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Pollution status evaluation of some heavy metals along some surface water sources by multivariate data analysis at Sulaimani governorate

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Abstract

In Sulaimani Governorate, Kurdistan Region, Iraq (KRI), the total concentration of eleven (11) transitional heavy metals were examined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) technique in water samples at 8 sites (S1 to S8) along Qalyasan Stream and Tanjaro River; also S9 was included in Darbandikhan Lake, S9 is a site located after the confluence of polluted Tanjaro River with Darbandikhan Lake water bodies by about 9 km. Water samples were taken on five dates (D1, D2, D3, D4, and D5) from March 2015 till July 2015 at each site of the total nine (9) selected sites along the water sources. Because those water sources are used as a direct sink for the untreated domestic and industrial wastewater effluents and they are in the meanwhile used as a main sources for multi human uses such as; drinking, irrigation purpose and industrial activities. Therefore, the objectives of this study were; evaluation the pollution status of the 11 transitional heavy metals by multivariate data analysis, the study also aimed to define the most polluted sites along the water sources during the studied period.

In the present study the results showed that the overall mean concentrations of the studied transitional metals illustrated the following abundance decreasing trend; Fe (6874.30) > Mn (378.98) > Cr (114.44) > Ni (77.63) > Zn (66.71) > V (21.10) > Cu (19.47) µg L^{-1}. Moreover, the concentrations were generally exceeded the criteria of WHO drinking water quality in some observations for those metals that have a defined guideline values by WHO. Additionally, S4 and S5 in D5 of sampling date had particularly the maximum levels for the upper and lower limit concentrations of the studied transitional metals. Consequently, S4 and S5 could be regarded as hot-spot sites or contaminated sites.

PCA results indicated a total variance of 82.34 % and 11.61 % among the studied transitional metals and sites respectively. On the other hand, the dendrogram plot classified the nine sites of the studied surface water into three major groups at a significant dissimilarity percent of about 48%. Furthermore, S1 and S9 revealed the highest similarity, in contrast to that, S1 showed the highest dissimilarity with S5.

Introduction

Surface water pollution due to the disposal of different heavy metals from; rapid population growth, accelerated industrialization processes and agricultural activities continues to be a serious problem today.

Natural phenomena such as weathering, volcanic eruptions, atmospheric deposition and soil erosion of metal ions have also been referred to play a significant contribution in surface water pollution by heavy metals [1 and 2].

Heavy metals are any chemical elements having an atomic weight greater than sodium (23) and forms soaps on reaction with fatty acids (e.g. mercury, chromium, cadmium, arsenic and lead), [3]. Whilst, [4] has defined the term of "heavy metals" as any metallic element that has a relatively high density and is toxic or poisonous even at low concentration. Heavy metals cannot be degraded or destroyed and to a small extent they enter our bodies via both ingestion through food and drink or inhalation of dust and fume through air [5]. Some transitional heavy metals have bio-importance, but the toxicity effects of many of them in biosystems are of great concern [6]. Hence, it is of prime concern to know the sources, concentrations, chemical conversions and modes of deposition of transitional heavy metals in surface water, in order to avoid their adverse toxicity effects to organisms and also to assess the occurrence and their level of contamination.

Discharging of high amounts of heavy metals into water bodies leads to several environmental and health impacts, because heavy metals are one of the most persistent pollutants in wastewater. Also, mixing of heavy metals with water bodies causes some negative impacts to aquatic ecosystems such as; death of aquatic life, algal blooms, habitat destruction and other short and long term toxicity [7]. Generally, the potential detrimental effects of heavy metal on the quality of receiving water bodies may depend on the source, volume and composition of the effluent that is discharged into the water bodies. [8 and 9].

In Sulaimani Governorate, Qalyasan stream with other small stream flow into Tanjaro River, this river then flows by/through other regions of the Governorate and combine with likewise rivers or tributes to end up finally into Darbandikhan Lake. Although, those sources are main water sources for different human uses and irrigation purposes along the entire paths of the sources. But unfortunately, large numbers of wastewater effluent and sewage outlets which may contain different transitional heavy metals are discharged directly into those sources of surface water without any pretreatment. The effluent discharge of wastewater and sewage are from different sources and activities (municipals, hospitals, industrial, academic centers, oil processing plants and agricultural) of Sulaimani City and the other area in the region. Also [10], have referred that many factors causes environmental pollution in and around Sulaimani city; the factors including untreated wastewater, contaminated agricultural fields, untreated solid waste, industrial waste and contamination of Tanjaro River and Darbandikhan Lake from these sources of pollution.

Since we recognize that a significant amount of the anthropogenic release of heavy metals ends up finally in wastewater [11]. Therefore, the objectives of this study were to evaluate the status and contamination level of 11 transitional heavy metals, namely; V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn and Cd by multivariate data analysis at different sites along the paths of Qalyasan Stream and Tanjaro River water sources and during some different season. Moreover, the study also aimed to define the most polluted sites by the selected transitional heavy metals.

Materials and Methods

1-Description of Sampling Sites

The sampling sites of; S1, S2, S3, S4, S5, S6, S7, S8 and S9 were selected along the water sources to provide a representative samples, the sites were situated in a geographical area between 35°34'58"- 35°13'07" N northern latitude and 45°22'41" - 45°51'47" E eastern longitude of Sulaimani governorate. As it is shown

Table (1) and Figure (1), the GPS (Global Position System) coordinates (Latitudes and Longitudes) were defined at each sampling site. The overall distance between the sampling sites of S1 to S9 was about 75 km and the elevation range was between 467 -752 m above sea level.

Table 1: GPS coordinates and sites description for the surface water sampling sites

No.	Sites Description	Symbol	GPS Coordination	
			Latitude	Longitude
1	Qalyasan stream-Near to the deconstructed cement factory at Sarchnar	S1	35° 34' 58"N	45° 22' 41"E
2	Qalyasan stream- Next to Awabara bridge	S2	35° 33' 17"N	45° 22' 15"E
3	Qalyasan stream- Next to Kani-Goma bridge	S3	35° 31' 33"N	45° 22' 22"E
4	Qalyasan stream-Near Kurd city community apartments	S4	35° 29' 55"N	45° 23' 14"E
5	Tanjaro River- Next to Tanjero bridge	S5	35° 28' 44"N	45° 25' 36"E
6	Tanjaro River- South west Arbat area- Near to Damarkan factory	S6	35° 26' 07"N	45° 29' 56"E
7	Tanjaro River- Next to Qaragol bridge	S7	35° 21' 20"N	45° 37' 36"E
8	Tanjaro River –Next to Tapekaram bridge	S8	35° 20' 14"N	45° 45' 05"E
9	Darbandekhan reservoir - Next to old Pir-Mohamad bridge	S9	35° 13' 07"N	45° 51' 47"E

The study area included the surface water sources of Qalyasan Stream, Tanjaro River and also a site (S9) in Darbandikhan Lake which located at about 9 km after the confluence site of meeting polluted Tanjaro River with the Lake water bodies.

Qalyasan stream flow into Tanjaro River and it is a watershed drains stream in Sulaimani city. The stream is fed by the following sources; melting snow and rainwater running off for the surrounding areas during the wet season, Chaq-Chaq stream, Sarchnar spring and untreated wastewater effluent and municipal sewage outlets of; Sarchnar area, industrial area and Sulaimani oil refining foundation [12 and 13].

Over the past three decades, Qalyasan stream became an ephemeral stream because the water sources of Chaq-Chaq stream disappears entirely during summer season and the stream's load became untreated wastewater effluents and municipal sewage.

