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Research Article

A SURVEY ON POLLUTION OF PAH COMPOUNDS AND CITY WASTE-WATER IN MASJEDSOLEIMAN AREA SURFACE-WATERS

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ABSTRACT
In order to investigate the contamination of surface water in Masjedsoleyman area and transport of anthropogenic and natural pollution from the stream of residential area and its impact on Tembi river, main anions and cations, biological oxygen demand (BOD) and chemical oxygen demand (COD) were analyzed and their measure were also compared to the standard values and chemical types. Water type, chemical faces of water samples, hydrogeochemical changes and impact of water mixing were also investigated. Statistical methods such as principle component analysis (PCA) and cluster analysis were used to find variables which have major impacts on classification of water samples to distinct hydrochemical groups. Based on these investigations, Na^{+} , SO_4^{2-} , Cl^{-} and Ca^{2+} have major values on first component. These components may be related to dissolution of Gachsaran evaporate Formation and mixing oilfield brines. Classification of water based on BOD5 suggests that Tembi River is considered as a severely polluted river. Because of occurrence of numerous oil seepages in the area, and importance of aromatic compounds from environmental point of view, concentration of polycyclic aromatic hydrocarbons in water and sediments sample were analyzed as well.

Keywords: *PAH; Cluster Analysis; PCA; Surface-waters; Sediments*

INTRODUCTION
Water quality is found as a major factor affecting human and animal health (Broekhuizen *et al.*, 2012; Singh *et al.*, 2005; Smith, 1990).

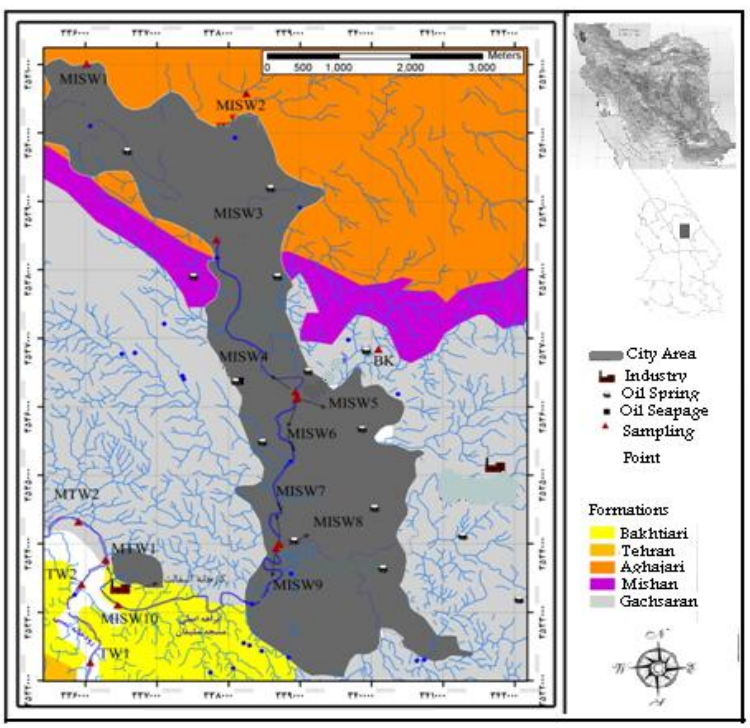

Figure 1: Location of the sampling points

Physical and chemical conditions of surface waters depend on natural phenomena such as weathering, sand erosion, industrial and city pollutions (Kazi *et al.*, 2005). Anthropological pollutions are the stable origin of the pollutions and their values usually increases with time (Smith *et al.*, 1996). Industrial heterogonous developments in one hand, and struggle of ecological comprehensive laws in the other hand duplicated the effect of anthropological pollutions in the underdevelopment countries relative to the developed and undeveloped countries. In this respect, illegal builders, absence of waste-water system, presence of oil springs and untreated waste-water related to the oil depended industries cause pollution of surface water of Masjedsoleyman ciy.
Masjedsoeliman is a city located in the North-Eastren corner of Khuzestan province in the north-east of Iran. This area is a part of folded Zagros located at in the nearby of Dezful. A big part of Masjedsoleyman area, especially its urban area is located over the third and the fourth part of Gachsaran Formation (Marn and Indrit). Other Formations are Mishan (grey Marne), Gachsaran formation (brown-grey limestone and reddish Marne with gypsum and redish silitstone (Figure 1).

