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Evaluation of Trace Elements in Drinking Water of Duhok province/Kurdistan region of Iraq

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ABSTRACT: *Good drinking water quality is essential for the well being of all people. One of the most important crises of the 21st century is the availability of drinking water, a resource basic to our survival and growth. The aim of this study was to evaluate the Trace metals of pre and post treated water resources of Duhok province in addition to evaluate the efficiency of water projects for purification of water. The areas of the study were water projects those of supporting Duhok governorate with their districts (Sumeel, Chambarakat, Zakho, Akre, Shekhan and Amedi). Results indicated that the concentration of trace metals Significantly decrease at Chambarakat and Zakho water project during water treatment processes, while the concentration Copper at (Shekhan) and Iron at (Duhok dam) significantly increased in post treated water compared with the pre treated water. Generally the concentrations of Cobalt, Copper, Manganese and Zinc of pre and post treated water were detected to be so much lower from WHO guidelines for drinking water standards (50, 1000, 50 and 3000 µg/L) respectively, except for Iron (fig.11) was higher than the WHO guidelines for drinking water standards, (50 µg.L^{-1}) Increasing the concentration of Trace metals during warm months compared with the cold months due to the dilution of waters by rain fall and evaporation, when raised the temperature, except Copper and zinc concentrations increase during wet months. The water supply of Duhok dam was contaminated with arsenic, although entire studied locations were polluted by studied heavy metals except chromium. According to this conclusion we recommend that all water projects must be monitored as well as a proper treatment*

Keywords: *Drinking water, Duhok Province, Trace Elements*.

I. INTRODUCTION

Good drinking water quality is essential for the well being of all people. Unfortunately in many countries around the world, including Kurdistan region, some drinking water supplies have become contaminated, which has impacted on the health and economic status of the populations (Akoto, 2008). Contaminants such as bacteria, viruses, metals, nitrates and salt have found their way into water supplies as a result of inadequate treatment and disposal of waste (human and livestock), industrial discharges, and over-use of limited water resources (Singh and Mosley, 2003).

Water covers about 73% of the earth's surface. It is the major constituent of the lithosphere and atmosphere and it is an essential requirement of all living organisms. The largest water requirement is for municipal use but standard of purity required for this purpose is one of the prime factors in deciding the growth of towns and cities as well as industries (WHO, 1984).

Extensive growth of industrial activities witnessed during this century had generated serious environmental problems throughout the world. Air, water and soil are being contaminated by countless harmful materials discharged to the environment without proper treatment. A good majority of these contaminants end up in drinking water sources threatening plant and animal lives (Kutty et al., 1995).

One of the most serious problems facing the world today is contamination of the environment by Trace metals and becoming a global phenomenon, metals contamination may become a major stress factor in the next decades (Bárány-Kevei et al., 2005)

Some of the metals have main role in biological systems. Especially trace metals that are essential for living organism. they founds in low concentrations in earth's crust and natural waters (Morrison et al., 1979 and Vagas etal., 2001).

Trace metals are among one of the significant pollutants of freshwater, with the development of mining, smelting and other industrial activities. Metal pollution not only affects the productivity of crops, but also the quality of the atmosphere and water bodies and threatens the health and life of animals and human beings by way of the food chain (Shashikanth et al ., 2008).

In other hands Most of these metals especially Iron, manganese, chromium and cupper in small amount are an essential elements for most life forms on earth, because of their participation in many significant physiological processes within the biological bodies including humans and animals. While exceeds their level

are associated with an increased risk for cancer, heart disease and other illness such as endocrine problem, arthritis, diabetes and liver disease (Niederau et al., 1996).
The major source of water supply in Duhok province, is drawn from ground water (Wells and spring) and some from Khapor River; all these issues provide a perennial source of water for drinking purposes and numerous activities.

The purpose of this study was To Determine the concentration of trace metals in drinking water resources in entire Duhok province in order to evaluate the efficiency of water project plant for purification of raw water. However the previous investigation on Duhok province (Al-Naqishbandi, 2002, Ahmed, 2007 and Hawrami, 2010) did not refer to trace metal concentration in water samples in the area. Never the less this paper may be regarded as base line information on Co, Cu, Fe, Mn and Zn in drinking water in this Province.

II. DESCRIPTION OF THE AREA

Duhok province is located at Kurdistan region of Iraq between Bekhir Mountain at north and White Mountain at south. It is boundaries extend from longitude (20-, 42°) (10-,44°)E and from latitude (40-,36°) (20-,37°) and the elevation of sea level of Duhok province varies from 445m to 1215m (Duhok meteorological directorate DMD,2008). The climate of Duhok area is similar to that of the other parts of Kurdistan region and the other northern parts of Iraq, which is semi-arid and characterized by hot summer and a moderately rainy cold winter. The total rainfall value for the studied area during the period of the study obtained from Duhok metrological office was (193.1mm) (DMD, 2008). The average annual values of temperature recorded during (2000–2008) were ranged (-11.1 - 41ºC) (DMD, 2008). The monthly average humidity values recorded for Duhok province during 2001 to 2004 was 43% (DMD, 2004).

