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Distribution and assessment of heavy metals and physicochemical parameters in riverine basin

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Abstract: Water is the most precious resource to sustain the life on earth. Rapid industrialization and urban development results in inclusion of variety of pollutants into rivers. In the present study, a comparison of characteristics of water quality with respect to heavy metal (Fe, Al, Mn and Se) and their interrelationships with some physiological parameters during different seasons of year 2015 has been investigated flowing through the two geographical regions, namely Kurdistan region (Chamsaghez, Chamkhorkhoreh, Jaghatoo Rivers) and West Azarbaijan Region (Sarough River) , in Zarrineh river basin one of the most important and longest rivers in the Lake Urmia basin in Iran which branches from the mountains of Chehelcheshmeh at the being of Kurdistan province. All observed values of Se in spring, observation of Al in 14 stations, observation of Fe in 11 stations and observation of Mn in 9 stations exceed WHO standard for drinking water. However, all of the observation of Se in winter are found with the standard limit. In the present study, the metals Fe, Al and Mn show negative correlation with pH and also the Mn and Se, show negative correlation with DO. Metals Al and Fe found to have strong positive correlation with each other. Distribution of Al and Se in river Chamsaghez and Al, Se and Mn in river Sarough systems, Al in Jaghatoo river and Fe in Chamkhorkhoreh river during entire study period shows significant difference at 95 % level of significance. Spatially all the metals in different river systems do not show any significant spatial difference in their distribution among different river systems.

Key words: Pollution, Dissolved heavy metals, spatial distribution, physicochemical parameters

1. INTRODUCTION

River water is often used for domestic needs and also supplied as potable water by municipal corporations which contamination of drinking water resources with hazardous chemicals like nitrate, nitrite, ammonium and heavy metals has become an increasing concern in developing countries. Regular monitoring of drinking water at the source of supply and at consumer end is of prime importance for generating the database on overall feature and chemical characteristics of water that can help minimize the health hazards to a large extent (Shah and Singh 2016). Physicochemical parameters play an important role to determine the water quality (Kouamé et al. 2014). The physical and chemical characteristics of water are important parameters as they may directly or indirectly affect its quality(Nevoh et al. 2015). During the last decades, there has been an increasing demand for monitoring water quality of many rivers by regular measurements of various water quality parameters (Khalilzadeh Poshtegal et al. 2016a, 2011). Quality of water is generally refers to component of water, which is to be present at the optimum level suitable for growth of aquatic plants and animals. Various factors like water temperature, turbidity, nutrient, hardness, alkalinity, dissolved oxygen (DO) play an important role for the growth of plants and animals in the water. The contamination of water with heavy metals is another major environmental problem. Anthropogenic activities continuously increase the amount of heavy metals in the environment, especially in aquatic ecosystem. Community development and growth of industrial and agricultural activities have led to increase in aquatic contamination such as heavy metals and nutrients (Shoaei et al. 2014). Pollution of heavy metals in aquatic system is growing at an alarming rate and has become an important worldwide problem (Malik et al. 2010; Shanur et al. 2015). Heavy metals have an adverse effect on riverine ecosystem that point sources of heavy metals in the water and sediments should be closely monitored (Mir Mohammad et al. 2016). Heavy metal and agricultural toxics in Garasou river for water quality assessment was investigated in Iran to show the distribution of pollution in the river basin (Fatehi et al. 2010). Transport of heavy metals through the soils may lead to the groundwater contamination and their accumulation in soils and crops (Khalilzadeh Poshtegal et al. 2016b). The use of wastewater in agricultural lands enriched soils with heavy metals to concentrations that may pose potential environmental and health risks in the long-term (Islam et al. 2014; Mirbagheri et al. 2014; Mirbagheri 2008; Yi et al. 2011). Assessment of the spatial and temporal variability of the heavy metal concentration can help determine the sources of these pollutants, and then provide better water quality management in the upper basins.