Tanjaro River is a permanent river flow into Darbandikhan Lake and it drains the area’s land around the river and forming by combining two streams; Qalyasan and Kani-Ban at a confluence. In addition to those two streams, many wastewater effluent and municipal sewage outlets of the areas; Industrial area, Albisaka, Qalawa, Wluba and Shekh-Abbas and Bakrajo boxes are discharged directly to Tanjaro River without any pretreatment. As it is shown in Figure (1), before discharging Tanjaro River into Darbandikhan Lake, it combines with some other small tributaries, such as Kane Shaswaer and Bestansur tributaries [12 and 13].

Darbandikhan Lake is located at about 60 km southeast of Sulaimani City and 230 km northeast of Baghdad. It is situated between 35°06′N north latitude and 45°41' E east longitude, with the altitude of 485 to 511 meters above the sea’s level. The surface area of the lake is about 114 to 121km^2 with a maximum depth of 75 m and the lake capacity is about 3 million m^3. Darbandikhan Lake is fed by two rivers, Tanjero River in the north and Sirwan River in the east, and surrounded by the mountains (Bashari, Zmnako, and Zawaly). Darbandikhan Lake discharged or flow into Diyala River which is one of the great tributaries of Tigris river [14, 15, and16].

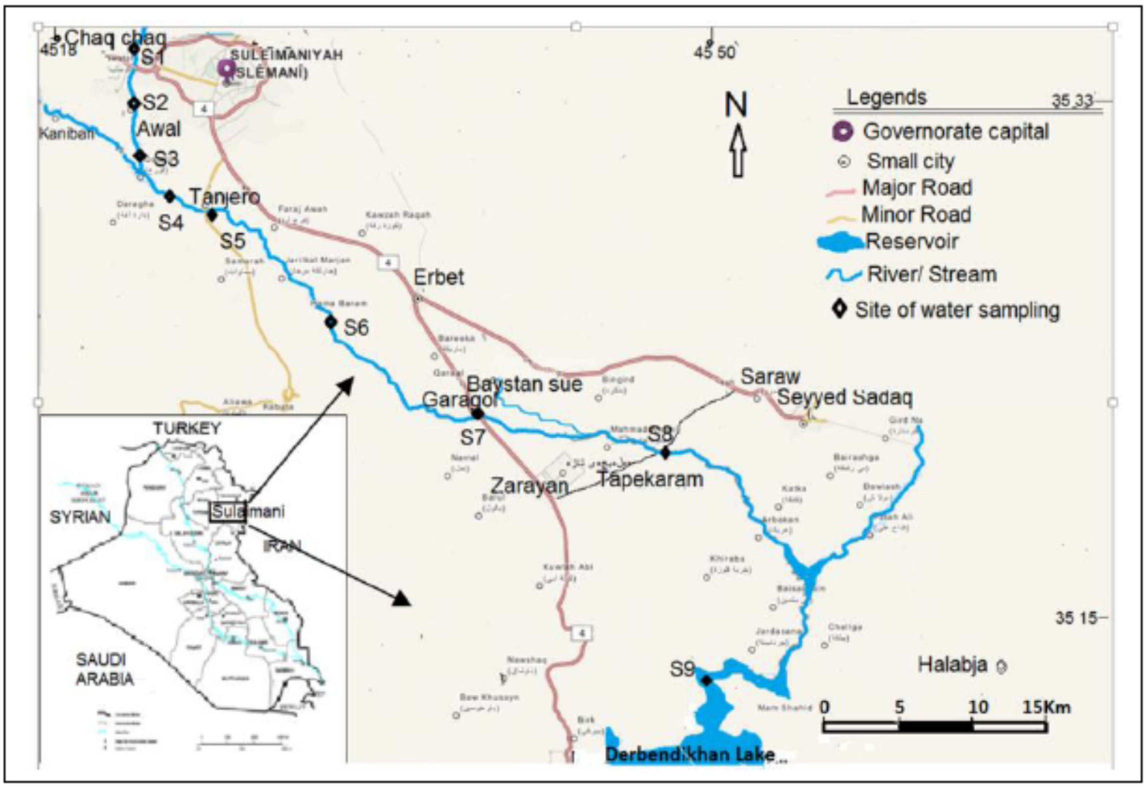


Figure 1: Sites for surface water sampling from Qalyasan stream, Tanjaro River and Darbandikhan Lakeat Sulaimani Governorate/KRI.(Source Google map).

2-Water Sampling and Preparations

Duplicate surface water samples were collected on five dates; D1, D2, D3, D4, and D5 at each site of the nine (9) selected sites during March 2015 till July 2015, the sampling dates were; 7th March, 5th April, 9th May, 15th June, and 22nd July 2015 respectively. Polyethylene terephthalate (PET) bottles of 1.5 L were used for collecting the samples. Before sampling, all the PET bottles were rinsed several times with the surface water of the concerned sampling site. The samples were taken below the surface, away from the edge of water bodies and in the center flow of the stream or river. A plastic jug which was joined with a plastic rod holder of a length about 2 m was used to collect the water samples. The unstable physicochemical properties of pH, EC and turbidity (Turb.) were measured directly after sampling in situ using portable meters according [17]. Then the sampling bottles were refilled again, labeled properly and immediately transported to the laboratory soon after sampling in portable cool boxes for the next processes of preservation and analysis.

3-Analytical Methods and Laboratory Analysis

As referred previously, the unstable physicochemical properties of pH, EC and turbidity (Turb.) were measured directly after sampling in situ using portable meters according [17]. The following instrument models were used; for pH model WTW 330i-Germany, while for EC the model LF 318/SET- WTW company- Germany and for turbidity the model Flex/ photo Flex Turb., WTW-Germany.

At the Laboratory, a sample of 500 mL volume was separated from each raw water sample for total analysis of the transitional heavy metal, then those separated samples were pretreated by acidifying them with concentrated nitric acid (HNO_3) to adjust the pH to about 2.0 [17]. The pretreated samples were then kept in a fridge at low temperature of 2-4°C for the integrated process of heavy metal analysis.

Total dissolved solids (TDS) as recommended by [18].

Total transitional metals: The concentration of the total transitional metals of; V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn and Cd were determined in the unfiltered sample after vigorous digestion.

According to [17], total metals are the sum of the concentrations of metals in the dissolved and suspended fractions.

Sample digestion: The well-mixed, acid-preserved samples were digested according to the method 3030 E as described in [17].

Finally, the total concentrations of the selected transitional metals of; V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn and Cd were measured in the digested sample solutions by inductively coupled plasma-optical emission spectroscopy ICP-OES instrument (PerkinElmer model) according [17]. The standard reference solutions for calibration curves were of analytical grade and from the National Institute of Standards and Technology (NIST), USA. The limit of detection (LOD) for the applied analytical method was addressed posit to each transitional metal in Table (4).

4-Statistical Analysis

For statistical data analysis, the XLSTAT version software was applied to interpret the data in a more relevant form and to predicate a high degree of interrelations among a set of variables by principal component analysis (PCA) and as described by [19]. Also in current study, Agglomerative Hierarchical Clustering (AHC), as one of the most statistic popular clustering methods of multivariate statistical analysis has been used for clustering (dendrogram) the sampling sites of the studied locations into groups by using the same XLSTAT statistical software.

Results and Discussion

1-Physicochemical Parameters

Table (2) presents results of the studied physicochemical parameters for the water samples. The pH values showed a slightly alkaline range of 7.04 to 7.93 with an overall mean of 7.38. The lower value of pH revealed at S4D3 while the highest pH value was at S8D5. Nevertheless, the obtained values of pH were in the highest desirable range of WHO standards for drinking water which is (7.0-8.5), [20].

