



## TRACE ELEMENTS ANALYSIS OF CROPS AND VEGETABLES GROWN AROUND INDUSTRIAL AREAS OF FAISALABAD AND GUJRANWALA CITIES USING INAA AND AAS

\*S.N. HUSAINI, J.H. ZAIDI<sup>1</sup>, MATIULLAH, M. AKRAM and K. SUBHAN<sup>2</sup>

Physics Division, Directorate of Science, PINSTECH, P.O. Nilore, Islamabad, Pakistan

PINSTECH, P.O. Nilore, Islamabad, Pakistan

<sup>2</sup>Equipment Maintenance Division, Directorate of S & S, PINSTECH, P.O. Nilore, Islamabad, Pakistan

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Industrial effluents pollution is a source of risk to the health of people living in industrial cities of Pakistan. Most of the untreated effluents are discharged to the nearby agricultural fields that pollutes the vegetation grown in such soil. A majority of the industries are not equipped with suitable recycling and effluent treatment plants. Consequently, toxic metals enter our food chain and results in significant health risks and serious diseases. In order to evaluate the concentration of toxic metals (namely As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb and Se), in crops and vegetable samples collected from the irrigated areas of Faisalabad and Gujranwala regions. Neutron activation analysis (NAA) and atomic absorption spectrometric (AAS) techniques have been used. All the observed metal concentrations were higher than the reported literature values. Moreover, the highest values of toxic metals of As ( $0.44 \pm 0.03 \mu\text{g/g}$ ) and Co ( $0.5 \pm 0.01 \mu\text{g/g}$ ), Mn ( $45.3 \pm 2.0 \mu\text{g/g}$ ) and Sb ( $0.1 \pm 0.01 \mu\text{g/g}$ ), Se ( $1.28 \pm 0.06 \mu\text{g/g}$ ) and Pb ( $3.84 \pm 0.27 \mu\text{g/g}$ ) were found in tomato, bitter gourd and rice samples respectively.

**Keywords:** Industrial pollution, Effluents, Toxic metals, Human health, NAA and AAS techniques

### 1. Introduction

Industrial pollution affects our environment, health of human beings and animals, oceans, lakes, rivers and underground water, making it a global concern for the sustainability of ecosystem [1]. There are serious consequences of the uncontrolled release of unprocessed effluents on the ecological balance of the atmosphere and is one of the most crucial problems of both developed and developing countries [2]. There are concomitant environmental risks with crude industrial effluents reuse, such as transport of harmful contaminants in soils, pollution of groundwater and surface-water, degradation of soil quality e.g salinity, impacts on plant growth etc. [3]. Untreated discharge of the effluents is a cognizable offence under the Environmental Protection Act 1997 (EPA-97) of Pakistan [4]. However, this law is not strictly implemented to limit the release and/or proper disposal of industrial effluents. Therefore, volume of the unspecified

industrial discharge is growing at an exponential rate without any specific safeguards. The problems related to industrial pollution have largely drawn attention of scientists and environmentalists of the country [5-12]. However, there are a few agronomic and economic benefits of effluents use in agriculture [13-15] such as they may increase the available water supply or release better quality supplies for alternative uses.

In Pakistan, industrial effluents and sewage water are also being used, due to inadequate sources of water, for the cultivation of crops and vegetables. People in some industrial cities consume these food articles due to lack of affordable food articles grown in the clean environment. The eminent concentrations of heavy metals are continuously entering into the food chain due to such agricultural practices leading to severe health hazard problems and may cause impairment of the vital organs of human body. There are some significant diseases [16-18] in

\* Corresponding author : husaini@pinstech.org.pk

Table 1. Analytical parameters for AAS analysis

Elements	Resonance Absorbance line $\lambda$ (nm)	Interfering agents	Instrument detection limit ( $\mu\text{g/ml}$ )	Sensitivity ( $\mu\text{g/ml}$ )	Optimum concentration range (ppm)
Cd	228.8	Silicon	0.002	0.025	0.05 – 6.0
Cu	324.8	NIL	0.01	0.1	0.2 – 30
Ni	232.0	NIL	0.02	0.15	0.3 – 10
Pb	217.0	Aluminum & Silicon	0.05	0.5	1.0 – 200

Table 2. Optimum experimental conditions and nuclear data employed for the neutron activation analysis

