ACCUMULATION OF TRACE METALS Pb AND Ni IN WATER, SOIL AND VEGETABLES GROWN IN SUBURBAN AREAS (A CASE STUDY)

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ABSTRACT: *The purpose was to study the accumulation of trace metals (Pb and Ni) in the edible parts of the vegetables, water and soil in the areas nearby river Ravi and Lahore, Pakistan. The areas selected were irrigated by river water, fresh water and sewage water. Five samples of Turnip, Radish, Coriander, Spinach and Brassica vegetables, ten samples of soil and two samples of water were collected from the selected areas. These samples were analyzed for Ni and Pb contents using atomic absorption spectrophotometer. All water samples for Pb were within safe limits but for Ni exceeded five times the maximum permissible limit. The concentration of Pb and Ni in soil samples irrigated with different water sources were below the critical levels. The concentration of Pb was found to be in all the vegetable samples exceeded three times greater than the maximum permitted limits in vegetables. The automobile emission, polluted atmosphere, dumping of untreated waste were found as major sources of Pb in vegetables, while Ni was found in most of the water samples. The content of Ni in selected vegetables was found within the maximum permissible limit. The lower Ni content in vegetables was may be due to the good texture of soil which did not allow the uptake of Ni while its content was higher in water.*

Key Words: Accumulation of Pb and Ni, sewage water, fresh water, river water, soils, vegetables

INTRODUCTION

Vegetables contain carbohydrates, proteins, vitamins; minerals as well as trace metals and make up an important part of the human diet [1]. In recent years due to increase awareness on the food value of vegetables, their consumption is increasing gradually [2]. However, vegetables contain toxic and essential elements. Trace metals are important contaminants that found in the tissue and on the surface of vegetables. Trace metals deposition in vegetables are related with many sources such as contaminated air, vehicular emission, re-suspended road dust, small scale industries, brick kilns and diesel generator. Other sources of trace metals in urban and rural areas include industrial effluent, sewage and farm waste leading to contaminated soils and vegetables [3]. Heavy metals, such as Lead (Pb), Nickel (Ni), Cadmium (Cd), Copper (Cu), Chromium (Cr) and Mercury (Hg) are environmental pollutants, particularly in areas under waste water irrigation. Trace metals accumulations in vegetables cause a direct threat to human health [4].

Water is very important for survival of life. It is used for household, industrial, farming, and entertaining purposes but about 90% of water is consumed by agricultural zone [5]. In many areas of Pakistan crops are irrigated by fresh, sewage waste and canal water. The drain water comes from houses and small industrial units in villages. It has been estimated 116590 million gallons of sewage is being produced per day from big cities of Pakistan such as Lahore, Karachi, Islamabad, Faisalabad, Multan, Hyderabad, Peshawar, Kasur, and Quetta. This sewage is used to irrigate 32000 hectares area of these cities and is major source of trace metals such as Lead, Nickel, Chromium, Cobalt, Cadmium, Copper, Zinc and Iron [6] in vegetables grown on these soils [7]. These contaminated vegetables can cause serious health problems to human beings and animals. Sewage is also a rich source of organic and inorganic nutrients for plants growth [8] because it has high values of soluble salts, nitrates, pH, nitrites, alkalinity, chemical oxygen demand and cations like potassium, sodium, and calcium [9].

The WHO panel on nutrition, diet, and prevention of unending diseases suggested an individual intake of at least 400 g of vegetables and fruits per day [10, 11]. In most regions of Pakistan fresh water, sewage water, and industrial waste water is used for irrigation purpose, which are usually a rich source of metals. In some parts around River Ravi near Lahore, this contribution is very common, so it is highly likely that vegetables being grown on such soils may build up high amounts of metals including Pb and Ni. In this context, the main purpose of carrying out this work and investigation was to determine the accumulation of heavy metals in the field soil the fresh water, sewage waste water, and River Ravi water used for irrigation, the vegetable samples like turnip, radish, coriander, spinach and brassica.

A comparison of concentration of metals like Pb and Ni were drawn to those vegetables which were grown on the soil irrigated by fresh water. The effect of washing on trace metals level in vegetables was also studied. Lead is found in many locations and products. The common cause of Lead poisoning is chips from old paint and dust. Lead is found in radiators for cars and trucks, batteries, and some colours of ink also contain lead. Lead may get into foods or liquids that have been stored in pottery and ceramics. Lead-glazed dishes usually come from other countries. Lead can be found in wrappers, pottery, candy, containers, and in certain cultural foods. In plants Lead reduces root hair development, decreases Hill activity, inhibits germination, stunted growth, reduces photosynthetic rate, increased closure of the stomata [12]. Senescence, thinning of the canopy, phenology (flowering and fruiting), necrosis, chlorosis and deterioration in shoot condition [13], alters relative proportion of chlorophyll a and chlorophyll b, reduces total chlorophyll production and gaseous exchange in leaves [14]. In animals and human beings Lead cause anemia, decrease reaction time and cause weakness in finger and ankles [15]. Lead hampers with many of body processes and is toxic to organs and tissues including the bones, heart, kidneys, intestines and nervous and reproductive systems. Lead is chiefly toxic to children because it interferes with the development of the nervous system and cause behavior and permanent learning disorders.