The conductivity results showed a large extent of variation among the sites and dates, the minimum value was 387 µS cm^{-1} at S9D4, but the maximum value of 4213 µS cm^{-1} revealed at S5D5 with an overall mean of 1270 µS cm^{-1}. According to [21] standards, water samples that have EC less than (<) 700 µS cm^{-1} can be considered as non-saline water for irrigation purposes, but those have EC ranges between 700 to 3000 µS cm^{-1} are slightly saline waters. Therefore, the quality of most of the studied water samples (91%) fall in slightly saline rating and that was due to wastewater discharge into the water sources.

The obtained TDS values ranged between 247.5 to 2696.4 mg L^{-1} at S9D4 and S5D5 respectively with an overall mean of 813.0 mg L^{-1}. Likewise for EC parameter the minimum value of TDS found at the same site and on the same date. Based on [21] standards , water samples with TDS values less than 500 mg L^{-1} are considered to be non-saline, while for those TDS values range from 500 to 2000 mg L^{-1} are slightly saline; for the 2000 to 4000 mg L^{-1} range, the water quality fall in medium saline grading. Accordingly, most (84.4%) of the studied water samples are slightly saline waters.

The turbidity values in this study also showed a wide range and fluctuated between 2.1 to 887.0 NTU at SID1 and S5D5 respectively with the average value of 188.4 NTU. The waters were found to be much more turbid at S4 and S5 on nearly all the dates. According to [22], a turbidity value of 5 NTU is usually acceptable for drinking water. This addressed standard value of 5 NTU was consistent with 80% of the measured values of water samples at S1 and in all the sampling dates. On the other hand, all the other sites and for all the sampling dates the turbidity values were much higher than the standard limit of 5 NTU due to the algal growth and phytoplankton's organic matter content.

Highly significant Pearson correlation coefficients were found between turbidity values and the values of each EC and TDS ($r = 0.826^{**}$ and $r = 0.826^{**}$) respectively (Table 3).

Table 2: Values of some physicochemical parameters of the wastewater samples at the selected sites during the sampling dates of the study.

Parameters	**Date of sampling**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**
pH	7th March 2015 (D1)	7.22	7.32	7.23	7.29	7.28	7.15	7.19	7.33	7.43
EC µS cm^{-1}		693	904	861	1293	1498	1150	1867	1136	832
TDS mg L^{-1}		443.6	578.5	551.1	827.8	959.0	736.2	1195.1	727.0	532.6
Turb. NTU		2.1	37.8	35.3	87.4	166.0	39.4	67.4	21.2	12.4
pH	5th April 2015 (D2)	7.44	7.55	7.41	7.34	7.35	7.20	7.31	7.43	7.53
EC µS cm^{-1}		754	954	921	1184	1511	1066	1164	1080	991
TDS mg L^{-1}		482.6	610.8	589.6	758.0	967.2	682.4	744.9	690.9	634.0
Turb. NTU		6.16	33.5	42.6	335.0	327.0	100.0	229.0	37.7	14.6
pH	9th May 2015 (D3)	7.24	7.28	7.41	7.04	7.05	7.26	7.31	7.23	7.33
EC µS cm^{-1}		767	795	1025	1735	1769	1324	1366	1217	701
TDS mg L^{-1}		491.2	508.9	656.0	1110.5	1132.1	847.2	874.0	778.8	448.7
Turb. NTU		2.2	176.0	55.7	883.0	634.0	80.3	278.0	54.4	15.2
pH	15th June 2015 (D4)	7.20	7.37	7.15	7.09	7.29	7.36	7.51	7.53	7.73
EC µS cm^{-1}		724	1137	1499	1800	1378	1598	1461	1645	387
TDS mg L^{-1}		463.2	727.8	959.1	1152.0	881.9	1023.0	935.0	1052.9	247.5
Turb. NTU		3.37	67.6	248.0	820.0	672	81.4	140.0	241.0	19.2
pH	22nd July 2015 (D5)	7.21	7.87	7.43	7.41	7.51	7.52	7.73	7.93	7.90
EC µS cm^{-1}		875	1239	1380	1965	4213	1743	1633	1439	487
TDS mg L^{-1}		560.3	792.8	882.9	1257.9	2696.4	1115.5	1045.3	921.1	311.7
Turb. NTU		5.01	79.2	225.0	796.0	887.0	78.2	184.0	139.0	18.6

2--Transitional Heavy Metals

Table (4) shows 495 measurements of the total concentration for the selected (11) transitional metals at the studied sites (S1, S2, S3, S4, S5, S6, S7, S8 and S9) along the surface waters in the sampling dates of (D1, D2, D3, D4 and D5) during March 2015 to July 2015. Through the recorded measurements many ND (not detected or undetectable) marks were observed particularly for the metals Mo, Co, Ag and Cd. Besides, the ND percentages in descending order were 97.8, 91.1, 73.3 and 35.6 for Cd, Ag, Mo and Co respectively. Accordingly, the water samples were mostly not contaminated with the metals of Mo, Co, Ag and Cd; hence the metals of Mo, Ag and Cd and those had more than 50% missed values were eliminated from the statistical analysis and also in depicting them through appropriate figures.

Table 3: Pearson correlation coefficient (r) values between the physicochemical properties and the transitional metals for the studied water sources.

Para.[1]	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**pH**	**EC**	**TDS**
Cr	__0.837**__										
Mn	__0.935**__	__0.68*__									
Fe	__0.968**__	__0.781*__	__0.944**__								
Co	0.463	0.322	0.467	0.421							
Ni	__0.939**__	__0.958**__	__0.837**__	__0.913**__	0.396						
Cu	__0.951**__	__0.712*__	__0.896**__	__0.944**__	0.462	__0.851**__					
Zn	0.485	0.229	0.536	0.522	0.455	0.376	__0.703*__				
pH	-0.319	-0.128	-0.524	-0.449	0.279	-0.254	**-0.392**	-0.429			
EC	__0.895**__	__0.802**__	__0.92**__	__0.906**__	0.557	__0.888**__	__0.859**__	0.578	-0.46		
TDS	__0.895**__	__0.802**__	__0.92**__	__0.906**__	0.557	__0.888**__	**0.859**	0.578	-0.46	__1.0**__	
Turb.[2]	__0.891**__	0.535	__0.968**__	__0.884**__	0.437	__0.723*__	__0.894**__	0.578	-0.517	__0.826**__	__0.826**__
Note	1 = Parameters; 2 = Turbidity. **Note:** the correlations have been conducted among all the related observations.										

Molybdenum was found only in 12 observations out of 45 and ranged between 3.1 to 9.8 µg L^{-1} at S5D2 and S7D2 respectively with an average of 5.18 µg L^{-1}, knowing that, Mo metal was revealed in all the dates of sampling of S9 (Darbandikhan Lake). This occurrence of Mo in S9 could be attributed to the fact that Mo at Darbandikhan Lake had other origin sources such as lithogenic source (molybdenum-bearing minerals) of the lake's bed rather than the pollution sources of Tanjaro River.

In general, the potential commercial and industrial sources of discarded Mo in wastewater include; corrosion control chemicals, truck washes, pigments, lubricants, catalysts, deicing products, antifreezes, hauled waste, steris sterilization units, water treatment chemicals and agriculture either for the direct treatment of seeds or in the formulation of fertilizers to prevent molybdenum deficiency [23 and 24].

According to [25], Mo was found in 32.7% of surface water samples from 15 major river basins in the USA at concentrations ranging from 2 to1500 µg L^{-1}.

The concentration of silver (Ag) was undetectable in 41 observation sites out of 45 (ND = 91.1%), it was found once at S3, S6 and both were in D3 and twice at S7 in D1 and D2 in the concentration range between 5.7 to 16.0 µg L^{-1}. This might be due to the dynamic input of the metal sources and ultimately the concentration change continuously.