Hydrologically Duhok province including Duhok city and their districts (Semeel, Zakho, Shekhan Akre and Amedy) has been studied by many authors during the last decade’s 80% of the Duhok city depend on the Mosul and Duhok dam and other remain 20% depend upon groundwater (Drilled wells) , Zakho city depends upon surface water (Khapor River) and other cities (Semeel, Shekhan Akre and Amedy) 100% depend upon Groundwater (Wells), and Groundwater (Spring) (Duhok Water and waste water Directory DWWD).Plate (1) illustrate the Satellite image of studied sites.

III. MATERIAL AND METHODS

The samples were collected from November 2008 to July 2009 at all selected Stations, this periods were occupy four seasons of year [Fall (November and December 2008), Winter (January, February and March 2009),Spring (April , May and June 2009) and Summer (July 2009)].

The sampling was took place monthly in two days; first start 10th each month at 10 am to 2 pm toward of Duhok city, Chambarakat, Semeel and Zakho, and the second 11th month start at 10am to 4 pm of each months toward Akre, Shekhan, and Amedy. Care was taken during sampling process to prevent any external contamination of samples with metals. Water samples were taken from each locations in pre and post treated water, and three replicate of water samples were taken at fife (5) minutes intervals. 500ml container polyethylene bottle and their lids previously washed by soaking in solution of 5 to 10 percent of nitric acid rinsed in deionized water, filled with 1% nitric acid and stored in sealed plastic bags. At the Sampling sites, the acid was removed; the bottles rinsed three times with the samples prior to filling, capping and being returned to plastic bag (APHA, 1999).

The samples were filtered though the (Watman No. 41) filter paper (if required) 0.45-µm pore size. The pH of the filtrate was adjust to 2±0.2 with 1M HNO3 then the samples were Preserving by acidified with 1:1HNO3/dIH2O 3ml .l-1 According to the APHA,(1999) to minimize the precipitation and adsorption to container walls, and stored in refrigerators for later determination of trace metals. Water samples were digested before analysis according to APHA, (1999) for a more accurate determination of these traces metals. 500ml of water sample was Placed in 600ml Pyrex-glass beaker, 5ml of concentrated HNO3 for each 100ml samples was added to the samples and slowly boiled on a hotplate (60-80°C) the evaporation process was carried out in a dust free room until reaching a final sample volume of 15-20ml ,the heating process continue and adding drops of concentrates HNO3until digestion is complete as show by the bright color, clear solution, and the digest samples were completed to50ml with deionized water in volumetric flask.

N	Location	Lat. - N	Long. - E	Elevation /m
1	Duhok	N 36°52'14.4"	E 42°58'44.4"	552m
2	Simmel	N 36°51'29.2"	E 42°51'18.0"	497m
3	Chamberkat	N 36°51'08.0"	E 42°50'03.5"	463m
4	Zakho	N 37°08'09.5"	E 42°41'40.8"	445m
5	Akre	N 36°40'34.8"	E 43°49'38.6"	578m
6	Shekhan	N 36°42'20.0"	E 43°21'22.0"	520m
7	Amedi	N 37°05'39.6"	E 43°29'23.8"	1215m

Plate (1) Satellite image shows the Duhok province are indicated all studied sites according to the Lat.N, Long.E and Elevation (Google Earth, 2008)

Water temperatures were measured in the field directly at the time of each sampling by a precise mercury thermometer (0-50°C) graduated up to 0.1 intervals, Hydrogen ion concentration was measured directly after transport the samples to the laboratory by electrometric method using pH-meter model (Inolab.WTW). As described by Mackereth et al.,(1978) Electrical conductivity was measured in the laboratory by using a EC-meter model (Inolab.WTW). As described by Mackereth et al., (1978).

The analyses were carried out using flame atomic absorption spectroscopy (AAS) for the determination of the total content of Co, Cu, Fe, Mn and Zn The instrument used was Aanalyst200 (Perkin-Elmer) spectrophotometer (continuum background correction) For Fe, Mn and Zn was used hollow cathode multi-element lamps, while for Co and Cu using an Electrode Less Discharge lamps (EDL System2), using acetylene gas as fuel and air as an oxidizer.

IV. STATISTICAL ANALYSIS

Randomize Complete Block Design (RCBD) was used for statistical analysis by using the Microsoft (SPSS Ver. 17). Analysis of Variance (ANOVA), Duncan multiple range tests was employed to examine statistical significance difference in the mean concentration of heavy metals among location, months and their interaction, probable level of ($P<0.01$) was conceded statistical significant. Multiple correlation models were used through measuring the correlation coefficient values between each calculated pairs of the studied variables.

V. RESULTS

Temporal variations of water temperature were observed during sample collection among the studied sites and sampling dates, as represents in Figure (1). The higher temperature values were observed in the wells (Shekhan, Akre and Semeel stations) and significantly differed from the values were observed in the surface water and spring (Duhok dam Chamberakat, Zakho and Amedi stations). Also no significant differences were observed between pre and post treated water during entire sampling sites. no significant differences was occured between entire sampling periods (seasons) as showed in figure (2).

Figure (3) represented the pH values of pre and post treated water. The pH values of pre treated water were higher than the post treated water except Shekhan station in post treated water was slightly higher than the pre treated water. No significant differences was observed between seasons, the higher value was recorded during summer was (7.82) and the lower value during fall was (7.64) (Figure 4).