Ni comes into the environment through sulphides, oxide ores and alloys. The sources of Ni in environment are combustion of fossil fuels (oil, gas and coal), storage batteries, electroplating, electrodes, aircraft and automobile parts, coins, spark plugs, pigments, paints, cooking utensils, printing fabrics and cosmetics. The uptake of Ni in plants is carried out mainly by active transport and passive diffusion [16]. The ratio of uptake of Ni in plants between active and passive transport varies with species, Ni form and concentration in the soil or nutrient solution [17, 18]. For example, soluble Ni compounds can be absorbed by the cation transport system [19-21].

The small amount of Ni is required for normal growth of plants therefore it is essential nutrient for plants. When the Ni pollution in the environment increased its toxic effects in plants also increased. In plants Ni reduces synthesis of Vitamin B-12 [22] and decreases dry matter production and yield [14]. In animals and human beings Ni cause respiratory disorder, nasal cancer and slows down activity of enzymes. Cigarette smoke causes the preservation of Nickel salts into the lungs. The inhalation of Nickel carbonyls causes dizziness, headache, pulmonary disorder, chest pain, vomiting, respiratory cancer, tremendous weakness and death. In drinking water Nickel causes intestinal and oral cancer [23].

Materials and Method

Apparatus

Hot Plates

STEDEC Rectangular Hot Plates (Temperature range 50 to 350 ^oC)

Electric Oven

Gallen Kamp Oven used for drying samples (Temperature Ranging 0 – 1000 ^oC).

Millipore Ultrapure Water Purification Unit

This type of unit was used to get Millipore ultrapure water.

Atomic Absorption Spectrometer

A Perkin Elmer AAnalyst 700 atomic absorption spectrometer equipped with HGA graphite furnace and a deuterium background corrector was used in the experiments. For graphite furnace measurements, argon was used as inert gas. Pyrolytic coated graphite tubes with a platform were used. Samples were injected into the graphite furnace using a Perkin Elmer AS-800 autosampler.

Chemicals

Ultra pure water used was supplied by a Milli-Q reagent water system (Millipore Corp., resistivity of 18.2 MΩ cm). HNO_3 and $HClO_4$ were of analytical grade quality (Merck, Darmstad, Germany).

Table 1: Instrumental Settings

Parameters	Lead (Pb)	Nickel (Ni)
Wavelength(nm)	283.3	232.0
Slit width (nm)	0.7	0.2
Lamp current (mA)	30	30
Argon flow (mL/min)	250	250
Sample volume (µL)	20	20
Signal type: Peak Area	AA-BG	AA-BG
Measuring Signal:	Peak Area	Peak Area
Detection Limit(mg/Kg)	0.001	0.001

Sampling

The ground water samples were collected from the bores constructed in the vegetable farms for supplying the ground water. The sewage water samples were collected directly from outlets of the sewage drains near the vegetable farms. The river Ravi water samples were collected at the point of river where vegetables were irrigated. The ground, sewage, and River Ravi water were collected in already cleaned and sanitized PTFE bottles (1.5 L). One from each of the collected samples was acidified with Nitric Acid (HNO_3). Then all the collected samples of water were transferred to laboratory and stored in refrigerator.

Pretreatment of Samples

Water sample for each was preserved in sampling bottles. The Nitric acid (HNO_3) was added in each water sample for the purpose of acidifying these samples. It avoided the ion exchange in the sample and preserved it for long time. The sewage sample was filtered by two micron filter paper before analysis to remove the suspended particles.

The soil samples were air-dried for 48 hours. Then these samples were later dried in an oven at 110^oC for 8 hours. After this these samples were crushed to pass a 200 mesh sieve by using Tema Mill. At the end the powdered soil samples were stored in air tight polythene bags.

The collected vegetable samples were cleaned with de-ionized water and air-dried these samples for 48 hours repeatedly. Then these samples were later dries in an oven at 100^oC for 1 hour. After this these samples were ground to powder using Tema mill of 200 -mesh size. At the end the powdered vegetable samples were stored in air tight polythene bags.

