

Monitoring and minimizing levels of some heavy metals in groundwater and water purification stations samples in El-Gharbiya Governorate- Egypt

AbdelRahman, Tarek A.*; Fayza A.Sdeek*, Ahmed A. El-Ghanam* and Abdel Baset A. El Saïdy**

* Central Agricultural Pesticides Laboratory, Agricultural Research Center, Dokki, Egypt

** Plant Protection Research Institute, Agricultural Research Center, Dokki, Egypt

Abstract: This study explored the heavy metals contamination of drinking water samples from El-Gharbiya Governorate. Microwave plasma - nitrogen plasma - atomic emission spectrometry was used for the determination of heavy metals in 20 water samples (10 samples was collected from groundwater sources and 10 samples collected from the water purification station), Heavy metal i.e. (As, Cd, Cr, Cu, Mn, Ni, Pb, Mo, and Zn) contents in the collected drinking water samples were found at different levels. The obtained results showed that, the contamination percentage of groundwater sources and the water purification station samples were reached 100%. Samples were contaminated with different amount of heavy metals. Each sample was contaminated with one or more of heavy metals. All samples were free from any detectable residues of Cr and Mo. As, Cu, and Pb were recorded the highest contamination in all samples, followed by Mn and Zn, while Cd and Ni recorded the lowest level one.

Keywords: drinking water, heavy metals, Microwave Plasma Atomic Emission Spectrometry, Microwave Digestion and statistical analysis.

1. INTRODUCTION

Water resources for domestic use are shrinking as a result of pollution of fresh water bodies by trace elements (TE) and other contaminants. Water TE contamination is a worldwide environmental problem, especially due to the strong toxicity of many of these elements even at low concentrations. The possible long term effects of extended exposure to toxins present in drinking water are one of the major concerns of water quality and public health. Natural substances leached from soil, runoff from agricultural activities, controlled discharge from sewage treatment works and industrial plants, uncontrolled discharges or leakage from landfill sites, and chemical accidents or disasters can all contribute to contamination in ground and surface water (Demir et al., 2015).

Toxic metals are usually present in industrial, municipal and urban runoff, which can be harmful to humans and biotic life. Increased urbanization and industrialization are to be blamed for an increased level of trace metals, especially heavy metals, in our water ways. Many dangerous chemical elements if released into the environment accumulate in the soil and sediments of water bodies. There are over 50 elements that can be classified as heavy metals, 17 of which are considered to be very toxic and relatively accessible. Characteristically, also the anions have its important role in drinking water; results also showed affecting the human health. Toxicity level depends on the type of metal, its biological role and the type of organisms that are exposed to it. Heavy metals have a marked effect on the aquatic flora & fauna which through biomagnifications enters the food chain and ultimately affect the human beings as well. The heavy metals in drinking water linked most often to human poisoning are lead, iron, cad

mium copper, zinc, chromium etc. They are required by the body in small amounts, but can also be toxic in large doses. They constitute one important group of environmentally hazardous substances if present (Chaitali and Dhote 2013).

2. MATERIALS AND METHODS

The determination of metals in water samples were performed according to the method of the Association of Official Analytical Chemistry (AOAC, 1995).

2.1. Sampling

Twenty samples (10 samples was collected from groundwater sources and 10 samples collected from the water purification station) were randomly collected during 2015. The drinking water samples were collected in pre-washed (with detergent, dilute HNO₃, doubly deionized distilled water respectively) double capped polyethylene bottles then transferred immediately to the Lab. All samples were maintained at 2-5°C until analysis. About 50 ml of the collected samples were digested by the microwave digestion system. The samples were transferred quantitatively into 25 mL volumetric flasks and completed to the mark with ultrapure water.

2.2. Chemicals and Standards

All chemicals and standards are of Analytical grade. Metals stock standards of As, Cd, Cr, Cu, Mn, Ni, Pb, Mo, and Zn were obtained from Merck, Darmstadt, Germany (1000 µg/ml).

