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Assessment of the physicochemical and microbiological water quality of Al-Zahrani River Basin, Lebanon

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Abstract

Lebanon is a mountainous country with an area of 10452 km², and it is characterized by a Mediterranean climate having a variable rainfall rate from which a significant amount is manifested as snow. The dense population of Lebanese is located in the coastal zone creating a strong anthropic pressure on the water resources. The civil war (1975-1990) and the post-war period (1990-2000) have led to a shortage in Lebanese watersheds data due to discontinuation of regular measurements.

This study aims at investigating the hydrological response of the Al-Zahrani River Basin by tackling various physicochemical and microbiological parameters that are related to human activities' influence on the water quality in six selection sites. The water tested physiochemical parameters of the basic temperature (T), the potential of hydrogen (pH), electrical conductivity (EC) and total dissolved solids (TDS), the anions $(NO_3^-, SO_4^{-2-} and PO_4^{-3-})$, the cations $(Na^+, K^+, Ca^{2+}, and Mg^{2+})$, and the heavy metals (Cd, Cr, Fe, Cu and Zn). The microbial parameters are Salmonella, Escherichia coli, Total Coliforms, Clostridium perfringens and Staphylococcus aureus. Furthermore, the most polluted site was assessed through conduction of principal component analysis (PCA) statistics.

Microbiological pollution was found at a high level in all sites with a total absence of heavy metals contamination. High nitrate levels were observable in two sites (WadiAkhdar 2 and Zahrani), in addition to a high potassium rate in NabehK farwah. The PCA assessment highlighted the Zahrani site as the most polluted. The main pollution causes are correlated with wastewater discharges and industrial activities.

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Keywords: Watershed, heavy metals, water quality, pollution, PCA, Mediterranean Region.

1. Introduction

The demand for water which is the key element for the survival of human beings is rising gradually. On one hand, the population growth with their associated modern way of living favors a high water consumption rate. On the other hand, scarcity in the water volume is the case due to the arising pollution problems with its adverse effects on natural water resources (Shaban, 2010).

In Lebanon, rivers, natural springs and groundwater continue to be negatively affected by sewage, various household and industrial wastes which are haphazardly discharged without any regulation or control from establishments. All water resources are susceptible to bacteriological contamination in agricultural areas (Naameh, 1995). Moreover, runoff and infiltration of residues from fertilizers and pesticides additionally contribute to their environmental degradation.

Rivers in Lebanese are affected by several sources of pollution resulting in the depopulation of numerous ones. This issue has had negative repercussions on the ecology of these causing many of them to lose their capacity for flow regulation (Comair, 2010) and CAL (1971).

The absence of land management has led to an increase in the erosion rate and a substantial decrease in the regulation of watercourses. This is because sustainable human activities are crucial to the ecological balance of watersheds (DGAC, 1999).

Lebanon has always stood out for having available water resources per capita (1350 m³/capita/ year) than neighboring countries. This is mainly attributed to its topography which favors a moderately high precipitation rate as rain and snow (Shaban, et al., 2004). More than 2000 karstic sources were discovered at the country (MOEW, 2010). The majority are used as a supply of drinking water and for irrigation purposes in the mountainous regions. The sources are known to have similar characteristics as reduced latency, a cloudy water outlet, and maximum floods around the period of March-May (Hakim, 1986). Among these sources which feed Ibrahim River are Afka Spring (1113 km altitude) has the highest flow rate (2.8 l/s), followed by the Roueiss Spring (1800 m altitude) with a flow rate of 1.7 l/s (Hakim, 1986).

The groundwater in Lebanon is studied to a much lower extent than the surface water. The main source of formation and recharge (i.e. feeds water resources by about 60%). The

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source rock massifs of Lebanon consist of limestone which is characterized by fractures and karstification allowing the absorption and infiltration of water from precipitation (Nehme et. al, 2020). The water infiltrates the limestone layers and collide with impermeable rock layers of marl, clay and basalt (Ayoub et al., 2000).

In the coastal region of Lebanon, there are 19 main watersheds, 35 intermediate and 40 minor secondary watersheds (Shaban and Darwish, 2010). The interior region of Lebanon has three major watersheds including Litani River that emerges from Bekaa Plain and outlets in the sea. In other words, it can be described as an interior coastal watershed, where water is captured. Two of these basins contain important rivers which divert water outside the Lebanese territory forming trans-boundary water resources. Within the interior region, it was detected four other transboundary watersheds which are commonly shared with Syria and one restricted hydrographic basin in the region of Yammounah (CNRS, 2005).