Digestion of Samples

1 g of the oven dried and sieved sample was weighed in a Teflon Beaker and moist with de-ionized water and then 2 mL of HF, 2 mL $HClO_4$ and 5mL of HNO_3 was added in it. Put the beaker on the hot plate placed in the Fume Hood. Let the beaker heat till the solution was evaporated near to dryness. After this 10 mL of 1:1 HNO_3 was added in the solution and kept watching the glass on the beaker. Continue leaching for 1 hour. At the end the samples were filtered into 25 mL volumetric flasks through Whatman Filter paper No. 41 and then made up to the mark with de-ionized water. In this way also prepared the Blank.

Calibration Standards

The Stock Solution of 1000 ppm of Nickel (Ni) and Pb were prepared. Standard solutions of 2.5 ppb, 5.0 ppb, 7.5 ppb 10.0 ppb for Ni and standard solution of 25 ppb, 50 ppb, 75 ppb and 100 ppb of Lead were prepared.

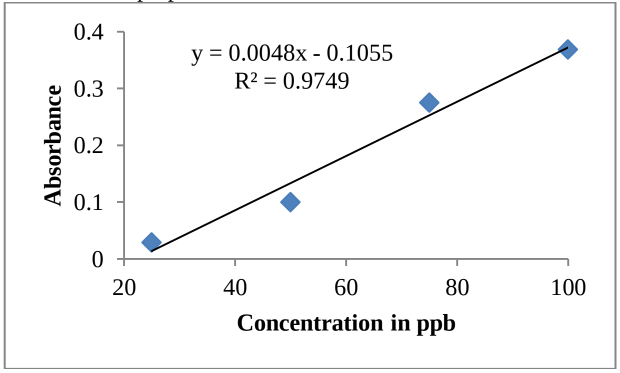

Figure 1: Calibration Curve for Lead

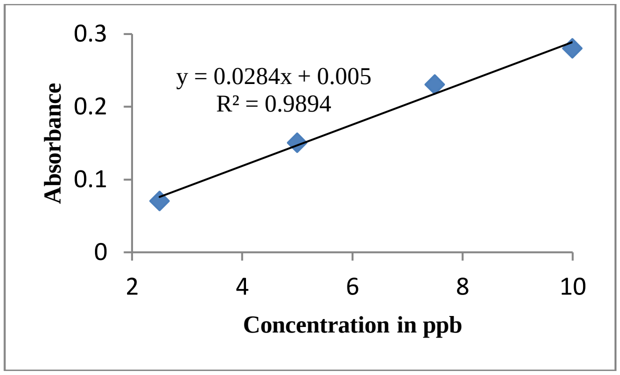

Figure 2: Calibration Curve for Nickel

Results and Discussion

The present work deals with the investigation of trace metals Lead and Nickel in the vegetables irrigated by sewage, Ravi and ground water. Sampling was carried out from Nain Sukh Lahore area, Saggian Khuda Yar area and River Ravi area near Saggian Bridge. The details are reported in tables 2.

Table No 2: Concentration of Pb and Ni (mg L^{-1}) water samples

Sr. No.	Sample ID	Description	Sampling Area	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	GW1	Fresh Water (non-acidified	Saggian Khuda Yar	0.74 ± 0.02	0.12 ± 0.01
2	GW1	Fresh Water (non-acidified	Saggian Khuda Yar	0.97 ± 0.01	0.18 ± 0.01
3	SW_1	Sewage water (non-acidified)	Nain Sukh	1.19 ± 0.03	0.35 ± 0.02
4	SW_2	Sewage water (acidified)	Nain Sukh	0.98 ± 0.02	0.44 ± 0.02
5	RW_1	Ravi water (non-acidified)	River Ravi	Not detected	0.53 ± 0.02
6	RW_2	Ravi water (acidified)	River Ravi	0.88 ± 0.01	0.30 ± 0.01

The maximum permissible limit for Pb and Ni recommended by Irrigation Water Quality Criteria is 5 mg L^{-1} and 0.2 mg L^{-1} respectively. Our value for Pb is within the permissible limit, whoever the value of Ni was found about 2 times more than the maximum permissible limits.

The maximum permissible limit of Pb and Ni established by Soil Science Society of America 85 mg kg^{-1} and 35 mg kg^{-1} respectively. Our values for Pb and Ni in soil are within the maximum permissible limit. The maximum permissible limit for Pb and Ni set by WHO for vegetables is 0.30 and 67 mg kg^{-1} respectively. Our values for Pb were about 2 times more than the maximum permissible limit. The relatively higher values of Pb in vegetables suggest that either the uptake was from the atmosphere or these species are hyper-accumulators. The maximum permissible limit according to WHO in air is 500 ng m^{-3} [24] but the survey conducted by Waheed indicates that the concentration of Pb in atmosphere of Lahore Pakistan is 4400 ng m^{-3} [25].