Table 1. Sampling locations and site characteristics

Sampling point	Location	Altitude (m)	Geographical position
CH-1	Chamsaqez after the Tamugheh village	1526	$N: 36^o12'03'', E: 46^o07'14''$
CH -2	Ghamsaghez, before Kileshin village	1717	$N: 36^o05'52'', E: 46^o00'20''$
CH -3	Ghamsaghez, before the Veis dam workplace	1540	$N: 36^o11'09.3'', E: 46^o06'34.1''$
CH -4	Ghamsaghez before entering the Saqez	1475	$N: 36^o13'35'', E: 46^o15'52.7''$
CH -5	Ghamsaghez exiting the Saqez	1458	$N: 36^o15'18.3'', E: 46^o18'10''$
CH -6	Ghamsaghez entering the Shahid Kazemi dam	1441	$N: 36^o18'25.05'', E: 46^o23'05.8''$
J -1	Jaghatooo after the Bastam village	1730	$N: 35^o48'02'', E: 46^o24'20''$
J -2	Jaghatooo , Talejar village	1540	$N: 36^o00'53.3'', E: 46^o18'38.1''$
J -3	Jaghatooo , Polgeshlagh village	1475	$N: 36^o05'59.7'', E: 46^o20'50.5''$
J -4	Jaghatooo entering the Bookan dam	1435	$N: 36^o12'31.5'', E: 46^o25'53.4''$
Kh-1	Chamkhorkhoreh, Mahidar Olia village	1600	$N: 35^o59'27.8'', E: 46^o28''38.5''$
Kh-2	Chamkhorkhoreh, Gataloo village	1530	$N: 36^o05'22.1'', E: 46^o29'47.6''$
Kh-3	Chamkhorkhoreh entering the Bookan Dam	1438	$N: 36^o17'28'', E: 46^o35'48.7''$
Sa-1	Entering Tekab city	1834	$N: 36^o22'24.7'', E: 47^o08'00.3''$
Sa-2	Downstream of Tekab city	1757	$N: 36^o26'18.4'', E: 47^o05'25.2''$
Sa-3	Madanchai, upstream of Zarnikh mine	2260	$N: 36^o43'21.3'', E: 47^o07'27.8''$
Sa-4	Aqh-Darreh, upstream of Pooyazarkan factory	1867	$N: 36^o36'53.8, E: 47^o05'29.6''$
Sa-5	Balacholeh, Shirmard village	1837	$N: 36^o35'54.9'', E: 47^o05'32.7''$
Sa-6	Balacholeh, Tekab Road	1716	$N: 36^o28'13.3'', E: 47^o01'38.1''$
Sa-7	Gugerdchi hydrometric station (right branch Alasaggal)	1725	$N: 36^o23'59.7, E: 47^o06'13.6''$
Sa-8	Sarough river before entering Bukan Dam	1442	$N: 36^o24'00.9'', E: 46^o39'18.7''$

2. MATERIALS AND METHODS

2.1 Study area and site description

Zarrineh river is one of the most important and longest rivers of the basin in the Lake Urmia which branches from the mountains of Chehelcheshmeh at the being of Kurdistan. The main branches of the river are as Chamghoreh, Chamkhorkhoreh and Sarough River. Zarrineh river basin area from its branches to the entrance of the Urmia Lake is about 11780 km^2 which is located between the longitudes 45º 45´ to 45º 15´ and the latitudes 35º 45´ to 37º 20´. All the rivers of the study area are grouped into four sectors: (a) River Chamsaghez System having 6 sampling/monitoring stations, (b) river Chamkhorkhoreh system having 3 monitoring/sampling stations (c) river Jaghatooo system having 4 sampling/monitoring stations and (d) Sarough river system having 8 sampling/monitoring stations which making a total of 21 sites. Sampling locations and site characteristics are given in Table 1 and Fig. 1. The locations are selected on upstream of Bukan Dam. Samples were collected during all different seasons of 2015.

2.1.1 Sample collection protection and analysis

1.5 liter water bottles for water sampling were used (samples later covered by a sheet of aluminum in disposable plastic containers were placed with a tight lid). At each station according to the calculated flow cross-section of the river and water in multi-axis average speed was estimated and evaluated. Water samples, if necessary, by special stabilizers (such as sulfuric acid and nitric acid) in fixed or hand-held and glaciers in sterile containers at temperatures below 4 °C (without freezing), maintenance and within 4 to 6 hours were sent to the laboratory. Heavy metals samples also stabilized in sterile containers and refrigerate within 2 days of manually maintained and were sent to the laboratory.