In USA, silver levels in drinking water that had not been treated with silver for disinfection purposes varied between non-detectable to 5 µg L^{-1} and the average concentrations in natural waters were 0.2-0.3 µg L^{-1} [26]. In an investigation of Canadian tap water sample, only 0.1% of them contained more than 1 to 5 ng L^{-1} Ag [27].

The maximum contaminant level (MCL) of silver in drinking water is 0.1 mg L^{-1} and it cause the following effects on human health when it exceeds the MCL level; skin discoloration; graying of the white part of the eye [28]. According to [29], no adequate data are available with which to address a health based guideline value for Ag in drinking water. Cadmium (Cd) occurred only once out of the 45 observation studies and it was 3.0 µg L^{-1} at S4 in D5 (ND = 97.8%). Nevertheless, the health guideline value that has been set by WHO (2011) [29] is 3.0 µg L^{-1} for Cd.

The frequent occurrences of undetectable observations for Mo, Ag and Cd would be either due to the unavailability of the metals at the site in that date of sampling or interestingly the concentration of Mo, Ag and Cd were below the detective level (limit of detection, LOD) according to the applied analytical method, and they were: 3.0, 5.0, and 2.0 µg L^{-1} for Mo, Ag and Cd respectively.

As it is depicted in Table (4) and Figure (2 & 3), the other studied transitional metals except Co were appeared in all of the investigated observations.

The overall vanadium (V) concentrations ranged between 2.9 to 190.0 µg L^{-1} at S1D3 and S5D5 respectively, while the average ranges for the entire sites and dates of sampling varied between 4.42 - 64.36 µg L^{-1} at S1 & S5 and 13.89 - 36.70 µg L^{-1} in D2 & D5 respectively. As observed in Figure (2), V showed high variability in the concentrations among the studied samples.

The concentration of vanadium in drinking water ranges from 0.2 to more than 100 µg L^{-1} and it depends also on geographical location [30]. The researchers [31] have referred that V often present in the water from volcanic springs, and they measured its concentration in 88 sources belonging to 5 catchments located in the volcanic area of Etna. Their findings showed that the average concentration of V varied from 15.5 ±4.2 to 188.0 ±7.7 µg L^{-1} and these results were relatively in agreement with the results of current study. In general, the measured concentrations of V in current study were below the levels of (140 µg L^{-1}) which imposed by the European and Italian Directive 98/83/CE in all observations except S5D5 [31].

Vanadium showed a highly significant positive correlation with each of; Cr, Mn, Fe, Ni, Cu, EC, TDS and turbidity by the correlation coefficient values of ; r = 0.837**, 0.935**, 0.968**, 0.939**, 0.951**, 0.895** and 0.895** respectively.

A high variation of chromium (Cr) concentrations were observed among its measurements and ranged between 3.8 to 536 µg L^{-1} with an overall mean concentration of 114.44 µg L^{-1}, the minimum level revealed at S9D3 while the maximum level was found at S5D5 (Table 4 and Fig 2 & 3). As indicated in Table (3), a highly positive significant correlations were found between Cr and each of V (r = 0.837**), Ni (r = 0.958**), EC (r = 0.802**) and TDS (r = 0.802**), while the correlations of Cr with each of Mn (r = 0.68*), Fe (r = 0.781*) and Cu (r = 0.712*) were only positively significant.

Table 4: Total and mean concentration of the studied transitional metals at selected sites along Qalyasan Stream and Tanjaro River from March 2015 till 22nd July 2015.

Heavy Metals	Date of Samp.*	Concentrations in µg L^{-1} (ppb)									Mean
		S1	S2	S3	S4	S5	S6	S7	S8	S9	
V	D1	5.1	7.6	5.1	33.4	36.5	14.7	55.4	14.7	10.5	20.3
	D2	4.6	16.5	7.9	19.1	29.5	9.1	15.6	11.6	11.1	13.9
	D3	2.9	4.5	2.9	59.8	50.7	6.2	9.2	14.3	7.4	17.5
	D4	4.2	3.0	10.5	44.6	15.1	9.8	16.7	43.8	6.0	17.1
	D5	5.3	11.0	8.2	36.4	190.0	18.2	18.9	33.1	9.0	36.7
	Mean	4.4	8.5	6.9	38.7	64.4	11.6	23.2	23.5	8.8	
	Limit of Detection (LOD) = 2.0 µg L^{-1} ; The overall Mean = 21.10										
Cr	D1	35.7	41.3	24.2	162.0	196.0	117.0	255.0	280.0	106.0	135.2
	D2	91.6	38.3	74.0	95.1	137	41.8	169.0	64.5	90.0	89.0
	D3	40.9	26.7	6.4	73.9	247.0	158.0	242.0	120.0	3.8	102.1
	D4	197	27.8	54.8	82.3	208	39.9	39.5	163.0	38.4	94.5
	D5	17.0	119.0	23.4	69.9	536.0	160.0	126.0	258.0	53.0	151.4
	Mean	76.4	50.6	36.6	96.64	264.8	103.	166.3	177.1	58.2	
	Limit of Detection (LOD) = 2.0 µg L^{-1} ; The overall Mean = 114.44										
Mo	D1	ND**	ND	ND	6.1	ND	ND	ND	ND	3.7	-
	D2	ND	ND	5.1	5.6	3.1	ND	9.8	8.8	7.8	-
	D3	ND	ND	4.2	ND	ND	ND	ND	ND	4.3	-
	D4	ND	ND	ND	ND	ND	ND	ND	ND	5.9	-
	D5	ND	ND	ND	ND	ND	ND	ND	ND	3.8	-
	Mean	-	-	-	-	-	-	-	-	-	
	Limit of Detection (LOD) = 3.0 µg L^{-1};										
Mn	D1	20.1	72.4	61.2	456.0	584.0	265.0	868.0	253.0	25.9	289.5
	D2	169.0	170.0	109.0	283.0	510.0	301.0	408.0	306.0	144.0	266.7
	D3	5.2	44.5	117.0	1310.0	1140.0	492.0	623.0	94.2	19.0	427.2
	D4	21.0	110.0	279.0	1420.3	563.0	198.0	169.0	470.0	15.7	360.7
	D5	14.4	226.0	265.0	1180.0	2350.0	500.0	196.0	198.0	28.2	550.8
	Mean	45.9	124.6	166.2	929.9	1029.4	351.2	452.8	264.2	46.6	
	Limit of Detection (LOD) = 0.5 µg L^{-1}; The overall Mean = 378.98										
Fe	D1	970.0	2410.0	839.0	13500.	13400.	4020.0	24300.	3100.0	1010.0	7061.0
	D2	1000.0	5740.0	1950.0	6530.0	10200.	1270.0	3860.0	1720.0	2540.0	3867.8
	D3	222.0	93.2	194.0	24600.	20900.	1340.0	2650.0	1760.0	322.0	5786.8
	D4	741.0	445.0	2780.0	8340.0	2470.0	980.0	1330.0	11100.	362.0	3172.0
	D5	485.0	1330.0	2180.0	13800.	81000.	23600.	1730.0	5890.0	341.0	14484.
	Mean	683.6	2003.6	1588.6	13354.	25594.	6242.0	6774.0	4714.0	915.0	
	Limit of Detection (LOD) = 5.0 µg L^{-1}; The overall Mean = 6874.30										
Co	D1	ND	1.2	1.1	8.3	10.0	2.7	18.0	3.0	1.3	5.7
	D2	ND	4.2	ND	5.2	6.8	2.5	4.4	2.7	ND	4.3
	D3	ND	ND	ND	17.0	16.2	2.4	4.2	ND	ND	10.0
	D4	ND	ND	2.8	3.7	4.3	ND	ND	8.1	2.6	4.3
	D5	ND	2.6	ND	11.2	59.2	4.0	2.6	5.0	ND	14.1
	Mean	0.0	2.7	2.0	9.1	19.3	2.9	7.3	4.7	2.0	
	Limit of Detection (LOD) = 2.0 µg L^{-1}.										
Note	*Sampling; **: Not detected.										

