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USE OF HYDROCHEMISTRY AND ENVIRONMENTAL ISOTOPES TO EVALUATE WATER QUALITY, LITANI RIVER, LEBANON

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The chemical and isotopic composition of water discharging from springs, surface and groundwater in the Litani river basin were studied. The data include field measurements of specific conductance, pH, total dissolved solids and laboratory measurements of major element chemistry, stable $^2H/^1H$ and $^{18}O/^{16}O$ isotope ratios (δ^2H and $\delta^{18}O$) of water. Water samples were collected during 2004 and 2005. Geochemical analysis indicates that sea spray influences the major ionic composition of the downstream river. Water quality changes over the course of the river in the central Bekaa plain near the Karaoun reservoir. This area drains percolated and infiltrated water that contains relatively elevated concentrations of nitrate originating from agricultural runoff. Isotopic results for $\delta^{18}O$ and δ^2H show that the river can be divided into three main parts relative to water quality. The upper part, near the headwaters, is directly influenced by precipitation input, while the mid course of the river is influenced by input from the Litani tributaries and the effluents from man's activities. The lower reaches of the river are exposed to high evaporation. In the Karaoun reservoir, isotope enrichment with respect to the Litani river is calculated to be more than 3‰ in $\delta^{18}O$ and 10‰ in δ^2H. The groundwater in Karaoun basin is recharged by direct river infiltration and infiltration from the reservoir. The percentage of reservoir recharge varies from 28.5% to 20.7% in the groundwater system.

INTRODUCTION

Rivers are fed by precipitation, by direct overland runoff, through springs and seepage, or from melt water at the edges of snowfields. The contribution of direct precipitation on the river water surface is usually minute, except where much of a catchments area is occupied by lakes and reservoirs (Berner and Berner, 1987). River water losses result from seepage and percolation into adjacent aquifers, and particularly from evaporation. The difference between the water input and loss sustains surface discharge or stream flow. Streams play a dominant role in the transport of inorganic and organic substances both as dissolved and as particulate matter. River discharges constitute the main source for dissolved matter in the seas. However, there is a marked difference between the average chemical composition of ocean and river water. The average salinity of the world's rivers is low. Major chemical constituents of river water are bicarbonate, sulfate, calcium, chlorine, sodium and magnesium (Garrels et al., 1975). In general, the composition of river water is controlled by water-rock interactions of the carbon dioxide-charged rainwater and soil waters with the minerals in continental rocks (Saad et al., 2004b). In general, the dissolved load of the world's rivers comes from the following sources: 7% from beds of halite (NaCl) and salt disseminated in rocks; 10% from gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$) deposits and sulfate salts disseminated in rocks; 38% from limestone and dolomite; and 45% from the weathering of one silicate mineral to another (Gaillardet et al., 1999).

Dissolved compounds in water are used in conjunction with naturally occurring stable and radioactive isotopes of water to study hydrological, hydrochemical and environmental processes in rivers and their catchment areas (Fritz, 1981; Gat, 1996). Special emphasis is placed on the water isotopes ^{2}H (deuterium) and ^{18}O (oxygen-18) because of their specific potential in addressing water balance, dynamics and interrelationships between surface and groundwater in river basins and catchment areas (Vrbka et al., 1993; Epstein and Mayeda, 1953). The water isotopes ^{2}H or ^{18}O are very useful because of their conservative behavior in water and the large variability of their isotopic ratios (Craig, 1961). Seasonal variations of these isotopes are larger in rivers where surface runoff from recent precipitation is the main source of flow, and smaller in streams where groundwater is the dominant source (Mook et al., 1974). Local precipitation events are an important component of river water in the headwaters of large basins. Isotopic composition of the river water is determined by contributions from different surface and subsurface sources, each with their characteristic isotope ratio (Mook, 2001). The oxygen and hydrogen isotopic composition of most of the world rivers was found to be close to the Global Meteoric Water Line, indicating that evaporation of river water is in most cases of insignificant influence on the isotopic composition of this water. However, in rivers and catchments of arid and semiarid zones, where evaporation can be an important factor, the combined measurement of ^{18}O and ^{2}H can be used to quantify the evaporation effect and to study mixing processes between river water and adjacent groundwater (Ikebuchi et al., 1988; Simpson and Herczeg, 1991). The relationship between the isotopic composition of precipitation (input) and newly formed groundwater and surface runoff (output) is built upon processes that differentiate between rain events on a meteorological or seasonal basis, and processes that fractionate between the different isotopic water species, primarily evaporation (Gat and Tzur, 1967).

The present study involves hydrochemical and stable isotopic monitoring of the Litani River that flows in the central Bekaa plain (semiarid climate) and reaches the sea in southwest Lebanon (Mediterranean climate). Many Lebanese farmers rely on the river and its tributaries for irrigation and other water needs, but over the years the basin has suffered from overuse and pollution.