Figure (5) represented the Electrical conductivity of water samples of Duhok province, Also no significant differences were observed between pre and post treated water, which no Significant differences were observed between months analysis for both pre and post treated water The higher value was recorded during winter (745.55µs.cm-1) and the lower value during summer (556.44µs.cm-1) (Figure 6).

Figure 7 showed that the Cobalt concentration of pre and post treated water, The (CO) concentration increased and decreased according to the process of treatment, the concentration in post treated water was increased only at Akre and other locations there were no significant differences between pre and post treated water. Seasonal variation of (CO) concentration during all studied periods ranged from (16.407 µg.L-1) to (36.278 µg.L-1), the higher mean value was found during summer that was differed significantly from all other seasons while, the lower mean value was recorded during Fall which was differed significantly from all other seasons (Fig. 8).

Figure (9) showed that the Copper concentration of pre and post treated water, Copper concentration in post treated water at Chambarakat and Zakho stations were significantly decrease, whereas Significantly increase their concentration after water process treatment at Akre and Shekhan stations while at Duhok, Semeel, Akre and Amedy water project which were no significant differences was observed between its concentration in pre and post treated water.

Seasonal variation of (Cu) concentration during all studied periods ranged from (6.53 $\mu g.L^{-1}$) to (2.41 $\mu g.L^{-1}$), the higher mean value was found during Fall that was differed significantly from all other seasons while, the lower mean value was recorded during Spring which was differed significantly from Fall and Summer (Fig. 9).

Figure (10) showed that the Iron concentration of pre and post treated water, the (Fe) concentration was significantly decreased during water treatment processes at Chambarakat and Zakho while at Duhok dam, its concentration was increased during water treatment processes. While at Sumeel, Akre and Shekhan there were no differ significantly.

Seasonal variation of (Fe) concentration during all studied periods ranged from (167.05 to 107.75 $\mu g.L^{-1}$), the higher mean value was found during summer which differed significantly from all other seasons while, the lower mean value was recorded during fall which no significantly differed from winter whereas differed significantly from spring and summer (Fig. 11).

Figure (12) showed that the Manganese concentration of pre and post treated water, The (Mn) concentration Significantly decreased during the treatment process, at Chambarakat and Zakho while its concentrations at all stations insignificantly differences were observed in pre and post treated water. Seasonal variation of Mn concentration during all studied periods ranged from (11.73 to 18.46 $\mu g.l^{-1}$), the higher mean value was found during summer which differed significantly from all other seasons while, the lower mean value was recorded during Fall which differed significantly from all other seasons (Fig. 12).

Figure (13) showed that the Zinc concentration of pre and post treated water, the Zinc concentration significantly decreased during the treatment process at Chambarakat and Zakho stations, while significantly increase during water treatment processes at Shekhan station.

Seasonal variation of (Zn) concentration during all studied periods ranged from (34.10 to 43.25 $\mu g.l^{-1}$), the higher mean was found during Spring which differed significantly from all other seasons while, the lower mean was recorded during winter which differed significantly from all other seasons (Fig. 14).

VI. DISCUSSION

Physical parameters such as (Temperature, pH, and Electrical conductivity) are one of the most important ecological features, they controls behavioral characteristics of organisms, solubility of gases and salts in water (Dixit and Tiwari, 2008). Generally annual water temperature variation as showed in Figure (1) during the study period was (7-24°C) which was similar to the previous study (Duhoki, 1997 ; Al-Nakshabandi, 2002 and Ahmed *et al*., 2007).The variation in water temperature was affected by Seasonal fluctuation and air temperature this was obvious throughout the present study.

The pH value of the current study lies in the alkaline side above pH 7, for pre and post treated water, figure (2) the obtained value of pH are considered as usual condition, because generally in Iraqi Kurdistan region the pH of water characterized by shift toward the alkaline side of neutrality due to the geological formation of the area which composed mainly of CaCO3 (Nabi, 2005), also the high pH value was recorded at the water project which depends upon surface water; River (Zakho) and, Impoundment (Chambarakat and Duhok). This could be contribute to increase photosynthetic activity (reduces the CO_2 amount in water), or may be due to the presence of dissolved carbonate and bicarbonate in the water. similar results recorded by Ahmed, (2007); and Othman,(2008). The decrease of pH values during water treatment processes (Fig. 5), May be due to the release of carbonate and bicarbonate in the water by the action of precipitation or filtration (Goher, 2002).

The pH values of all studied samples in pre and post treated water was on the safe side for drinking purposes (6.5-8.5) according to WHO and Iraqi guideline for drinking water standards (WHO, 2006 and Abbawi and Hassan, 1990).