RESULTS AND DISCUSSION

Discussion

In order to evaluate and refine pollution initiated from waste-water of the city and oil springs. Sampling is done from urban area and Tembi River based on global standards. To do so, 14 water samples are drawn with topological maps for determining values of BOD, COD, cations and anions. 7 water sediment samples are also drawn for analysis of PAH. Location of the sampled points is indicated in Figure1.
Results of descriptive statistics of physical and chemical properties and concentration of major ions of water samples of the area are shown in Table 1 (Ouyang, 2005). In this study MIS1 are taken from a natural spring and are chosen as a blank sample. This sample had the least pH and the most Eh among all of the area water samples.

Table 1: Statistical information of some chemical and physical properties of ions in the samples

Skew	Standard Deviation	Maximum	Minimum	Median	Mean	
-0.6	0.3	8.0	7.0	7.6	7.6	pH
-0.6	26.4	-19.0	-116	-61.5	-62.6	Eh (mV)
-1.4	1.7	32.3	26.7	31.4	30.9	Temperature (^{0}C)
1.8	1673.2	6283	952.0	1826	2515.2	EC (µmho/cm)
1.6	1324	5946	791.8	1681	2091.9	TDS (mg/L)
0.6	144.1	696.8	243.9	400.2	434.8	HCO_3^-(mg/L)
2.7	6.8	23.1	0.00	0.00	2.60	CO_3^{2-}(mg/L)
0.4	344.8	1235	136.7	515.8	597.8	SO_4^{2-}(mg/L)
1.9	523.1	1702	115.1	327.6	504.6	Cl^-(mg/L)
-0.3	127.8	483.0	119.0	353.6	328.0	Ca^{2+}(mg/L)
1.4	19.1	100	34.9	47.5	54.70	Mg^{2+}(mg/L)
2.0	329.2	1050	53.6	149.5	291.5	Na^+(mg/L)
1.9	3.10	19.3	5.80	10.7	10.8	K^+(mg/L)

Investigating pH vs Eh chart helps evaluating both of those properties in the different samples. As depicted in Figure 2, moving down, the stream tends to be reduced and acidity tends to be decreased. Since the major part of the municipal waste-water is released in the stream, viewing such a phenomenon is probable. Based on the recent studies done on Tembi River revealed the presence of H_2S soluble in water (Alijani, 1384), so that reduction condition of Tembi River can be justified.
Papyri chart is used for determining water type, hydrochemical faces, hydrogeochemical changes of water samples and mixing effect of water. Figure 3 shows variations of sulfate ion concentration in MISW1 and MISW2. As seen sulfate contents are increasing from upstream to downstream. From geological view

point MISW1 and MISW2 are located in Aghajari Formation, and this change in lithology of basement of the stream is clearly distinguishable.
Entering to the Gachsaran evaporate Formation, content of chloride and sulfate increase, However moving toward downstream just shows increase of sulfate ion concentration, and chloride ion concentration does not increase significantly.