Table No 3: Concentration of Pb and Ni in soil irrigated by fresh water (Saggian Khuda Yar)

Sr. No.	Sample ID	Description	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	S_1	Turnip soil	6.81 ± 0.15	12.53 ± 0.56
2	S_2	Turnip soil	10.20 ± 0.26	12.63 ± 0.57
3	S_3	Radish soil	11.75 ± 0.30	15.24 ± 0.63
4	S_4	Radish soil	9.14 ± 0.20	15.05 ± 0.61
5	S_5	Coriander soil	9.23 ± 0.19	13.79 ± 0.58
6	S_6	Coriander soil	9.14 ± 0.22	14.56 ± 0.58
7	S_7	Spinach soil	10.49 ± 0.28	11.95 ± 0.35
8	S_8	Spinach soil	10.11 ± 0.23	12.14 ± 0.38
9	S_9	Brassica soil	12.43 ± 0.40	13.21 ± 0.40
10	S_{10}	Brassica soil	11.75 ± 0.35	13.30 ± 0.41

The maximum permissible limit for Pb and Ni recommended by Irrigation Water Quality Criteria is 5 mg L^{-1} and 0.2 mg L^{-1} respectively. Our value for Pb is within the permissible limit, whoever the value of Ni was found about 2 times more than the maximum permissible limits. The maximum permissible limit of Pb and Ni established by Soil Science Society of America 85 mg kg^{-1} and 35 mg kg^{-1} respectively. Our values for Pb and Ni in soil are within the maximum permissible limit. The maximum permissible limit for Pb and Ni set by WHO for vegetables is 0.30 and 67 mg kg^{-1} [26] respectively. Our value for Pb in Brassica was about 2 times more than the maximum permissible limit. The value of Pb in Coriander exceeded the maximum permissible limit set by WHO. Although the concentration of Pb found in water and soil was within the permissible limit in this area.

Table No 4: Concentration of Pb and Ni in soil irrigated by sewage water (Nain Sukh)

Sr. No.	Sample ID	Description	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	SS_1	Turnip soil	20.86 ± 0.56	12.53 ± 0.45
2	SS_2	Turnip soil	17.57 ± 0.58	11.66 ± 0.42
3	SS_3	Radish soil	28.03 ± 0.75	12.82 ± 0.48
4	SS_4	Radish soil	29.78 ± 0.95	13.01 ± 0.51
5	SS_5	Coriander soil	17.57 ± 0.63	14.18 ± 0.55
6	SS_6	Coriander soil	17.66 ± 0.59	14.56 ± 0.58
7	SS_7	Spinach soil	25.90 ± 0.78	13.89 ± 0.53
8	SS_8	Spinach soil	26.48 ± 0.88	13.98 ± 0.54

9	SS_9	Brassica soil	16.31 ± 0.61	15.53 ± 0.67
10	SS_{10}	Brassica soil	16.41 ± 0.67	15.63 ± 0.69

Table No 5: Concentration of Pb and Ni in soil irrigated by Ravi water (River Ravi near)

Sr. No.	Sample ID	Description	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	RS_1	Turnip soil	16.50 ± 0.55	13.79 ± 0.53
2	RS_2	Turnip soil	17.66 ± 0.68	13.89 ± 0.53
3	RS_3	Radish soil	14.08 ± 0.41	14.37 ± 0.57
4	RS_4	Radish soil	13.79 ± 0.39	14.56 ± 0.58
5	RS_5	Coriander soil	13.69 ± 0.33	13.11 ± 0.51
6	RS_6	Coriander soil	16.31 ± 0.50	13.21 ± 0.52
7	RS_7	Spinach soil	11.08 ± 0.29	11.27 ± 0.41
8	RS_8	Spinach soil	10.98 ± 0.26	11.37 ± 0.43
9	RS_9	Brassica soi	28.13 ± 0.88	15.15 ± 0.63
10	RS_{10}	Brassica soil	28.52 ± 0.93	15.24 ± 0.64

Table No 6: Concentration of Pb and Ni in Vegetables irrigated by fresh water (Saggian Khuda Yar)