Isotope	Half-life	$\gamma$ -peak (keV)	Irradiation time	Cooling time
$^{56}\text{Mn}$	2.58 h	846.8	10 m	3 h
$^{76}\text{As}$	26.3 h	559.1	25 m	2 d
$^{51}\text{Cr}$	27.7 d	320.1	5 h	2 w
$^{124}\text{Sb}$	60.2 d	1691.1	5 h	2 w
$^{75}\text{Se}$	119.8 d	264.7	5 h	2 w
$^{60}\text{Co}$	5.27 y	1173.2	5 h	2 w

m = minutes, h = hours, d = days, w = week, y = year

humans due to the consumption of toxic metals through contaminated crops and vegetables that are cultivated with untreated effluents. These diseases include brain damage, typhoid, cholera, leukemia, dysentery, gastroenteritis, diarrhoea, vomiting, lung cancer and ulcers, pigmentation of fingers and nails, hypertension, pregnancy toxemia, impair growth, heart failure, low blood pressure, bones disorderness, myocardial infarction, hepatic neurosis, skeletal abnormalities, Parkinson syndrome, loss of hair, depression, dermatitis, alcapia tumor, kishan disease, etc.

The prime objective of this research was to investigate the accumulation of toxic and other metals in the crops and vegetables which were cultivated within the vicinity of industrial areas of Faisalabad and Gujranwala regions. In crops, the samples of wheat (*Triticum aestivum*) and rice (*Oryza sativa*) were examined. Similarly, for vegetables, the samples of brinjal (*Solanum melongena*), tomato (*Solanum lycopersicum*) and bitter gourd (*Momordica charantia*) were studied.

## 2. Experiment Procedures

### 2.1. Sampling and Sample Preparation

Crops and vegetables samples were collected in different seasons in the vicinity of the selected industrial areas of Faisalabad and Gujranwala

regions using Grab sampling technique [19]. Vegetable samples consisted of tomato, brinjal and bitter guard whereas crop samples included wheat and rice. During Grab sampling, the interested areas were selected and proper codes were assigned for those areas to collect various samples in different seasons from them. Samples preparation process involved different standard steps. All samples were washed with distilled water to remove any surface contamination, then with deionized water and subsequently dried with hot air blower. The samples were then freeze-dried, ground to fine powder, sieved and homogenized. The samples were stored in pre-cleaned polyethylene capped bottles.

### 2.2. Neutron Irradiations

For NAA [21], the samples, (each weighing 150 mg) alongwith the appropriate amounts of reference materials, namely NIST-SRM Citrus Leaves (CL-1572) and Lichen (IAEA-336) for biological samples and Lake sediment (IAEA-SL-1) and Soil-7 for geological samples, were irradiated for 10 minute to 5 hour depending on the requirement. Samples were taken in triplicate and heat-sealed in pre-cleaned polyethylene and quartz ampoules for short and long lived radionuclides respectively. The quartz ampoules were placed in irradiation aluminum cans and cold-welded. Irradiations were carried out in thermal tubes and

core of a 10 MW swimming pool- type research reactor (PARR-I). Thermal neutron flux density at the irradiation site of the reactor is  $7 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ . Thermal neutron flux monitors, e.g. Au, Co, and Al foils, were inserted between the samples and the standards to determine fluctuations in the thermal neutron flux gradient. The irradiated samples and standards were transferred to the pre-weighed polyethylene vials and reweighed to determine the exact weight.

### 2.3. $\gamma$ -ray Spectrometry

The  $\gamma$ -ray spectra of the samples and standards were recorded, after appropriate cooling, for varying times ranging from 3 hour to 2 week employing a 4k series 85 a Canberra multi-channel analyzer coupled with a EurisyS coaxial 245  $\text{cm}^3$  HPGe detector. The system has a resolution of 1.9 keV for 1332.5 keV  $\gamma$ -peak of  $^{60}\text{Co}$  and Peak/Compton ratio of 40:1. The data, transferred from MCA to the central computer facility, was processed by using locally developed software.

### 2.4. AAS Technique

For AAS analysis, 0.5 gram international atomic energy agencies (IAEA) certified reference materials (SL-1 and Soil-7) were taken in a Teflon beaker and dissolved in 10 ml Aquaregia (3 ml conc. HCl & 1 ml conc.  $\text{HNO}_3$ ). The mixture was dried on a hotplate at 80 °C. Filtrate and precipitates were separated through filtration technique. 5 ml conc. HF and 1 ml conc.  $\text{H}_2\text{SO}_4$  were added in the residue. Heating and fuming was done for two times. Then 1 ml conc. HF, 0.5 ml conc.  $\text{HClO}_4$ , 0.5 ml conc.  $\text{H}_2\text{SO}_4$  and 2 ml Aquaregia were added in it. Heating was done up to fuming. Again 5 ml Aquaregia was added and filtrate was also mixed. The final volume was made up to 50 ml with demineralized water. All atomic absorption spectrometric [20] measurements were carried out using Hitachi Zeeman Atomic Absorption Spectrometer model Z-8000 with a Zeeman Effect background correction mode. It consists of a light source, atomizer unit, monochromators, detector and readout device, computer & printer. The instrument was also equipped with a graphite furnace, an auto-sampler and a computer based programmed for analysis. Argon was used as an inert purging gas; the flow was interrupted during the atomization step. Signal evaluation was based on integrated absorbance values. The analytical parameters, instrumental detection limits, sensitivity and optimum concentration range for

AAS analysis are shown in Table 1. The measurements of cadmium (Cd), copper (Cu), nickel (Ni) and lead (Pb) were carried out with an electro-thermal atomization technique. The adjusted operating parameters for such measurements were burner height 7.5 cm, lamp current 7.5 mA, slit width 1.3 cm and acetylene was used as a fuel with 2.2 l/min flow rate.