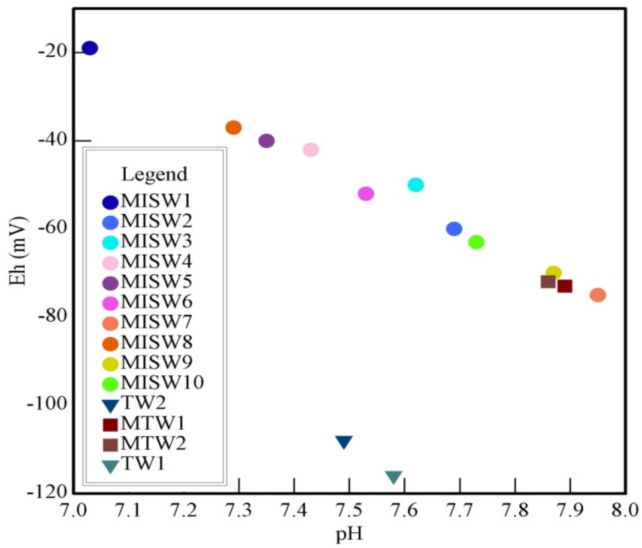

Figure 2: Chart of Eh versus pH of the samples

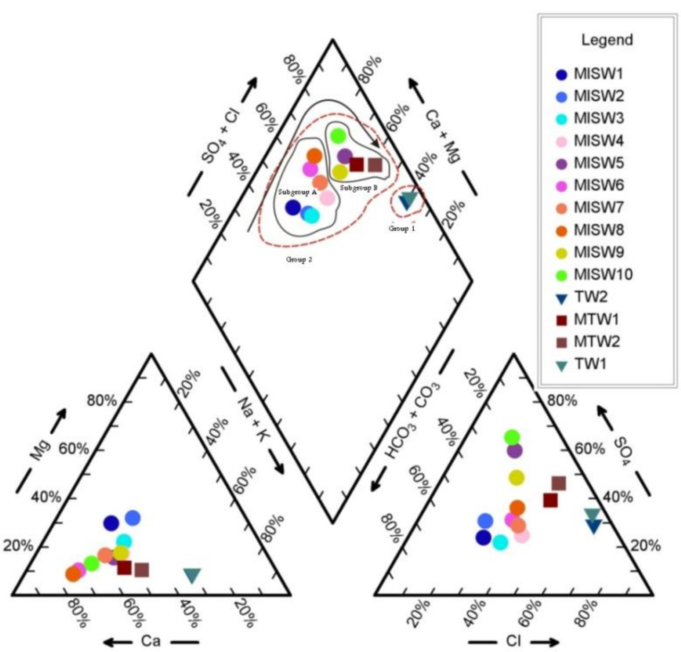

Figure 3: Papyri chart of water samples of the studied area. Arrows indicate completion trend of water faces in the movement toward the downstream.

Evaluating cation concentrations indicate that calcium content is dramatically increasing in the mai stream of Masjedsoleyman. Chloride and sodium ions contents are dominant ions in Tembi River, but calcium and sulfate have a similar importance. Joining the stream to Tembi River is clearly indicated in papyri charts such that sample MTW1 and MTW2 in both of the triangles are located between samples of

Tembi River and the stream of the city. Water face of MISW1-3 samples is calcium carbonate as it was predictable. MISW1-10 has water face of calcium sulfate and this fact reflects dissolution of gypsum of Gachsaran Formation. Combination of calcium sulfate water of the stream with that of sodium chloride water of Tembi River changes hydrochemical face of Tembi River into calcium chloride. However the effect of evaporative beds of Gachsaran Formation lead into hydrochemical water face into calcium sulfate just 700 m after joining the stream to Tembi river. Cluster analysis is one of the beneficial and empirical methods of precise evaluation of water samples and their classification into discrete groups of hydrochemichals (Hussain *et al.*, 2008; Ismail and Ramadan, 1995; Ke *et al.*, 2011). In order to identify variables having the greatest effect on the data collection, amounts of calcium, carbonate, chloride, and sulfate were evaluated with principal component analysis from 14 samples prior to cluster analysis. The results were summarized in table 2. As the results show sodium, sulfate, chloride, and calcium are the most important parameters determining water chemical faces of water samples, respectively. Projecting sample chemical information into the coordinate axis composed of the first and the second or the third principal components provides projection of most information into two dimensional spaces. As seen in Figure4 and 5, samples taken from Tembi River are completely from those of the Masjedsoleyman main stream. MTW1 and MTW2 samples which correspond to Tembi River just after joining the stream to Tembi River. And MISW4, MISW5, and MISW9 are also separated from the others. However samples MISW1 and MISW3 which are representative for carbonate water of Gachsaran and Mishan Formations are discriminated from the other samples good enough. But sample MISW2 is located within samples correspond to subgroup “B”. Samples MISW4, MISW6, MISW7, and MISW8 are discriminated from other samples in both of the charts. However, projecting the first principal component versus the third one show the proximity of these points more efficiently.