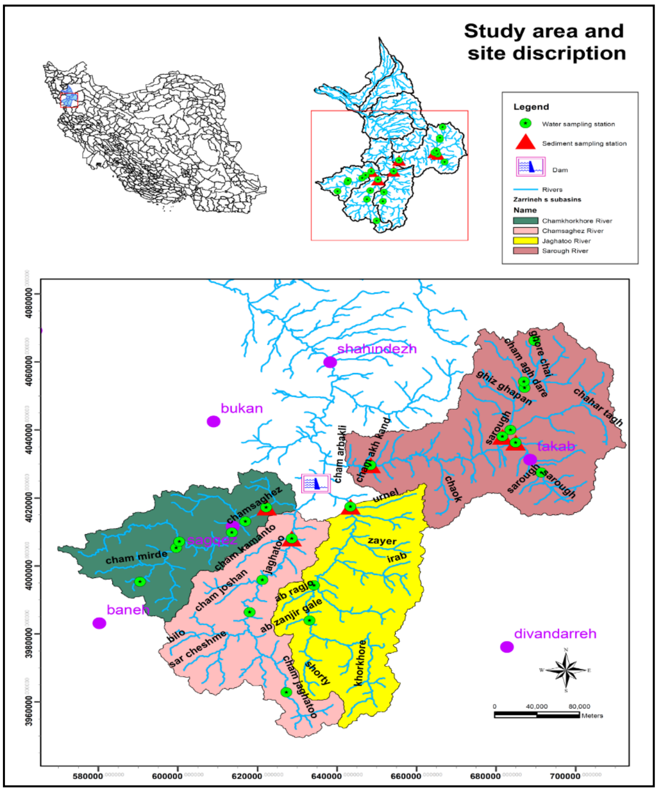

Figure 1. Site location map

2.2.2 Sample transfer device

A number of water samples after the packaged ice in glaciers were transferred to the laboratory, with the assurance of receipt by the director of the lab. Water samples after fixation of heavy metals and minerals were delivered to the laboratory to perform the needed analysis. Water samples were preserved at pH < 2 in separate 300-ml plastic bottle by adding concentrated HNO_3 for heavy metal analysis.

Table 2. Mean, standard deviation, range of the analyzed data for heavy metals in different seasons in two geographical regions of the study area

Statistics	Al (mg/l)	Fe (mg/l)	Mn (mg/l)	Se (mg/l)
Kurdistan region (Chamsaghez, Chamkhorkhoreh, Jaghatoo Rivers)				
Mean	0.31	0.39	0.07	0.05
SD	0.34	0.25	0.06	0.04
Min	0.01	0.12	0.02	0.008
Max	1.18	1.28	0.23	0.10
West Azarbaijan Region (Sarough River)				
Mean	0.08	0.18	0.14	0.05
SD	0.10	0.10	0.17	0.04
Min	0.01	0.01	0.02	0.01
Max	0.30	0.41	0.60	0.10
WHO Standard 2008 for drinking water	0.1	0.3	0.4	0.01
Institute of Standards and Industrial Research of Iran, ISIRI,1053, 5th.Revision	0.1	0.3	0.1	0.01

Due to the primary analyzes between all the 14 measured metals, only four heavy metals were analyzed and mention in the research as their role was important. Observed values for various parameters were statically analyzed by using correlation study on MS Excel and SPSS software. All instruments used for analysis are calibrated with standard solutions to check their precision and accuracy. A blank sample had been run for each parameter, and necessary corrections have been made to achieve accurate results. At least three readings for each parameter had taken for getting precise information**.**

3. RESULTS AND DISCUSSION

Average concentration, range, and standard deviation along with values of different standards are given in Table 2. Temporal and spatial variations of studied heavy metals, namely Al, Fe, Mn and Se are presented at Figs. 2, 3, 4 and 5, respectively. However, mean concentration and standard deviation of Al, Fe, Mn and Se in the Chamsaghez, Chamkhorkhoreh, Jaghatoo and sarough rivers systems in winter and spring are presented in Figs. 6, 7, 8, and 9, respectively.

