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Study of Metallic Pollutants in Water and Food Items of an Industrial City by Atomic Absorption Spectrophotometry

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Abstract: To evaluate the base line levels of potentially toxic and essential trace metals namely, Cd, Pb, Cr, Mn, Ni, Cu and Zn in water, locally grown vegetables, cereals and vegetable ghee-oil samples of a highly industrial city 'Gujranwala' have been measured after wet digestion by employing AAS technique. Sampling was made from selected sites in and around the city over a period of three months. The concentration of Mn, Ni, Zn, Cu and Pb was found significantly higher in vegetables ranging from 3-63, 2-81, 5-92, 7-70 and 6-60 ppm respectively. Nickel and Cu concentration was found higher in cereals whereas, Cd was found at ppb level in all variety of samples studied. Tap water, vegetable ghee-oil have recorded lower concentration of these metals. Vegetables collected from urban area have shown elevated level of contamination than those of taken from canal irrigated farms. The overall level of trace metals with few exceptions of vegetable samples was found within the permissible limits fixed by WHO. The analytical method was checked by applying on SRM of wheat and spinach. The results were found in agreement with the certified values within experimental error. The major polluting sources of the city such as automobile, man made activities, soil and road dust, metallic corrosion and industrial activities have been indicated. The environmental impacts of pollutants on water and food quality of an industrial and non-industrial city are briefly discussed in the light of their adverse effects on human health.

Key words: Determination, metallic pollutants, water, vegetable, cereals, wet digestion

Introduction

With an ever increasing amount of industrial toxic waste being poured into our lakes, rivers, chemical fertilizers, residues of toxic sprays used on land, untreated sewage dumped into the water ways and even our wells and springs are likely to be loaded with toxic chemicals, viruses, bacteria and unwanted minerals. The use of various chemicals by municipal organizations creates carcinogens by combining with other water-borne pollutants (Lo and Chen, 1990). Talib (1991) has reported that toxic agents such as asbestos, pesticides, Pb, Cd, Cr, As and many other cancer causing substance in our water and vegetables are responsible for majority of human cancers. Water is among the major sources of pollution carrier and about 80% of all the diseases are related to water. As a result 40% adult and 60% infant death occurs (Rasool, 2000 and Laghari, 2000). According to Anonymous (1995), drinking water in Pakistan is generally contaminated by both highly toxic chemicals and microbiological organisms. WHO recorded 315 cases of water-borne diseases out of 0.1 million in Pakistan (Irshad, 2001). Anonymous (1971) surveyed that nearly 55% of the population is deprived of safe water. Metallic pollutants enter into the food chain either directly or through irrigating growing plants with contaminated water and get cumulate in the vital organs of human body thereby adversely affect on their functions. Thus, chemical and biological contamination of foods due to polluted water and air is becoming a serious threat to our environment.

Gujranwala is the fourth largest city and third largest industrial center of the Punjab province of Pakistan. The current population of the city is exceeding 2 million. The random scattering of industrial establishments throughout the city has adversely affected the physical growth of industries and infrastructural facilities. Thirty five of the 541 industries are rated as highly polluting industrial units which are located within the heart of the city. More than 90% major polluting industries discharge their waste water into the municipal sewerage system without adequate treatment. The sewerage and drainage system of the city is antiquated, poorly adequate and extremely deficient in term of quality and network coverage (Baird, 1995). About 90% of daily garbage from various sources is collected and disposed off in open dumps and ponds inside and outside of the city. These are the major causes of environmental nuisance and public health hazard in industrial cities. The alarming role of metal pollutants has attracted attention of researchers towards adopting measures for their effective control. Though progress has been made in this direction (Talib, 1991; Mannan *et al.*, 1992; Haleem, 2002) but much have to be done to save our environment. Prior to any attempt on their control, it is necessary to study the base-line level of these metals in water and common food items. In continuation to our previous communication (Haleem, 2002), present study was undertaken to determine the concentration level of some essential and some toxic trace metals such as Mn, Ni, Cu, Zn, Cr, Cd and Pb in water, vegetables and cereals consumed by the people living in and around a typical industrial city.

