicochemical characteristics of soil but effected the change in temperature and rainfall [34]. The heavy metals concentration in water samples (Table 1) was higher than the recommended levels and the contaminated water was a big source of heavy metals accumulation in vegetables. The heavy metal content in all vegetable samples was little higher than the critical limits [29, 35]. The results obtained from the analysis in current study were compared with the previously reported level of heavy metals concentration in vegetables. The limit of heavy metal concentration in vegetables as reported by Perveen et al. for Ni, Cr, Zn, Pb, Cu, and Cd metal was slightly higher than the safe limits provided by WHO standards [10]. Similarly, Jagtap et al. and Sana et al. also investigated the flux of heavy metal concentration and observed the excessive toxic heavy metals quantification in the edible portion of vegetables [36, 37]. Muchuweti et al. measured the content of toxic metals in the vegetables grown with wastewater in Zimbabwe [38].

Table 1. Heavy metals concentration in wastewater (mgL⁻¹) and soil (mgkg⁻¹).

Sample	Elements	Observed Range	Average Value	Standard Deviation	WHO safe limit mgkg ⁻¹	References
Wastewater used	Zn	25.3-32.37	31.31	±4.25	0.002	[27]
for Irrigation	Cu	7.86-12.14	9.33	± 2.32	0.0002	[27]
(mgL^{-1})	Cd	0.98-9.41	3.57	±3.15	0.00001	[27]
	Pb	0.96-2.34	1.42	±0.59	0.005	[27]
Soil	Zn	37.9-66.29	49.67	±9.61	0.3	[28]
(mgkg ⁻¹)	Cu	8.32-16.40	12.01	±2.59	0.1	[28]
	Cd	0.42-1.92	1.15	±0.52	0.003	[28]
	Pb	0.98-4.42	2.79	±1.21	0.1	[28]
	Hg	0.84-1.84	0.80	±0.43	0.0003	[28]

Table 2: Accumulation of heavy metal in various vegetables (mgkg⁻¹).

Vegetables	Element	Pb	Cd	Cu	Zn	Hg
Beet	Range	1.50-2.64	0.93-2.37	3.78-6.24	12.30-18.32	0.025-0.032
	Average	2.082	1.633	4.433	15.077	0.029
	STDV±	0.37	0.42	0.82	1.71	0.013
Lady's Finger	Range	3.44-3.62	0.86-0.93	3.27-4.77	22.36-28.40	N.D
	Average	3.538	0.893	3.907	24.511	N.D
	STDV±	0.012	0.067	0.02	3.22	N.D
Spinach	Range	0.87-22.12	0.93-1.87	6.34-10.12	20.14-24.11	0.018-0.021
	Average	15.103	1.218	8.485	22.044	0.019
	STDV±	8.39	0.33	1.35	1.58	0.005
Cauliflower	Range	4.88-6.12	0.77-1.12	4.02-6.37	20.29-24.42	0.009-0.012
	Average	5.439	0.972	4.576	21.972	0.01
	STDV±	0.45	0.15	0.68	1.29	0.0028
Pumpkin	Range	1.23-2.40	0.86-1.30	6.92-7.80	27.36-30.12	N.D
	Average	1.659	1.054	7.18	28.926	N.D
	STDV±	0.37	0.20	0.32	0.9099	N.D
Brinjal	Range	0.37-1.84	0.36-1.054	2.86-3.92	14.05-20.47	N.D
	Average	0.656	0.72	3.18	18.926	N.D
	STDV±	0.56	0.11	0.40	2.54	N.D
Zucchini	Range	0.47-1.83	1.34-1.40	3.84-4.48	10.96-18.96	N.D
	Average	0.919	1.37	4.184	13.519	N.D
	STDV±	0.49	0.034	0.334	2.80	N.D

Conclusion

The data obtained from analysis of limited numbers of sewage water, soil and vegetables samples lead to the following conclusion:

- The content of Pb, Zn, Cd and Cu was detected little higher in the sewage water than the limits provided by WHO, except Hg that found in safe limits, used for irrigation purpose in the study area.
- The content of Cd, Cu, Pb, Zn, and Hg in all the soil samples was found in safe limits.
- In vegetables, the content of Pb, Hg, Zn, Cu, and Cd is also slightly greater as compared to the safe limits provided by WHO (1996, 2007) and FAO (1985), the concentration of all the heavy metals varies in vegetables.
- The concentration of Pb is greater in leafy vegetables than roots.
- Monitoring of these toxic metals on regular basis from sewage and effluents and in vegetables is necessary to avoid their excessive build up in the food chain. In order to avoid any worse situation regarding the further increase in the concentration of these heavy metals, wastewater treatment plant should be installed in the concerned area as well as the concerned industries.