Lebanon's largest dam, the Karaoun dam, has been located on the upper Litani River, near the town of Karaoun (Srour and Sleiman, 1998). It regulates downstream flow of the river to generate power and irrigate the upper and lower reaches of the Litani. The amount of groundwater recharge in the Litani river basin is greatly increased by the Karaoun reservoir when compared to natural recharge. This positive effect occurs mainly due to the prevention of flow losses beyond the recharge area, and due to the extension of the infiltration duration (Saad et al., 2005c).

The objective of this study is to evaluate river water quality and its influence on recharged groundwater in its drainage basin. As groundwater is a major source of water for agricultural and drinking purposes in this area, it is important to know the impacts of Litani river chemistry, geological formations and agricultural activities. Also the role of the Karaoun reservoir is investigated with regard to its impact on recharge to groundwater.

EXPERIMENTAL SECTION

Catchment areas

Surface and groundwater samples were taken from the course of Litani River and its basin (Figure 1). The Litani River is Lebanon's primary river, running southward for 170 km from the Bekaa Valley through the center of the country. Its annual average discharge is 9.34 m^3/sec with an average annual flow estimated at $920x10^6$ m^3. Flow rises to 14.2 m^3/sec in the wet season and drops to 4.4 m^3/sec in dry season (Khair et al., 1994). The Litani river basin area is estimated at 2.17 km^2 and is considered the largest drainage area in Lebanon. The main sources of the river are the Berdauni, Yahfufah and Ghazeyel springs. It is characterized by a laminar flow in summer and a turbulent one in winter when the discharge of the river is highest. The cross sectional profile is V-shaped and most of its floodplains appear before the estuary. The largest single withdrawal from the Litani is the diversion of 236 million cubic meters annually through the Markaba tunnel to the Awali River for hydroelectric generation to supply Beirut and other coastal areas. In fact, 35 percent of Lebanon's total production of electricity comes from the Litani waters directly or from the Markaba-Awali diversion.

Sample collection

Evaluation of water quality was conducted by surface water sampling every two months between 2004 and 2005 from 10 sites located upstream of the estuary (Figure 1a). These sites are designated respectively from 1 to 10 as follows: Tyre, Khaysaran, Yohmor, Joub Janninne, after dam, Ghozayel, Berdawni, Chtoura, Riyak, Fouar source Litani. The samples were collected from the banks of the river at 5 cm from the top surface of the flow.

To assess the surface-groundwater interaction, additional surface and groundwater points are sampled: Four surface water sites in the Karaoun Reservoir (K1-K4), four surface sites in the Litani river before and after the dam (S1- S4), and six groundwater sites surrounding the dam (W1-W6) (Figure 1b). Groundwater was pumped for 2 minutes before collection in polyethylene bottles of 5 liters. At each site, conductivity, pH and total dissolved solids were measured directly on the samples.

Water analysis

Water samples were filtered through 0.45 μm pore size cellulose acetate syringe filters (Millipore filters), then samples were acidified with nitric acid (15% v/v) and stored at 4°C before analysis. Calcium, magnesium, sodium and potassium were measured using Atomic Absorption