It can be considered that there are three large rivers shared between Lebanon and the neighboring regions. One exists in the north and constitutes the border with Syria forming the El-Kabir River. Another one originates from the plain of Bekaa and called Orontes River (named domestically as Al-Assi River) and runs in the northern direction towards Syria. The third one referred to as Hassbani-Wazzani that shared with Palestine at the South forming a major tributary of Jordan River.

The areas of the watersheds excluding the Litani River, the Orontes River and the Hassbani-Wazzani River are relatively small. According to the MEDRUSH model, they can be described as small hydrographic basins or subwatersheds compared to the nested Ladders. This suggests that the entire Lebanese coastal zone constitutes an ordinary watershed that spans several valleys due to the steep slope and the relatively short distance between the thresholds and the outlets (Shaban and Darwish, 2010). This hypothesis is not only limited to Lebanese territory but also extends northward to Syria and to Palestine in the south, which means that the entire area including the regional watershed that supplies water to the Mediterranean.

The surface runoff of the Al-Zahrani River is almost west of the sea. Therefore, the Al-Zahrani River has been described as a coastal watershed since it first entered the sea. According to Shaban (2003), watersheds in Lebanon have been divided into three main types. These are: major, intermediate and minor watersheds. Large watersheds are those linked to rivers with permanent water flows. Al-Zahrani River watershed is considered an important watershed. The main objectives of this study are to present a general overview of the Al-Zahrani River: its route, the limits of its watershed and land use. The present study investigates the sources of contamination of the river with its watershed using statistical methods.

2. Materials and methods

2.1. Study area

In this study, the Al-Zahrani River basin, including major and minor watersheds, which has its source at Nabeh Al-Tasseh Spring between Jarjouh and Al-Lowaizeh (governorate of Al-Nabateyyeh) at 695m a.s.l. The peripheral zones of Jarjouh, Arabsalim, KafarRumman, Habbush, HouminFawqa, Azza, Deir Al-Zahrani, Kfarwah, and Al-Hajjeh end in the Mediterranean on the coast of Al-Zahrani. Al-Zahrani River has an average annual discharge of about 202 Mm³/year (Litani River Authority, 2012), where it collects water in a catchment area of approximately 140 km² (Shaban et al., 2009). The length of the river is approximately 25 km. The region of our study is located in south Lebanon and extends from the source "Nabeh El-Tasseh Spring" to the region "Al-Zahrani" (Figure 1).

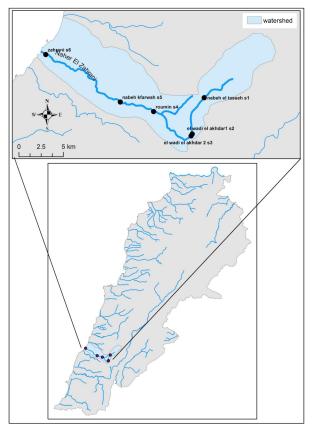


Figure 1. The study area of Al-Zahrani River Basin.

According to the physical and hydrological characteristics, two main parameters are used to characterize the Al-Zahrani watershed:

- Dimensional parameters: which are expressed through the identification of the Al-Zahrani watershed. The dominant form has L shape. The area extends more than 140 km² with an altitude of the threshold or upstream more than 700 m.
- Hydrological parameters: This includes the length of the primary stream around 25 km, and the number of outing games in the sea is 1 game with an average volume of discharged water around 202 Mm³/year.

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The sites that have been selected in this study are Nabeh El-Tasseh Spring, Wadi Al-Akhdar 1, Wadi Al-Akhdar 2, "Roumin, and NabehK farwah. Water samples were collected from six selected sites at the outlet of the Zahrani coast.

These sites represent typical source points for investigating pollution since they are situated at different geographic localities (Table 1).

