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Physiochemical and Microbial Assessment of Water Quality in the Upper Litani River Basin, Lebanon

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Abstract
Water resources in Lebanon are witnessing serious challenges and reached depletion. One of the major challenges is the quality deterioration, which is accompanied with uncontrolled resources management, and thus the increasing demand. There are several consumption aspects, mainly the domestic, industrial and irrigation. Yet, exploitation of water resources in Lebanon implies both the surface and groundwater. However, surface water resources are most used due to the ease of exploitation processes, and more certainly water from rivers. Typically, the Litani River is the largest one in Lebanon. The river has been lately subjected to several aspects of deterioration in its quality. This includes the major physiochemical characteristics. This study aims to assess the seasonal variations in water quality in the Upper Litani River Basin, including the Qaraaoun Lake. Samples were collected from particular sites along the river, and at several dates during the years of 2010 and 2011. The carried analysis implies the physical (pH, T°, TDS, Ec), chemicals (Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NH_3^+, NO_3^-, PO_4^{2-}, K^+, BOD_5 and COD, Heavy metals (Fe, Ni, Zn, Cu, Cr, Al, Ba, Pb, Mn) and microbiological parameters. This resulted numeric data are being compared with WHO guidelines. In addition, PCA was applied to evaluate the data accuracy. We can conclude that the variables used are very efficient and the dry season shows the worst water quality with nitrate, metal and microbial enrichments.
Keywords: Water Contamination, Human Interference, Litani River, Principal Component Analysis.

1. Introduction

Water is the essential element for tremendous uses and it has a vital role in human daily activities. However, there are many challenging conditions govern water supply-demand management, and yet water becomes a rare commodity in some cases. The recent changing climatic conditions accompanied with population growth have become a geo-environmental issue of concern after water problem has been raised on the regional and international levels. This is well pronounced in arid and semiarid regions where water resources are rare and the per capita does not exceed 500 m^3/ year in many regions.

Compared to the Middle East and neighboring countries, water resources in Lebanon are still available in sufficient amounts. The per capita exceed 1350 m^3 a year (Shaban, 2011). However, more than 8.8 billion m^3 of the rainwater falling, but only 2.2 billion m^3 are available for use and this rain is mainly concentrated in winter months from October till April (Qumair 1998). The average rainfall rate in Lebanon ranges between 800 mm and 1400 mm annually and may decline to few hundred millimeters in some regions like in the northern Bekaa plain (Hajjar 1997). In addition, snow at the higher altitudes often covers more than 2000 km^2 and feeds the existing springs and rivers. Thus, Lebanon encompasses fifteen rivers and more than 2000 major springs. There are twelve coastal rivers and three inner ones that area created from the Bekaa plain.

The Litani River flows from the Bekaa plain southward, and diverted in the south towards the Mediterranean Sea (Figure 1). It is the largest Lebanese rivers with a length of about 172 km and basin area of 2186 km^2. The estimated discharge from the Litani River is about 360 million m^3/ year (LRA, 1999).

The average water discharge in the (Upper Litani Basin) ULB is highly fluctuated between winter and summer as shown in the Table 2. During the summer season, the litany ULB often becomes dry. Figure 1 shows the annual discharge rate along five major stations along the ULB. Moreover, the impact of climate change is seriously influenced the river basin. Impact of sewage releases could be greatly attenuated with higher effluents. However, under low runoff rate, sewage pollutant loading of the same magnitude could render water hazardous for most uses.

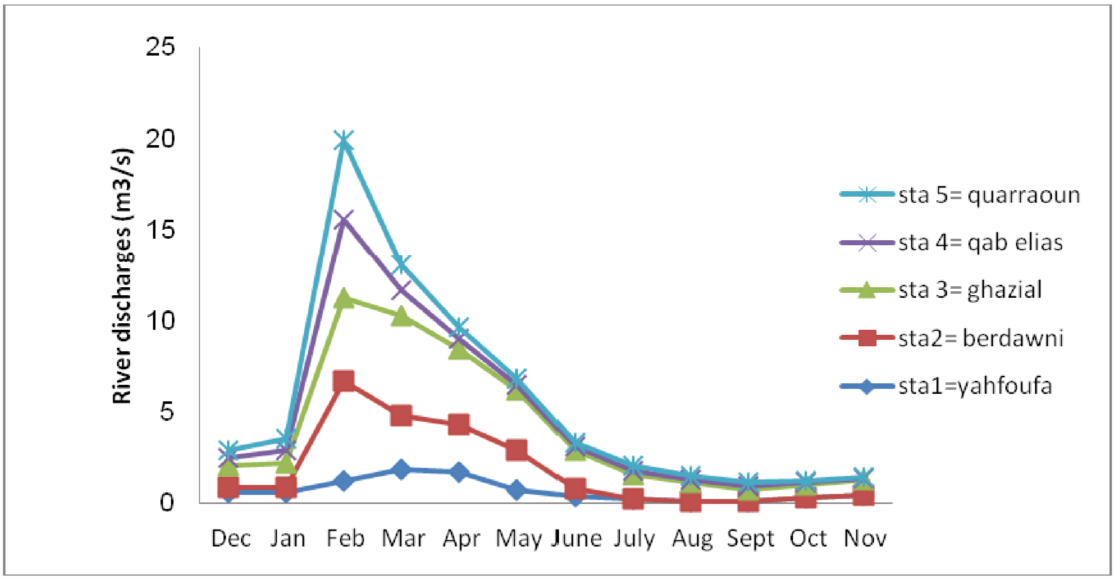

Figure 1: River discharges 2010-2011

The figure shows that the discharges in these stations are at their climax in February and March.

The geomorphologic setting of the Litani River Watershed shows two major units. These are the Upper Litani Basin and Lower Litani Basin, which are joined in the middle part of the watershed at the Qaraaoun Lake. This lake, with an area of about 4km^2 and capacity of 220milion m^3, has been artificially executed since the 1956.

The long distance that the Litani River crosses among a miscellany of land uses, notably the agricultural lands, makes it vulnerable to many pollution aspects. Therefore, pollutants are loaded into the rivers from industrial and municipal wastewater and even from the solid wastes, whilst agricultural pollutants are tremendous, with a special emphasis those derived from fertilizer. Therefore, components of pollution can be diagnosed as follows:

- Progressive urbanization (metals such as Fe, Zn, Cu, Cd, Pb, bacteria),
- Socio-economic growth (bacteria, metals),
- Agricultural activities (nitrate, nitrite, Phosphate, sulfate)
- Tourist and car pollution (bacterial, metals: pb, Cd, ..)
- Development of industries (metals).