Table 4: Continued: Total and mean concentration of the studied transitional metals at selected sites along Qalyasan Stream and Tanjaro River from March 2015 till 22nd July 2015.

Heavy Metals	Date of Samp.*	Concentrations in μg L^{-1} (ppb)									Mean
		S1	S2	S3	S4	S5	S6	S7	S8	S9	
Ni	D1	13.4	20.4	10.6	92.0	118.0	71.9	238.0	130.0	36.4	81.2
	D2	38.6	30.2	40.6	53.9	88.5	27.4	87.2	35.8	23.8	47.3
	D3	18.1	9.3	5.0	118.0	197.0	85.7	138.0	63.4	30.2	73.9
	D4	104.0	21.7	32.7	116.7	130.0	33.4	29.6	107.0	22.2	66.8
	D5	8.8	55.6	21.3	86.8	553.0	102.0	78.2	137.0	31.8	119.4
	Mean	36.6	27.4	22.1	93.5	217.3	64.1	114.2	94.6	28.9	
	Limit of Detection (LOD) = 5.0 μg L^{-1}; The overall Mean = 77.63										
Cu	D1	6.2	8.4	8.9	28.6	27.3	12.2	36.2	10.5	8.0	16.3
	D2	7.0	15.1	11.6	19.6	21.5	8.3	15.9	10.5	13.0	13.6
	D3	5.7	4.4	5.7	40.1	35.3	8.6	10.8	9.1	4.8	13.8
	D4	8.0	6.5	32.9	25.7	11.1	12.1	12.7	34.4	8.9	16.9
	D5	14.1	22.2	40.6	36.4	150.0	13.7	12.1	20.5	20.8	36.7
	Mean	8.2	11.3	19.9	30.1	49.0	11.0	17.5	17.0	11.1	
	Limit of Detection (LOD) = 2.0 μg L^{-1}; The overall Mean = 19.47										
Ag	D1	ND**	ND	ND	ND	ND	ND	7.0	ND	ND	-
	D2	ND	ND	ND	ND	ND	ND	5.7	ND	ND	-
	D3	ND	ND	8.5	ND	ND	16.0	ND	ND	ND	-
	D4	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
	D5	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
	Mean	-	-	-	-	-	-	-	-	-	
	Limit of Detection (LOD) = 5.0 μg L^{-1}										
Zn	D1	26.6	28.3	78.5	64.0	73.8	70.0	89.1	23.8	29.0	53.9
	D2	46.3	44.4	86.8	78.8	88.1	67.2	79.2	38.4	70.9	66.7
	D3	8.1	9.8	29.3	81.0	68.4	94.8	82.2	98.8	6.0	53.2
	D4	12.5	13.4	239.0	104.2	35.9	31.3	17.8	63.0	16.5	59.3
	D5	18.8	34.8	261.0	114.0	316.0	23.3	13.0	34.1	91.8	100.8
	Mean	22.4	26.1	138.9	88.4	116.4	57.3	56.3	51.6	42.84	
	Limit of Detection (LOD) = 3.0 μg L^{-1}; The overall Mean = 66.71										
Cd	D1	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
	D2	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
	D3	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
	D4	ND	ND	ND	ND	ND	ND	ND	ND	ND	-
	D5	ND	ND	ND	3.0	ND	ND	ND	ND	ND	-
	Mean	-	-	-	-	-	-	-	-	-	
	Limit of Detection (LOD) = 2.0 μg L^{-1}										

Although Cr(III) is an essential nutrient to humans but the metal become hazards for human and aquatic ecosystem health when its concentration in water exceed the guideline values of (50 μg L^{-1}) which has been set by [30]. In current study a number of 30 observations had higher Cr concentration than the allowable guideline values of 50 μg L^{-1} which has been set by [24] and those exceeding were mainly in all of the observations of S4 and S5. In a research study on heavy metal concentration in wastewater effluent by [32], a concentration of 21 μg L^{-1} for Cr metal was detected in sugar industry effluent in Chittoor District, India.

As it is shown in Table (4) and Figure (2 & 3), manganese (Mn) likewise Cr levels showed a wide range concentrations among the studied observation and varied between 5.2 - 2350.0 μg L^{-1} at S1D3 and S5D5 respectively, with an overall mean of 378.98 μg L^{-1}. Our findings for Mn concentrations were relatively consistent with the results of [33] who found the concentration range of 52 - 1800 μg L^{-1} in surface water of the Bay of Bengal coast, and also with [34] who obtained a concentration range of 46 to 1272 μg L^{-1} in surface water sources in an industrial region of central India.

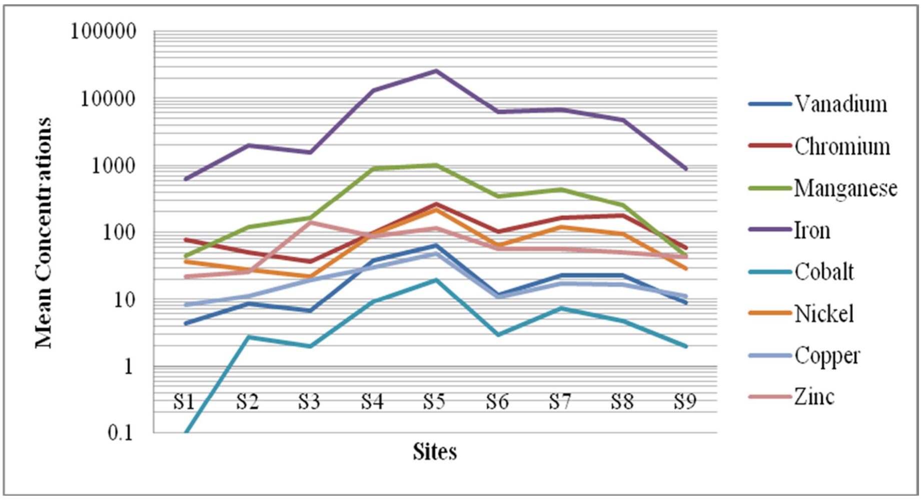


Figure 2:Relaionship between means of transitional metals concentration(μg L^{-1}) with different sites

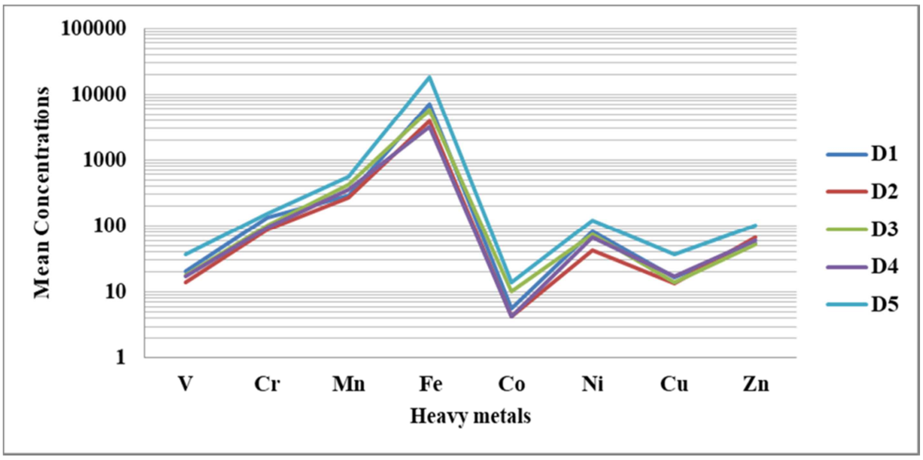


Figure 3: Mean concentrations (μg L^{-1}) of the studied transitional metals *for differentsampling dates*.