2.3. Sample preparation

Microwave digestion was used to prepare the spice samples. Ten mL of HNO₃ was added to accurately weighed ≈ 50 ml of the sample. A preloaded method for the MARS6.

Table 1: Microwave Digestion System Parameters

(CEM, Corporation, USA) microwave was used to digest

Options	Internal Fiber Optic Temperature Control
	Internal Pressure Control
	DuoTemp Control
Temperature	210°C
Pressure	800 PSI
Time	Ramp : 21 min
	Hold : 15 min
Power	400- 1800 Watt
Vessels	EasyPrep Full Starter Set, P/T Control

the samples. Once cooled, the solution was diluted quantitatively to 25 ml using ultrapure water. The microwave digestion parameters were according to Table 1.

2.4. Instrumentation

All measurements were performed using the innovative Agilent microwave plasma atomic emission spectrometry model 4200 MP-AES with nitrogen plasma gas supplied via an Agilent 4107 Nitrogen Generator. The generator alleviates the need and expense of sourcing analytical grade gases. The sample introduction system comprised a double-pass cyclonic spray chamber and the Oneneb nebulizer. The innovative 4200 MP-AES features a second generation waveguide and torch, with mass flow controlled nebulizer gas flow (Cauduro, 2013). The 4200 MP-AES has robust toroidal plasma with a central channel temperature of $\approx 5,000$ K which eliminates many of the chemical interferences that are present in FAAS and also expands the concentration working range of the 4200 MP-AES when compared with the FAAS. This means that the element specific sample preparation that is commonplace when using FAAS is not necessary when using the 4200 MP-AES, improving ease of use and reducing cost. An Agilent SPS 3 auto sampler was used to deliver samples to the instrument, allowing the system to be operated unattended. The instrument operated in a fast sequential mode and featured a Peltier-cooled CCD detector. Background and spectral interferences could be simultaneously corrected easily and accurately using Agilent's MP Expert software. Method parameters are given in Table 2. The average recoveries ranged between 91.4 % and 99.3%, and limit of determination was ranged between 0.044×10^{-3} to $4.500 \times 10^{-3} \mu\text{g/ml}$.

Limit of determination (LOD) were determined on samples at spiking levels 0.01 – $0.05 \mu\text{g/ml}$ from the elements standard. Correlation Coefficient was ranged between 0.8719 to 0.99996.

2.5. Statistical Analysis

Data were statistically evaluated by one-way analysis of variance. Determination of the differences among means was

Table 2: Metals Determined in water and their Wavelengths and Calibration Ranges.**Table 3: Microwave Plasma Atomic Emission Parameters.**

*As is determined by HG-AAS

Table 4: Limit of Detection (LOD) and Limit of

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	15 seconds
Rinse time	30 seconds
Stabilization time	15 second
Fast Pump during Uptake and Rinse	On (80 rpm)
Nebulizer	OneNeb
Spray chamber	Double pass cyclonic
Autosampler	Agilent SPS 3
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Quantification (LOQ) and % recovery of Metals Determined in drinking water.

LOD: The Limit Of Detection ($=3X$ standard deviation of

Element	Wavelength (nm)	Calibration Range ($\mu\text{g/ml}$)	Correlation Coefficient
As*	193.7	0 – 0.020	0.8719
Cd	228.8	0 – 2.500	0.9992
Cr	425.4	0 – 2.000	0.9998
Cu	324.8	0 – 2.500	0.9992
Mn	403.1	0 – 2.000	0.9999
Mo	379.8	0–2.200	0.9992
Ni	352.5	0 – 2.000	0.9999
Pb	405.9	0 – 2.500	0.99996
Zn	213.9	0 – 1.500	0.9904

10 measurements in blank matrix).

LOQ: The Limit Of Quantification ($= 3XLOD$).