Table 1. Coordinates of the sampling sites of the study area and the types of activities.								
Sites		Coordinates		Types of economic activities				
Siles	Latitude	Longitude	Altitude (m)	Types of economic activities				
Nabeh El- Tasseh (S1)	33°27′08.3" N	35°31′56.9" E	690	Agriculture, irrigation and tourist area.				
Wadi Al-Akhdarl (S2)	33°24′54.7" N	35°31′07.8" E	447	Agriculture and tourist area.				
Wadi Al-Akhdar 2 (S3)	33°24′47.5" N	35°31′03.0" E	471	Agriculture and tourist area.				
Roumin (S4)	33°26′14.2" N	35°28′17.1" E	435	Agriculture, irrigation and urban zone.				
NabehKfarwah (S5)	33°26′46.9" N	35°25′50.9" E	405	Agriculture, irrigation and tourist zone.				
Zahrani (S6)	33°29′35.5" N	35°20′21.1" E	12	Urban and industrial zone and outlet.				

It is worth mentioning that the study area includes vegetation cover, arable lands and urban areas. The sites are considered as forest areas which are surrounded by vast agricultural areas. Contrarily, the final Zahrani site (S6) which is a coastal one is located in an urban area.



Figure 2. Land cover/ use map of Al-Zahrani River and its surrounding.

2.2. Sampling and treatment methods of water

Water samples were collected from various locations in the river basin of the mentioned sites. To assess adequately the pollution factor from each site 2000 ml were collected. Furthermore, each sample was replicated twice from each site. To conserve water samples polyethylene bottles were used. The method of sampling and collection followed the Standards Methods by WHO and Lebanese standard for drinking water (2016).

The physiochemical parameters of the water were analyzed to quantify its quality. The pH and EC of water samples were determined using a pH /ECmeter (HANNA, number type 8417 serial number 1143732). The concentration of heavy metals was determined using Atomic Absorption using the Atomic Absorption Spectrophotometric method (Spectrophotometer (RAYLEICH - MFX-210) with an air/ acetylene flame and background correction and a deuterium lamp to remove solid impurities before testing (AOAC 974.27). Ammonia, sulfate, nitrate and phosphate were determined using Spectrophotometer Jenway (Type 6300 serial number 6734. Several microbiological estimations have been conducted in this study such as total colony

counts, total coliforms group, Escherichia Coli, Salmonella, Staphylococcus aureus and Clostridium Perfringens.

2.3. Statistical analysis

The Spearman correlation examines whether there is a relationship between the rank of observations for two characters X and Y, which makes it feasible to detect the existence of monotonic relationships as increasing or decreasing, and whatever their precise form if linear, exponential or power. This coefficient is appropriate when one or both variables are skewed or ordinall and is robust when extreme values exist.

Data analysis by principal component analysis (PCA) is performed by SPAD software. PCA is a technique for reducing the dimensionality of numerical datasets that increase interpretability and at the same time minimize information loss. It creates new uncorrelated variables that successively maximize the variances and exploratory tools for data analysis. PCA allows the reduction in the number of variables, and detection the type of structure in the relationships between variables, which amounts to ordering the variables. In this study, two potentials of this statistical tool were applied. Finally, the unsupervised learning k-means clustering was used to classify the sites.

4. Results and discussion

4.1. Physical and chemical assessment

The results obtained revealed that the temperature, pH, EC and TDS in the water samples of the underground tanks conform with the permissible limits of WHO (Table 2). The nitrate concentrations were significantly high in both sites of Wadi El Akhdar 2 and Al-Zahrani concerning the other ones. The sulfate concentrations ranged between 3 and 35 mg/L with the highest concentration detected at Al-Zahrani (42.75 mg/L). All the sites have sulfate concentrations below the maximum acceptable WHO threshold (250mg/L) indicated the absence of any sort of contamination from this parameter. The same applies to calcium and magnesium cations (Table 2). The average concentration of sodium at Nabeh El Tasseh, Kfarwah, Roumin and Zahrani surpassed the acceptable WHO standard (>150 mg/L), whereas the potassium level of Kfarwah exceeded the maximal allowable limit by 1mg/L (Table 2).