## 3. Results and Discussion

All the samples were analyzed using instrumental neutron activation analysis (INAA) and atomic absorption spectrometric (AAS) techniques. After irradiation of samples, the short-lived indicator radio-nuclides (i.e.  $^{56}\text{Mn}$  and  $^{76}\text{As}$ ) were measured employing short irradiation time whereas relatively long-lived indicator radio-nuclides, (i.e.  $^{124}\text{Sb}$ ,  $^{60}\text{Co}$ ,  $^{51}\text{Cr}$  and  $^{75}\text{Se}$ ) were measured employing long irradiation time after appropriate cooling (Table 2). The  $\gamma$ -peaks of all the radio-nuclides were well resolved. Most of the elements were determined without any spectral interference with few exceptions. To avoid interference of  $^{134}\text{Cs}$  at 604.7 keV with full intensity peak of  $^{124}\text{Sb}$  at 602.7 keV, the concentration of antimony was determined by using less intense, interference free peak at 1691.0 KeV with long counting times. The photo-peak of  $^{75}\text{Se}$  at 279.5 keV interfered with the photo-peak of  $^{203}\text{Hg}$ . This problem was overcome [22] by calculating the concentration of selenium from the non-interfering peak at 264.7 keV.

The reliability of the method was checked by analyzing reference materials, including Lichen (IAEA-336) and Citrus Leaves (NIST/ CRM-1572) for biological samples and Lake Sediment (IAEA-SL-1) and IAEA-Soil-7 for geological samples. Our values are fairly in good agreement with the certified values, as shown in Tables 3 and 4. For IAEA Lichen and CL (Table 3) variation coefficient between cited values of Lichen and observed values is 0.93 – 5.48%. Similarly, the range of percent deviations between recommended values of Citrus leaves and observed values is 1.81 – 3.79%. In Table 4, for SL-1 and S-7 CRMs, the range of percent deviations between cited values of SL-1 and observed values is 1.06 – 4.58%. Similarly, the range of percent deviations between recommended values of S-7 and observed values is 1.49 – 5.88%.

Table 3. INAA of IAEA and NIST bio- standard reference materials (concentration in  $\mu\text{g/g}^*$ )

Elements	IAEA-336 (Lichen)		NIST/ CRM-1572 (Citrus Leaves)	
	IAEA Values	Our Values	NIST Values	Our Values
As	0.63 $\pm$ 0.08	0.61 $\pm$ 0.09	3.1 $\pm$ 0.3	2.99 $\pm$ 0.36
Co	0.29 $\pm$ 0.05	0.28 $\pm$ 0.06	(0.02)	0.017 $\pm$ 0.01
Cr	(1.06)	1.05 $\pm$ 0.21	0.8 $\pm$ 0.2	0.74 $\pm$ 0.02
Mn	63.0 $\pm$ 7.0	61.6 $\pm$ 7.8	23.0 $\pm$ 2.0	22.3 $\pm$ 2.9
Sb	0.073 $\pm$ 0.01	0.069 $\pm$ 0.02	(0.04)	0.038 $\pm$ 0.03
Se	0.22 $\pm$ 0.04	0.23 $\pm$ 0.05	(0.025)	0.02 $\pm$ 0.01

\*95% Confidence Interval

Values in parenthesis ( ) are information values

Table 4. INAA of IAEA geo-standard reference materials (concentration in  $\mu\text{g/g}$ )

Elements	IAEA-SL1		IAEA-S7	
	IAEA Values	Our Values	IAEA Values	Our Values
As	27.5 $\pm$ 3.02	28.3 $\pm$ 2.3	13.4 $\pm$ 0.85	13.2 $\pm$ 0.95
Co	19.8 $\pm$ 1.5	19.4 $\pm$ 1.2	8.9 $\pm$ 0.85	8.60 $\pm$ 0.9
Cr	104.1 $\pm$ 9.05	103 $\pm$ 9.9	60 $\pm$ 12.5	59.1 $\pm$ 13.5
Mn	3400 $\pm$ 160	3516 $\pm$ 182	631 $\pm$ 23	616 $\pm$ 27.0
Sb	1.31 $\pm$ 0.12	1.37 $\pm$ 0.15	1.7 $\pm$ 0.2	1.6 $\pm$ 0.5
Se	(2.9)	2.78 $\pm$ 1.21	(0.4)	0.38 $\pm$ 0.3