Mean value of (a) Al is found 0.17, 0.30, 0.62 and 0.08 mg/l; (b) Fe is found 0.33, 0.36, 0.53 and 0.18 mg/l; (c) Mn is found 0.06, 0.08, 0.10 and 0.14 mg/l; (d) Se is found 0.05 mg/l in Chamsaghez, Jaghatoo, Chamkhorkhoreh, and Sarough rivers respectively. However, concentration of Al and Fe varied spatially with higher levels in Jaghatoo and Chamkhorkhoreh river system and the concentration of Mn varied spatially with higher level in Sarough river system. Al is detected in 42 samples with mean value of 0.31 and 0.08 mg/l in Kurdistan and West Azarbaijan region respectively. The highest value of 1.18 mg/l of observed in river Chamkhorkhoreh of Kurdistan region. Iron is detected in all samples with mean value of 0.39 and 0.18 mg/l, respectively, in Kurdistan and West Azarbaijan regions, respectively. The highest value of 1.28 mg/l of observed in river Chamkhorkhoreh of Kurdistan region. Manganese is detected in 42 samples and the mean values are 0.07 and 0.14 mg/l in Kurdistan and West Azarbaijan regions, respectively. The highest value of 0.60 mg/l of observed in river Sarough of West Azarbaijan region. Selenium is detected in all samples and the mean value is 0.05 mg/l for both Kurdistan and West Azarbaijan regions. The highest value of 0.10 mg/l observed in mostly all stations in four rivers in spring. Selenium did not show much variation in winter in all stations and regions of study area. 14 observation of the Al, 11 observations of Fe, 9 observations of Mn and all observed values of Selenium only in spring were exceeded with the WHO standard for drinking water (WHO 2009).

Two observations of Mn in Sarough river in West Azarbaijan regions, found to be exceeded with the Institute of Standards and Industrial Research of Iran ISIRI, 1053; 5th Revision. As compared with the standards for fresh water as prescribed under Environment Protection Rules some rivers are found not suitable for drinking; Locations where Fe exceeded with 0.5 mg/l , Al exceeded with 0.1 mg/l in Chamkhorkhoreh, Jaghatoo rivers in Kurdistan region and for Mn which exceeded with 0.1 mg/l in Sarough River in West Azarbaijan Region, are also not suitable for drinking.