Materials and Methods

Sampling: Almost 90% of the vegetables grown in rural area are normally irrigated by canal water or tub wells, whereas, in urban area are irrigated by municipal sewage water and industrial waste water containing health hazardous wastes from various sources. Keeping in view the type of irrigation, common vegetables were collected from both rural and urban area during March to May 1996. Selected sampling sites of water and food items from in and around the city were People colon***y*** (PC), Gondlawala (GW), Masaikywala (MW) andruni Mandi(AM), Baruni Mandi (BM), Chicherwali (CW), Rahwali (RW), Saiduwali (SW), Darvashki (DV), Abida steel area (AS), Sultan baud mill (SM), Azmat industry area (AI), Textile industry area (TI), Mirza steel area (MS), Rahwali cantt. (RC), Shahan da kot(SK), Nickel-chromium blunting(NCB), Kheialee(KL), Sharanwala bagh (SB), Azmat baco light (ABL), domestic waste water (DW) and Mandiala (MD). Sufficient amount of representative samples of each type of fresh vegetables namely, potato (solanum tubirosum), tomato (locoperscon esculentum), onion (allium cipa), spinach (spinacia oleracea) and chilies (capsicum annum) were collected (Table 1), washed and kept in deep freezer for further process. Both locally grown and otherwise rice (*oryza sativa*) and wheat (T*riticum vulgare*) samples were randomly purchased from whole sale markets and small stores of the city for determination purpose (Table 2).

Vegetable ghee-oil sampling was made among the most commonly used six different brands namely, Dalda, GCP and Shan vanaspati ghee, Dalda, Pakwan and Planta cooking oils. These samples were procured from local markets in factory packing during April 1996 (Table 2).

Drinking or tape water samples were collected from hand pumps at a depth of 45-50 feet, tube wells outlets and municipal water supply pipelines. All samples were taken in pre-cleaned I.5 liter capacity plastic bottles and kept air-tight till analyzed. Sewage water samples from industrial and domestic area of the city were collected in pre-washed plastic bottles (Table 3 and 4).

Sample preparation: The vegetable samples were washed with distilled water to remove debris and soil particles before proper storage in polyethylene bags. Wheat and rice samples were also washed with distilled water. A known weight (5.0 g) of each wet vegetable and food sample was taken in teflon beaker and oven dried at 80°C for 6 h and then pulverized in a grinder. One gram dried powdered of each sample was digested in a 100 cm^3 pyrex glass beaker by adding 10 cm^3 nitric acid first for cold digestion for 24 h and then heated at 50°C for 4 h. The solution was finally boiled with 1:5 mixture of $HClO_4$: HNO_3 respectively to digest all organic matter (Lag and Kary, 1978) and then filtered on cooling. Final volume was made in a 25 cm^3 measuring flask with de-ionized distilled water.

Ten grams of each sample of oil and ghee was taken in a 100 cm^3 conical flask containing 10 cm^3 CCl_4 and 5 cm^3 of HNO_3 to dissolve the sample. The contents were shaken vigorously for 1h for extraction of trace elements of interest (Ali and Faridi, 1977) and then diluted up to 50 cm^3 with distilled water. The extraction was repeated for half an hour and flask was allowed to stand for phase separation. Aqueous layer was collected in a pre-cleaned polystyrene tube and kept in a refrigerator at 5°C till analysis of trace metals.

Ten cm^3 of each drinking and waste water sample was taken in 25 cm^3 measuring flasks containing 0.5 cm^3 concentrated HNO_3 after proper filtration. Final volume was made with water sample and stored at 4°C till analyzed. Reagent's blanks were also prepared in the same manner.

Reagents and Solutions: Analytical reagent grade chemicals of E. Merck, Germany were used in these determinations. Certified standard stock solutions of Cr, Mn, Ni, Cu, Zn, Cd and Pb for atomic absorption spectrophotometric determination were obtained from BDH, England, for calibration purpose. All working solutions were prepared in doubly distilled de-ionized water.

Instrumentation and Determination: Perkin-Elmer double beam atomic absorption spectrophotometer, model AA2380 with automatic background correction was employed for these measurements (Gurdeep and Sham,1990; Talib, 1991; Haleem, 2002) The analyses were carried out by using hollow cathode lamp of respective metallic element under standard instrumental operational conditions. Air-acetylene was used as fuel. Fresh solutions of metal ions of 5×10^{-5} M were prepared by appropriate dilution of their standard stock solution. All determinations are based on triplicate results.