Electrical conductivity is an important water quality measurement because it gives a good idea of the amount of dissolved minerals in the water (Muhammad, 2004). The EC values at Duhok dam and Semeel were exceed WHO guideline for drinking water (700 $\mu S.cm^{-1}$) in both *pre* and *post* treated water, (Table 6a and b) this may be related to present of high dissolved ions, input of allochthonus organic material from the catchments area and high mineral salts concentration from the dissolution of minerals in the soil (Shekha, 2008). These two stations are not suitable for domestic use. Health effects in humans for consuming water with high EC may include disturbances of salt and water balance; and adverse effect on certain Myocardic patients and individuals with high blood pressure (Fatoki and Awofol, 2003), similar EC values were recorded at the same area (Duhoki, 1997 and Al-Naqishbandi, 2002). Fig.(5) indicate that, There was no significant differences observed between EC in pre and post treated water, at each stations, this may be due to the inactivity of treatment processes in trapping total ions or may be related to new contamination of water with ions during treatment process. Also seasonal fluctuation of EC values illustrates that (Fig.6), during rainfall increase EC values because of runoff or by effluent different ions in to the water body.

Among Trace metals Cobalt, Copper, Iron, manganese and Zinc in small amount are an essential element for most life on earth, including humans and animals. high level of them are associated with an increased risk for cancer, heart disease and other illness such as endocrine problem, arthritis, diabetes and liver disease (Niederau et al., 1996)

Also these metals that is essential for living organism (Vargas, 2001). Nitrogen fixing organism and some Microorganisms need these elements for metabolism and growth but it causes digestion failure so much as other trace metals when the concentration of these elements exceeds from a certain level (Atashi, et al., 2009 trace 2). When the concentration of these elements exceeds, it could be dangerous for human health. Toxic doses of trace metals causes bad effect such as asthma, pneumonia, vomiting, vision problems, hearth problems (Agency for Toxic Substances and Disease Registry, 2004 trace 2)

In general, the concentration of trace metals Significantly decrease at Chambarakat and Zakho water project during water treatment processes may be due to the precipitation and sand filtration unit, present in both water project but these decreasing for (Fe) was not reach to the acceptable limit,(Fig.11) because of the effect of solder , galvanized pipesand storage tanks on the treated water (Dixit and Tiwari, 2008), on the other hand paints of water reservoirs as well as relatively old and poorly maintained distribution systems of drinking water may be the main cause of elevation concentrations of Iron in drinking water.

Unfortunately the concentration Copper at (Shekhan) and Iron at (Duhok dam) significantly increased in post treated water compared with the pre treated water (Fig.9 and 11) This may be due to the household plumbing systems in which the pipes solder, fittings, or service connections to homes contain both metals pipes also contain and Cu and Fe compounds that can be leached in to drinking-water (Schock, 1990 and Rajaratnam *et al*., 2002).

Seasonal variation of Co, Iron and Manganese (Fig. 8, 12 and 14), revealed that their concentration significantly increased during summer and decrease during fall Similar results were observed by Khan, (2005) and Othman,(2008). This may be due to the evaporation during warm and dry season and dilution during rainfall or may be related to increase dust deposition during dry and dusty months, recorded by Duhok Metrological Directorate during, May, June and July 2009.whil the concentration of Copper and Zinc, were significantly increased during Wet season (Fig.10 and 16) this may be due to the increase weathering and erosion by heavy rain during wet season lead to runoff in to the near water body or may be transition of metals between water and sediment due to oxidation and reduction condition and change water pH, whereas decrease their conc. During hot periods may be relate to increase of abundance of green organisms including phytoplankton growth and activities (because their essentiality for them) throughout summer (Mallick and Rai, 1989). Same results recorded observed by Khan,(2005);Virkutyte et al.,(2006) Sajidu et al.,(2007).

Generally the concentrations of Cobalt, Copper, Manganese and Zinc of pre and post treated water were detected to be so much lower from WHO guidelines for drinking water standards (50, 1000, 50 and 3000 µg/L) respectively, Zn concentration is adequate in the studied sites, if the water is used for only domestic purposes. However, Zn could be a problem in water for other uses, for example, in the use of the aquatic ecosystem. The acceptable range for Zn in water for the use of aquatic ecosystem is (0 to 20µg/L). Hence Zn concentration was exceeded in the all studied sites. Thus, water from the studied stations is unsuitable for the aquatic ecosystem as it could be detrimental to fish and other aquatic lives (Akoto, 2008).

The concentrations of these metals in studied drinking water resources was found much lower than the permissible limits except for Iron (fig.11) was higher than the WHO guidelines for drinking water standards, (50 $\mu g.L^{-1}$) this may be due to the discharge of industrial effluents and municipal wastes, geological formation, weathering and erosion of soil during rainy seasons (Kaushik et al., 2009). Or may be related to distribution pipes, therefore, the use of the water for domestic supply is not safe without the proper treatment.

Table (1) Multiple Correlation between the Heavy Metals for the entire of the present study.

		EC	pH	Co	Cu	Fe	Mn	Zn
EC	Correlation	1						
	Sig.(2Tailed)							
pH	Correlation	-0.085	1					
	Sig.(2Tailed)	0.507						
Co	Correlation	-0.05	0.065	1				
	Sig.(2Tailed)	0.699	0.611					
Cu	Correlation	-0.010	-0.027	-0.143	1			
	Sig.(2Tailed)	0.936	0.832	0.263				
Fe	Correlation	-0.271*	0.351**	395**	0.001	1		
	Sig.(2Tailed)	0.031	0.005	0.001	0.158			
Mn	Correlation	-0.122	0.336**	0.075	0.178	0.678**	1	
	Sig.(2Tailed)	0.342	0.007	0.557	0.163	$1.04*10^{-9}$		
Zn	Correlation	-0.081	-0.010	-0.050	-0.089	-0.101	-0.096	1
	Sig.(2Tailed)	0.527	0.940	0.699	0.490	0.431	0.454	

***Correlation is Significant at the 0.05 level (2Tailed)**

**** Correlation is Significant at the 0.05 level (2Tailed)**

Possible metal-metal, metal-pH and metal-EC relationships were investigated throughout the study, using the Pearson correlation coefficient, r, $p<0.05$ and 0.01. as sowed in Table (21), This correlation supports by many authors such as Soyalk et al.,(2002); Papafilippaki et al., and (2007) ;Akoto et al.,(2008).