High significant positive correlations were revealed between Mn and each of V (r = 0.935**), Fe (r = 0.944**), Ni (r = 0.837^{**}), Cu (r = 0.896**), EC (r = 0.92^{**}), TDS (r = 0.92^{**}) and turbidity (r = 0.968^{**}), while the correlations between Mn and Cr was only positively significant (r = 0.68*), (Table 3).

The occurrence of Mn in aquatic environment is basically in the two main forms of Mn(II) and Mn(IV), the change in their forms are always governed by abiotic or microbial medium through oxidation and reduction reactions [33]. Mn is a naturally occurring element and present in soil, water and air. The manganese content of natural surface waters that are essentially free of anthropogenic inputs can range from 10 to usually less than 200 μg L^{-1}. The chemistry of Mn and its environmental aspects is largely controlled by pH and redox conditions; the divalent oxidation state form of Mn(II- divalent) dominates at lower pH and redox potential, with an increasing proportion of colloidal manganese oxyhydroxides above pH 5.5 in non-dystrophic waters [35]. The main anthropogenic sources of manganese release to the environment are combustion of fossil fuels, and, to a much lesser extent, emissions from the combustion of fuel additives, emissions from alloy of steel and iron production, municipal wastewater discharges, sewage sludge, mining and mineral processing (particularly nickel), [36 and 37]. According to [29], the acceptable concentration of Mn in drinking water to consumers is below 100 μg L^{-1}, because Mn even at concentration of 200 μg L^{-1} causes a coating on pipe due to the formation of a black precipitate. The findings of Mn concentration in this study have exceeded the addressed acceptable limit of 100 μg L^{-1} by [29] in all of the observations of S4, S5, S6, and S7. Also, the detected concentration of Mn metal in the observations of other sites has mostly exceeded the acceptable limit.

Iron (Fe) had the highest and widest concentrations range among the other studied transitional metals and varied between 93.2 to 81000 µg L^{-1} at S2D3 and S5D5 respectively with an overall average of 6874.3 µg L^{-1} (Table 4 and Fig. 2 & 3) . The obtained results were found to be somewhat in good agreement with the results of [33] which were 60.5 to 60454.0 µg L^{-1}, but in our results were much more, as compared to the detected upper limit by [38] who obtained 25 to 5490 µg L^{-1} in surface water of Ganga River in West Bengal. High significant positive correlations were revealed between Fe and each of V (r = 0.968**), Mn r = (0.944**), Ni (r = 0.913^{**}), Cu (r = 0.944**), EC (r = 0.906^{**}), TDS (r = 0.906^{**}) and turbidity (0.884^{**}), while the correlations between Fe and Cr was only positively significant (r = 0.781*), (Table 3).

Table (4) and Figure (2 & 3) showed that cobalt (Co) had the smallest and narrowest variation range as compared to the other studied transitional metals of V, Cr, Mn, Fe, Ni, Cu and Zn along the selected sites and during the dates of sampling. In general, the concentration of Co varied between 1.1 - 59.2 µg L^{-1}, the lowest concentration was revealed at S3D1 while the highest level was found at S5D5. Additionally, Co was not detected in 16 observations and this equivalent to 35.55% of the total observations. Incidentally, Co has not showed any significant correlation with the other studied transitional metals as well as the physicochemical properties. Earlier studies by [39] showed a much higher concentration level for cobalt in wastewater of Kubanni stream channels in Zaria, Kaduna State, Nigeria who found the range of 3.77-15.20 mg L^{-1} for the year 2013 and 4.74-15.20 mg L^{-1} in 2014.

Likewise Cr, Mn and Fe, the concentration of nickel (Ni) showed a wide range and varied between 5.0 to 553.0 µg L^{-1} at S3D3 and S5D5 respectively, and the overall average was 77.6 µg L^{-1} (Table 4 and Fig. 2 & 3) . As mentioned previously, Ni had highly significant positive correlation with each of V (r = 0.939**), Cr (r = 0.958**), Mn (r = 0.837**), Fe (r = 0.913**), Cu (r = 0.851**), EC (r = 0.888**), and TDS(r = 0.888**), but the correlation was only positively significant with turbidity (0.723*), but no significant correlations were found between Ni and each of Co, Zn and pH. Our findings for Ni were not compliant with those of the investigators; [38] who found 11.0 to 54.0 µg L^{-1} in surface water of Ganga river in West Bengal, [40] who obtained 1400 to 4400 µg L^{-1} in wastewater from an industrial area in Ibadan, Nigeria, and [12] who detected 1020 to 2220 µg L^{-1} in sewage water of Tanjaro Rivers, Sulaimani City, Iraq.

Nickel is ubiquitous in nature and found in several oxidation states including divalent form which is the predominant state, while trivalent state may be formed by redox reactions [41]. As referred by [29], Ni is used mainly in the production of nickel alloys and stainless steel, Furthermore, Ni like some other metals is an essential element for healthy plant life and required for various biochemical and physiological functions in different organisms. The addressed guideline value of Ni by [29] is 70 µg L^{-1}, thus most of the observations of S4, S5, S6, S7 and S8 could be regarded as polluted sites by Ni also, because its concentration has exceeded the guideline value of 70 µg L^{-1}. Also, the investigator [12] has pointed out that the metals Cd, Cu, Ni, Pb, and Zn as well as other pollutants in Tanjaro River has exceeded the international and local standards due to the sewage and industrial effluents discharge in the river.

The levels of copper (Cu) concentrations were between 4.4 to 150.0 µg L^{-1} at S2D3 and S5D5 respectively and had an overall average of 19.47 µg L^{-1}. However, previous studies showed the following results, 0.38 to 0.5 mg L^{-1} buy [**12**] in sewage water of Tanjaro Rivers, Sulaimani City, Iraq; 1.6 to 6.7 mg L^{-1} by [40] in wastewater from an industrial area in Ibadan, Nigeria; and 0.2 mg L^{-1} in domestic wastewater, and 0.04-26 mg L^{-1} in commercial wastewater in Munich by [42]. As it is depicted in Table (3), Cu had highly significant positive correlation with each of V (r = 0.951**), Mn (r = 0.896**), Fe (r = 0.944**), Ni (r = 0.851**), EC (r = 0.859**), TDS (r = 0.859**) and turbidity (r = 0.894**), while the correlation of Cu with each of Cr and Zn were positively significant, but no significant correlations was found between Cu and Co.

According to [29], the occurrence concentrations of Cu appear to be less than 0.001, 0.2 and 5.0 µg L^{-1} in groundwater, surface water and drinking water respectively. Cu imparts a color and undesirable bitter taste to water at concentration level above 5 mg L^{-1}, therefore the prescribed guideline value by [29] is 20.0 µg L^{-1}. In current study Cu has exceeded the prescribed guideline value of WHO in 15 observations out of the entire 45 observations.

The range concentration of zinc (Zn) in this study was found to be 6.0 to 316 µg L^{-1} at S9D3 and S5D5 respectively with an overall average of 66.71 µg L^{-1} (Table (4) and Figure 2 & 3). Inconsistent findings for Zn concentration in surface water were reported by the following researchers; [12] who detected 530 to 1330 µg L^{-1} in sewage water of Tanjaro Rivers, Sulaimani City, Iraq and with [43], who obtained a range of 2000–5000 µg L^{-1} in surface water of Alahsa farms, Saudi Arabia. But our results for Zn concentrations were somewhat in agreement with the findings of [38] who found a concentration range 12 to 370 µg L^{-1} in Ganga River in West Bengal during 2004 -2005 and with [34] who detected a concentration range of 9 to 397 and 108 to 341 µg L^{-1} in pre-monsoon and post-monsoon samples respectively in surface water sources of an industrial region of central India.