* As is determined by HG-AAS

Element	LOD ($\mu\text{g/mL}$)	LOQ ($\mu\text{g/mL}$)	% recoveries
As*	0.044×10^{-3}	0.1467×10^{-3}	99.3
Cd	2.100×10^{-3}	7.000×10^{-3}	91.4
Cr	0.100×10^{-3}	0.333×10^{-3}	92.6
Cu	0.700×10^{-3}	2.333×10^{-3}	93.11
Mn	0.200×10^{-3}	0.667×10^{-3}	95.3
Mo	0.050×10^{-3}	0.150×10^{-3}	96
Ni	0.900×10^{-3}	3.000×10^{-3}	95.3
Pb	3.300×10^{-3}	0.011	97.23
Zn	4.500×10^{-3}	0.015	93.11

carried out by using the least significant differences test. All statistical analyses were done using the Statistical Package for Social Sciences (SPSS 16.0) program.

3.Results and Discussion

Minimum, maximum, mean, standard deviation, contamination, Maximum Permissible Limits (MPL) and violation of As, Cd, Cr, Cu, Mn, Mo, Ni, Pb and Zn in drinking water are presented in Tables (5, 6 and 7). Some types of metals, such as Cu, Fe and Zn, are the natural essential components of enzymes and coenzymes and are important for growth, photosynthesis and respiration. Although other metals, such as Pb and Cd, have nobiochemical or physiological importance, so they are considered as very toxic pollutants.

Data in Tables (5 and 6) demonstrated the amounts of heavy metals residues and their percentages of contamination in 20 samples of groundwater sources and the water purification stations. The obtained results showed that, the percentage of contamination of groundwater sources and the water purification station samples were reached 100%. Samples found contaminated with different amount of heavy metals. Each sample was contaminated with one or more of heavy metals. All samples were free from any detectable residues of Cr and Mo.

As, Cu, and Pb were recorded the highest contamination in all samples, followed by Mn and Zn, while Cd and Ni recorded the lowest level contamination in samples.

3.1.Arsenic:

The essential role of As was discovered 1977 and it was believed that it is responsible for growth in humans and animals, however its metabolism in the body has been still unknown (Meharg & Hartley-Whitaker, 2002). The toxicity of arsenic is well known historically (Berman, 1980). Arsenic combines readily with proteins due to its great affinity for sulfhydryl groups. This results in the precipitation of proteins, producing gastrointestinal irritation and irreversible inhibition of important enzyme systems. Recent advances in our knowledge of arsenic carcinogenesis include the development of rat or mouse models for all human organs in which inorganic arsenic is known to cause cancer—skin, lung, urinary bladder, liver, and kidney (Kitchin, 2001). From Table (7), data revealed that, the arsenic varied in water from groundwater sources samples between 0.00231-0.00399mg/L. while in water samples after treatment were 0.001875- 0.003988mg/L. the mean rate of reduction was recorded 4.85%. All the water samples after treatment in the present study were contaminated with Arsenic. All the water samples after treatment in the present study had lower As levels than the maximum permissible limit (0.05mg/L) specified by the EU Council Directive (2001).

3.2.Cadmium:

Cadmium is a highly toxic metal (Berman, 1980). Cadmium inhibits the sulfhydryl containing enzymes and affects the hydroxyl, carboxyl, phosphatyl, cysteinyl, and histidyl side chains of proteins, purines, and porphyrin. It can also disrupt

the pathways of oxidative phosphorylation. Cadmium competes with the absorption of some essential elements such as iron, zinc, and copper. It can be seen from Table 7. that cadmium contamination was detected in 5 water samples from groundwater sources. The Cadmium varied in water from groundwater sources samples between N.D-0.005 mg/L. The mean of five samples was 0.0005 mg/L. on the other hand, water samples after treatment were recorded N.D-0.01 mg/L. the mean rate of reduction was recorded 34.65%. The percentage of contamination of water samples after treatment in the present study was 30 %. Two samples after treatment in the present study had higher Cd levels than the maximum permissible limit (0.005mg/l) specified by the EU Council Directive (2001).

3.3.Chromium and molybdenum:

All collected samples were free from any detectable concentrations of Cr and Mo.