These pollutants strongly affect flow rates and the concentration of river pollution. (Fawaz, 1992; Jaber, 1993; Hajjar, 1993). Both solid and liquid wastes are directly disposed into the river tributaries without any treatment (Jurdi, 1992, 1998); especially in inland villages and this is the common case of the ULB.

The Qarraoun Lake was considered as open water systems with regular inflows and outflows and could be compared to the water of the LRB. As such, periodical physical, chemical and microbiological analysis of these water systems is generally necessary (Oxfam technical Brief, 2006).

The objective of this study is to evaluate the physical, chemical and microbiological characteristics of water in the ULB, as well as in the Lake of Qaraaoun. The study targets to monitor the seasonal variations in water quality at the ten representative selected sites (Fig. 2 and Table 1). These sites are named as:, El Ouleik (Site-1), Houch el rafika (Site-2), Bednayl (Site-3), Berdawni 1(Site-4), Berdawni 2(Site-5), Darzanoun (Site-6), Masabki (Site-7), Qarraoun 1(Site-8), Qarraoun 2 (Site-9), Qarraoun 3 (Site-10).

The description of site's location will help identifying the sources of physiochemical and microbiological pollutants. Consequently, recommendations can be well illustrated.

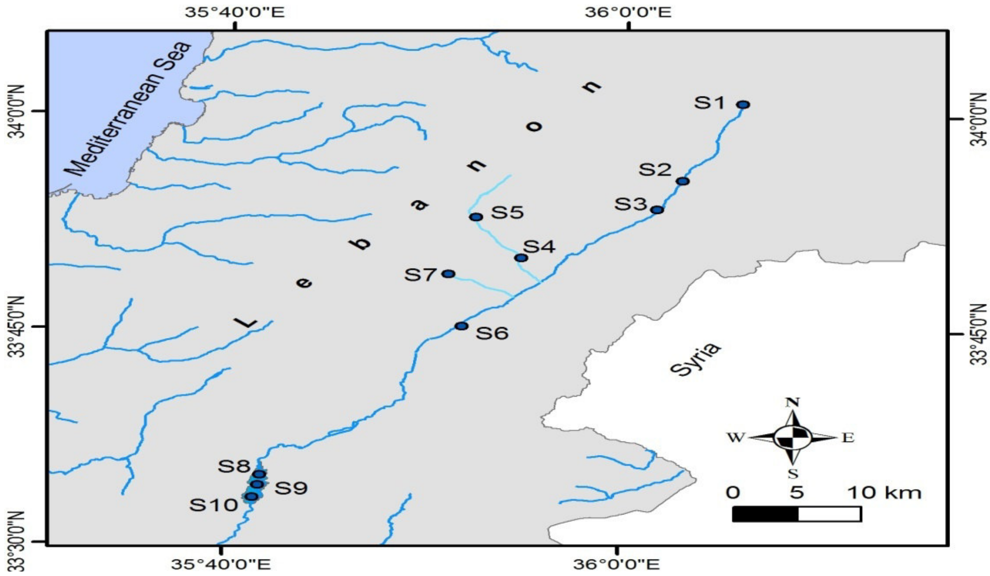

Figure 2: Location of sites in the Upper Litani River Watershed and Qarraoun.

2. Material and methods

2.1. Sampling and data collection

Water samples were collected on seasonal bases; i.e. Winter (February), Spring (May) and Summer (September) from the eight determined sites from the primary watercourse of the Upper Litani River; While, three samples were collected from the Qaraaoun Lake. Clean polyethylene bottles were used to conserve the water samples, and they were presoaked overnight in 10% (v/v) nitric acid; and then rinsed three times with distilled water. Samples for analysis were picked from the surface using two 1 L polyethylene bottles. While, the selection of samples from the lake was distributed at three geographic points, these are: at contact between the river and the lake, middle of the lake and at the outlet of the lake.

Each bottle was supplied by 2 % of nitric acid to acidified (pH < 2) and stored in portable coolers before transport them to the laboratory. For microbiological analysis, 500 ml were collected in borosilicate glass bottles. Physical parameters were in-situ tested including: pH, T°, Total Dissolved Solid and electrical conductivity. The instrument (Hanna instruments: pH Meter Model HI 98103 and Hach Model 44600 Conductivity/TDS Meter*)* immersed into lake for fifteen minutes where it is able to take a measurement every minute. The method of sampling and collection followed the Standards Methods WHO and Libnor (1992). In order to facilitate the graphic representation of numeric results, the sampling were numerated as in Table 1.

Table1: Number of sampling in each site over the three seasons.

Sites	Coordinates			Winter (February)	Spring (May)	Summer (September)
	Latitude	*Longitude*	Altitudes m			
Ouleik	36º05'54	34º00'53	1000	1	11	21
Houch el Rafika	36º02'56	33º55'32	957	2	12	22
Bednayl	36º01'40	33º53 '31	925	3	13	23
Berdawni 1	35º53'07	33º52'00	1150	4	14	24
Berdawni 2	35 º 54'49	33º50'05	923	5	15	25
Darzanoun	35º38'55	33º46'40	890	6	16	26
Masabki	35º51'09	33º48'56	934	7	17	27
Qarraoun 1	35 º 42' 19.	33 º 34'9.6	840	8	18	28
Qarraoun 2	35 º 42'11	33 º 33'58.6	846	9	19	29
Qarraoun 3	35º41'06	33º34'04	857	10	20	30

2.1. Experimental analysis

The rest of parameters were determined in laboratory following the Standard Methods WHO and Lebanese Standards Institution (Libnor) (1992) as follows:

- pH measurements were taken with a Hanna instruments pH Meter Model HI 98103, with a pH range from 0.00 to 14.00 and a resolution of 0.01 pH. The accuracy of the pH meter is ±0.2 pH at 20ºC.
- Temperature, electrical conductivity (EC) and total dissolved solids (TDS) were measured directly in-situ using Hach Model 44600 Conductivity/TDS Meter (resolution Conductivity 0.1 $\mu S\ cm^{-1}$, TDS 0.1 $mg\ L^{-1}$).
- Water samples were filtered through an 0.45 μm filter (Merck) and divided into two parts: one bottle was acidified with nitric acid (pH < 2) and stored at 4 ◦C for metal analysis (Fe, Zn, Cu, Cr, Al, Ba, Pb, k, Ni, Mn) by atomic absorption spectrophotometer with an air/acetylene flame and background

correction with a deuterium lamp to remove solid impurities before (AOAC 974.27).