Significance correlation between metals may be indicate whether there is any common source of pollution (Wakida, 2008) or may be as a result of co-existence and co-precipitate with each other, based on the redox condition, on other hand most metals in the water are affected by many physico-chemical change in their environment, such as pH, Temperature, DO, COD and Redox potential (Akato et al., 2008).

VII. CONCLUSION AND RECOMMENDATION

All drinking water resources in Duhok province severely contaminated with iron therefore cannot be use for drinking purposes, while other metals (Co, Cu, Mn and Zinc) found to be low in this investigation and lie under WHO guidelines for drinking water.

Chamberkat and Zakho are the best water treatment plants for purification of raw water in the Duhok province.

All water projects must be continuously monitored as well as a proper treatment of raw water, in order to eliminate the concentration of metals before the water enters the aqueduct web, by using Granular activated carbon filtration and sand filters inoculated with heavy metal biosorbing and bioprecipitating bacteria there is a unique way for removing excess heavy metal

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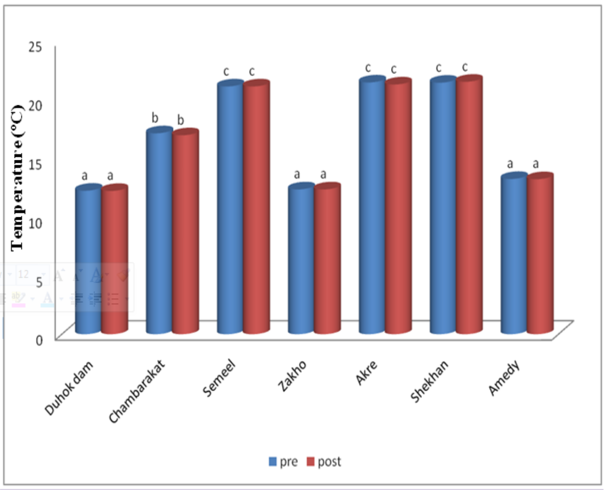

Fig. (1) Temperature (°C) of pre and post Treated Water at studied sites, different letters means significantly different at (P<0.01) level.

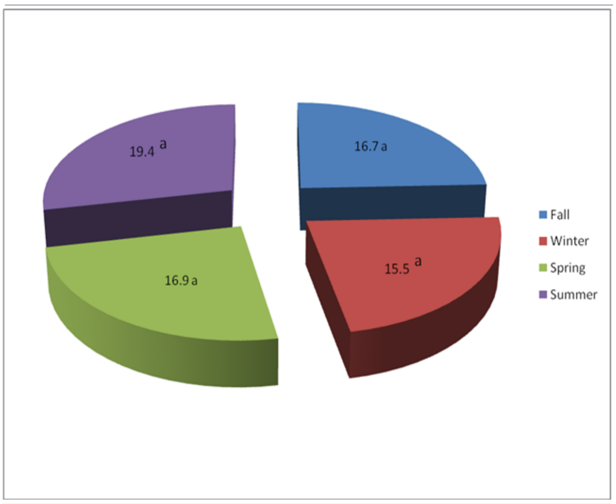

Fig.(2) Seasonal variation of temperature (°C) during studied periods, different letters means significantly different at (P<0.01) level.

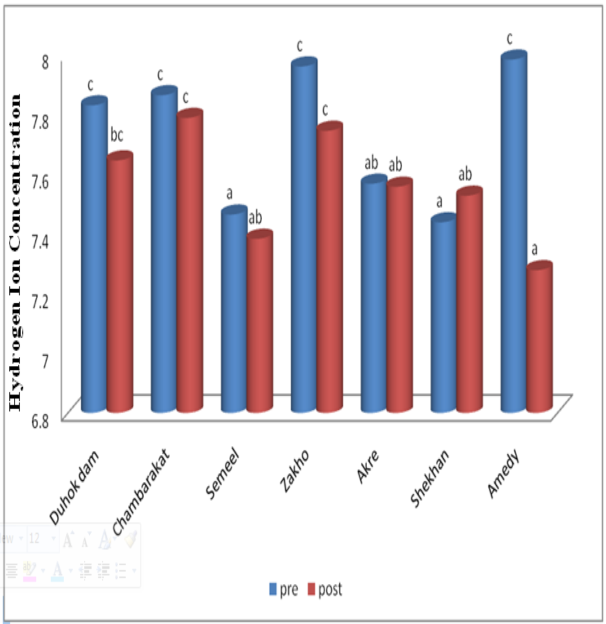

Fig.(3) pH values of pre and post Treated Water at studied sites, different letters means significantly different at (P<0.01) level.