Table 2: Results of principal component analysis of the major ions in the samples

PC3	PC2	PC1	
-0.72	-0.58	-0.27	HCO_3^-
-0.20	-0.12	0.45	Cl^-
0.23	-0.17	0.46	SO_4^{2-}
0.08	-0.55	0.42	Ca^{2+}
0.02	-0.54	0.30	Mg^{2+}
-0.62	0.56	0.49	Na^+

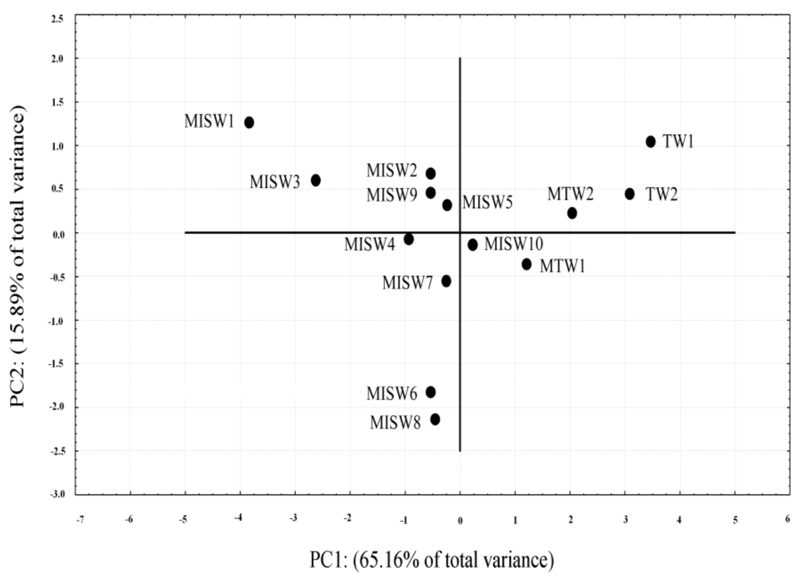

Figure 4: The first principal component versus the second principal component for the water samples

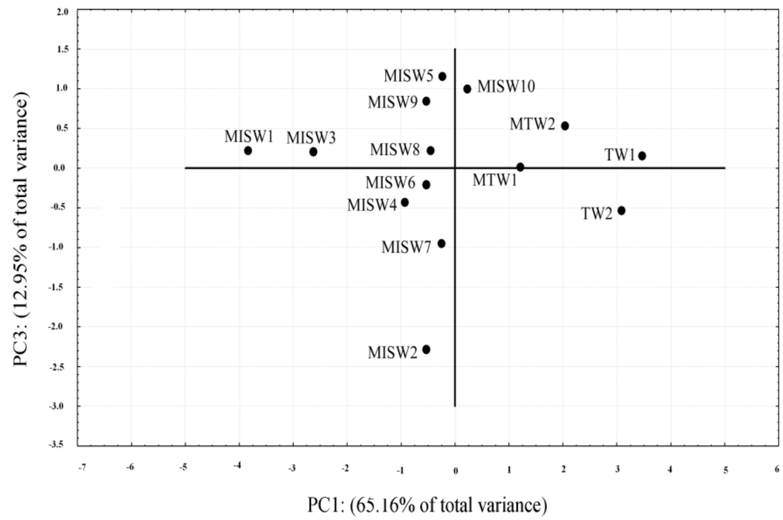

Figure 5: The third principal component versus the first principal component for the water samples