- The Hydride generator Mercury vaporizer unit was used to detect Arsenic, Selenium and Mercury.
- IRI Spectrophotometer Method: EPA 352.1 and EPA 354.1, was used to measure nitrate NO_3, Nitrites NO2. While, ISO 6878:2004 was used to determine the total phosphates; the Sulphate was determined by AOAC 973.57.
- The alkalinity was determined by the phenolphthalein method (ISO 7980:1986) as calcium carbonates $CaCO_3$.
- The biochemical oxygen demand, 5 days, BOD_5 as O was detected by (EPA 405.1) and by (ISO 6060:1989), the chemical oxygen demand, as O.
- All water quality parameters are expressed in ppm except pH, EC (μS cm^{-1}), temperature (° C), the CT, GMA, staphylococcus, salmonella (MPN/ 100 ml) and CF (MPN/ 200ml)

2.3. Microbiological analysis

Water samples for the microbiology test were collected from the ten selected sites during the three seasons dry, wet and mid wet. Standard method Total Coliforms NF EN ISO 9308-1. ISO 4831 & R1/FT/04 was employed to determined the total Coliforms and (NF EN ISO 9308-1) for FC, salmonella by (NF V08-052), Staphylococcus aureus (NF V08-057-1/2 R1/FT/O6), clostridium per-fringes.

3. Results and Discussion

Water-quality monitoring of the ULB and the Qarraoun Lake was regularly conducted over a period of years (2010- 2011) at the ten sites. All the samples were analyzed for various parameters and the results of physic-chemical, heavy metals and microbiological properties obtained during the study was found inconsistent with the standard values of water quality given by the World Health Organization (WHO, 2008) and Libnor (1999).

The water of ULB and the Qarraoun Lake is characterized by $CaCO_3 > K^+ > Mg^{2+} > Na^+ > Fe^{2+} > NH_4^+ > Cu^{2+}$: $NO_3^- > Cl^- > SO_4^{2-}$ (Table 2). Heavy metals such as Cd, Ni, Zn, Al, Ba, Mn are not detectible, and Clostridium perfigens was not detectible.

For data analysis, three different multivariate statistical techniques were applied. The statistical computations of the physico-chemical parameters was performed using the SPSS software (SPSS for Windows, version 16, correlation matrix), Excel 2007 and Principal Component Analysis (PCA) were applied to evaluate both the spatial and temporal variations in water-quality data matrix of the Upper Litani River without losing important information.

Table 2. Physical, Chemical, heavy metals in mg/ l and Microbial constituent of the water at various stations in the UBL.

Parameter	**Average values (range)**			**WHO (2006)**	**Libnor (99)**
	Winter (February)	Spring (May)	Summer (September)		
PH	7.2-8.0	7.1-8	7.3-8.4	6.5-8.5	6.5-8.5
T	13-17	13-19.1	19.5-24.1	15.57-21.10	15.57-21.10
EC	264- 884	471- 597	384-1484	Max 1500µs/cm	Max1500µs/cm
TDS	230-297	226-350	159- 321	<500 mg/L	<500 mg/L
NH_4^+	0.01-0.30	0.2-7	0.08-12	Max 0.5 ppm	<500 mg/L
NO_3^+	1.80-4.05	0.02-12.3	0.08-12	Max 50 ppm	45 ppm
NO_2^+	0.08-3.34	0.1-0.4	0.1-1	Max 0.1ppm	0.05 ppm
PO_3^{4+}	0.2-0.5	0.13-0.5	0.50-0.89	Max 1 ppm	1 ppm
K^+	20.79-51.99	2.7-5.1	4.5-7.6	Max 12 ppm	12 ppm
Cl^-	120-170	0.5-55	0.5-81	Max 250 ppm	200 ppm
SO_4^{2-}	19.1-51.4	0.03-0.1	0.04-0.4	Max 250 ppm	250 ppm
$CaCo_3$	200-266	210-370	250-370	Max 200 ppm	200 ppm
Na^+	0.1-7.8	0.1-9.7	0.1-8.7	Max 150 ppm	150 ppm
Cr^{3+}	0.3-0.5	0.02-0.1	0.01-0.09	0.05 ppm	0.05 ppm
Cu^{2+}	0.05-0.10	0.05-0.1	0.05-0.10	1 ppm	1 ppm
Fe^{3+}	0.11-0.4	2-3.5	2-7.2	0.3 ppm	0.3 ppm
Mg^{2+}	1-6	2-9	2-7	50 ppm	50 ppm
BOD_5	5-7	5-29	5-12	25 ppm	25 ppm
COD	20-30	20-90	20-97	25 ppm	25 ppm
Staph	0-20000	250-5000	1000-5000	5 ppm	5 ppm
CT	0-2600	0-300000	0-300000	0.01 ppm	0.01 ppm
CF	0-1000	0-300000	0-300000	0.2 ppm	0.2 ppm
Sal	0	0-1000	0-1000	0.5 ppm	0.5 ppm
GMA	0-240000	0-300000	0-300000	0.02 ppm	0.02 ppm
Averages of Discharges	20.94 m/s^3	13.01 m/s^3	8.01 m/s^3		

**(Cd, Ni, Zn, Al, Ba, Mn, Clostridium Perfiregens: Not Detect)

3.1. Correlation matrix

The temporal variations of the river water-quality parameters were first evaluated through season-parameter correlation matrix using the Pearson correlation coefficient. The correlation matrix determines the variance of each constituent can be explained by the relationship with each of the others. Therefore, the following remarks were resulted:

- **pH** tends to be at acceptable levels, and it is almost basic. Some sites in the ULB have pH ranges from 7.1 to 8.1, and in the sites of the Qaraaoun Lake, the pH has high values and approach to 8 or 8.4, which is typical of water bodies underlain by carbonate rocks (Stumm and Morgan, 1996; Korfali and Davies, 2000). The prevalence of carbonate sedimentary rocks in the Qarraoun reservoir drainage basin is reflected in the water chemistry. pH showed positive correlation with potassium, chloride, sulfate, Cr, GMT, salmonella.
- **Temperature (T)** measures the intensity of heat stored in a volume of water, experimental results show the variation in temperature which is due to the variation of seasonal heat change, and it indicates multi-source water effluents into the river and the Lake.
- **Specific conductivity** varied from 264 to 1484µs/cm. About 90% of the specific conductivity values are higher than the acceptable level (i.e. 400 µs/cm). It was detected that Houch El Rafika, Bednayl and Dairzanoun has high levels of contamination over all seasons. In the dry season, the higher level of conductivity was observed in Dairzanoun, and can be related to the presence of many industries which release wastewater in this part of the river. In the Lake high level of conductivity was detected in the upper western part (in the enter part of the lake). Table 3 shows the significant correlation of Ec with all the parameters. For examples, The correlations between EC and TDS ($r = 0.69$, $p= 0.00 < 0.05$) are moderate and significant, which means that the concentration of ion is high and this suggest the contamination and in summer the quantity of water is not enough to dilute the pollutants and in this case, specific conductivity should be correlated. TDS, EC and nitrate ($r = 0.32$,) are positive but not significant $p> 0.05$ and the positive correlation between EC and the bacteria such as, salmonella, CT, staphylococcus CF, and GMA, show that only significant correlation found between EC the first two one and this meaning that the bacteria nourish the ion or the nutrient. There is positive correlation, but it is not significant between EC and BOD and COD which meaning that is not due to the addition of waste.
- **Total Dissolves Solids (TDS)** refer to any minerals, salts, metals, cations or anions dissolved in water. This includes all elements present in water other than the pure water (H20) molecule and suspended solids. A TDS meter is based on the electrical conductivity (EC) of water, in this study the EC is the double of TDS. The correlation between TDS and all the chemical and heavy metals are low and not significant, and it is moderate only with Cr, but it was due to hazard.

3.2. Correlations

Chemicals compositional relations in water show that Ammonium has a significant correlation with NO_3^-, CaCO3, Na^+, Cu^{2+},Fe^{3+}, and CF. The ammonia/Nitrate association ($r = 0.45$, $p < 0.01$) indicates inputs of fertilizers and other agricultural sources. Nitrate has a moderate correlation with sulfate, Cl^- and K^+ ($p < 0.01$). K^+ has strong correlation with Cl^-, SO_4^{2-} and Cr. The potassium/sulfate association is due to the inputs of potassium sulfate as fertilizers. Chloride has a moderate correlation with SO_4^{2-} and Cr. SO_4^{2-} showed a strong correlation with Cr^{3+} and moderate with staphylococcus. $CaCO_3$ has a moderate correlation Na, Fe and Cu. Na has a moderate correlation with Cu^{2+}, Fe^{3+}, and good correlation with BOD_5, COD and this significant association can explain by the reject or discharges of sewage and domestic wastewater. The uniform correlation between Fe^{3+} and CT and CF can be explained by industrial discharges from dying and tanning, mineral processing and electroplating and wastewater discharges. In addition, correlation between DOB5 and DOC was moderate. CT and CF ($r =0.658$, $p < 0.05$). CF and salmonella ($r =0.53$, $p < 0.05$) and CF and GMA ($r =0.59$, $p < 0.05$), can indicate inputs of sewage and municipal solid wastes in the lack of treatment planets. As the correlation is important, it means that seasonal effects and localization are important and need to evaluate the evolutions in space and time.

3.3. BOD5 and COD in different locations of the ULB

To evaluate the degree of contamination of the ULB and the Qaarraoun Lake, the values of biological oxygen demand (BOD_5; Norms 25 mg/L) and chemical oxygen demand (COD; Norms 25 mg/L) were measured during the three seasons Winter (February), Spring (May) and Summer (September) from the eight determined sites from the primary watercourse of the Upper Litani River Basin; in addition, three sites in the Qaraaoun Lake shows in figure 2.

Figure 3 shows that the site 3 was contaminated in all the season and especially in summer. This is attributed to the discharge of wastewaters from many cities and villages into this site. The microbial activity was increased with the increasing of the temperature. Also, the contamination was observed during spring as a result of the decrease in the level of water (13.01 m/s^3) and the intensive agriculture activity. The variation of seasons was observed in the sites 6 and 7 while the level of contamination increase in summer and this is due to many reasons: the decrease in the level of water (8.01 m/s^3), the activity of industry and the reject of waste water was increase. In addition in the sites 7 the tourist activities increase in summer. The degree of contamination is high in site 9, which may be due to the presence of agricultural opposite to herbaceous vegetation and fruits tree.

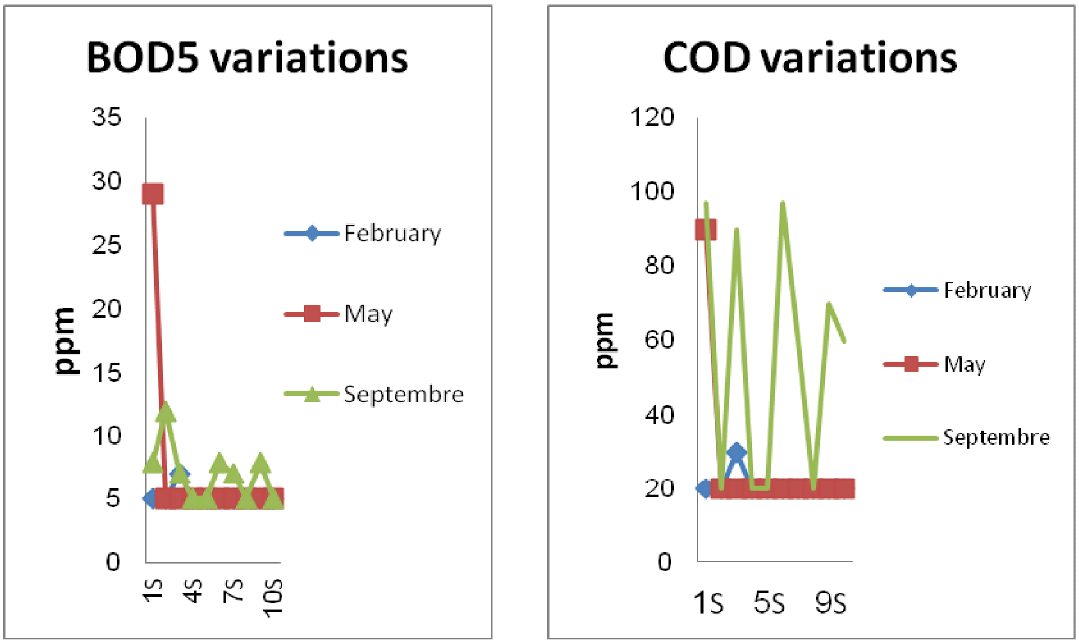

Figure 3 Seasonal Variation of COD and BOD_5 in the UBL.