Element	Average	Standard WHO	Situation
pН	7.59	(6.5-8.5)	Basic media:Wadi al akhdar 1&2, Zahrani
EC (ųs/cm)	220	1500	Acceptable
TDS (ppm)	229	<1000	Acceptable
Nitrate (mg/L)	0.193	0.2	Only Al-Zahrani not accepted:0.67 mg/L
Sulphate (mg/L)	13.8	50	No contamination
Calcium (mg/L)	54.8	250	No contamination
Magnesium (mg/L)	18.52	50	No contamination
Sodium (mg/L)	168	150	Nabeh El Tasseh : 170 Nabehkfarwah: 160 Roumin : 190; Zahrani: 192 mg/L
Potassium (mg/L)	2	12	Roumin : 13mg/L

Table 2. Physical	and chemical	parameters of wat	er samples

4.2. Microbial Assessment

The results of this study revealed a high level of microbial contamination in most of the investigated sites. Thus, Salmonella and staphylococcus aureus were highly detectable in all sites with figures significantly above the WHO threshold limits (Table 3) (Figures 3 and 4). Moreover, Nabeh El Tasseh Spring, Roumin and Zahrani zones recorded

exceedingly high levels of total coliforms (>10000) (Table 3) (Figure 5). Total coliforms do not usually cause a disease, but their presence indicates contamination of the water by other more harmful bacterial microorganisms (Subin, 2013). No contamination from E.Coliand Clostridium perfringens was detected in any site.

Table 3. Microbial quality of water samples.							
Sites	Coliforms totaux	EC	Salmonella	Staphylococcus aureus	Clostridium perfringens		
Nabeh El Tasseh Spring	>10000	0	2000	20000	0		
El Wadi Al Akhdar 1	1200	0	2200	2400	0		
El Wadi Al Akhdar 2	1000	0	300	200	0		
Kfarwah	1000	0	10	100	0		
Roumin	>10000	0	4300	4200	0		
Zahrani	>10000	0	>10000	20000	0		

This study highlight on the danger of using this microbial polluted water for drinking purposes due to the associated negative impacts on human health and the environment regarding the norms of WHO.

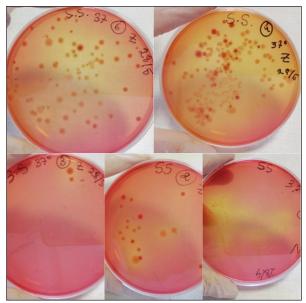


Figure 3. Photomicrograph showing Salmonella in the culture medium.

Figure 4. Photomicrograph showing Staphylococcus aureus in the culture medium.

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Figure 5. Photomicrograph showing total Coliforms in the culture medium.

4.3. Correlation analysis of water quality parameters

Water quality parameters were evaluated using the Spearman Correlation (Table 4). Total coliforms and Staphylococcus aureus are directly correlated with the conductivity of water and the total dissolved matter. Thus, as the concentration of dissolved solids increases, the conductivity factor mounts parallel causing an increase in the Total coliforms and Staphylococcus aureus counts. Salmonella is highly susceptible to pH mode. As the pH becomes more basic, the presence of Salmonella elevates.

able 4. Correlation between bacteria and physicochemical parameters									
	pН	EC	TDS	Nitrate	Sulfate	Ca	Mg	Na	K
ColiformesTotaux	Weak	Very strong	Very strong	Very strong	Average	Strong	Average	Strong	Average
Salmonella	strong	No Relation	No Relation	Very strong	Average	Strong	Very strong	Strong	Average
Staphylococcus aureus	Weak	Strong	Strong	Very strong	Average	Strong	Average	Strong	Weak
Very Strong correlation: r>0.8				•	Average correlation : 0.2 <r<0.5< td=""><td></td></r<0.5<>				
• Strong correlation : 0.5 <r<0.8< td=""><td>•</td><td>Weak correl</td><td>ation: 0<r<0< td=""><td>.2</td><td></td><td></td></r<0<></td></r<0.8<>				•	Weak correl	ation: 0 <r<0< td=""><td>.2</td><td></td><td></td></r<0<>	.2		

Excess of the magnesium is not harmful for kidneys, but a prolonged overdose can have a laxative and hypertensive effect (Rylander, 2014). However, an increase in magnesium concentration results in another increase of Salmonella in the water

4.4. Analysis of the Main Components

The principal component analysis is a statistical procedure that allows summarizing the information content in large data tables through a smaller set of "summary indices" that can be more easily visualized and analyzed (Mahapatra, et. al, 2012). The analysis considered on three bacteria as illustrative variables. The eigenvalue corresponds to the inertia intercepted by the factorial axis, obtained by the diagonalization of the inertia matrix, from which we choose the largest eigenvalues λi , which helps to determine the numbers of factorial axes for establishing a

reduced dimension subspace. The choice of axes carrying the maximum inertia is equivalent to the construction of new variables that are associated with the axes of maximum variance. The principal axes of inertia are called the direction axes; the eigenvectors of the matrix of variancescovariance's normalized to 1. The number of axes is decided based on the Scree Plot, the Kaiser criterion, the modified Kaiser criterion and the Anderson criterion.