\*95% Confidence Interval Values in parenthesis ( ) are information values

For comparison purposes, in Tables 5 and 6, observed data has been compared with the reference values from literature [15, 23-27] for vegetables (i.e. Brinjal, Tomato & Bitter gourd) collected from industrial areas of Faisalabad and Gujranwala regions respectively. For Faisalabad, in case of brinjal, all the obtained metal concentrations are higher than reported values in literature. However, the observed values of Mn (9.0 $\pm$ 0.03  $\mu\text{g/g}$ ) and Sb (0.05 $\pm$ 0.004  $\mu\text{g/g}$ ) are low as compared to the literature values (13.6 $\pm$ 0.6  $\mu\text{g/g}$ ) and (0.068 $\pm$ 0.007  $\mu\text{g/g}$ ) respectively. Moreover, the observed values of As (0.26 $\pm$ 0.01  $\mu\text{g/g}$ ), Co (0.35 $\pm$ 0.02  $\mu\text{g/g}$ ), Cr (11.6 $\pm$ 0.5  $\mu\text{g/g}$ ), Cu (8.3 $\pm$ 0.5  $\mu\text{g/g}$ ), Ni (2.1 $\pm$ 0.1  $\mu\text{g/g}$ ) Pb (0.9 $\pm$ 0.01  $\mu\text{g/g}$ ) and Se (0.29 $\pm$ 0.08  $\mu\text{g/g}$ ) are 2-15 times higher than the literature values of (0.115 $\pm$ 0.01  $\mu\text{g/g}$ , 0.12 $\pm$ 0.03  $\mu\text{g/g}$ , 0.97 $\pm$ 0.1  $\mu\text{g/g}$ , 2.8 $\pm$ 0.2  $\mu\text{g/g}$ , 0.8 $\pm$ 0.05  $\mu\text{g/g}$ , 0.06 $\pm$ 0.006  $\mu\text{g/g}$  and 0.028 $\pm$ 0.003  $\mu\text{g/g}$ ) respectively. In case of tomato, all the current values of metal concentrations were higher than literature values. However, the observed value of Mn (10.8 $\pm$ 0.9  $\mu\text{g/g}$ ) was low as compared to the literature value (12.2 $\pm$ 0.6  $\mu\text{g/g}$ ). Moreover, the observed values of Cd (0.1 $\pm$ 0.01  $\mu\text{g/g}$ ), Pb (0.5 $\pm$ 0.01  $\mu\text{g/g}$ ) and Se (0.18 $\pm$ 0.02  $\mu\text{g/g}$ ) were 2-5 times higher than the literature values for these

elements (0.075 $\pm$ 0.003  $\mu\text{g/g}$ , 0.255 $\pm$ 0.004  $\mu\text{g/g}$  and 0.039 $\pm$ 0.004  $\mu\text{g/g}$ ) respectively. In case of bitter gourd, all the current values of metal concentrations were higher than literature values. However, the observed values of Ni (3.1 $\pm$ 0.1  $\mu\text{g/g}$ ) and Pb (1.7 $\pm$ 0.1  $\mu\text{g/g}$ ) were lower than the literature values of (8.32  $\mu\text{g/g}$  and 2.15  $\mu\text{g/g}$ ) respectively. Moreover, the observed values of Mn (45.3 $\pm$ 2.0  $\mu\text{g/g}$ ), Se (0.1 $\pm$ 0.01  $\mu\text{g/g}$ ) and Cr (5.7 $\pm$ 0.8  $\mu\text{g/g}$ ) were 2-4 times higher than the literature cited values of (26.3 $\mu\text{g/g}$ , 0.06  $\mu\text{g/g}$  and 1.5 $\pm$ 0.1  $\mu\text{g/g}$ ) respectively. The higher elemental values in all samples may be due to the contribution of industrial effluents and nature of soil.