3.4. Microbiological characteristics
The total coliform (TC) includes fecal coliform (FC) and non-fecal coliform.

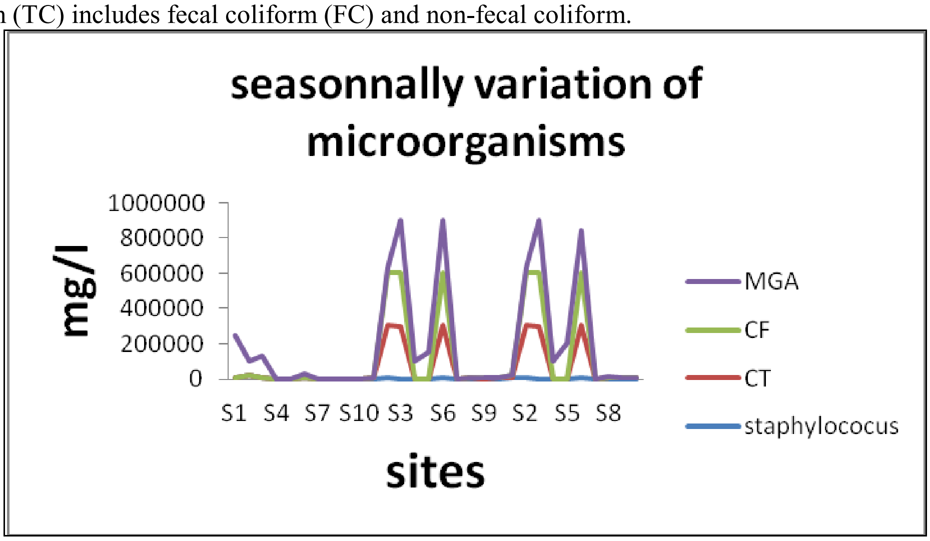

Figure 4: Seasonally variation of microorganisms.

FC may be separated from the TC group by their ability to grow at higher temperature and they are associated only with fecal materials. Therefore, *Escherichia Coli* is the major practical indicator of fecal contamination (Shaban and Nassif, 2007).
The maximum level of TC and FT in the river was found to reach about 300000 col/100mL, which occurs in sites 2, 3 and 6. Figure 4, shows that the level of contamination of all micro-organisms is much higher in summer than in winter and some bacteria such as *salmonella* is present (sites 6) only in summer, so the season factor is important in the presence of bacteria and in increasing the level of contamination.
3.5. Principal Analysis Compound PCA
The second type of multivariate Statistical used in this study was Principal Analysis Compound (PCA), it is a very powerful technique applied to reduce the dimensionality of a data set consisting of a large number of inter-related variables, while retaining as much as possible the variability present in data set. This reduction is

achieved by transforming the data set into a new set of variables, the principal components (PCs) are orthogonal (non-correlated) and are arranged in decreasing order of importance. (Wunderlin et al., 2001).

PCA techniques extract the eigen values and eigenvectors from the covariance's matrix orthogonal variables. PC provides information on the most significant parameters, which is describing whole data set affording data reduction with minimum loss of original information. Factor analysis reduces the contribution of less significant variables obtained from PCA and the new group of variables known as varifactors is extracted through rotating the axis defined by PCA (Helena et al., 2000).

PCA was applied on the analyzed water (physicals, chemicals and microbials) of the ULB and the Quaraoun Lake in order to extract significant PCs which are subjected to varimax rotation raw generating VFs, and to identify the factors that influences each one. Since there were different elements that may influence the pollution of the lake water; however, a PCA was conducted. In this study we apply PCA to chemicals, heavy metals and bacteriological parameters for all sampling sites.

PCA of the entire data set (Table 1) evolved seven PCs with eigenvalues > 1explained about 80.68% of the total variance in the water quality data.

- The first PC accounting for 27.53 % of total variance was correlated with Cr, sulfate, potassium, Cl^-, nitrate and Fe.
- The second PC accounting for 13.26% of total variance was correlated with Ammonium, Na+, Cu, $CaCO_3$ and CT.
- The third PC accounting for 13.05% of total variance was correlated with Nitrite, GMA, Salmonella and CF.
- The fourth, fifth, sixth and seventh PC accounting for the total variance of 8.07%, 7.26%, 6.92% and 4.59%; respectively, correlated with none of the parameters.

Analysis of the results and the Table 3 shows that the majority of information is explained by the first three factorial axes, because it is necessary that the thresholds of PCs must be less than 0.95.

Table 3. Thresholds intervals of 0.95

Number	Inferior extremity	Eigenvalues	Superior Extremity
1	3.33	6.88	10.42
2	1.60	3.31	5.02
3	1.58	3.26	4.94
4	0.97	2.01	3.05
5	0.88	1.81	2.74

The variance of different parameters in the formation of three first factorial axes C1, C2, and C3 are 27. 53%, 13.65% and 13.05% or 61.91 %; respectively of total information explained.

As a result, the maximum cumulative of total inertia is formed by the planes of factorial axes C1 × C2 and C1xC3. Thus, the physicochemical and microbial meaning of the factorial axes C1, C2 and C3 are necessary. This is because of the projection that can sometimes be unreliable. It is advisable to see the importance of square cosine of the angle formed by the vector of this and the projection plane of the variable to assess the quality of the projection of this variable on this particular factor axis. SPSS shows that the cosine square is higher more the variable is related to the axis factorial. Conversely, plus the square cosine is close to 0 (zero) less the variable is bound to this axis (Eby Ould M, at el 2008). The analysis of correlations between variables and the factorial axes reveals the nature of these axes. Some variables are having low squared cosines from unity, and consequently they are not well represented in projection of the circles where they should not take much space in explaining the factorial axis concerned.