Results and Discussion

Gujranwala being a big industrial city, have various environmental degradation factors. Ever increasing transportation, rapid urbanization, industrialization and unplanned extension of city is continuously polluting the environment of this area. To study the level of exposure of human being to various metallic pollutants, representative samples of water and basic food items were analyzed by employing atomic absorption spectrophotometry (AAS), possible contamination sources and adverse effects of these metals on human health have been discussed. The validity of analytical method was checked by decomposing and analyzing the Standard Reference Material (SRM), NBS-1567 (wheat) and NBS-1570 (spinach). The results were found in agreement with the reported values within expected experimental error. General parameters for tape water quality such as pH, hardness, TDS and total bacterial counts have been checked and found within the permissible limits recommended by WHO (Talib, 1991). There are 36 tube wells which draw 33 million gallons of underground water that is fed into 33,000 connection through overhead reservoirs and a looped net work, yet only half of the city is served and other half get pumps from shallow polluted prone. Similarly about half of the built up area is served by sewer and remaining rely on open drain sewer. This water is directly consumed for the purpose of drinking and food cooking. A large amount of municipal sewage water is generated per day in and around the city.

The mean concentration of Cr in various samples was found to be 22.6 ppb in dw, 20.0 ppm in sw, 17.6 ppm in pt, 14.84 ppm in tt, 27.67 ppm in sp, 30.75 ppm in on, 20.25 ppm in ch, 5.17 ppm in rc, 7.0 ppm in wt and 5.16 ppm in ghee-oil (Table 1 and 4). These results indicated lower level of Cr contamination than those recorded for most of the samples taken from urban area. This may be due to the difference in irrigation sources of these vegetation. The crops grown in rural area are mainly irrigated by canal water and tube wells whereas, farms around the city and along the bank of busy roads are being irrigated by municipal sewage water/ sludge containing hazardous waste effluents from various types of industries located within the municipal limits. Chromium sources are various industries, combustion of fossil fuel, lather discharges, electroplating, municipal refuses, stainless steel alloys, printing material and magnetic taps etc. Chromium is among the carcinogenic element having important biological activities. Its compounds are highly mobile, easily penetrate into the soil and are taken up by the vegetables through roots. Excessive intake of Cr may causes irritation of respiratory tract, ulceration,

Table 1: Determination of trace metals in potato (pt), tomato (tt), spinach (sp), onion(on) and chilies (ch) (Concentration in ppm unless stated otherwise)

SSC/ SC*.	Cr	Mn	Ni	Zn	Cu	Cd[a]	Pb
PC-pt	11	19	39	92	42	01	60
GW-pt	13	25	20	21	14	---	13
AM-pt	21	21	27	48	18	02	06
BM-pt	18	18	22	32	11	02	16
RW-pt	15	17	10	10	09	---	07
MS-pt	25	28	20	35	11	05	14
Mean	**17. 16**	**21.34**	**23.00**	**39.67**	**17.5**	**2.50**	**19.34**
TI- tt	13	21	25	19	17	07	10
AL-tt	17	28	37	32	21	11	37
PC-tt	19	16	47	16	07	02	25
GW-tt	17	11	23	22	12	---	22
RW-tt	13	06	07	13	08	---	13
MW-tt	10	16	28	29	18	03	30
Mean	**14.84**	**16.34**	**27.84**	**21.84**	**13.84**	**5.75**	**22.84**
SW-sp	16	31	81	31	30	70	35
PC-sp	33	20	17	43	52	18	17
AM-sp	42	59	28	25	34	28	24
GW-sp	11	71	72	34	68	12	09
SW-sp	49	63	57	28	70	13	33
RW-sp	12	27	55	16	45	90	08
Mean	**27.67**	**45.17**	**51.67**	**29.5**	**48.84**	**38.5**	**21.0**
PC-on	23	37	52	37	19	07	17
RW-on	33	18	51	17	15	19	23
GW-on	37	14	43	15	29	13	09
BM-on	40	25	48	36	19	23	14
Mean	**30.75**	**23.5**	**48.5**	**26.25**	**20.5**	**15.5**	**15.75**
RW-ch	27	12	03	05	09	---	13
BM-ch	20	21	07	08	12	02	17
MW-ch	21	16	02	11	07	01	12
PC-ch	13	03	52	13	08	07	21
Mean	**20.25**	**13.0**	**16.0**	**9.25**	**9.0**	**3.34**	**15.75**