3.4.Copper:

Copper is an essential element for all living organisms (Berman, 1980). The essential role of copper became clear when its value in diets and consequently its necessity, in addition to iron, in blood formation was demonstrated in 1928. Copper is involved in the formation of several enzymes such as tyrosinase, ascorbic acid oxidase, cytochrome oxidase, monoamine oxidase, and uricase. It is also essential for the cross-linking of elastin. In Table 7 copper was found to be low in the water from groundwater sources samples and water samples after treatment far below the maximum allowed levels at 0.115 -0.13 mg/L, and 0.11-0.125 mg/L. the mean rate of reduction was recorded 7.30%. The maximum allowed limit of copper in drinking water is 1 mg/l. specified by the EU Council Directive (2001). All samples of water after treatment were lower than maximum permissible limit (MPL).

3.5.Nickel:

Nickel is used as alloys product, nickel-plating for anti-corrosion and in the manufacture of batteries. It is regarded as an essential trace metal but toxic in large amount to human health. It is considered as carcinogenic to human. Ambrose et al. (1976) reported that high-dose of nickel in rats and dogs were significantly decreasing their body weights. Data in table (7) show that, 8 samples of groundwater sources samples were contaminated with Ni. The varied in water from groundwater sources samples between N.D-0.03 mg/L. and the mean was 0.044 mg/l. On the other hand, water samples after treatment were recorded N.D-0.055 mg/l. the mean rate of reduction was recorded 44.68%. The percentage of contamination

tion of water samples after treatment in the present study was 40 %. Two samples after treatment in the present study had higher Ni levels than the (MPL) (0.05 mg/L) specified by the EU Council Directive (2001).

3.6. Lead:

Lead For lead it was found that, the concentrations in the present study lied between 0.105-0.13mg/L and of a mean of 0.117mg/L of groundwater sources samples, Table (7). In water samples after treatment the lead concentrations were at the levels of 0.02-0.055mg/L. and of a mean of 0.033 mg/L . The mean rate of reduction was recorded 72.38 % .The percentage of contamination of water samples after treatment in the present study was 100 %. One sample after treatment in the present study had higher Pb levels than (MPL) (0.05 mg/L) specified by the EU Council Directive (2001).

3.7. Zinc:

Zinc has been known as an essential element since 1869 (**Berman, 1980**). A number of enzymes, such as alkaline phosphatase and lactic acid dehydrogenase, are zinc dependent. The element also influences the growth rate and bone development, the integrity of the skin, and development and function of the reproductive organs. The lowest found zinc limits were (N.D-N.D) and the maximum was (0.06 and 0.055 mg/L) samples of groundwater sources and the water purification station, respectively. (Table 7).whole the mean of samples groundwater sources and the water purification station were (0.0255-0.025 mg/L) , respectively . The mean rate of reduction was recorded 7.98 % .The percentage of contamination of water samples after treatment in the present study was 80 %. All samples after treatment in the present study had lower Zn levels than the (MPL) (5 mg/L) specified by the EU Council Directive (2001). (Table 8) summarizes inter TE correlation coefficient in groundwater sources samples in the studied area. Some studied elements showed moderate positive significant correlation at the 0.05 level like Pb–Mn ($r = 0.5862$) and Zn–Ni ($r = 0.6551$). There are also very weak positive significant correlations at 0.05 level for Cd–As ($r = 0.2334$), Cd–Mn ($r = 0.1924$) , Cu–Mn ($r = 0.0782$), Pb–Ni($r = 0.3975$) and Pb–Zn($r = 0.3655$) . Some studied elements showed moderate negative significant

correlation at the 0.05 level like Cd–As ($r = 0.6057$) and Zn– Mn ($r = 0.3102$), As –Pb ($r = 0.6542$), weak negative significant correlation like Cd–Cu ($r = 0.3663$) and Zn– Mn ($r = 0.3102$). There are also very weak positive significant correlations at 0.05 level for As–Ni ($r = 0.0511$), Cu–Ni ($r = 0.0799$), Ni –Mn ($r = 0.0947$) and As–Pb ($r = 0.6452$).