3.6. Factorials axes C1, C2, and C3

Figure 5 shows that C1, which explains 27.53% of total variance, has strong positive correlation with Fe^{3+}, $CaCO_3$, ammonium, iron, and moderate positive correlation with nitrate, temperature and FC. C1 has strong negative correlation with Cr, So_4^{2-}, Cl^-, K^+. The first principal component C1 is associated with a combination of various hydrogeochemical processes, which can be interpreted as a minerals component of the river water. It indicates the chemical weathering of feldspar by water and ferro minerals together with anthropogenic sources (Hem 1991; Zhang *et al* 1995 and Satyanarayana and Periakali 2003). The presence of FC indicates that anaerobic fermentation undergoes which leads to the formation of ammonia.

However, the variables that contribute in a major way the constitution of the C2 axis are the Na^+, Cu^{2+}, pH and phosphates of positive side towards negative (Figure 5), this axis shows a gradient increasing concentration of Na^+, Cu^{2+}, to decrease pH and PO_4^{2-}. For instance, the presence of Na^+ ion suggests ion exchange on the clay or feldspar by weathering materials (Hem 1991). Cu^{2+} is due to the reject of waste water from several industries. The process of dissolution of Na^+ and Cl^- ions indicates a higher rate of weathering in the area. There is no relationship between Na^+ and Cl^- and this means that their presence in water has from different sources. Na^+ comes from the domestic reject and Cl^- comes from fertilizers.

The positive correlation between Phosphate and CT may be explained by the using of phosphate as source of nutrition to the bacteria.

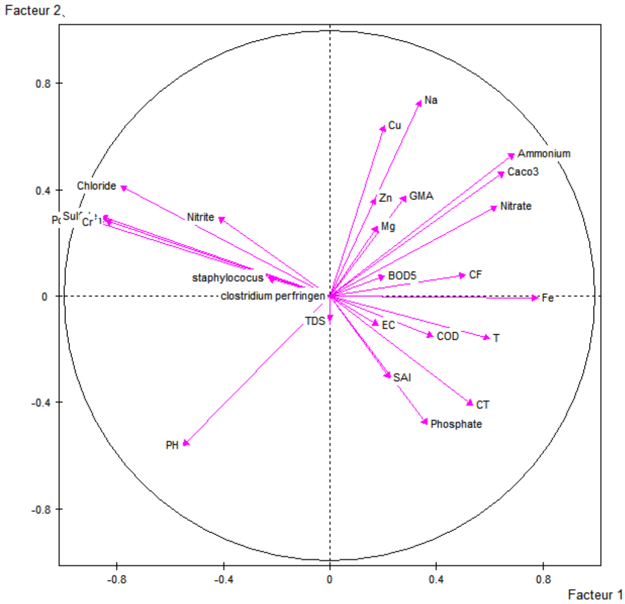

Figure 5. Circle of correlation of different variables in C1 and C2

The potassium sulfates association and potassium chloride association and their presence due to the utilization of them as source of fertilizers.
C1 and C2 are insensitive to a microorganism that means there presences are natural (carbonate) and increase by the rejects of wastewater and by utilization of different form of fertilizers.

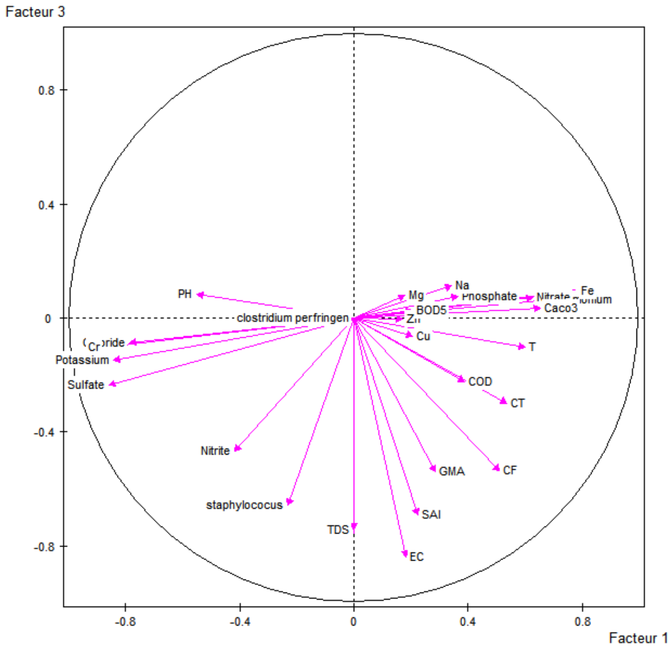

Figure 6: Circle of correlation of different variables in C1 and C3

Figure 6 shows that F3 has negative correlations with EC, TDS, staphylococcus, nitrite, salmonella, FC and GMA. The higher concentrations of TDS observed in the F3 is related to conductivity which is an indication of human pollution due to domestic wastes (Chettri and Smith 1995; Fisher and Mullican 1997 and Scheytt 1997). NO2 indicates the presence of cycle of nitrification which increases the concentration of oxygen and has positive effect in the increasing of concentration of bacteria; such as staphylococcus, CF, CT, Salmonella. Their presence in the water is also anthropogenic (irrigation return flow, fertilizers, and domestic wastes).

3.7. Analysis of factorial designs C1 X C2 and C1 X C3

Analysis of the factorial map C1 x C2 (Figure 7) allows distinguishing three groups of samples. The first class (1/3) has found in positive side of the axis of C2 and it was done during winter, in opposite situation a third class (3/3) correspond to summer sampling and has found in the positives side of C2; the second class (2/3), which corresponds to spring has found in negatives side in the axis of C2.