For Gujranwala, in case of brinjal, all the current values of metal concentrations were higher than reported values in literature. However, the observed values of Mn (11.0 $\pm$ 0.03  $\mu\text{g/g}$ ) and Sb (0.04 $\pm$ 0.004  $\mu\text{g/g}$ ) were low as compared to the literature values (13.6 $\pm$ 0.6  $\mu\text{g/g}$ ) and (0.068 $\pm$ 0.007  $\mu\text{g/g}$ ) respectively. Moreover, the observed values of As (0.21 $\pm$ 0.01  $\mu\text{g/g}$ ), Co (0.3 $\pm$ 0.02  $\mu\text{g/g}$ ), Cr (11.0 $\pm$ 0.5  $\mu\text{g/g}$ ), Cu (7.3 $\pm$ 0.5  $\mu\text{g/g}$ ), Ni (1.9 $\pm$ 0.1  $\mu\text{g/g}$ ) Pb (0.8 $\pm$ 0.01  $\mu\text{g/g}$ ) & Se (0.2 $\pm$ 0.08  $\mu\text{g/g}$ ) were 2 to 13 times higher than the literature values of (0.115 $\pm$ 0.01  $\mu\text{g/g}$ ), (0.12 $\pm$ 0.03  $\mu\text{g/g}$ ), (0.97 $\pm$ 0.1

Table 5. Comparisons between present data and values reported in the literature for studied vegetables grown in industrial areas of Faisalabad

Elements	Brinjal		Tomato		Bitter gourd	
	This Works	Reference values	This Works	Reference values	This Works	Reference values
As	0.26±0.01	0.115±0.01 <sup>23</sup>	0.44±0.03	0.69±0.07 <sup>23</sup>	0.2±0.02	0.177±0.02 <sup>23</sup>
Cd	0.09±0.001	0.07±0.004 <sup>25</sup>	0.1±0.01	0.075±0.003 <sup>25</sup>	0.07±0.001	0.06 <sup>15</sup>
Co	0.35±0.02	0.12±0.03 <sup>25</sup>	0.5±0.01	0.43±0.14 <sup>27</sup>	0.21±0.04	0.168±0.01 <sup>24</sup>
Cr	11.6±0.5	0.97±0.1 <sup>24</sup>	2.68±0.02	2.4±0.2 <sup>24</sup>	5.7±0.8	1.5±0.1 <sup>24</sup>
Cu	8.3±0.5	2.8±0.2 <sup>24</sup>	12.2±0.6	10.8±0.9 <sup>24</sup>	11.5±1.0	9.4±0.8 <sup>24</sup>
Mn	9.0±0.03	13.6±0.6 <sup>24</sup>	10.8±0.09	12.2±0.6 <sup>24</sup>	45.3±2.0	26.3 <sup>15</sup>
Ni	2.1±0.1	0.8±0.05 <sup>25</sup>	1.9±0.1	1.365±0.01 <sup>26</sup>	3.1±0.1	8.32 <sup>15</sup>
Pb	0.9±0.01	0.06±0.006 <sup>26</sup>	0.5±0.01	0.255±0.004 <sup>25</sup>	1.7±0.1	2.15 <sup>15</sup>
Sb	0.05±0.004	0.068±0.007 <sup>23</sup>	0.08±0.001	0.057±0.006 <sup>23</sup>	0.1±0.01	0.082±0.008 <sup>23</sup>
Se	0.29±0.08	0.028±0.003 <sup>23</sup>	0.18±0.02	0.039±0.004 <sup>23</sup>	0.1±0.01	0.06 <sup>15</sup>

(µg/g) is the unit for concentration of all studied elements

Table 6. Comparisons between present data and values reported in the literature for studied vegetables grown in industrial areas of Gujranwala

Elements	Brinjal		Tomato		Bitter gourd	
	This Works	Reference values	This Works	Reference values	This Works	Reference values
As	0.21±0.01	0.115±0.01 <sup>23</sup>	0.54±0.03	0.69±0.07 <sup>23</sup>	0.21±0.02	0.177±0.02 <sup>23</sup>
Cd	0.08±0.001	0.07±0.004 <sup>25</sup>	0.09±0.01	0.075±0.003 <sup>25</sup>	0.065±0.001	0.06 <sup>15</sup>
Co	0.3±0.02	0.12±0.03 <sup>25</sup>	0.51±0.01	0.43±0.14 <sup>27</sup>	0.19±0.04	0.168±0.01 <sup>24</sup>
Cr	11.0±0.5	0.97±0.1 <sup>24</sup>	2.58±0.02	2.4±0.2 <sup>24</sup>	5.1±0.8	1.5±0.1 <sup>24</sup>
Cu	7.3±0.5	2.8±0.2 <sup>24</sup>	11.2±0.6	10.8±0.9 <sup>24</sup>	10.5±1.0	9.4±0.8 <sup>24</sup>
Mn	11.0±0.03	13.6±0.6 <sup>24</sup>	9.0±1.0	12.2±0.6 <sup>24</sup>	34.3±2.0	26.3 <sup>15</sup>
Ni	1.9±0.1	0.8±0.05 <sup>25</sup>	1.7±0.1	1.365±0.01 <sup>26</sup>	4.6±0.1	8.32 <sup>15</sup>
Pb	0.8±0.01	0.06±0.006 <sup>26</sup>	0.4±0.01	0.255±0.004 <sup>25</sup>	1.1±0.1	2.15 <sup>15</sup>
Sb	0.04±0.004	0.068±0.007 <sup>23</sup>	0.07±0.001	0.057±0.006 <sup>23</sup>	0.09±0.01	0.082±0.008 <sup>23</sup>
Se	0.2±0.08	0.028±0.003 <sup>23</sup>	0.11±0.02	0.039±0.004 <sup>23</sup>	0.08±0.01	0.06 <sup>15</sup>