* Sampling site code/sample code, 'a'= µg dm^{-3}

Table 2: Determination of trace metals in rice (rc), wheat (wt) Vanaspati ghee(g) and cooking oil (o) (Concentration in ppm unless stated otherwise)

SSC/SC*.	Cr	Mn	Ni	Zn	Cu	Cd[a]	Pb
PC-rc	02	09	09	15	05	02	13
GW-rc	08	08	22	22	04	01	09
MW-rc	03	11	15	13	07	03	08
AM-rc	07	13	79	14	04	06	02
BM-rc	05	17	34	17	10	09	05
PPCW-rc	11	19	21	13	08	07	12
RW-rc	---	16	46	21	07	03	03
SW-rc	01	18	34	18	04	---	07
DV-rc	04	23	58	28	07	---	04
Mean	**5.17**	**14.9**	**35.33**	**17.88**	**6.22**	**4.42**	**7.0**
AM-wt	07	15	21	21	13	11	06
GW-wt	04	17	20	25	08	02	05
BM-wt	14	13	14	15	04	15	03
MW-wt	13	16	16	27	05	07	05
RW-wt	07	31	32	22	27	11	11
CW-wt	06	27	27	10	17	---	18
SW-wt	03	29	28	11	09	11	04
MD-wt	02	22	21	34	73	14	05
Mean	**7.0**	**21.25**	**22.37**	**20.62**	**19.5**	**10.14**	**7.12**
DA-g	03	05	26	06	03	16	04
GCP-g	05	07	35	08	05	37	06
SN-g	07	03	49	08	07	29	05
PK-o	12	04	07	07	06	86	04
PL-o	03	02	03	04	02	25	04
DA-o	01	02	02	03	03	12	01
Mean	**5.16**	**3.8**	**20.33**	**6.0**	**4.33**	**34.16**	**4.0**

* Sampling site code/sample code, ' a'= µg dm^{-3}

Table 3: Concentration of trace metals in drinking water (dw) samples of an industrial city (Concentration in ppm unless stated otherwise)

SSC/SC*	Cr [a]	Mn	Ni	Zn	Cu	Cd [a]	Pb
PC-dw	09	02	03	07	02	---	03
GW-dw	12	02	03	09	01	01	04
MW-dw	13	03	05	07	12	02	03
AM-dw	14	04	07	09	15	03	02
BM-dw	15	04	02	10	03	04	05
CW-dw	19	01	04	06	11	03	04
RW-dw	16	02	03	03	03	---	02
SW-dw	11	01	02	02	02	---	02
DV-dw	14	02	01	02	03	---	04
AS-dw	14	08	06	10	03	03	06
SB-dw	12	03	05	09	02	---	02
AI-dw	30	06	08	10	04	05	07
TI-dw	35	10	09	08	02	07	04
MS-dw	27	07	04	10	05	11	07
RC-dw	12	02	01	05	07	---	01
SK-dw	30	03	01	06	04	01	02
KL-dw	50	06	03	02	02	01	01
ABL-dw	80	07	03	18	04	03	01
MD–dw	10	05	02	04	03	04	02
Mean	**22.26**	**4.11**	**3.77**	**7.22**	**4.63**	**3.7**	**3.26**

Table 4: Concentration of trace metals in sewage water (sw) (Concentration in ppm unless stated otherwise)

SSC/SC*.	Cr	Mn	Ni	Zn	Cu	Cd	Pb
PC-sw	11	21	11	11	04	03	31
DW-sw	10	25	20	18	43	04	37
AS-sw	18	44	14	37	11	05	30
SM-sw	12	24	11	19	05	02	19
AI-sw	27	52	48	30	24	09	34
TI-sw	17	38	63	27	29	13	26
MS-sw	20	33	32	36	21	11	21
NCB-sw	38	49	37	24	42	---	24
SB-sw	17	37	09	09	09	02	16
ABL-sw	30	16	19	12	04	03	38
Mean	**20**	**33.9**	**26.4**	**22.3**	**19.2**	**5.8**	**27.6**