References

- A. Khan, S. Javid, A. Muhmood, T. Mjeed, A. Niaz and A. Majeed. *Soil Environ.*, 32 (2013) 49. <u>http://agris.fao.org/agris-</u> <u>search/search.do?recordID=PK2013000982</u>
- 2. M. Tüzen., *Microchem. J.*, 74 (2003) 289. <u>https://doi.org/10.1016/S0026-</u> <u>265X(03)00035-3</u>.
- D. Mendil, Ünal ÖF, M. Tüzen and M. Soylak, *Food Chem. Toxicol.*, 48 (2010) 1383. https://doi.org/10.1016/j.fct.2010.03.006.
- 4. M. Tüzen, *Microchem. J.*, 74 (2003)105. <u>https://doi.org/10.1016/S0026-</u>265X(02)00174-1.
- D. Mendil, Z. Demirci, M. Tuzen and M. Soylak, *Food Chem. Toxicol.*, 48 (2010) 865. <u>https://doi.org/10.1016/j.fct.2009.12.023</u>

- 6. S. S. Asaolu, *Pak. J. Sci. Ind. Res.*, 1995. http://www.pjsir.org/documents/journals/020 42011003408_PJSIR-VOL.38-(11-12)-1995-Abstract.pdf
- K. Ahmad, Z. I. Khan, S. Yasmin, M. Ashraf and A. Ashfaq, *Pak. J. Bot.*,46 (2014) 511. <u>https://www.pakbs.org/pjbot/PDFs/46(2)/15.</u> <u>pdf</u>
- J. U. Ahmad and M. A. Goni, *Environ Monit.* Assesst., 166 (2010) 347. https://doi.org/10.1021/es200374c
- G. Uzu, J. Sauvain, A. Baeza-Squiban, M. Riediker, M. Sánchez Sandoval Hohl and S. Val, *Environ. Sci. Technol.*,45 (2011) 7888. doi.org/10.1021/es200374c
- S. Perveen, Ihsanullah I-u, Z. Shah, W. Nazif, S. S. Shah and H. Shah, 42 (2011) 220. <u>https://inis.iaea.org/search/searchsinglerecord.aspx?recordsFor=SingleRecord&RN=4206 9372</u>
- 11. F. Marshall, (2004). <u>https://www.gov.uk/dfid-research-</u> <u>outputs/enhancing-food-chain-integrity-</u> <u>quality-assurance-mechanisms-for-air-</u> <u>pollution-impacts-on-fruit-and-vegetable-</u> <u>systems-final-technical-report</u>
- 12. J. S. Kanwar and M. S. Sandha, *Agric. Rev.*, 21 (2000) 133. https://www.arccjournals.com/uploads/article s/ar212011.pdf
- M. B. Kirkham, Agri. Ecosystems Environ., 9 (1983) 281. <u>https://doi.org/10.1016/0167-</u> 8809(83)90102-0.
- K. Yusuf and S. Oluwole. *Res. J. Environ. Sci.*, 3 (2009) 292. dhttps://doi.org/10.3923/rjes.2009.292.298.
- A. Mitra and S. Gupta. J. Indian Soc. Soil Sci., (India), 47 (1999) 99. <u>http://agris.fao.org/agris-</u> search/search.do?recordID=IN2001000628
- 16. S. Williams and Arlington, Assoc. of Analyt.Chem., (1984) www.aoac.org
- 17. R. Ronaq, I. Haider, M. Qadir and N. Hussain, *National Chem. Conf.*, (2005). 63.
- I. Säumel, I. Kotsyuk, M. Hölscher, C. Lenkereit, F. Weber and I. Kowarik. *Environ. Pollut.*, 165 (2012) 124. <u>https://doi.org/10.1016/j.envpol.2012.02.019</u>.