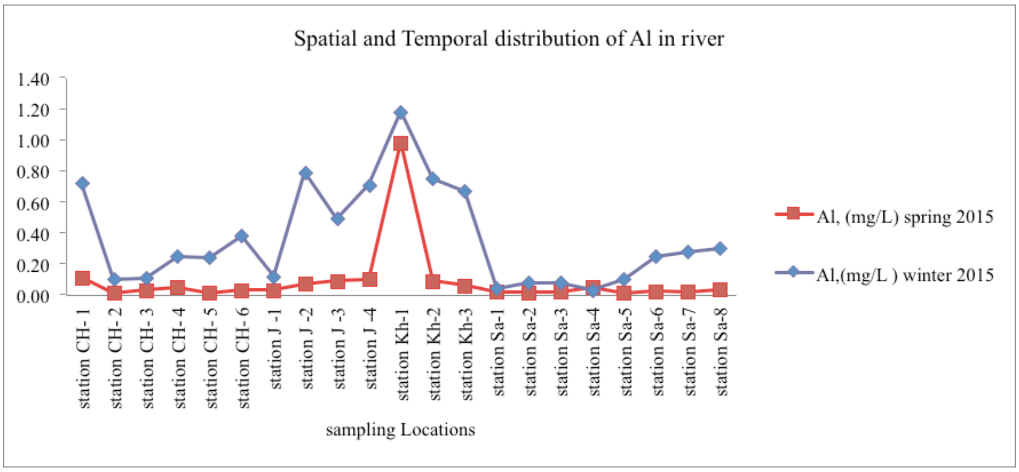

Figure 2. Temporal and spatial distribution of Al

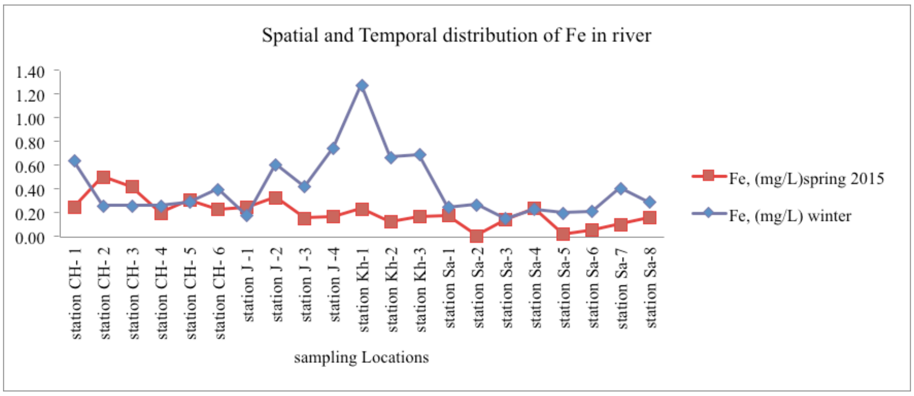

Figure 3. Temporal and spatial distribution of Fe

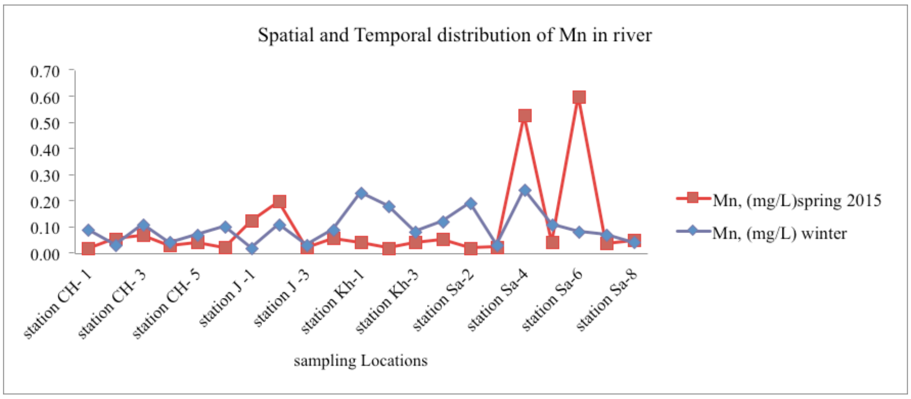

Figure 4. Temporal and spatial distribution of Mn

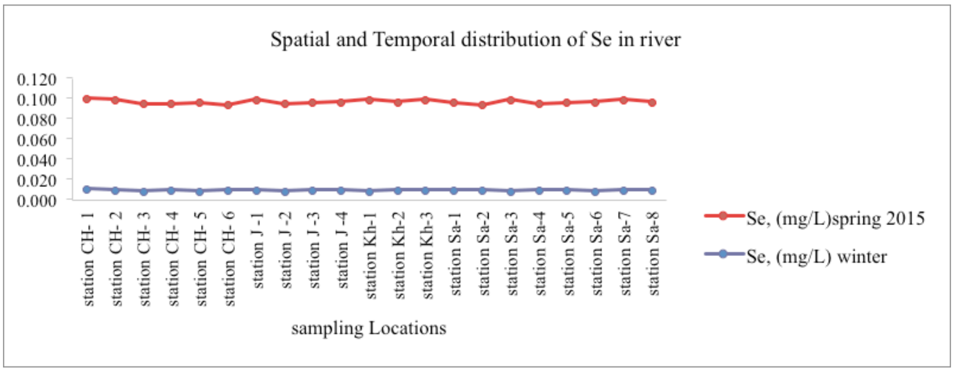

Figure 5. Temporal and spatial distribution of Se

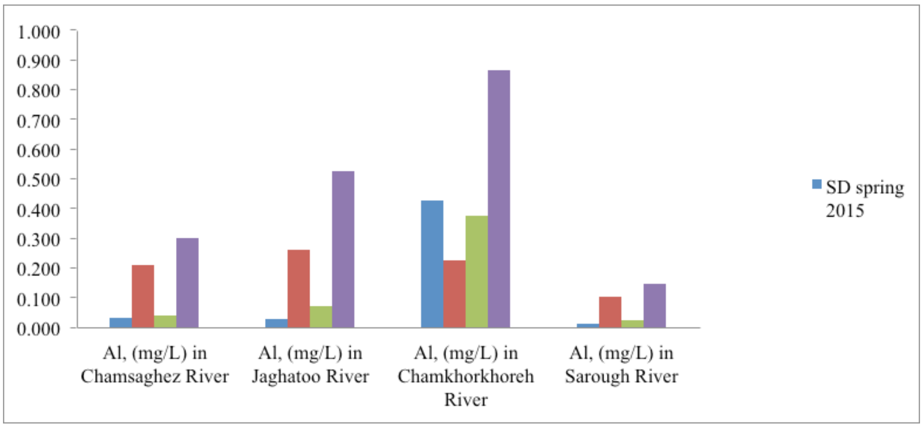

Figure 6. Mean and standard deviation of Al

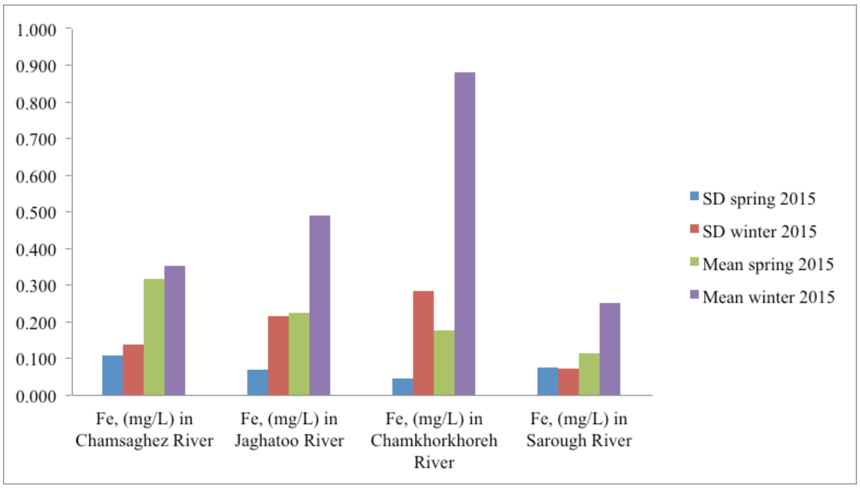

Figure 7. Mean and standard deviation of Fe

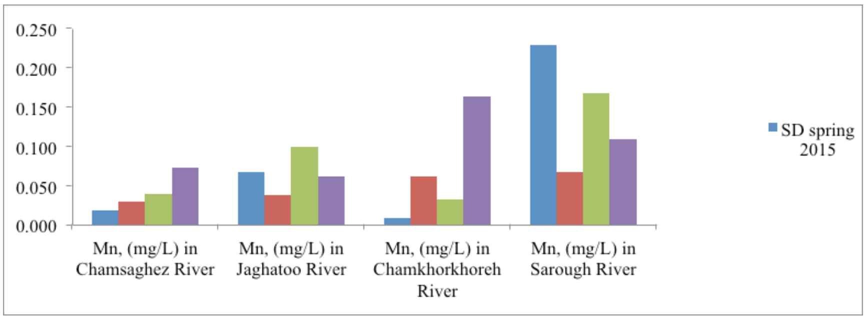

Figure 8. Mean and standard deviation of Mn

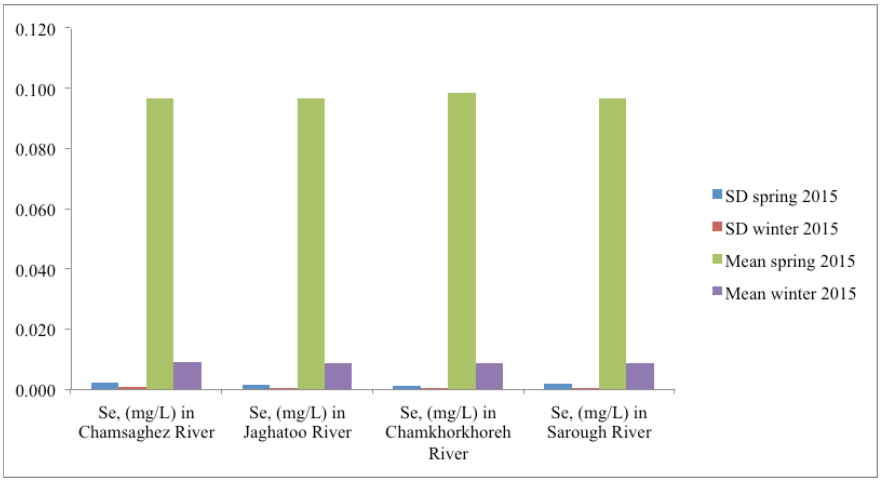

Figure 9. Mean and standard deviation of Se

Average concentration of dissolved oxygen, pH, and electrical conductivity and their correlation are presented in Tables 3 and 4, respectively. In the present study, the metals Fe, Al and Mn show negative correlation with pH and also the Mn and Se, show negative correlation with DO which indicates that the more organic load in the water bodies, the more will be the concentration of heavy metals because organic matter provides surface for lechation of metals in acidic conditions; While in the other hand Se shows positive correlation with pH; Al and Fe also show positive correlation with DO. Metals Al and Fe showed negative correlation with electrical conductivity that Mn and Se show positive correlation with electrical conductivity which may be the result of rock–bed interaction with flowing water (Kansal et al. 2013). Metals Al and Fe found to have strong positive correlation with each other in the present study.