4.4.1. Scree plot

A scree plot is a graph that displays the proportion of variance explained and the number of principal components found. Choosing the number of principal components by eyeballing the scree plot and identifying a point at which the proportion of variance explained by each subsequent principal component drops off (Figure 6).

		-+		+		+	+
N	UMERO	Ì	VALEUR PROPRE	Ì	POURCENTAGE	POURCENTAGE CUMULE	
	1	1	6.3508 1.6947		70.56	1 70.56 1 89.39	· · · · · · · · · · · · · · · · · · ·
	3	÷.	0.7511	i	8.35	97.74	****
	4	1	0.1727	1	1.92	99.66	***
	5	1	0.0308	1	0.34	100.00	*
	6	1	0.0000	i	0.00	100.00	*

Figure 6. The graph of scree plot.

It can be noticed from the scree plot in Figure 6 that the point at which the proportion of variance explained by each subsequent principal component drops off from the second principal component.

4.4.2. Kaiser's criterion

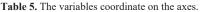
The number of axes was taken according to Kaiser's criterion modified by Sapota and Karlin. In this case, the main components were retained corresponding to the eigenvalues λ such as: $\lambda > 1 + 2\sqrt{((p-1)/(n-1))}$, where p=9 the number of active variables, and n = 6 the number of individuals. According to the Figure 6 the value of $\lambda 1 = 6.3508$ and $\lambda 2 = 1.6947$, therefore it is used 2 axes to collect and classify most of the datasets that are explained at 89.39% of the revealed results.

4.4.3. Variables Coordinates and Correlation Circle

The correlation circle shows an effect on the first axis since the first main component is negatively correlated with all the variables that give information to this axis (Table 5). The second component is positively correlated with pH, EC, Mg, TDS and Nitrate, and negatively with K, Na, Ca, and Sulfate.

It can be noticed on the graph of the illustrative and active variables that the bacteria Salmonella and Staphylococcus Aureus influence negatively on axis 1, so there is a correlation with these bacteria with TDS, Nitrate, Ca, Mg and sulfate. The total coliform bacteria negatively influences on axis 2, and this evidences a correlation with Na (Figure 7).

Elements	Axe 1	Axe 2
РН	-0.13	0.53
EC	-0.38	0.18
TDS	-0.39	0.09
Concentration of Nitrate	-0.39	0.13
Concentration of Sulfate	-0.37	- 0.08
Concentration of Ca	-0.38	- 0.19
Concentration of Mg	-0.39	0.12
Concentration of Na	-0.31	- 0.46
Concentration of K	-0.05	- 0.63



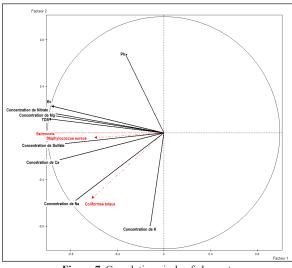


Figure 7. Correlation circle of elements.

The individuals who positively influence on axis 1 areNabehKfarwahSpring with a contribution of 6.69, Wadi Akhdarl with a contribution of 7.46, Wadi AKhdar2 with a contribution of 5.12, while Roumin has the smallest contribution on axis 1 with 1.19. The individuals who negatively influenced on axis 1: Al-Zahrani with a large contribution of 74.86 and Roumin with a contribution of 1.19 (Figure 8).

On axis 2 theWadiAlkhdar 1, wadiAlKhdar 2 and Al-Zahrani influence positively on axis 2 with contributions from 21.79, 11.01 and 6.2, respectively, while Roumin, Nabeh el Tasseh Spring and NabehKfarwah Spring influenced negatively on axis 2 with the contributions of 56.16, 3.73 and 1.10, respectively.