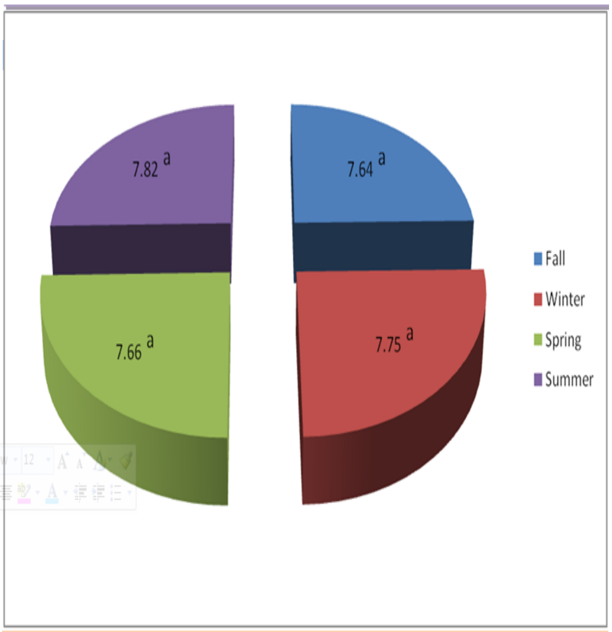

Fig.(4) Seasonal variation of pH values during studied periods, different letters means significantly different at (P<0.01) level.

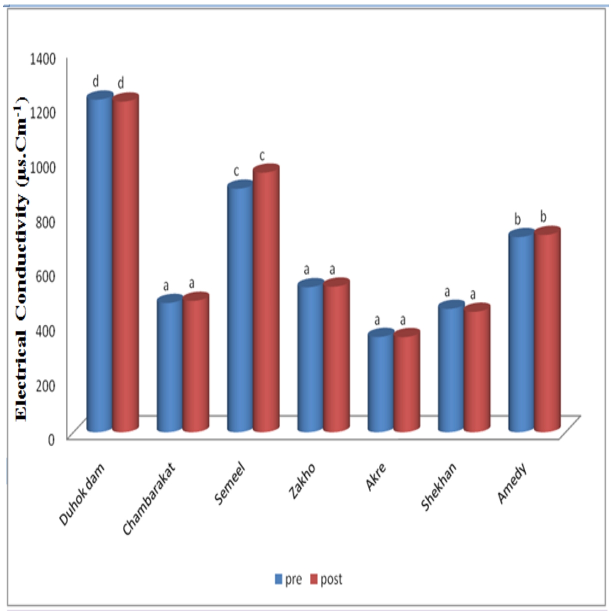

Fig.(5) Specific EC (µs.cm^{-1}) of pre and post Treated Water at studied sites, different letters means significantly different at (P<0.01) level.

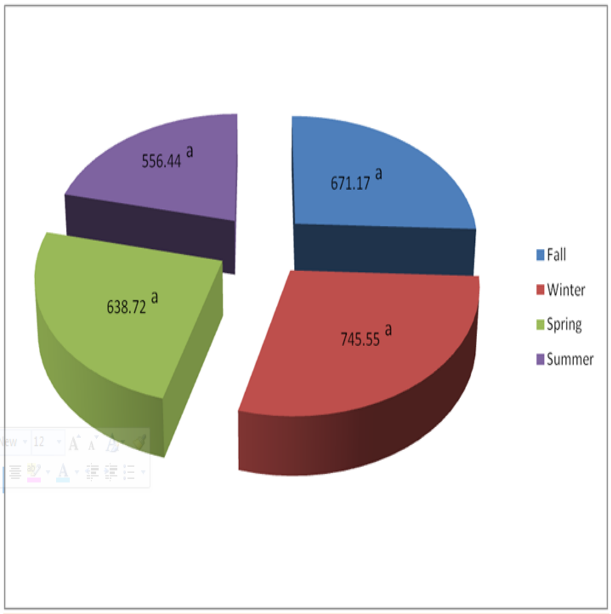

Fig.(6) Seasonal variation of Specific EC (µs.cm^{-1}) during studied periods, different letters means significantly different at (P<0.01) level.

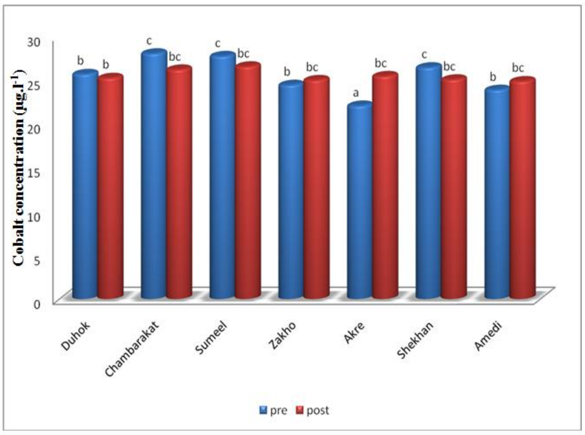

Fig.(7) Cobalt concentration (µg.l^{-1}) of pre and post Treated Water at studied site, different letters means significantly different at (P<0.01) level.