Based on the results of principal component analysis, sodium, sulfate, chloride, and calcium ions are selected for evaluating samples by using cluster and hierarchical analysis. Figure6 shows dendrograms of water samples based on the aforementioned ions. As seen Tembi river samples are separated from the stream well. The samples of the stream themselves are subdivided into two subgroups. Samples MISW4, MISW6-8 placed in a different cluster of subgroup "A" which are representative the stream. These samples have not show sever increase of sulfate contents. Samples MISW1, MISW2, MISw5, MISW9, and MISW10 are located in subgroup "B" and represent an intense increase in sulfate contents.
Concentration of chloride in MISW1 and MISw2 samples are also intensively increased due to joining the sodium chloride waters of Tembi River. This fact caused locating these two samples in a cluster of quit different from the other samples. To evaluate extent of pollution of domestic and industrial waste-waters of the area, the effect of entrance of hydrocarbon compounds into ecology of water system, an estimate of organic compound contents present in surface-water of the area, BOD, and COD of samples are determined and the results were summarized in Table 3.

Table 3: BOD and COD of the water samples of the studied area

Eh (mV)	pH	COD (mg/L)	BOD (mg/L)	Sample Point
-19	7.0	5.0	2.00	MIS1
-60	7.7	47	30.0	MIS2
-50	7.6	50	39.0	MIS3
-42	7.4	70	10.0	MIS4
-40	7.4	826	531	MIS5
-52	7.5	67	52.0	MIS6
-75	8.1	47	38.0	MIS7
-37	7.3	44	36.0	MIS8
-70	7.9	61	49.0	MIS9
-63	7.7	39	21.0	MIS10
-73	7.9	35	28.5	MTW1
-72	7.9	40	23.0	MTW2
-116	7.6	24	19.0	TW1
-108	7.5	48	3300	TW2

Since the results corresponding to BOD and COD of the area are the same, plotting of similar charts for COD's were avoided. Figure7 shows BOD contents in MISW5 station which is entrance of oil pollutants initiated from oil springs. There are lots of oil springs in the passage of the water stream such that oil spots are obvious. Entrance of hydrocarbon compounds into the stream causes a noticeable increase in BOD and COD and also causes decrease of soluble oxygen in water. On the hand degradation of such organic chemicals causes increase of Eh in the downstream. For example, MISW6 and MISW7 have shown 12, and 35 mV decrease in Eh, respectively. Inspecting Table 3 indicates that contents of BOD and COD in TW2 sample are increasing relative to TW1 sample, and this is probably due to the addition of waste-water from asphalt-industry in the distance between the two stations.

Diversity of oil springs in the area and entrance of crude oil into the area surface-waters cause several physical and chemical problems for domestic animals and resident of the area. On the other hand, entering insoluble compounds to those surface-waters can risk health of that ecosystem. As polyarmomatic hydrocarbons (PAHs) is toxic, soluble, cancer causing and mutagenic, so their investigations are of great importance. In this research, 7 water samples and 7 sediment samples are taken from different location of the area. For determining concentration of PAHs using ICP-MS instrument. Based on the results obtained the water samples do not show significant pollution due to PAHs, but sediment samples have shown a significant pollution due to some chemicals. So the results of chemical analysis of the sediment samples were just considered in Table 4. Setting up the optimization standard and pretreatment of sediments in the river bed were both based on the guides for determining risky levels of pollutants for human and microorganisms of the ecosystem. For alluvial sediments such standards are known as qualitative standard of sediment. Environmental protection agencies (EPAs) of the different countries have provided different guidelines which differ dramatically. For examples some of them consider a certain level of pollutants as harmful level while the others consider it as a harmless level. Mc. Donald and coworkers (Mc. Donald *et al.,* 2000) introduced the lowest concentration in the guidelines as threshold effective concentration (TEC) and the upper limit as probable effective concentration (PEC). TEC represents the lowest concentration lower which is harmless for microorganisms resident in the sediment, while PEC represents the highest concentration upper which has a dreadful impacts on that microorganisms in the sediment.

Total PAH contents in all of the samples were found lower than that of Tec and PEC, and PAHs pollution were not found in the area overall. However evaluating each of the compounds individually shows that concentration of fluren in TS1 sample is greater than that of accepted PEC, so that this compound indicates a severe pollution in the sediments. Phenanterene is also indicates an intense pollution in MISS5 sample and its concentration are greater than that of accepted TEC in the other sediments. Hence it has toxic potential for bioorganisms resident in the sediments. However pyrene does not indicate any pollution in none of samples.