* Sampling site code/sample code, 'a' = $\mu g\ dm^{-3}$

Table 5: Comparison of mean concentration of various elements in food items of some cities (concentration in ppm unless stated otherwise)

Name of city and food items	Cd [a]	Pb	Cr*	Cu	Ni	Mn*	Zn*
LHR (water)	44	08	07	03	---	---	---
Sewer water	97	65	78	24	85	---	---
Vegetables (rural)	19	67	19	39	14	---	---
Vegetables (urban)	56	13	27	46	18	---	---
Wheat	11	07	19	09	05	---	---
Rice	23	13	10	12	08	---	---
Vegetable- oil	39	26	23	6.5	---	---	---
Vegetable-ghee	56	28	13	5.3	08	---	---
M. Abad (water)	---	03	---	01	01	1.5	02
Sewer water	3.6	36.8	---	7.4	9.1	17.0	13.3
Vegetables	1.35	13.5	---	8.9	15.16	21.3	17.45
Wheat	01	3.8	---	03	06	12.8	15.4
Rice	01	6.6	---	3.5	7.2	20.6	13
Pulses	01	09	---	4.3	9.2	14.8	11.7
GWLA (water)	3.7	3.26	22.26	4.6	3.8	7.2	4.10
Sewer water	5.8	27.6	20	19.2	26.4	22.3	33.9
Vegetables	13.11	18.93	22.15	21.9	33.4	25.3	23.9
Wheat	10.14	07	5.12	6.2	35.3	17.9	14.9
Rice	4.42	7.12	07	19.5	22.4	20.6	21.25
Vegetable ghee-oil	34.16	04	5.16	4.3	20.3	06	3.8

LHR = Lahore; M. Abad = Muzaffarabad; GWLA = Gujranwala (present work), 'a' = $\mu g\ dm^{-3}$, *= Con. of Mn and Zn is not reported for LHR Concentration of Cr is not reported for M. Abad.

perforation of nasal septum, skin ulcer and pneumonia (Khurshid and Iqbal, 1984). Although, Cr concentration reported herein is within the safe limits, but our values are also higher and comparable to those reported for some other industrial cities (Talib, 1991).

The mean concentration of Cd in dw, sw, vegetables, cereals and vegetable ghee-oil samples was noted to be 3.7 ppb (dw), 5.8 ppm (sw), 2.5 ppb (pt), 5.75 ppb(tt), 38.5 ppb(sp), 15.5 ppb(on), 3.34 ppb(ch), 4.42 ppb(rc), 10.14 ppb(wt) and 34.16 ppb (ghee-oil) respectively. These results revealed comparatively lower concentration of Cd with exception of sewer water. Cadmium is a highly toxic metal and its food contamination may occur from various pre-existing sources present in this area such as fertilizers, fungicides, metallurgy, electrical work, paints, plastic products and smoking. Due to low boiling point and high vapour pressure, Cd readily volatilize to form fine air borne particles into the environment which reacts with oxygen to form respirable cadmium oxide fumes (Talib, 1991). Its toxicity appears in the form of vomiting, nausea, renal damage and many other complications. The Cd concentration found in these studied falls within the safe intake limits reported by Anonymous (1973).

The mean concentration of Pb was found to be 27.6 ppm in sw, 3.26 ppm in dw, whereas, 15.75-22.8 ppm of Pb was noted in various vegetables (Table 1). However, concentration of Pb in cereal and vegetable ghee-oil samples was found to be lower (4.0-7.12 ppm) than those noted for other food items. These results showed reasonably higher concentration of Pb in almost all samples with exception of ghee and oil. Common sources of lead contamination in urban area are the use of tetra-alkyl lead in gasoline, lead arsenate as fungicide, plasters, paints, house dusts, waste water and newsprint. Elevated level of Pb in human body reduce plasma copper which leads irreversible damage to brain (Khurshid and Iqbal, 1984). Lead absorption also increases in iron deficiency and inhibits enzymatic activities which causes hemoposis. Lead toxic effects are anemia, headache, irritability and renal damage.