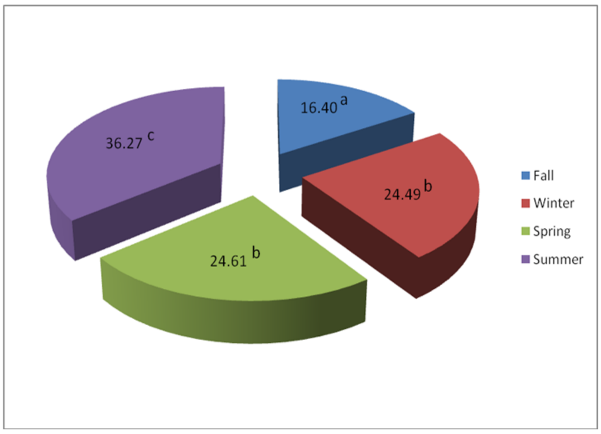

Fig.(8) Seasonal variation of Cobalt concentration (µg.l^{-1}) during studied periods, different letters means significantly different at (P<0.01) level.

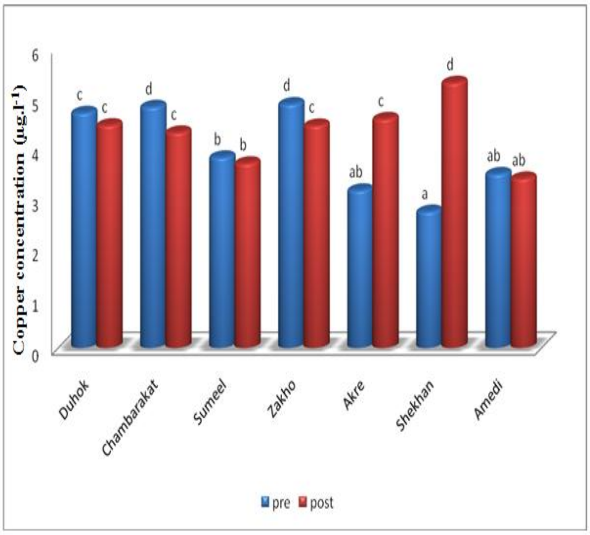

Fig.(9) Copper concentration (µg.l^{-1}) of pre and post Treated Water at studied site, different letters means significantly different at (P<0.01) level.

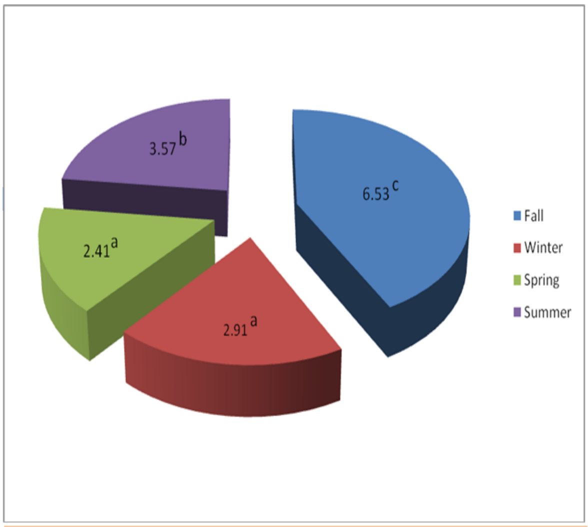

Fig.(10) Seasonal variation of Copper concentration (µg.l^{-1}) during studied periods, different letters means significantly different at (P<0.01) level.

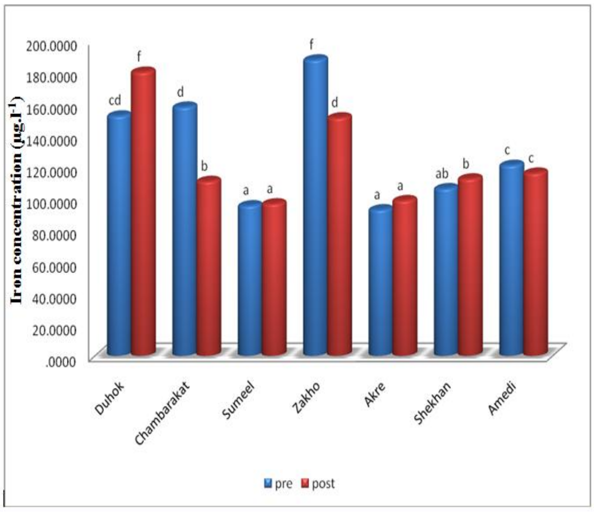

Fig.(11) Iron concentration (µg.l^{-1}) of pre and post Treated Water at studied site, different letters means significantly different at (P<0.01) level.

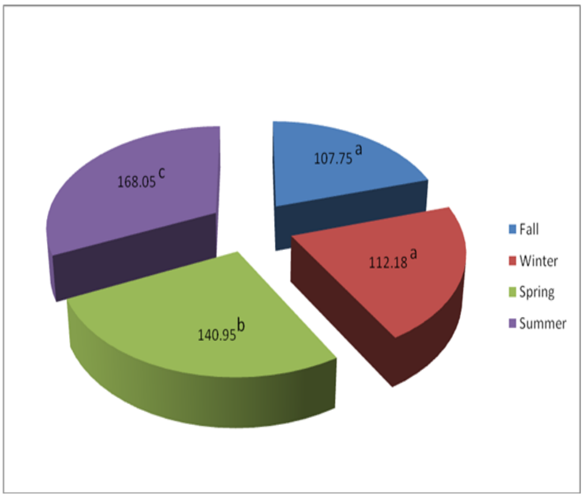

Fig.(12) Seasonal variation of Iron concentration (µg.l^{-1}) during studied periods, different letters means significantly different at (P<0.01) level.