Table 9 summarizes inter TE correlation coefficient in water purification station samples in the studied area. Some studied elements showed strong positive significant correlation at the 0.05 level like Cu–Mn ($r = 0.811$) and Pb– Mn ($r = 0.7521$) and Ni–Zn($r = 0.7308$). Some studied elements showed moderate positive significant correlation at the 0.05 level like Cd–As ($r = 0.2594$), Pb–Ni ($r = 0.5241$). There are also very weak positive significant correlations at 0.05 level for Cu–Pb ($r = 0.3498$) and Pb–Zn($r = 0.2085$). Some studied elements showed very negative significant correlation at the 0.05 level like As –Pb ($r = 0.8252$). Some studied elements showed moderate negative significant correlation at the 0.05 level like Ni–As ($r = 0.5683$) and As – Mn ($r = 0.5553$), weak negative significant correlation like Cd–Ni ($r = 0.4171$), Zn–As ($r = 0.4973$) and Zn–Cd ($r = 0.3687$).

Our results agree with (**Idrisi, 2000** , **Meghdad Pirsahab et al 2013** and **Chennaiah et al 2014**).Drinking water from these areas is mixed up with about 25% underground water (**Idrisi, 2000**). The underground water is closed to the Ismailia canal and the agricultural activities that would explain how heavy metals contaminated drinking water in these areas. The main source for heavy metals that contaminated drinking water in the studied areas is from industrial wastes and agriculture activities. In another words, industrial and agriculture waste is carried out to the reservoirs that supply drinking water for the studied areas. Also, we should consider the old pipe systems in these areas, from which copper could have another source from the corrosion of water pipes. (**Meghdad Pirsahab et al 2013**) , they collected 165 water samples from water supply resources (128 wells), 25 water reservoirs and water distribution network (tap water) of Kermanshah City (with a population of about one million). Heavy metals concentrations (Aluminum, Arsenic, Cadmium, Lead, Chromium, Mercury, Copper, Cobalt, Iron, Manganese, Selenium, Molybdenum, Vanadium, Antimony, Nickel

Table 5. Trace elements concentrations and % reduction in water samples collected from groundwater sources and water purification station.

Sample	Element	As (µg/L)		Cd(mg/L)		Cr(mg/L)		Cu(mg/L)		Mn(mg/L)		Mo(mg/L)		Ni(mg/L)		Pb(mg/L)		Zn(mg/L)	
		*	**	*	**	*	**	*	**	*	**	*	**	*	**	*	**	*	**
1		2.31	1.87	N.D	N.D	N.D	N.D	0.13	0.125	0.05	0.046	N.D	N.D	0.025	0.016	0.13	0.055	0.025	0.02
2		2.39	2.27	N.D	N.D	N.D	N.D	0.12	0.11	0.015	0.005	N.D	N.D	0.04	0.035	0.12	0.04	0.04	0.03
3		2.95	2.814	0.001	N.D	N.D	N.D	0.12	0.11	0.02	0.005	N.D	N.D	0.3	0.055	0.125	0.04	0.06	0.05
4		2.96	2.95	0.005	N.D	N.D	N.D	0.125	0.11	0.005	0	N.D	N.D	0.005	0.005	0.115	0.025	0.051	0.04
5		3.09	2.71	N.D	N.D	N.D	N.D	0.13	0.11	0.01	0.005	N.D	N.D	0.03	0.025	0.115	0.03	0.03	0.02
6		3.18	3.179	0.008	0.005	N.D	N.D	0.12	0.11	0.035	0.005	N.D	N.D	0.01	N.D	0.115	0.03	0.011	0.01
7		3.30	3.23	0.005	0.005	N.D	N.D	0.12	0.11	0.075	0.005	N.D	N.D	0.015	N.D	0.12	0.025	0.016	0.01
8		3.39	3.34	0.005	N.D	N.D	N.D	0.115	0.11	0.005	0.005	N.D	N.D	N.D	N.D	0.105	0.035	N.D	N.D
9		3.76	3.65	N.D	N.D	N.D	N.D	0.12	0.12	0.005	0.005	N.D	N.D	0.02	N.D	0.105	0.02	0.022	0.02
10		3.99	3.98	N.D	0.001	N.D	N.D	0.12	0.115	0.04	0.01	N.D	N.D	N.D	N.D	0.12	0.025	N.D	N.D
MPL		5		0.005		0.1		1		0.1		0.01		0.05		0.05		5	
* : groundwater sources		** : water purification station										MPL: the maximum permissible limits							

Table 6. Trace elements % reduction in water samples collected from groundwater sources and water purification station.