Sr. No.	Sample ID	Description	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	V_1	Turnip (washed)	0.50 ± 0.05	7.06 ± 0.56
2	V_2	Turnip (washed)	0.41 ± 0.03	7.11 ± 0.59
3	V_3	Radish (washed)	0.45 ± 0.04	5.48 ± 0.34
4	V_4	Radish (washed)	0.32 ± 0.02	5.43 ± 0.29
5	V_5	Coriander (washed)	0.77 ± 0.06	1.49 ± 0.10
6	V_6	Coriander (washed)	0.45 ± 0.04	1.58 ± 0.12
7	V_7	Spinach (washed)	0.54 ± 0.06	4.98 ± 0.26
8	V_8	Spinach (washed)	0.41 ± 0.05	5.07 ± 0.27
9	V_9	Brassica (washed)	1.31 ± 0.09	3.17 ± 0.18
10	V_{10}	Brassica (washed)	0.77 ± 0.06	3.30 ± 0.19

The maximum permissible limit for Pb and Ni recommended by Irrigation Water Quality Criteria is 5 mg L^{-1} and 0.2 mg L^{-1} respectively. Our value for Pb is within the permissible limit, whoever the value of Ni was found about 2 times more than the maximum permissible limits. The concentration of Ni found in this area is between the safe limit set by WHO. The maximum permissible limit of Pb and Ni established by Soil Science Society of America 85 mg kg^{-1} and 35 mg kg^{-1} respectively. Our values for Pb and Ni in soil are within the maximum permissible limit. The maximum permissible limit for Pb and Ni set by WHO for vegetables is 0.30 and 67 mg kg^{-1} [26] respectively. Our value for Pb in Coriander and Brassica was about 2 times more than the maximum permissible limit. The value of Pb in Turnip and Spinach exceeded the maximum permissible limit set by WHO. Although the concentration of Pb found in water and soil was within the permissible limit in this area. The concentration of Ni found in this area is between the safe limit set by WHO.

Table No 7: Concentration of Pb and Ni in Vegetables irrigated by Sewage water (Nain Sukh)

Sr. No.	Sample ID	Description	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	SV_1	Turnip (washed)	0.33 ± 0.05	5.72 ± 0.35
2	SV_2	Turnip (unwashed)	0.20 ± 0.03	6.85 ± 0.49
3	SV_3	Radish (washed)	0.15 ± 0.02	5.54 ± 0.33
4	SV_4	Radish (unwashed)	0.06 ± 0.01	5.17 ± 0.31
5	SV_5	Coriander (washed)	0.51 ± 0.07	2.32 ± 0.15
6	SV6	Coriander (unwashed)	0.24 ± 0.03	2.55 ± 0.16
7	SV_7	Spinach (washed)	0.33 ± 0.04	6.31 ± 0.45
8	SV_8	Spinach (unwashed)	0.06 ± 0.01	6.85 ± 0.48
9	SV_9	Brassica (washed)	0.42 ± 0.04	2.82 ± 0.17
10	SV_{10}	Brassica (unwashed)	0.74 ± 0.06	3.41 ± 0.21

Table No 8: Concentration of Pb and Ni in Vegetables irrigated by Sewage water (River Ravi)

Sr. No.	Sample ID	Description	Conc. of Pb (mg L^{-1})	Conc. of Ni (mg L^{-1})
1	RV_1	Turnip (washed)	0.45 ± 0.09	5.12 ± 0.31
2	RV_2	Turnip (unwashed)	0.41 ± 0.08	6.93 ± 0.43
3	RV_3	Radish (washed)	0.54 ± 0.09	5.70 ± 0.35
4	RV_4	Radish (unwashed)	0.36 ± 0.04	6.16 ± 0.41
5	RV_5	Coriander (washed)	0.69 ± 0.07	1.78 ± 0.07

6	RV_6	Coriander (unwashed)	0.38 ± 0.04	2.19 ± 0.11
7	RV_7	Spinach (washed)	0.47 ± 0.07	5.49 ± 0.32
8	RV_8	Spinach (unwashed)	0.20 ± 0.02	5.85 ± 0.36
9	RV_9	Brassica (washed)	0.47 ± 0.06	3.45 ± 0.17
10	RV_{10}	Brassica (unwashed)	0.78 ± 0.08	3.91 ± 0.19

Conclusion

The results and discussion show that the amount of Pb in all the water samples of Saggian Khuda Yar near Faizpur Motorway, Nain Sukh Lahore and River Ravi near Saggian Bridge used for the irrigation purpose was found within the maximum permissible limits, whereas the amount of Ni was two times higher in sewage and River Ravi water than the maximum permissible limits. It is interesting to note that the amount of Ni found highest in sewage and River Ravi water could not contaminate the vegetation. Almost in all the soil samples the concentration of Pb and Ni was found to be within the safe limits.

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