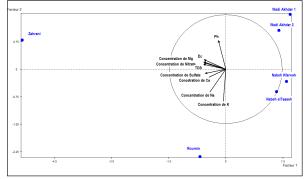


Figure 8. Graph showing the sites along with the correlation circle.

4.4.5. Clustering of sites

K-means clustering was used to classify the sites into clusters. It is the process of partitioning the entire data set into disjoint groups or clusters that are based on the pattern in the datasets, so the specific clustering criteria are optimized. It can be noticed that the sites can be classified into three clusters (Figure 9).

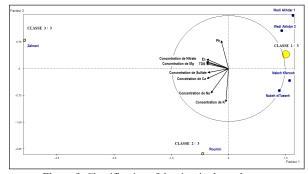


Figure 9. Classification of the sites in three clusters.

The elements which affected the clustering of the sites are: EC, TDS, Nitrate and Magnesium, the concentration of these elements in the clusters are all within WHO standards, but according to the correlation table, EC, TDS, Nitrate and Magnesium have a strong correlation with Total Coliform Bacteria, Salmonella and Staphylococcus aureu. It can be noticed Staphylococcus aureu that has a medium correlation with Mg. It can be concluded that all the sites are contaminated by three types of bacteria and that the Al-Zahrani Site is the most contaminated one since it represents the highest average for the four elements. The second cluster contains Roumin site, it is the only site that has a high concentration of Potassium. The least affected cluster is the one having sites WadiAkhdar 2, NabehKfarwahSpring, NabehElTassehSpring, WadiAkhdar 1, since it has lower averages.

5. Conclusions and recommendations

Generally, the discharge of Al-Zahrani River is decreasing over the last few decades. This may compose an external element affecting the water balance of Al-Zahrani River and its basin. This element is believed to be the limited human impact of water consumption, as mentioned earlier in connection with the large number of villages that benefit from drinking water drawn from the source of Nabeh Al-TassehSpring by large-scale water supply network and because of unlicensed wells in the river basin.

The coastal river in Lebanon appears to be a very important element that could be useful in various active sectors of the population's life, from domestic uses to agriculture and industrial. Emphasis should be paid to the common surface and groundwater resources and their hydrological characterization in this area. The Zahrani River Basin is a typical example showing the absence of integrated studies and management approaches and lack of comprehensive datasets. This study helps to provide some of the comprehensive information necessary for the management of the Al-Zahrani River and its watershed and to highlight the hydrological and flow characteristics of the river. The results of this study are essential for the continuation of the future proposed works on the Al-Zahrani River basin. These include water strategies and policies, notably in the view of dams for the construction, and the supply canals and the abstraction of groundwater.

In this study, six sites were studied along the Al-Zahrani River. It is based on the evaluation of the physico-chemical parameters of water (T, pH, EC and TDS), anions of NO_3^{-7} , SO_4^{-2-} and PO_4^{-3-} , cations of Na⁺, K⁺, Ca²⁺, Mg²⁺ and metals of Cd, Cr, Fe, Cu and Zn, in addition to the evaluation of the levels of bacteria as Salmonella, Escherichia coli, Total coliforms, Clostridium perfringens and Staphylococcus aureus.

It obvious that the sites are not contaminated with Mg, Ca and PO_4^{-3} , since their concentrations are generally lower than the standards set for the WHO, while they are contaminated by Nitrate, Sulfate, Potassium, Sodium and bacteria since their concentrations are higher than the standards in certain sites. This pollution is linked to the use of fertilizers in agriculture on one hand, and a mixture with sewage on the other hand. Thus, the quality of the water is deterioratedat these sites. However, the values of heavy metals in the water were not detected. The microbiological analysis indicated that all sites are contaminated by total coliforms that have a very high contamination, which exceeds the limit acceptable by WHO. The contamination with Salmonella and Staphylococcus aureus are high, which indicates that all the sites are discharges of wastewater and agricultural waste.Onthe other hand all the sites are not contaminated by Escherichia Coli and Clostridium perfringens. The results of the physico-chemical parameters for the values of TDS, EC

and pH for all sites are acceptable. The PCA of the statistical analysis showed that the Zahrani site is the most polluted.

Finally, legislation must be made to control and protect the Lebanese watersheds against pollution including water strategies, construction of wastewater treatment unit and adopting efficient irrigation approached in the agricultural areas.

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