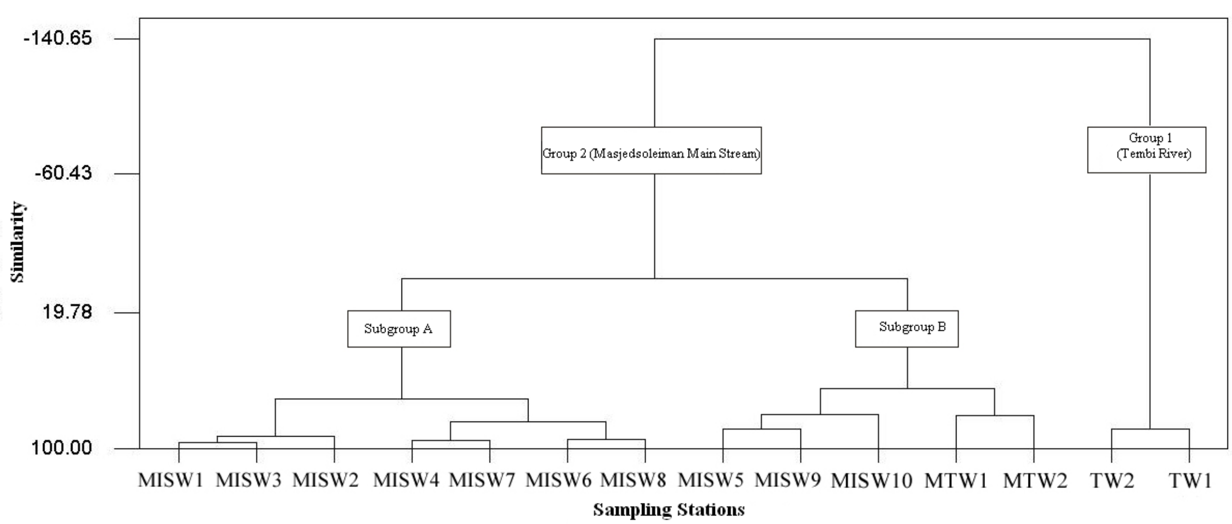

Figure 6: Dendrogram of the water samples based on the concentration of sulfate, chloride, bicaribonate, and sodium ions, Ward repetition method and Euclidian distance was used

Table 4: Analytical results of PAH compounds in the sediment samples (ng/g of sediment)

Total PAH	Pyrene	Phenantherene	Fluorene	Sample
1427	-	1427	-	MISS6
787	130	381	271	MISS9
467	-	316	151	MISS10
1431	-	481	950	TS1
1126	-	778	348	TS2
671	53	434	184	TMS1
1044	45	728	271	TMS2
22800	1520	1170	536	PEC
1610	195	204	77.4	TEC