Table 3. Mean concentration and standard deviation DO (milligrams per liter), pH, PO_4 and EC (micromhos per centimeter)

Rivers	pH		DO		EC		PO_4	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Chamsaghez	7.38	0.63	7.66	2.05	551.54	278.37	1.01	1.68
Jaghatoo	7.41	0.56	8.81	1.71	412.69	191.54	0.45	0.76
Chamkhorkhoreh	7.29	0.545	8.952	1.269	377	136.2	0.26	0.178
Sarough	7.34	0.53	8.31	2.03	1058.44	612.64	0.21	0.27

Table 4. Correlation of physicochemical parameters with heavy metals

	Fe	Mn	Se	pH	DO	EC	PO_4
Al	0.797**	0.029	-0.462**	-0.410**	0.443**	-0.405**	-0.185
Fe		0.110	-0.459**	-0.406**	0.375*	-0.317*	0.012
Mn			0.002	-0.093	-0.085	0.007	-0.037
Se				0.680**	-0.770**	0.225	0.351*
pH					-0.361*	0.348*	0.250
DO						-0.134	-0.367*
EC							-0.002

**Correlation is significant at the 0.05 level, **Correlation is significant at the 0.01 level*

Data are also analyzed statistically for analysis of variance (ANOVA) on SPSS. ANOVA is a measure to test the data statistically for its significant difference with the compared values at different levels of significance. In its simplest form, ANOVA provides a statistical test of whether or not the means of several groups are all equal and therefore generalize t test to more than two groups. In the present study, ANOVA is used to find the significant variation of data while analyzing in different seasons and at different sites, i.e., temporal and spatial variation; such data are presented in Table 5, 6 and 7, respectively.

Table 5. T test for heavy metals in different river systems

Parameter	Temporal variation							
	Chamsaghez river		Jaghatoo river		Chamkhorkhoreh river		Sarough river	
	t	Sig.	t	Sig.	t	Sig.	t	Sig.
Al	5.818	0.037	6.621	0.042	2.780	0.171	44.025	0.000
Fe	0.172	0.688	4.749	0.072	10.971	0.030	0.283	0.603
Mn	1.875	0.201	1.429	0.277	5.362	0.082	9.476	0.008
Se	9.657	0.011	3.419	0.114	3.200	0.148	7.860	0.014

Table 6. Spatial ANOVA for heavy metals in different river systems

Parameter	Spatial variation							
	Chamsaghez river		Jaghatoo river		Chamkhorkhoreh river		Sarough river	
	F	Sig.	F	Sig.	F	Sig.	F	Sig.
Al	0.693	0.648	0.396	0.764	2.241	0.254	0.470	0.832
Fe	0.480	0.781	0.543	0.678	0.282	0.772	0.410	0.871
Mn	0.562	0.728	2.449	0.204	0.267	0.782	1.600	0.262
Se	0.001	1.000	0.001	1.000	0.000	1.000	0.000	1.000

Table 7. Spatial ANOVA for heavy metals in river systems

Parameter	Spatial variation	
	All river system	
	F	Sig.
Al	7.182	0.001
Fe	4.255	0.011
Mn	1.158	0.339
Se	0.001	1.000

From the ANOVA, it is found that distribution of Al and Se in river Chamsaghez and Al, Se and Mn in river Sarough systems, Alminium in Jaghatoo river and Fe in Chamkhorkhoreh river during entire study period shows significant difference at 95 % level of significance. Spatially all the metals in different river systems do not show any significant spatial difference in their distribution among different river systems. It can conclude that the region of three Chamsaghez, Chamkhorkhoreh and Jaghatoo Rivers are located in Kurdistan province and due to few industrial activities along these river, concentration of pollutants in this river system is found less as compared to other river systems in the basin. Comparing the ANOVA test for all the rivers system, it can be also, concluded that among all the metals only the Al and Fe show significant spatial difference among all the river systems. Scope of further research Present study is limited to quarterly analysis of water quality of major water bodies. It may extend up to monthly and even daily monitoring. Apart from that, only four heavy metals have been analysed among almost the 14 metals which be available and cause problem in water quality. Future work in this area may be expanded in analysis of more trace metals, covering more monitoring points in another water bodies. Ground water deterioration cannot be denied due to discharge of industrial effluent and direct injection of effluent into ground water strata. Further scope of work may be elaborated to monitoring of groundwater quality in the Zarrineh river basin.