(µg/g) is the unit for concentration of all studied elements

µg/g), (2.8±0.2 µg/g), (0.8±0.05 µg/g), (0.06±0.006 µg/g) and (0.028±0.003 µg/g) respectively. In case of tomato, all the reported values are higher than literature values. However, the observed value of Mn (9.0±1.0 µg/g) was low as compared to the literature value (12.2±0.6 µg/g). Moreover, the observed values of Pb (0.4±0.01 µg/g) and Se (0.11±0.02 µg/g) were 2 and 3 times higher than

the literature values (0.255±0.004 µg/g) and (0.039±0.004 µg/g) respectively. In case of bitter gourd, all the current values of metal concentrations were higher than reported values in literature. However, the observed values of Ni (4.6±0.1 µg/g) and Pb (1.1±0.1 µg/g) were low as compared to the literature values (8.32 µg/g) and (2.15 µg/g) respectively. Moreover, the observed

Table 7. Concentrations ( $\mu\text{g/g}$ ) of trace elements in wheat crop, grown in the vicinity of industrial areas of Faisalabad and Gujranwala regions and values quoted from literature

Elements	Faisalabad's Samples	Gujranwala's Samples	Reference Values
As	0.13 $\pm$ 0.02	0.11 $\pm$ 0.02	0.058 $\pm$ 0.006 <sup>23</sup>
Cd	0.09 $\pm$ 0.004	0.08 $\pm$ 0.004	0.18 $\pm$ 0.07 <sup>28</sup>
Co	0.11 $\pm$ 0.01	0.07 $\pm$ 0.01	0.014 $\pm$ 0.002 <sup>24</sup>
Cr	0.46 $\pm$ 0.08	0.65 $\pm$ 0.08	0.2 $\pm$ 0.02 <sup>24</sup>
Cu	8.9 $\pm$ 1.1	9.9 $\pm$ 1.1	3.6 $\pm$ 0.2 <sup>24</sup>
Mn	8.65 $\pm$ 0.3	18.6 $\pm$ 0.3	16.2 $\pm$ 1.2 <sup>24</sup>
Ni	3.9 $\pm$ 0.8	4.9 $\pm$ 0.8	1.49 $\pm$ 0.88 <sup>28</sup>
Pb	3.84 $\pm$ 0.27	3.4 $\pm$ 0.27	0.86 $\pm$ 0.79 <sup>28</sup>
Sb	0.05 $\pm$ 0.002	0.03 $\pm$ 0.002	0.06 $\pm$ 0.001 <sup>23</sup>
Se	0.81 $\pm$ 0.02	0.68 $\pm$ 0.2	0.22 $\pm$ 0.028 <sup>23</sup>

Table 8. Concentrations ( $\mu\text{g/g}$ ) of trace elements in rice crop, grown in the vicinity of industrial areas of Faisalabad and Gujranwala regions and values quoted from literature

Elements	Faisalabad's Samples	Gujranwala's Samples	Reference Values
As	0.16 $\pm$ 0.04	0.13 $\pm$ 0.04	0.087 $\pm$ 0.009 <sup>23</sup>
Cd	0.1 $\pm$ 0.01	0.1 $\pm$ 0.01	0.11 $\pm$ 0.07 <sup>28</sup>
Co	0.018 $\pm$ 0.003	0.08 $\pm$ 0.003	0.031 $\pm$ 0.004 <sup>24</sup>
Cr	0.6 $\pm$ 0.04	0.86 $\pm$ 0.04	0.43 $\pm$ 0.04 <sup>24</sup>
Cu	10.2 $\pm$ 1.2	14.2 $\pm$ 1.2	4.9 $\pm$ 0.4 <sup>24</sup>
Mn	33.7 $\pm$ 2.6	31.7 $\pm$ 2.6	8.6 $\pm$ 0.4 <sup>24</sup>
Ni	2.4 $\pm$ 0.4	5.2 $\pm$ 0.04	0.97 $\pm$ 0.66 <sup>28</sup>
Pb	4.8 $\pm$ 0.07	4.0 $\pm$ 0.07	0.6 $\pm$ 0.3 <sup>28</sup>
Sb	0.04 $\pm$ 0.001	0.03 $\pm$ 0.001	0.011 $\pm$ 0.002 <sup>23</sup>
Se	1.28 $\pm$ 0.06	1.0 $\pm$ 0.06	0.75 $\pm$ 0.074 <sup>23</sup>