Zinc exhibited a significant positive correlation only with copper (r = 0.703*) and had no other significant positive or negative correlation with the other studied transition metals and physicochemical parameters. This might be due the synergistic effect between Zn and Cu; this can be supported by [44] who found a synergistic effect between ternary iron-zinc-copper mixed oxides and grapheme for better photocatalytic activities of water decontamination.

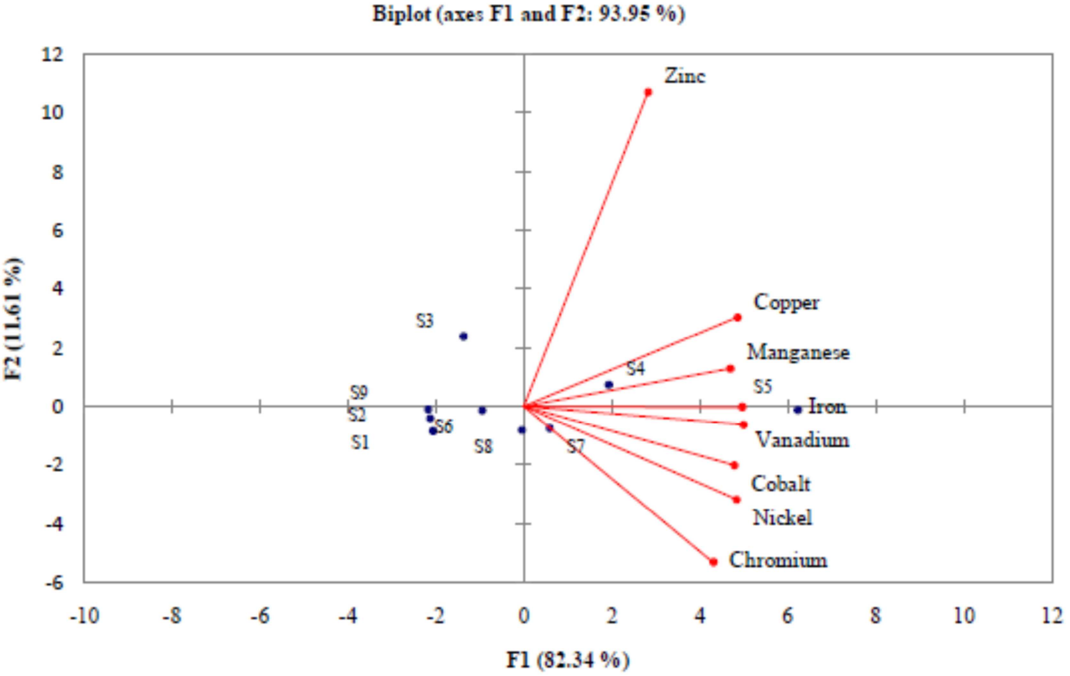
As indicated by [29], the Zn content of surface water and groundwater normally do not exceed 0.01 and 0.05 mg L^{-1}, respectively. But in tap water the concentrations can be much higher due the dissolution of zinc from pipes and undesirable astringent taste to water will be formed on the threshold concentration of about 4 mg L^{-1} zinc as zinc sulfate. Moreover, water becomes opalescent and develops a greasy film when containing zinc in excess concentrations of 3-5 mg L^{-1}. Regarding maximum permissible limits content of Zn in drinking water, no health-based guideline value was proposed. But drinking water may not be acceptable to consumers if Zn concentration become at levels above 3 mg L^{-1}.

Based on the overall averages of the detected transitional metals in all the observations of the current study (Table 4), it has been appeared that the occurrence level of the metals were found to decrease in the following sequence; Fe (6874.30) > Mn (378.98) > Cr (114.44) > Ni (77.63) > Zn (66.71) > V (21.10) > Cu (19.47) µg L^{-1} (Fig. 3). Nevertheless, the extreme variation in concentration range of the studied transitional metals, and particularly for (Fe, Mn, Ni, Cr, Zn, Cu, V and Co) throughout this study could be explained on the basis of the potential difference in metal pollutant supply by the sites and with the sequence of sampling's dates.

Additionally, the detected levels of the studied transitional metals in some of the observations (particularly for the site of; S3, S4, S5, S6, S7 and S8) have exceeded the health guideline values that have been set by WHO for drinking water. Consequently, those observations were contaminated with the following metals V, Cr, Mn, Ni, and Cu as compared with the defined health guideline values by WHO. But for the transitional metals of Mo, Ag, Co, Fe, and Zn the contamination status could not have evaluated because no health-based guideline values were proposed by WHO.

In order to assess the degree of variations for the studied transitional *metals* among the sites and also to give the best *graphical representation for them;* principle component analysis (PCA) was used to interpret the relations between the studied transitional metals by reducing the dimensionality and revealing hidden structure in the data set. As it is depicted in the plot of Figure (4), x-axis explains that the first component (principle component) had 82.34 % of the variation among the metals because the greatest variance of the data set comes usually to lie on the first axis, while y-axis represent the second components and explains 11.61 % of the variation within the sites. Thus, the cumulative explained variance among the transitional through the sites of the studied surface water was % 93.95.

The cosines of the angels between the vectors of the metals in Figure (4) express an approximation of the correlation among the averages of the studied metals in dates of sampling along the sites. A small angle (less than 90^{o} degree); such as the angels between the vectors of Cu, Mn, Fe, V, Co, Ni and Cr indicates that the metals are positively correlated. Angles of ninety (90^{o}) degrees indicate that the metals are not correlated. The cosine of 0 (zero) is equal one and this means that the variables are high significantly and positively correlated. Moreover, an angle of more than (90^{o}) degree; such as the angel between the vector of Zn and Cr express a negative correlation between the metals. If the angle is approaching 180° degree, the relation then expresses a strong negative correlation between them.



Where: F1 stand for component 1 or the heavy metals, while F2 stand for component 2 or the sites of sampling.
Figure 4: Principle component analysis (PCA) plot showing distribution of the studied sites on scatter plot based on the metal results.

On the other hand, Figure (5) shows a scree plot between the eigenvalues (the corresponding values of each eigenvectors) and the associated component or factor (metals) in descending order to visually assess which components or factors explain most of the variability in the data. In general, the transition metals showed the following variability decreasing trend; V> Cr > Mn > Fe > Co > Ni > Cu > Zn. Incidentally, the corresponding eigenvalue is a number to reveal how much variance is in the data along that eigenvector (or principal component).

According to the agglomerative hierarchical clustering (Dendrogram) in Figure (6) and depending on the concentration levels of the studied transitional metals, the studied nine sites of water sampling were classified into three major groups at a significant dissimilarity percent of about 48%. The first group contained only site 5 (Tanjaro River- Next to Tanjaro bridge) which had almost the highest concentration levels of the metals. The second group included only site 4 (Qalyasan stream-Near Kurd city community apartments), and this site also was characterized by relatively highly concentration level of the metals. Finally, the third group covered all the remained 7 sites in two subgroups of about 29 % dissimilarity, the subgroups in turn were also clustered into two sub-subgroups of about 7 % dissimilarity for the following sites; S1+S9 and S2+S3 for the first sub-subgroup, but the second sub-subgroup covered the following sites; S8 alone and S6+S7. Obviously this explains that the clustered sites under one sub-subgroup had always close concentrations for the studied transitional metals due to the conditions that are more likely in metal supply to the studied surface water sources.