Manganese has been recognized as an essential element, is distributed in all the tissues and organs of human body (Khurshid and Iqbal, 1984). The mean concentration of Mn in sw (33.9 ppm), sp (45.17 ppm), on (23.5ppm) and pt (21.34 ppm) were found higher. A daily intake of 2.5-5.0 mg of Mn by humans contributes to the well being of the cells and its deficiency results in growth inhibition and many other abnormalities (Khurshid and Iqbal, 1984). Elevated level of Mn get accumulated in kidney, liver and bones thereby causing "manganese Psychosis", which is an irreversibly brain disease. The possible sources of contamination of Mn in an industrial city are workshops, dry battery cells, ferro-manganese, iron alloys, glass, ceramics, fossil fuel, domestic waste water discharge, street run-off and ground water infiltration from soil to the sewerage system (Khurshid and Iqbal, 1984).

The concentration of Cu in various vegetable samples was found to be ranged between 9.0 - 48.84 ppm whereas, in rice, wheat and ghee-oil it was noted to be ranged between 5.16 - 7.0 ppm. In dw and sw, Cu was recorded to be 4.63 and 19.2 ppm respectively (Table 3 and 4). Highest concentration of Cu was found in sp (49.0 ppm), wheat (19.5 ppm) and sw (19.2 ppm). Possible sources of Cu are corrosion of Cu-alloys, metal plating, roofing material, cooking utensils, coins and pigment material. The elevation of Cu in human body (>15 mg) causes nausea, vomiting, diarrhea, jaundice, cirrhosis, haemolytic anemia and tuberculosis (Khurshid and Iqbal, 1984).

The mean concentration of Ni in water and various food items was found to be very high i.e, 26.4 ppm in sw, 51.67 ppm in sp, 48.5 ppm in on, 35.33 ppm in rc, 22.37 ppm in wt and 27.84 ppm in tt samples. Most of these samples were taken from urban polluted area (Table 1 and 4). Consumption of fossil fuel, non-ferrous metallurgy and use of nickel plating objects are the main sources of Ni contamination. Excessive intake of Ni causes, allergy, bronchial asthma, dermatitis, eczema, myocardial infarction, larynx, kidney, prostate and stomach cancers (Murti and Viswanathan, 1989)

Significantly high concentration of Zn was found in pt (39.67 ppm), sp (29.5 ppm), on (26.25 ppm) and in tt (21.84 ppm) samples. Common sources of Zn are the presence of welding workshops, electric batteries and various other factors existing in urban area mentioned else where. It is also reported that Zn bearing magnetite present in the soil act as one of the main sources of food toxicity Table 5 reflected the comparison of metal contamination levels reported for various other cities. The data reveals significantly higher concentration of Cd, Pb, Cr and Cu for LHR (Talib, 1991) than those reported in the present study. The significant variation in data (Table 5) may be due to various factors existing among these cities such as old sewerage system, random industrialization, transportation, over and congested population and unhygienic environment. The concentration of various elements reported herein was found higher than those of M.Abad (Haleem, 2002). The sole reason may be the difference of industrial and non industrial set up of these cities.

The baseline levels of potentially essential and toxic trace metals namely, Cd, Pb, Cr, Mn, Ni, Cu and Zn in water, vegetables and cereal items commonly used by the inhabitants of the city have been measured. The concentration of Mn, Ni, Cu, Zn and Pb was found significantly higher in vegetables (2-92 ppm) whereas, only few cereal samples have shown higher values of Mn, Ni, Zn and Cu. However, the concentration of Cd was found at ppb level. Tap water and vegetable ghee-oil samples have recorded lower concentration of these elements. Because of unavailability of data regarding trace metals concentration in food commodities of this city, the measurements reported herein will help in monitoring and improvement in hygienic conditions. The factors and sources responsible for up take of trace metals such as environmental conditions, availability of trace metals from soil, nature of vegetables to be an efficient interceptors of metals, use of agriculture related chemicals, method of handling, processing and effect of pollutants on health need to be studied carefully. The data reported herein may be useful for evaluation of dietary intake amounts of toxic elements and their ultimate effects on human health.

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