value of Cr (5.1 $\pm$ 0.8  $\mu\text{g/g}$ ) was 4 times higher than the literature cited value (1.5 $\pm$ 0.1  $\mu\text{g/g}$ ). Among all studied vegetables, the concentrations for observed values of Se (0.29 $\pm$ 0.08  $\mu\text{g/g}$ ) and Cr (11.6 $\pm$ 0.5  $\mu\text{g/g}$ ) were highest in brinjal. Similarly, the concentrations for observed values of As (0.44 $\pm$ 0.03  $\mu\text{g/g}$ ), Cd (0.1 $\pm$ 0.01  $\mu\text{g/g}$ ), Co (0.5 $\pm$ 0.01  $\mu\text{g/g}$ ) and Cu (12.2 $\pm$ 0.6  $\mu\text{g/g}$ ) were highest in tomato. In the same way, the concentrations for current values of Mn (45.3 $\pm$ 2.0  $\mu\text{g/g}$ ), Ni (3.1 $\pm$ 0.1  $\mu\text{g/g}$ ), Pb (1.7 $\pm$ 0.1  $\mu\text{g/g}$ ), Sb (0.1 $\pm$ 0.01  $\mu\text{g/g}$ ) and Zn (99.8 $\pm$ 7.0  $\mu\text{g/g}$ ) were highest in bitter gourd.

The current data for different crops (wheat and rice) is presented in Tables 7 and 8 collected from the vicinity of industrial areas of Faisalabad and Gujranwala regions. Moreover, it is also compared with literature values [24-25, 29]. Table 7, for wheat samples from Faisalabad, shows that all the current values for studied elements are higher than

the cited values. However, the observed values of Cd (0.09 $\pm$ 0.004  $\mu\text{g/g}$ ), Mn (8.65 $\pm$ 0.3  $\mu\text{g/g}$ ), and Sb (0.05 $\pm$ 0.002  $\mu\text{g/g}$ ) were low as compared to the literature values (0.18 $\pm$ 0.07  $\mu\text{g/g}$ ), (16.2 $\pm$ 1.2  $\mu\text{g/g}$ ) and (0.06 $\pm$ 0.001  $\mu\text{g/g}$ ) respectively. Moreover, the observed values of As (0.13 $\pm$ 0.02  $\mu\text{g/g}$ ), Co (0.11 $\pm$ 0.01  $\mu\text{g/g}$ ), Cr (0.46 $\pm$ 0.08  $\mu\text{g/g}$ ), Cu (8.9 $\pm$ 1.1  $\mu\text{g/g}$ ), Ni (3.9 $\pm$ 0.8  $\mu\text{g/g}$ ), Pb (3.84 $\pm$ 0.27  $\mu\text{g/g}$ ) and Se (0.81 $\pm$ 0.02  $\mu\text{g/g}$ ) were 2-8 times higher than the literature cited values (0.058 $\pm$ 0.006), (0.014 $\pm$ 0.002  $\mu\text{g/g}$ ), (0.2 $\pm$ 0.02  $\mu\text{g/g}$ ), (3.6 $\pm$ 0.2  $\mu\text{g/g}$ ), (1.49 $\pm$ 0.88  $\mu\text{g/g}$ ), (0.86 $\pm$ 0.79  $\mu\text{g/g}$ ) & (0.22 $\pm$ 0.028  $\mu\text{g/g}$ ) respectively. In wheat samples which were collected from Gujranwala region, all the studied elements were higher than the cited values in literature. However, the observed value of Cd (0.08 $\pm$ 0.004  $\mu\text{g/g}$ ) was low as compared to the literature value (0.18 $\pm$ 0.07  $\mu\text{g/g}$ ). Moreover, the observed values of As (0.11 $\pm$ 0.02  $\mu\text{g/g}$ ), Co (0.07 $\pm$ 0.01  $\mu\text{g/g}$ ), Cr (0.65 $\pm$ 0.08  $\mu\text{g/g}$ ), Cu (9.9 $\pm$ 1.1

$\mu\text{g/g}$ ), Ni ( $4.9\pm 0.8 \mu\text{g/g}$ ), Pb ( $3.4\pm 0.27 \mu\text{g/g}$ ) & Se ( $0.68\pm 0.2 \mu\text{g/g}$ ) were 2-5 times higher than the literature values ( $0.058\pm 0.006 \mu\text{g/g}$ ), ( $0.014\pm 0.002 \mu\text{g/g}$ ), ( $0.2\pm 0.02 \mu\text{g/g}$ ), ( $3.6\pm 0.2 \mu\text{g/g}$ ), ( $1.49\pm 0.88 \mu\text{g/g}$ ), ( $0.86\pm 0.79 \mu\text{g/g}$ ) & ( $0.22\pm 0.028 \mu\text{g/g}$ ) respectively.