Sample	Element								
	As (µg/L)	Cd(mg/L)	Cr(mg/L)	Cu(mg/L)	Mn(mg/L)	Mo(mg/L)	Ni(mg/L)	Pb(mg/L)	Zn(mg/L)
1	19.14	0	N.D	3.84	8	N.D	36	57.69	12
2	4.93	0	N.D	8.33	66.66	N.D	12.5	66.66	12.5
3	4.65	100	N.D	8.33	75	N.D	81.66	68	8.33
4	0.50	100	N.D	12	100	N.D	0	78.26	5.88
5	12.29	0	N.D	15.38	50	N.D	16.66	73.91	16.66
6	0.15	37.5	N.D	8.33	85.71	N.D	100	73.91	9.09
7	2.35	9.09	N.D	8.33	93.33	N.D	100	79.16	6.25
8	1.53	100	N.D	4.3	N.D	N.D	N.D	76.19	N.D
9	2.84	0	N.D	N.D	N.D	N.D	100	66.66	9.09
10	0.15	0	N.D	4.16	75	N.D	N.D	83.33	N.D
MPL	5	0.005	0.1	1	0.1	0.01	0.05	0.05	5

MPL: the maximum permissible limits

Table 7. Minimum, maximum, mean, standard deviation, contamination, % reduction, maximum permissible limits (mpl) and violation of heavy metals monitored in 20 samples of water from groundwater sources and the water purification station.

	Range: (Minimum-maximum) (mean ± SD) (mg/l).	Range of % reduction (Minimum-maximum) (mean ± SD)	Contami- nated Samples af- ter purifica- tion	MPLs (mg/l)	Violated Samples after puri- fication		
Element	*	**	**	No.	%.	No.	%.
	N=10	N=10	N=10				
As*	(0.00231-0.00399)	(0.001875-0.003988)	(0.15-19.14)	10	100	0.05	0
	(0.00313±0.52)	(3.001±0.62)	(4.85±6.18)				
Cd	(N.D-0.005)	(N.D-0.01)	(0-100)	3	30	0.005	2
	(0.0005±0.0015)	(0.0003±0.0041)	(34.65±46.51)				20
Cr	(N.D- N.D)	(N.D- N.D)	0	0	0	0.1	0
							0
Cu	(0.115-0.13)	(0.11-0.125)	(0-15.38)	10	100	1	0
	(0.122±0.004)	(0.113±0.0053)	(7.30±4.41)				0
Mn	(0.005-0.075)	(N.D-0.046)	(0-100)	9	90	0.1	0
	(0.122±0.004)	(0.0091±0.013)	(55.37 ±38.95)				0
Mo	(N.D- N.D)	(N.D- N.D)	0	0	0	0.01	0
							0
Ni	(N.D-0.03)	(N.D-0.055)	(0-100)	4	40	0.05	2
	(0.044±0.09)	(0.015±0.01)	(44.68±45.5)				20
Pb	(0.105-0.13)	(0.02-0.055)	(57.69-83.33)	10	100	0.05	1
	(0.117±0.007)	(0.033±0.01)					10
			(72.38±7.60)				
Zn	(N.D-0.06)	(N.D-0.055)	(0-16.66)	8	80	5	0
	(0.0255±0.02)	(0.025±0.018)	(7.98±5.26)				0
Σ				10	100		4
							40

*:groundwater sources

**: water purification station

Table 8. Correlation matrix of selected Trace elements in groundwater samples before treatment.