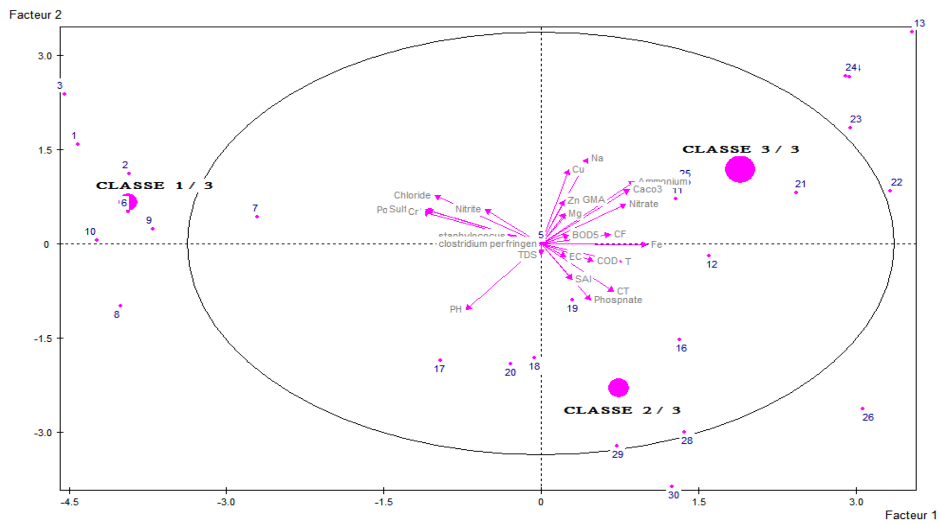

Figure 7: factorial map C1 × C2 (Not full title)

The effect of the factor "Season" is important between winter and summer, the class1\3 and class 3\3 are opposite to C2 and the class 3\3 and class2\3 are opposite of C1 and the effect of parameters varies by seasons due to the variation in temperature as well as the rainfall periods.

Some sites of first class (6, 7, 8, 9 and 10) were found in negatives side of the axis of C1 and are characterize by the presence of Cr, SO_4^{2-}, Cl^-, K^+ and nitrite. In sites 6 and 7 the presence of many industries and the reject of waste water without recycling (Cr and Cl^-). SO_4^{2-}, K^+, nitrite is present because near the site 9 and 10 many land are cultivated by olive and fruits tree. Sites 1, 2, and 3 of this class have the same characteristics of the positive site of C2: strong correlation with Na^+, Cu^{2+}, Zn^{2+} and Mg^{2+}. This is normal in the sites 3 because all around villages reject their waste without treatments. In the sites 1 and 2 in this time the around land is not cultivated and the debit is low (13.27 m/s^3).

The second class (2/3) was found in negatives part of the axis C2 corresponding to mix sampling of spring samples 12,16,17,18,19 and 20 and summer sampling (26,28,29,30) which was found in negative side of the axis of C2 and this meaning that this sites are characterizes by the presence of high pH, CT and phosphates.

The third class (3/3) formed by summer sampling of the first seven sites (21, 22,23,24,25 and 27), and sampling of four spring sites (13, 14 and 15). The sites 21, 22, 23 are correlated to the positive part of C1. $CaCO_3$, ammonium, Fe, nitrate, temperature and FC are present in these sites and this is normal because bacteria increases with temperature and the first three sites are agricultural sites and they are cultivated with potatoes and wheat. Sites 13, 14 and 24 have strong positive correlation with the positive part of C2, like the sites 1, 2 and 3. Sites 25, 15, 27 and 11 have low correlation to the two axes.

Figure 8 shows that the physico-chemical metal and bacterial characteristic of the sites 4 and 5 are not influenced by the season (14, 24, 15, and 25) which means that they don't have considerable pollution.

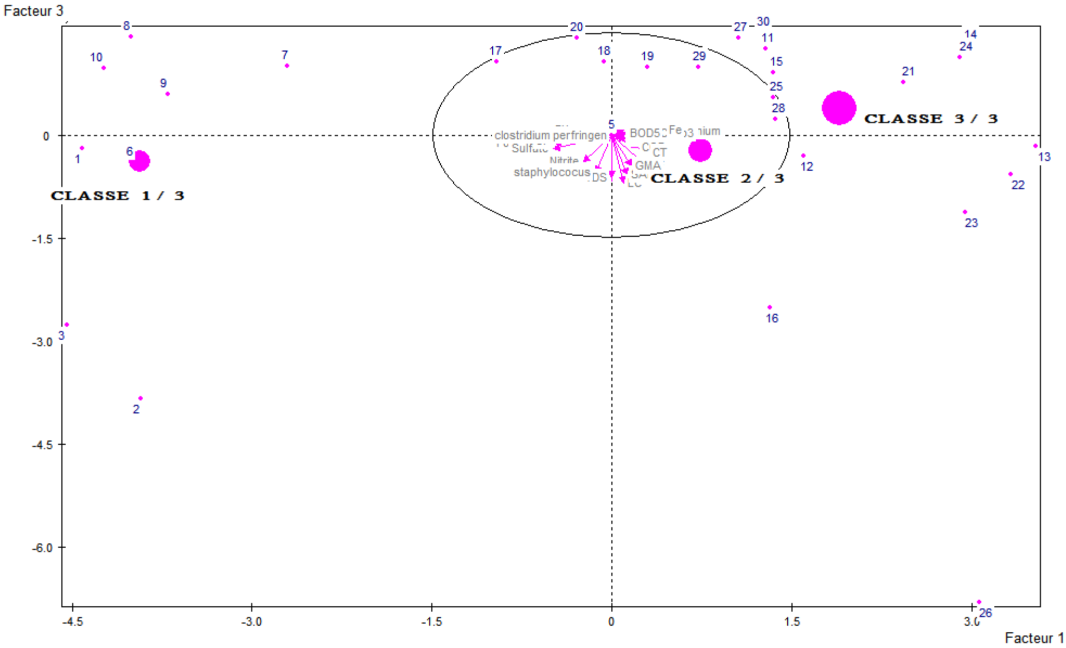

Figure 8: Factorial map C1xC3

The plan C1 × C3 shows three groupings of records: a first grouping note class 1\3 gathering winter surveys, class 2\3 of spring and another class 3\3 of summery readings. It is obvious that there is no difference between the spring and summer sampling. Only site 16 was correlated negatively to C3 and the others sites are positive related to C3.

Concerning ammonium, nitrates and Fe^{2+}, K^{+}, the records show that summer submitted to the higher levels. Moreover, there is a positive correlation in ammonia, which supposed to be derived from wastewater. It is noted that the FC have an exclusively fecal habitat and that the nitrates can also be derived from feces by oxidation of ammonium (Gaudreau and Mercier, 1998).

In summer, the increased temperature and evaporation rates raise the dissolution of rocks and these results in the concentration of Ca^{2+} and all the sites are examples of this case. The salinity gradient representing by the concentrations of Na^{+} and K^{+} which are higher in site 3 during summer.