Table 8, represents concentrations of studied elements in rice samples, collected from industrial areas of Faisalabad and Gujranwala regions, all the current values were higher than reported values in literature. However, for Faisalabad, the observed value of Co ( $0.018\pm 0.003 \mu\text{g/g}$ ) was low as compared to the literature value ( $0.031\pm 0.004 \mu\text{g/g}$ ). Moreover, the observed values of As ( $0.16\pm 0.04 \mu\text{g/g}$ ), Cr ( $0.6\pm 0.04 \mu\text{g/g}$ ), Cu ( $10.2\pm 1.2 \mu\text{g/g}$ ), Mn ( $33.7\pm 2.6 \mu\text{g/g}$ ), Ni ( $2.4\pm 0.4 \mu\text{g/g}$ ), Pb ( $4.8\pm 0.07 \mu\text{g/g}$ ), Sb ( $0.04\pm 0.001 \mu\text{g/g}$ ) and Se ( $1.28\pm 0.06 \mu\text{g/g}$ ), were 2 to 8 times higher than the literature values of ( $0.087\pm 0.009 \mu\text{g/g}$ ,  $0.43\pm 0.04 \mu\text{g/g}$ ,  $4.9\pm 0.4 \mu\text{g/g}$ ,  $8.6\pm 0.4 \mu\text{g/g}$ ,  $0.97\pm 0.66 \mu\text{g/g}$ ,  $0.6\pm 0.3 \mu\text{g/g}$ ,  $0.011\pm 0.002 \mu\text{g/g}$  and  $0.75\pm 0.074 \mu\text{g/g}$ ) respectively. All studied elements in rice samples from Gujranwala region were higher than literature values. Moreover, the observed values of As ( $0.13\pm 0.04 \mu\text{g/g}$ ), Co ( $0.08\pm 0.003 \mu\text{g/g}$ ), Cr ( $0.86\pm 0.04 \mu\text{g/g}$ ), Cu ( $14.2\pm 1.2 \mu\text{g/g}$ ), Mn ( $31.7\pm 2.6 \mu\text{g/g}$ ), Ni ( $5.2\pm 0.04 \mu\text{g/g}$ ), Pb ( $4.0\pm 0.07 \mu\text{g/g}$ ) and Sb ( $0.03\pm 0.001 \mu\text{g/g}$ ) were 2-7 times higher than the literature values of ( $0.087\pm 0.009 \mu\text{g/g}$ ,  $0.031\pm 0.004 \mu\text{g/g}$ ,  $0.43\pm 0.04 \mu\text{g/g}$ ,  $4.9\pm 0.4 \mu\text{g/g}$ ,  $8.6\pm 0.4 \mu\text{g/g}$ ,  $0.97\pm 0.66 \mu\text{g/g}$ ,  $0.6\pm 0.3 \mu\text{g/g}$  and  $0.011\pm 0.002 \mu\text{g/g}$ ) respectively. In the studied crops (rice and wheat) the concentrations of As, Cd, Cr, Cu, Mn, Ni, Pb and Se are high in rice samples. Similarly, the concentrations for Co and Sb are highest in wheat crop. Arsenic is high due to use of Arsenical insecticidal spray on crops and high selenium is due to the uptake of this element from soil.

The difference between the current data and the reported literature values may be attributed to many factors such as origin of samples, local characteristics and nature of soil, irrigation with sewage water or untreated industrial effluents especially from metallurgical industries, pesticides, spray of toxic chemicals, artificial fertilizers, mechanized farming, different environmental conditions, tendency of each plant species for uptake and accumulation of toxic metals, etc.

#### 4. Conclusion

Toxic and other elements have been studied in vegetables and crops samples collected from the vicinity of industrial areas of Faisalabad and Gujranwala regions. INAA and AAS techniques have been successfully used to quantify these elements with relatively good precision. Relatively higher concentration values of toxic elements have been observed as compared to their values reported in literature. The rice crop has more toxic elements than wheat crop. Similarly, in vegetables, bitter gourd has more toxic elemental concentration while tomato is moderate and brinjal has the least concentration level. Moreover, industrial areas of Faisalabad are more polluted than those of Gujranwala region. Keeping present data in consideration, untreated effluents are not suitable for irrigation purposes. Enforcement of environmental laws and public awareness campaigns about adverse effects of industrial pollution would be beneficial to reduce the pollution.

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