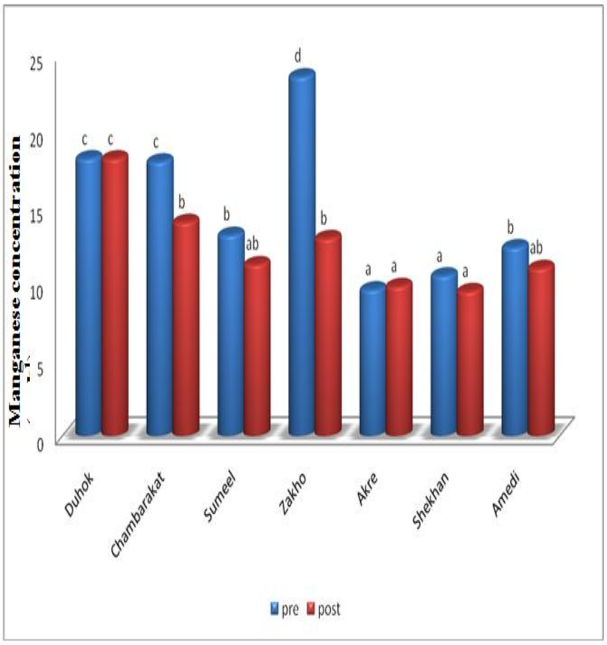

Fig.(13) Manganese concentration ($\mu g.l^{-1}$) of pre and post Treated Water at studied site, different letters means significantly different at (P<0.01) level.

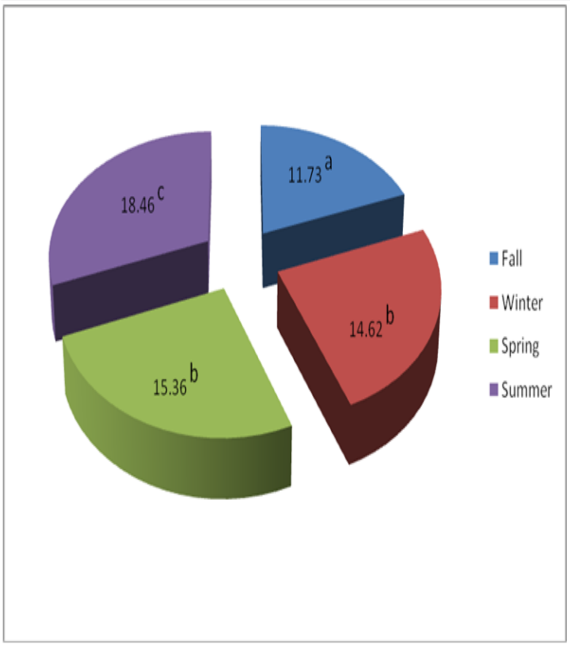

Fig.(14) Seasonal variation of Manganese concentration ($\mu g.l^{-1}$) during studied periods, different letters means significantly different at (P<0.01) level.

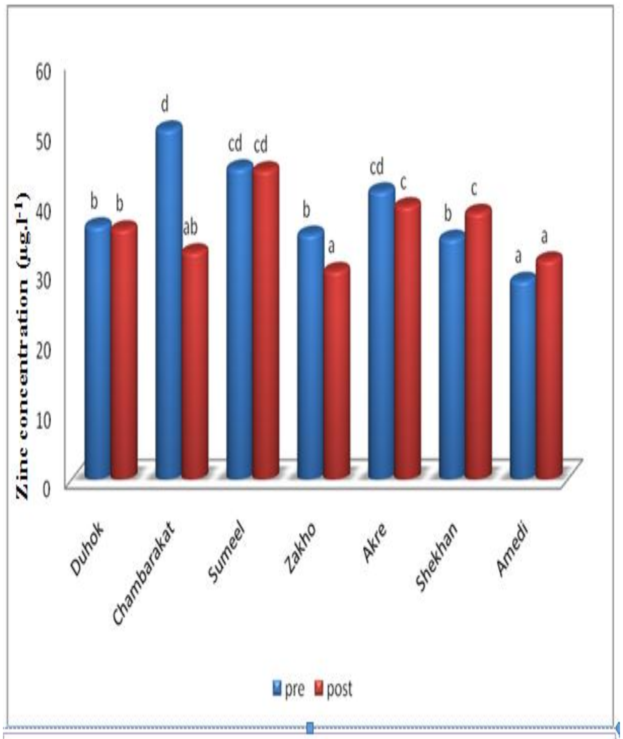

Fig.(15) Zinc concentration ($\mu g.l^{-1}$) of pre and post Treated Water at studied site, different letters means significantly different at (P<0.01) level.

Fig.(16) Seasonal variation of Zinc concentration ($\mu g.l^{-1}$) during studied periods, different letters means significantly different at (P<0.01) level.