In summer, the level of FC, FT and salmonella are increased and this due to rejects of wastewater. PCA shows that nitrite, sulfate, phosphate, Mg and Zn are not significant in determining the type and physicochemical metals of the medium studied.

PCA shows that sites 2, 3 and 6 are contaminated in all seasons by an important domestic (wastewater effluents), agricultures activities, farmers, industrials reject and organic pollutants. Concerning the sites in the Lake, the results show that site 8 was more polluted because there is a perceptible difference between the various sites, and that the source out of nitrates can have different origins all along the river from the Litani. This difference seems to be influenced by the geographical location of the intake points.

4. Conclusion

The statistical computations of the physico-chemical parameters (SPSS method) shows that some parameters are significant correlated such as Total Dissolved Solid (TDS) and electrical conductivity (EC), Ammonium, Nitrate, Potassium and Phosphate. The application of multivariable statistical techniques on the data collected in this study showed that the Upper Litani Basin (ULB) and the Qarraoun Lake water quality are changed seasonally. Pollution has been clearly identified as a cause of water quality degradation in the lake of Qarraoun. In fact, other parameters, such as geology, land use, topography, storm flow and weather, can control or increase the amount of nutrients released.

Different seasons revealed the presence of either mineral or anthropogenic or both sources of pollution and for that the degree of pollution is different from one site to another. Pollution caused by human interference was shown to come from municipal wastewater and agricultural purposes discharged into the River between the sampling at Yafoufa, Berdawni and Ghazial stations. Temporal effects were associated with seasonal variations of river flow, which caused the dilution of pollutants and, hence, variations in water quality. Therefore, the sewage treatment processing is not carried in all the cities along the river which makes the water in river is not suitable for use.

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References
Chettri M and Smith G D 1995 Nitrate pollution in ground water in selected districts of Nepal; *Hydrogeol. J.* **3**, 71–76.
Eby Ould M., Ahmed L., El Housseine R., Mustapha L., Mohamed F., Maxime P., Abdel Kader M. et Mohamed F. 2008, Typologie physico-chimique et métallique des eaux du fleuve Sénégal au niveau de la ville de Rosso (Mauritanie). Journal of Afrique Science, **3**, 394 – 409.
Fawaz, M.: 1992, 'Water Resources in Lebanon', in *Proceedings of the National Workshop of the Status of Water in Lebanon*, Beirut, Lebanon, pp. 17–29.
Fisher R S and Mullican W F 1997 Hydrochemical evolution of sodium-sulfate and sodium-chloride ground water beneath the northern Chihuahuan Desert, Trans-Pecos,Texas, USA; *Hydrogeol. J.* **5**, 4–16.
Hajjar, Z.: 1993, 'Water Needs in Lebanon: Potable, Agricultural and Industrial', in *Proceedings of the Workshop on Water Affairs in Lebanon and Peace-Process in Project Series of Lebanon Life Studies-5*, Beirut, Lebanon, pp. 67–80 (in Arabic).
Hajjar, Z. K. 1997 Lebanese Water and Peace in the Middle East. Dar el ilm lilmalayin, Beirut, Lebanon (in Arabic).
Hem J D 1991 Study and interpretation of the chemical characteristics of natural water: Book 2254, 3rd edn., (Jodhpur, India: Scientific Publishers) 263 p.
Jaber, B.: 1993, 'Water Availability in Lebanon', in *Proceedings of the Workshop on Water Affairs in Lebanon and Peace- Process an Project Series of Lebanon Life Studies-5*, Beirut, Lebanon, pp. 53–66 (in Arabic).
Jurdi, M.: 1998, 'Follow up National Environmental Surveillance, 1996', Unicef Publications, Beirut, 1998 (in Arabic).
Jurdi, M.: 1992, 'A National Study on the Quality of Potable Water in Lebanon', in *Proceedings of the National Workshop of the Status of Water in Lebanon*, Beirut, Lebanon, pp. 145–173 (in Arabic).
Gaudreaud, D., and M. Mercier. 1998. La contamination de l'eau des puits privés par les nitrates en milieu rural. Montérégie, Canada : Régie Régionale de la Santé et des Services Sociaux, Direction de la santé publique.
Lebanese Norm for Drinking Water, n˚161, ICS 13.060.20, 1999.
LRA, 1999. Technical Report. Litani River Authority
Mansour, H.: 1994, 'Field Report on the Pollution of Al-Litani Waters', Al-Litani National Water Authority.
Oxfam Technical Brief, 2006. Water quality analysis in emergency situations. pp: 1-8.
Qumair, F. 1998, Pollution problems and surface water losses. Abaad **7**, 14–19 (in Arabic).
Satyanarayana M and Periakali P 2003 Geochemistry of ground water in ultrabasic peninsular gneissic rocks, Salem district, Tamil Nadu; *J. Geol. Soc. India* **62**, 63–73.
Scheytt T 1997 Seasonal variations in ground water chemistry near lake Belau, Schleswing-Holstein, northern Germany; *Hydrogeol. J.* **5**, 86–95.
Shaban, A. 2011. Analyzing climatic and hydrologic trends in Lebanon. Journal of Environmental Science and Engineering, 5 (3), 2011.
Shaban, A. and Nassif, N. 2007. Pollution in Qaraaoun Lake, Centre Lebanon. . Journal of Environmental Hydrology, **15**, 11.
Stephenson, A., Labounskaia, I. and Stringer, R.: 1998: *Heavy Metal and Organic Screen Analysis of Environmental and Waste Samples Associated with Industrial Activities in Lebanon, September, 1997*, Greenpeace Research Laboratory, University of Exter, U.K.
Stumm, W. and Morgan, J. J.: 1996, *Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters*, 3rd ed., Wiley & Sons, New York, U.S.A.
World Health Organization (WHO) « A Proposal for Updating Lebanese Norm of Drinking Water (1999) based on WHO Guidelines », 2006.
Wunderlin, D.A., Pilar, D.M., Valeria, A.M., Fabiana, P.S., Cecilia, H.A., Bistoni, M.A., 2001. Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. Water Research **35**, 2881–2894.
Zhang J, Huang W W, Letolle R and Jusserand C 1995 Major element chemistry of the Huanghe (Yellow River), China – Weathering processes and chemical fluxes; *J. Hydrol.* **168,** 173–203.