Element	Function	As (µg/L)	Cd(mg/L)	Cu(mg/L)	Mn(mg/L)	Ni(mg/L)	Pb(mg/L)	Zn(mg/L)
As (µg/L)	Pearson Correlation Coefficient	1.						
	<i>R Standard Error</i>							
	<i>t</i>							
<i>p-value</i>								
Cd (mg/L)	Pearson Correlation Coefficient	0.2344	1.					
	<i>R Standard Error</i>	0.1181						
	<i>t</i>	0.6820						
<i>p-value</i>								
Cu (mg/L)	Pearson Correlation Coefficient	-0.6057	-0.3663	1.				
	<i>R Standard Error</i>	0.0791	0.1082					
	<i>t</i>	-2.1533	-1.1133					
<i>p-value</i>								
Mn (mg/L)	Pearson Correlation Coefficient	-0.2529	0.1924	0.0782	1.			
	<i>R Standard Error</i>	0.1170	0.1204	0.1242				
	<i>t</i>	-0.7392	0.5547	0.2217				
<i>p-value</i>								
Ni (mg/L)	Pearson Correlation Coefficient	-0.0511	-0.2399	-0.0799	-0.0947	1.		
	<i>R Standard Error</i>	0.1247	0.1178	0.1242	0.1239			
	<i>t</i>	-0.1446	-0.6989	-0.2266	-0.2690			
<i>p-value</i>								
Pb (mg/L)	Pearson Correlation Coefficient	-0.6542	-0.2815	0.4666	0.5862	0.3975	1.	
	<i>R Standard Error</i>	0.0715	0.1151	0.0978	0.0820	0.1053		
	<i>t</i>	-2.4464	-0.8298	1.4920	2.0468	1.2252		
<i>p-value</i>								
Zn(mg/L)	Pearson Correlation Coefficient	0.0402	0.4307	0.1740	0.0749	0.2553		
	<i>R Standard Error</i>	-0.2618	-0.2387	0.3354	-0.3102	0.6551	0.3655	1.
	<i>t</i>	0.1164	0.1179	0.1109	0.1130	0.0714	0.1083	
<i>p-value</i>								
		-0.7673	-0.6952	1.0069	-0.9228	2.4524	1.1106	
<i>t</i>								
		0.4649	0.5066	0.3435	0.3831	0.0398	0.2990	
<i>p-value</i>								

Table 9. Correlation matrix of selected Trace elements in water purification station samples after treatment.

Sample size		10	Critical value (5%)			2.306		
		As (µg/L)	Cd(mg/L)	Cu(mg/L)	Mn(mg/L)	Ni(mg/L)	Pb(mg/L)	Zn(mg/L)
As (µg/L)	Pearson Correlation Coefficient	1.						
	R Standard Error							
	t							
	p-value							
Cd(mg/L)	Pearson Correlation Coefficient	0.2594	1.					
	R Standard Error	0.1166						
	t	0.7596						
	p-value	0.4693						
Cu(mg/L)	Pearson Correlation Coefficient	-0.1829	-0.2784	1.				
	R Standard Error	0.1208	0.1153					
	t	-0.5262	-0.8199					
	p-value	0.6130	0.436					
Mn(mg/L)	Pearson Correlation Coefficient	-0.5553	-0.1626	0.811	1.			
	R Standard Error	0.0865	0.1217	0.0428				
	t	-1.8883	-0.4662	3.9213				
	p-value	0.0957	0.6535	0.0044				
Ni(mg/L)	Pearson Correlation Coefficient	-0.5683	-0.4171	-0.1812	0.0323	1.		
	R Standard Error	0.0846	0.1032	0.1209	0.1249			
	t	-1.9537	-1.2982	-0.5211	0.0914			
	p-value	0.0865	0.2304	0.6164	0.9294			
Pb(mg/L)	Pearson Correlation Coefficient	-0.8252	-0.2972	0.3498	0.7521	0.5241	1.	
	R Standard Error	0.0399	0.114	0.1097	0.0543	0.0907		
	t	-4.1318	-0.8803	1.0562	3.2282	1.7407		
	p-value	0.0033	0.4044	0.3217	0.0121	0.1199		
Zn(mg/L)	Pearson Correlation Coefficient	-0.4973	-0.3687	-0.1783	-0.1277	0.7308	0.2085	1.
	R Standard Error	0.0941	0.108	0.121	0.123	0.0582	0.1196	
	t	-1.6212	-1.1219	-0.5124	-0.3642	3.0284	0.6029	
	p-value	0.1436	0.2944	0.6222	0.7252	0.0163	0.5633	