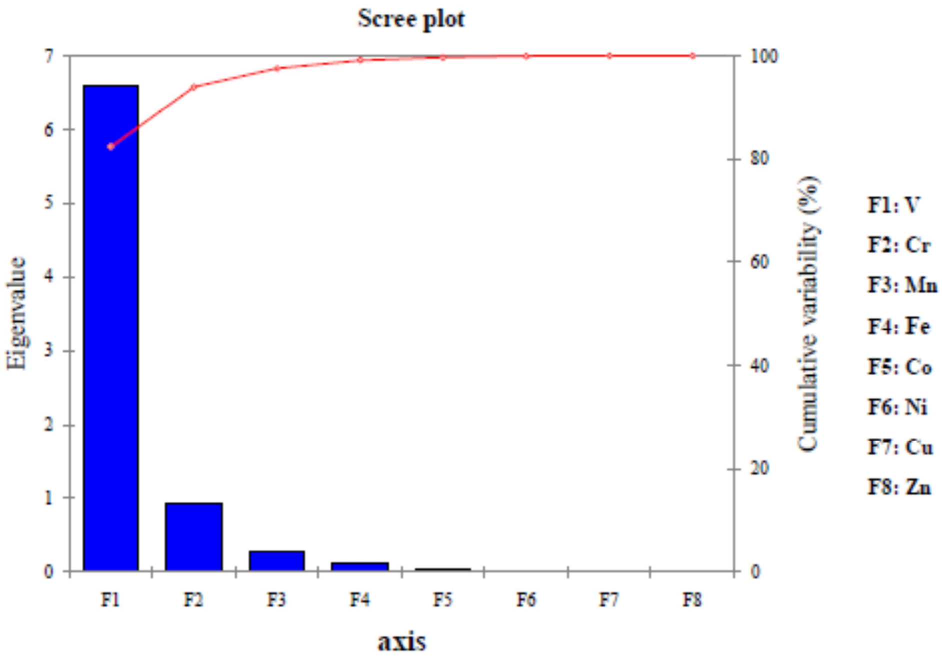


Figure 5: A scree plot displays the eigenvalues associated with a component of the studied transitional metals in descending order.

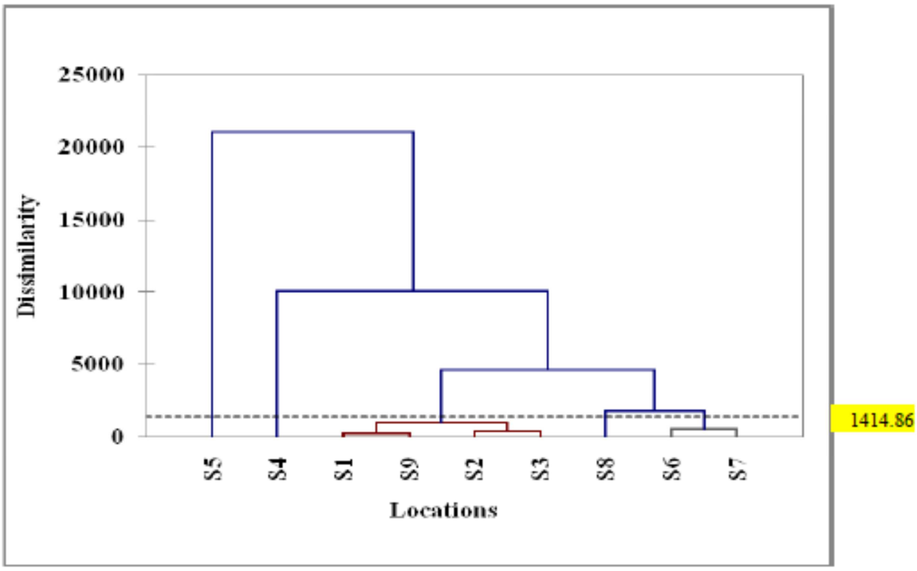


Figure 6: Dendrogram for clustering of the water sampling's sites based on the average concentrations of transitionalmetals.

Depending on the average concentration values of the eight studied transitional metals along the studied surface water, cluster analysis as a method of multivariate analysis was carried out by using Euclidean distance coefficient (Table 5). The maximum distance of (24976.422) was found between S1 and S5 (Qalyasan stream-Near to the deconstructed cement factory at Sarchnar and Tanjaro River- Next to Tanjaro bridge), this means that highest dissimilarity was detected between those two sites. This can be due to the differences in water quality supply of the sources as well as the chemical composition that discharged in the water at both sites.

On the other hand, the minimum distance coefficient of (277.931) was appeared between S1 and S9 (Qalyasan stream-Near to the deconstructed cement factory at Sarchnar and Darbandikhan reservoir - Next to old Pir-Mohamad bridge); hence the highest similarity was found between S1 and S9. This can be attributed to the fact of similarity of the water quality that flows into or discharged in both sites.

Table 5: Euclidean distance coefficients values showing dissimilarity among the nine sites of the surface water source according to the studied transition metals

S	S1	S2	S3	S4	S5	S6	S7	S8	S9
S1	0								
S2	1367.560	0							
S3	965.650	432.414	0						
S4	12746.470	11379.445	11790.687	0					
S5	**24976.422**	23609.755	24022.896	12242.264	0				
S6	5611.957	4245.055	4658.470	7135.717	19365.366	0			
S7	6150.243	4784.116	5196.562	6597.808	18829.506	548.407	0		
S8	4083.055	2717.938	3132.196	8666.084	20894.731	1532.626	2068.819	0	
S9	**277.931**	1091.546	691.283	12470.685	24700.351	5336.029	5874.820	3807.695	0

Finally, the divergence between the highest and the lowest dissimilarity values (Euclidean distance coefficients) confirms the variation in chemical composition and water quality, as well as the contamination levels along the sites of the studied water source. Also, the dendrogram supports the results of PCA in the classification of the sites into groups, subgroups and sub-subgroups at the studied water sources.

Conclusions and Recommendations

A high degree of variability in the concentrations of the studied transitional metals were observed among the sites and during the date of sampling in the studied surface water sources due to the direct discharge of untreated wastewater effluents into the studied water sources. Undoubtedly, this causes a variety of health and environmental impacts, when wastewater is released directly into receiving surface water bodies.

Based on the overall averages of the detected transitional metals in all the observations, it has been observed that the abundance level of the metals were found to decrease in the following sequence; Fe (6874.30) > Mn (378.98) > Cr (114.44) > Ni (77.63) > Zn (66.71) > V (21.10) > Cu (19.47) µg L^{-1} . However, the variability decreasing of the transition metals among the sites showed the following trend; V> Cr > Mn > Fe > Co > Ni > Cu > Zn.

Additionally, PCA results confirmed that there was a high variability in the concentrations level of the studied transitional metals. Besides, the dendrogram plot classified the nine sites of the studied surface water sources into three major groups as well as clustering to subgroups and sub-subgroups at a significant dissimilarity due to the variation in concentration levels along the sites of the water resources.

Because those water sources are used as a direct sink for the untreated domestic and industrial wastewater effluents as well as human uses for different purposes such as; drinking, irrigation and industrial activities. Therefore, continuous monitoring and water quality assessment through regulatory testing is required to be carried out by the authorities for the surface water sources of Qalyasan Stream, Tanjaro River and Darbandikhan Lake in order to minimize the harmful effects of those sources on population's health and also to reduce the detrimental impacts on the aquatic ecosystem.

On the other hand, proper wastewater treatment plants are recommended to be established in order to conduct some pretreatments processes for the wastewater effluents before their direct mixing with the surface water sources.

Additionally, complimentary studies and research are needed to expand our knowledge beyond the studied metals and selected sites of water sources in current study.

Finally, in order to obtain a composite picture about the whole aquatic system in our region, other studies are recommended to study the possible side effect of the transitional metals on plants and food chain system, also phytoremediation experiments are recommended for cleaning up the contaminated water sources by heavy metals.

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