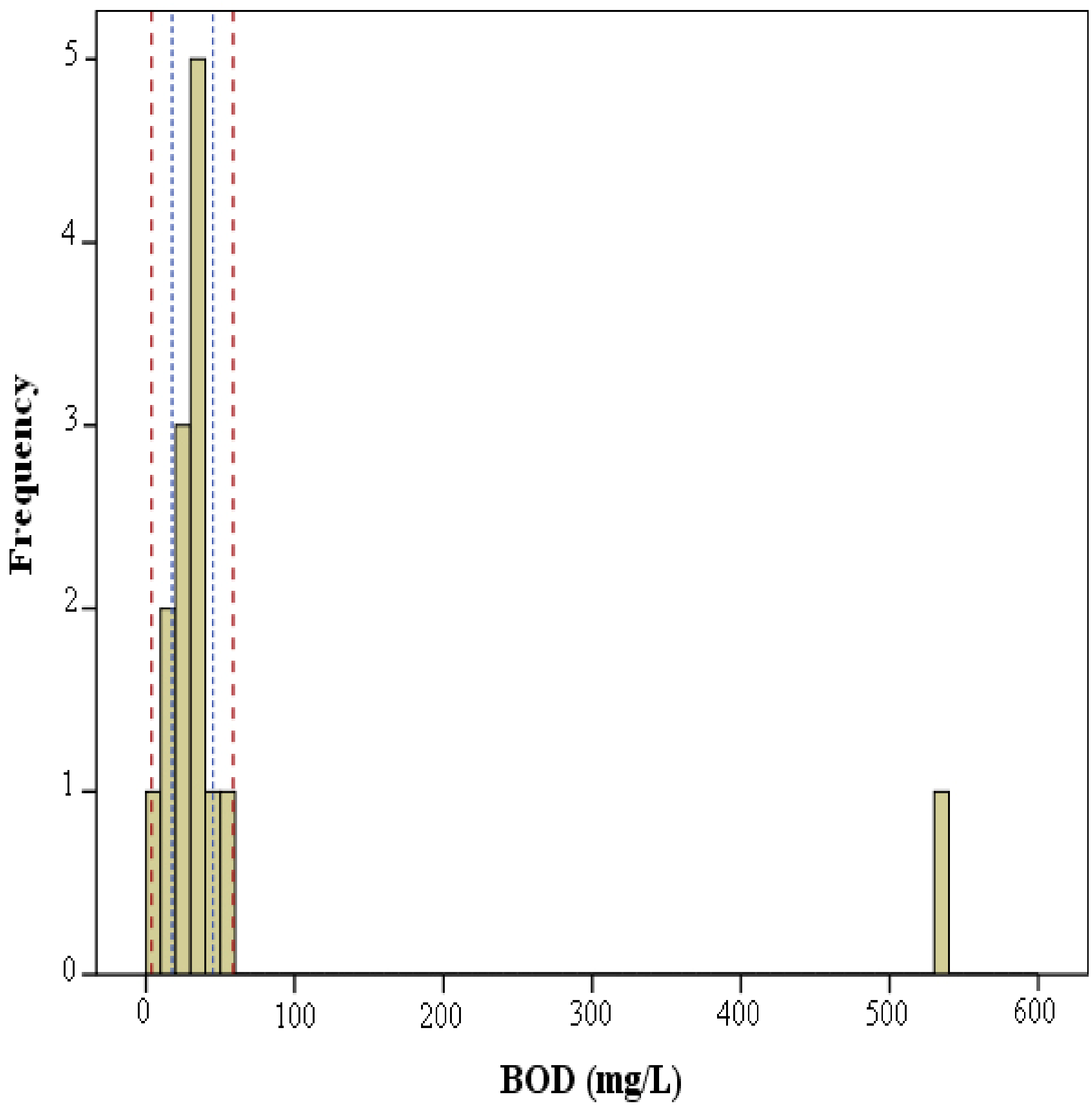

Figure 7: Histogram of biological oxygen demand contents of the surface waters of the studied area, the blue lines show background and the red lines show outliers.