Correlation is significant at the 0.05 level (2_tailed).

ples were measured by the Varian atomic absorption device. Results indicated that concentrations of all measured metals (except the amount of Aluminum, Iron and Manganese in some samples of water resources, distribution network and water reservoirs) were lower than the national standards and guidelines recommended by the World Health Organization (WHO). Continuous monitoring of heavy metals concentrations in urban water systems from source of production to consumption site is recommended to identify the source of pollution.also, (Chennaiah et al 2014) They assess the status of drinking water quality in the rural areas of the Bhongiri region, India. A total of 42

drinking water samples were collected from different areas. All the samples were analysed for three physico-chemical parameters Such as Conductivity, Total dissolved solids (TDS), pH and Twelve heavy metals (As, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, V, Mo ,Zn) and cations like (Na,K, Ca, mg)using standard procedures. All the Cations (Na, Mg, K, and Ca) concentrations exceeded the permissible limits of WHO and BIS. Out of twelve heavy metals six heavy metals (Cr, Fe, Mn, Ni, Pb, and Zn) concentration exceeded the WHO and BIS permissible limits, this could poses serious health diseases. It is recommended that potable water sources in the study area should be routinely monitored to ascertain its suitability for drinking and other purposes.

REFERENCES

- Ambrose, A.M., D.S. Larson, J.R. Borzelleca and G.R. Hennigar, Jr., (1976)** .Long-term toxicologic assessment of nickel in rats and dogs. *J. Food Sci. Technol.* 13: 181-187.
- AOAC, (1995).**Assoc. Official Anal.Chem., 16th ed. AOAC Int., Arlington, Virginia, USA.
- Chaitali V. Mohod , JayashreeDhote (2013).** Review of heavy metals in drinking water and their effect on human health. *International Journal of Innovative Research in Science, Engineering and Technology* Vol. 2, Issue 7, July 2013.
- Berman, E,** Toxic Metals and Their Analysis, Heyden & Son Ltd., London(1980)
- Cauduro, J.; (2013).** Determination of major, minor and trace elements in rice flour using the 4200 Microwave Plasma- Atomic Emission Spectrometer (MP-AES) , Agilent Technologies, (available on <https://docs.google.com/viewer?url=http://www.chem.agilent.com/Library/applications/5991-3777EN.pdf>) last accessed on January 7, 2015)
- Demir. V., Dere. T, Ergin. S, Y. Cakr and F. Celik (2015).** Determination and health risk assessment of heavy metals in drinking water of tunceli, Turkey. *Water Resources*, 2015, Vol. 42, No. 4, pp. 510–518.
- Idrisi, M., 2000:** Personnel communication.
- Chennaiah. Bala. J, M.A. Rasheed and D.J. Patil (2014).** Concentration of heavy metals in drinking water with emphasis on human health. *International Journal of Plant, Animal and Environmental Sciences* vol 4, No. 2, pp205-214.
- Kitchin, K.T., Recent Advances in Arsenic Carcinogenesis (2001):** Modes of Action, Animal Model Systems, and Methylated Arsenic Metabolites, *Toxicology and Applied Pharmacology*, Academic Press 172, 3, 249-261(13)
- Meghdad Pirsaeheb, Touba Khosravi, Kiomars Sharafi, Leila Babajani and Mansour Rezaei (2013)** Measurement of Heavy Metals Concentration in Drinking Water from Source to Consumption Site in Kermanshah – Iran. *World Applied Sciences Journal* 21 (3): 416-423, 2013.
- Meharg, AA & Hartley-Whitaker, J 2002,** 'Arsenic uptake and metabolism in arsenic resistant and non-resistant plant species' *New Phytologist*, vol 154, no. 1, pp. 29-43.