86

- R. P. Kinnersley and L. K. Scott, *J. Environ. Radioactivity*, 52 (2001) 191. <u>https://doi.org/10.1016/S0265-</u> <u>931X(00)00033-3</u>.
- 20. D. A. Grantz, J. H. B. Garner and D. W. Johnson, *Environ. Int.*, 29 (2003) 213. https://doi.org/10.1016/S0160-4120(02)00181-2.
- R. Nair, S. H. Varghese, B. G. Nair, T. Maekawa, Y. Yoshida and D. S. Kumar, *Plant Sci.*, 179 (2010) 154. https://doi.org/10.1016/j.plantsci.2010.04.012.
- 22. N. I. Ward, Sci. Total Environ., 93 (1990) 277. <u>https://doi.org/10.1016/0048-</u> 9697(90)90117-D.
- 23. T. Eichert, A. Kurtz, U. Steiner and H. E. Goldbach. *Physiol. Plant.*, 134 (2008) 151. <u>https://doi.org/10.1111/j.1399-</u>3054.2008.01135.x.
- T. T. Xiong, T. Leveque, A. Austruy, S. Goix, E. Schreck and V. Dappe, *Environ. Geochem. Health*, 36 (2014) 897. https://doi.org/10.1007/s10653-014-9607-6.
- C. Larue, H. Castillo-Michel, S. Sobanska, L. Cécillon, S. Bureau and V. Barthès, J. Hazard. Mater., 264 (2014) 98. https://doi.org/10.1016/j.jhazmat.2013.10.053.
- C. Larue, H. Castillo-Michel, S. Sobanska, N. Trcera, S. Sorieul and L. Cécillon, J. Hazard. Mater., 273 (2014) 17. https://doi.org/10.1016/j.jhazmat.2014.03.014.
- 27. V. Fernández and T. Eichert. *Critical Rev in Plant Sci.*, 28 (2009) 36. https://doi.org/10.1080/07352680902743069.
- J. H. J. Ensink, R. W. Simmons and W. Van Der Hoek, Wastewater use in irrigated agriculture., 1 (2004) 91. https://doi.org/10.1079/9780851998237.0091.
- 29. WHO. Guidelines for drinkng water quality, Health Criteria and other supporting information. In. Geneva, Switzerland World Health Organization, (1996). https://apps.who.int/iris/handle/10665/38551
- 30. FAO. Water Quality for agriculture Paper No. 21 (Rev. 1). In. Rome; (1985) 96. http://www.fao.org/3/T0234E/T0234E00.htm

- 31. A. Jawahar and M. Javed, J. Eng. Appl. Sci., 16 (1997) 43. <u>https://journals.uetjournals.com/index.php/JE</u> <u>AS/article/view/2820</u>
- 32. Z. Mian and T. Ahmed, Proc. Nat. Symp. Modern Trends Contemy Chem. Environ. Pol., (1997) 24. <u>https://inis.iaea.org/search/search.aspx?orig_</u> q=RN:30047447
- 33. Z. I. Khan, A. Ahmad, M. Sher, I. Noorka, A. Batool and S. Hamid, *Fres. Environ. Bul.*, 25 (2016) 5676. <u>https://www.researchgate.net/profile/Naunai</u> <u>n_Mahmood2/publication/316657883_Bioac</u> <u>cumulation_of_heavy_metals_from_contami</u> <u>nated_soil_to_the_vegetable_commonly_con</u> <u>sumed_in_Pakistan_Implications_for_public</u> <u>health/links/592b84f5458515e3d46c9994/B</u> <u>ioaccumulation-of-heavy-metals-fromcontaminated-soil-to-the-vegetablecommonly-consumed-in-Pakistan-Implications-for-public-health.pdf</u>
- 34. S. Farid, Sci. Technol. Develop., 22 (2003) 58. <u>https://doi.org/10.1016/S0009-</u> 2509(03)00161-1.
- 35. WHO. WHO Expert standards program codex Alimentation Commission. In. Geneva, Switzerland; (2007). www.fao.org/input/download/report /686/al31_13e.pdf
- 36. M. Jagtap, M. Kulkarni and P. Puranik, *American-Eurasian J. Agric. Environ. Sci.*, 8 (2010) 487.

https://www.idosi.org/aejaes/jaes8(5)/1.pdf

37. S. Chaoua, S. Boussaa, A. El Gharmali and A. Boumezzough. *J. Saudi Soc. Agric. Sci.*, (2018).

https://doi.org/10.1016/j.jssas.2018.02.003

 M. Muchuweti, J. W. Birkett, E. Chinyanga, R. Zvauya, M. D. Scrimshaw and J. N. Lester. Agric. Ecosys. Environ., 112 (2006) 41.

https://doi.org/10.1016/j.agee.2005.04.028.