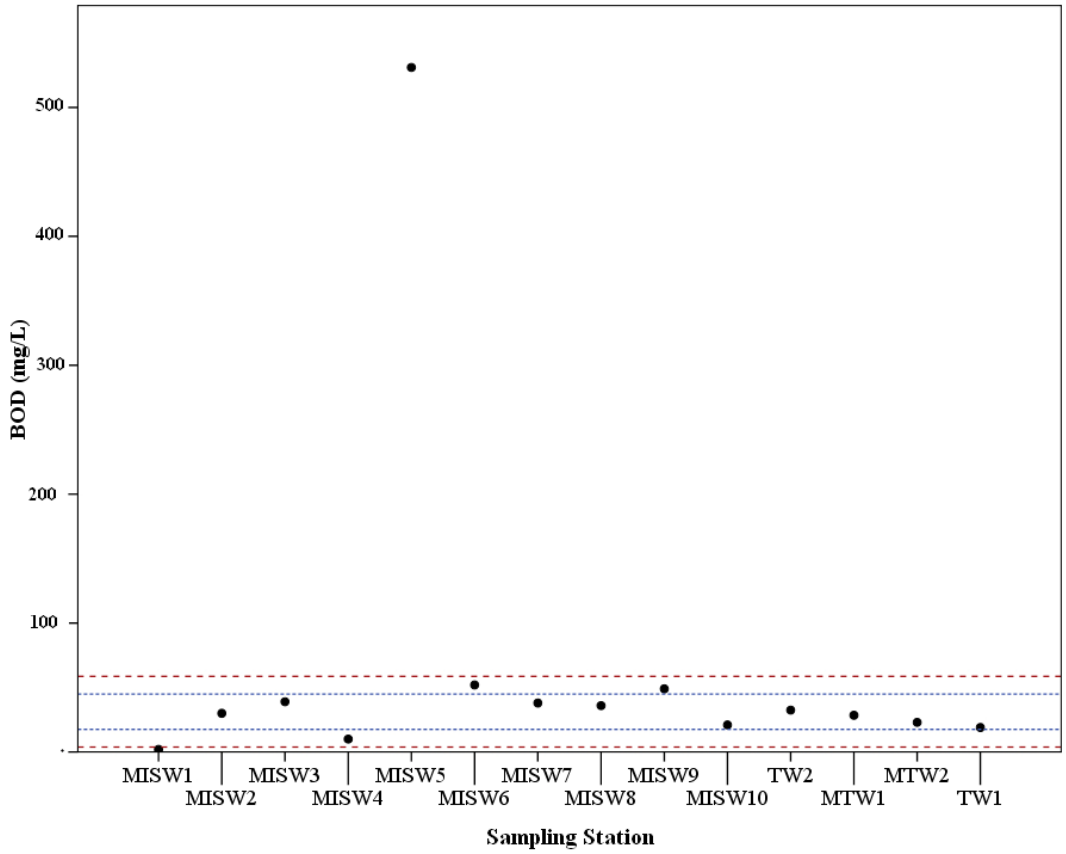

Figure 8: Biological oxygen demand changes in the water samples, the blue lines show background level, and the red line indicates hazard level.

Conclusion

Geochemical investigation done on the surface water resources in the studied area indicates a collection of anthropological and allochtonus sources controlling hydrochemical condition of the water system. The most important effect of presence of outcrops and oil seepages into the stream and river Tembi was entrance of a huge amount of organic compounds into water and reduction trend of water system due to the decrease of such organic compounds. Overall, moving downward of Masjedsoleyman stream, the surrounding becomes more reduced and less acidic. This condition harms life of marine living organisms of the area. hydrochemical faces the stream. hydrochemical faces of the stream are determined with basement lithology of the stream, such that water type of the up stream is calcium carbonate but moving down through the stream it changes to calcium sulfate due to the salvation of gypsum of Gachsaran Formation. Water type of river Tembi is sodium chloride just before junction of the stream which is mainly due to the salty springs over the area. However it changes to calcium sulfate after junction of the stream. Based on the results of principal component analysis sodium, sulfate, chloride, and calcium are the most important factors determining hydrochemical faces of the studied area. On the other hand, presenting water sample on coordinate system composed of the first and the third principal components provides feasibility of classification of samples effectively. The first principal component can be attributed to the salvation of Gachsaran Formation and also mixing with salty waters. Based on the PCA results, sodium, sulfate, chloride, and calcium ions are also found as the most important factors controlling changes in surface water faces; hence these ions were used for cluster analysis of the samples. Results of cluster analysis show that hierarchical clustering based on the Ward repetition method and Euclidian distance on the aforementioned ions has had the most efficiency in the classification of water

samples on the basis of hydrochemical faces. Results of cluster analysis have also had a good consistence with that of papyri chart. Based on the achieved results sodium, sulfate, chloride, and calcium ions are found as the most important parameters controlling the changes in water faces in the studied area.
Surface waters of the studied area are inconvenient for marine animals based on the biological oxygen demand content. Tembi River was classified as one of the extremely polluted rivers in the world. Regarding the amounts of PAHs water and sediments of the studied area are not considered as polluted, however in some cases, some individual compounds have shown little pollution in some sediment samples.

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