REFERENCES

Fatehi E, Monavari SM, Hasani AH, Karbasi AR, Mirbagheri SA (2010) Heavy Metal and Agricultural Toxics Monitoring in Garasou River in Iran for Water Quality Assessment. Asian J Chem 22:2991-3000

Islam M, Ahmed M, Habibullah-Al-Mamun M, Islam K, Ibrahim M, Masunaga S (2014) Arsenic and lead in foods: a potential threat to humanhealth in Bangladesh. Food Addit Contam Part A 31:1982–1992

Kansal A, Siddiqui NA, Gautam A (2013) Assessment of heavy metals and their interrelationships with some physicochemical parameters in eco-efficient rivers of Himalayan region. Environ Monit Assess 185:2553–2563

Khalilzadeh Poshtegal M, Jafari A, Noury M (2016a) River Quality and Quantity Modeling Using Neural Wavelet Network. Technical Journal of Engineering and Applied Sciences

Khalilzadeh Poshtegal M, noury m, mirbagheri sa, Nikoo s (2016b) Investigation of heavy metal and susepended sediment in river. Paper presented at the 8th National Conference on Environmental Engineering, Iran

Khalilzadeh Poshtegal M (2011) Investigation the relationship between the land use and the rainfall, run off and sediment by GIS and RS (case study: Shaharchai River, Orumieh, Iran). In: Proceedings of the International Conference on Environmental Science and Technology, 2011, University of the Aegean, Rhodes Island (Greece)

Kouamé MK, Safiatou C, Boua CA, Essetchi PK (2014) Survey of heavy metals concentrations in water and sediments of the estuary bietri bay, Ebrie Lagoon, Cote d'Ivoire. International Journal of Research In Earth & Environmental Sciences 1

Malik N, Biswas A, Qureshi T, Borana K, Virha R (2010) Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal Environ Monit Assess 160:267-267

Mir Mohammad A, Mohammad Lokman A, Islam M, Rahman M (2016) Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. Environmental Nanotechnology, Monitoring & Management 5:27–35

Mirbagheri S, Biglarijoo N, Keyhanezghad M (2014) Pilot plant studies for the removal of heavy metals from industrial wastewater using adsorbents. Turkish J Eng Env Sci 38:159-166

Nevoh GO, Akhionbare SMO, Uzoma HC (2015) Water Quality Aspects of River Okpoka in Relation to Watershed Activities Resources and Environment 5:124-133 doi:10.5923/j.re.20150504.03

S.A.Mirbagheri AB, and A. H. Javid (2008) Heavy Metals Transport in the Soil Profiles under the Application of Sludge and Wastewater. International Journal of Civil, Environmental, Structural, Construction and Architectural Engineering 2

Shah AB, Singh RP (2016) Monitoring of hazardous inorganic pollutants and heavy metals in potable water at the source of supply and consumers end of a tropical urban municipality. Int J Environ Res:149-158

Shanur JH, Mohosena BT, Md.Istiaque Haidar, Tayfa A, AKM SAR (2015) Physico-chemical characteristics and accumulation of heavy metals in water and sediments of the river Dakatia, Bangladesh. International Journal of Fisheries and Aquatic Studies 2:300-304

Shoaei SM, Mirbagheri SA, Zamani A, Bazargan J (2014) Dissolved Heavy Metals in the Reservoir of Shahid Rajaei Dam, Sari, Iran. Int J Environ Res 8:997-1004

WHO (2009) Global health risks: mortality and burden of disease attributable to selected major risks. World Health Organization

Yi Y, Yang Z, Zhang S (2011) Ecological risk assessment of heavy metals insediment and human health risk assessment of heavy metals in fishes in themiddle and lower reaches of the Yangtze river basin. Environ Pollut 159:2575–2585