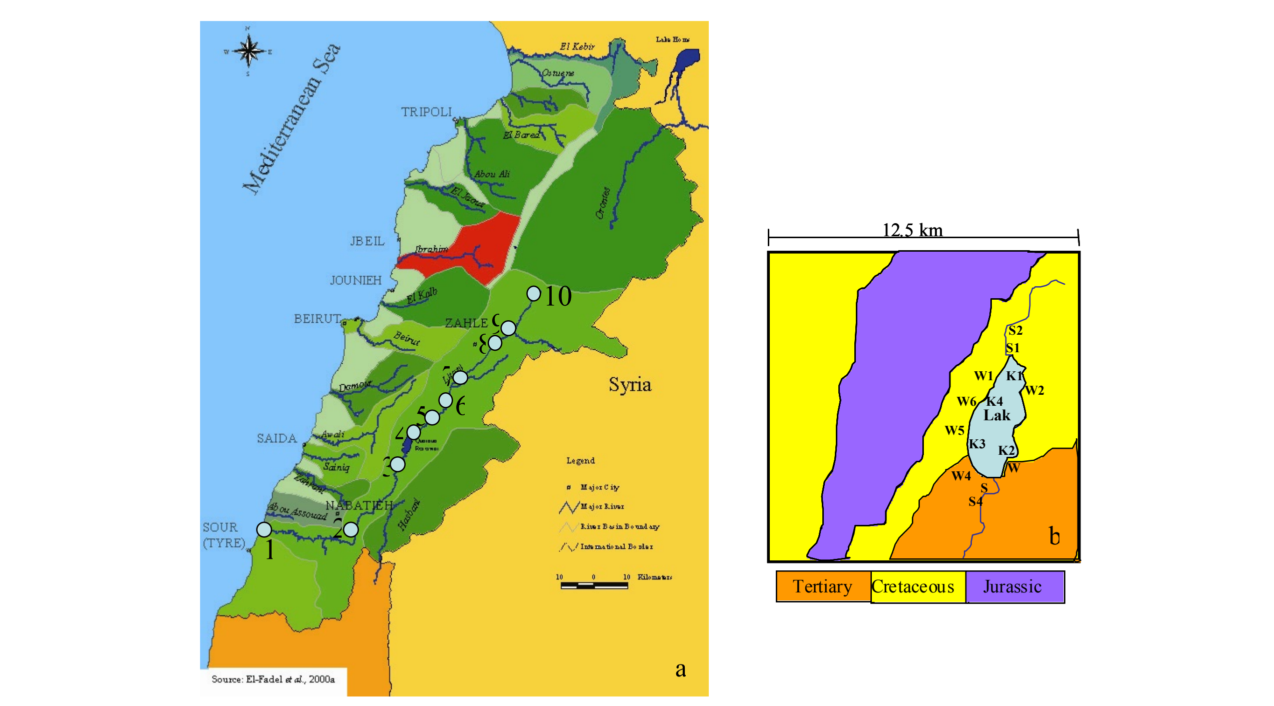

Figure 1. a- Location of sampled surface water along the course of Litani river. b- Location of surface and groundwater around Karaoun dam.

Spectrometry using air-acetylene flame after addition of lanthanum chloride to minimize the interference phenomena. Nitrate, sulfate and chlorine were measured using Ion Chromatography. Standard reference material was used for quality assurance. The mean concentrations of cations and anions determined in the reference standard material were within their certified concentration ranges. Each sample was measured in triplicate. The stable isotopic composition of the water samples was determined by the chromium technique (^{2}H) with an analytical precision of ±0.8‰, and the standard H_2O-CO_2 equilibration method (^{18}O) (Epstein and Mayeda, 1953) with an analytical precision of ±0.1‰ in an IRMS delta S (Finnigan MAT). The results of the hydrogen and oxygen isotope measurements are expressed as delta notations ($\delta^{18}O$ and $\delta^{2}H$), relative to the Vienna Standard Mean of Ocean Water (VSMOW).

RESULTS AND DISCUSSION

Evolution of Litani River surface water quality

Analysis of physical and chemical parameters

The locations of sampling sites with their longitude, latitude and elevation above sea level is presented in Figure 2. Litani surface water samples range from 5 m elevation in the coastal Tyre region to the highest spring source at 950 m in the Fouar region. Physical analysis results of sampled surface water along the course of the river are presented in Figure 3 which shows the variation of total dissolved solids, TDS, and Electrical Conductivity, Ec. The range of TDS and Ec progressively increases from the headwaters of the river to its estuary. This could be attributed to an increased input of both particulate and dissolved particles that originate from sea salt spray and intensified agricultural activity in coastal plains.

TDS usually ranges from 0.5 to 1.0 times the Ec. In our study, a mean factor of 0.7 was found between TDS and Ec along the course of the river. The values of TDS and Ec fall into the highest

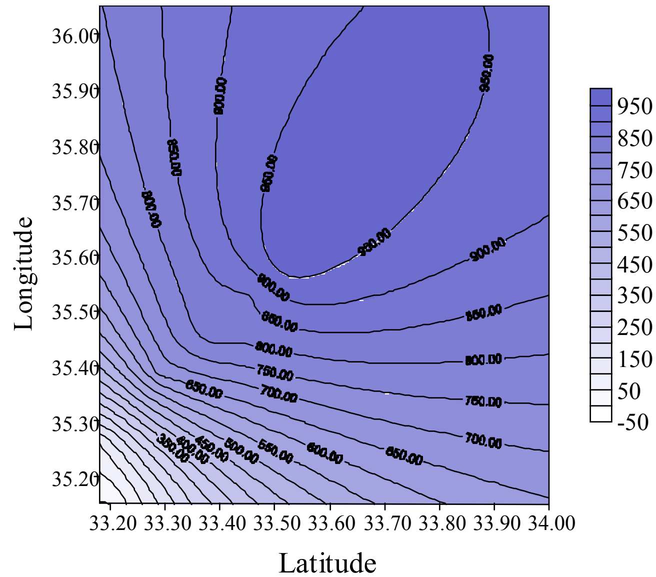

Figure 2. Distribution of sites elevation (m) as a function of latitude and longitude.

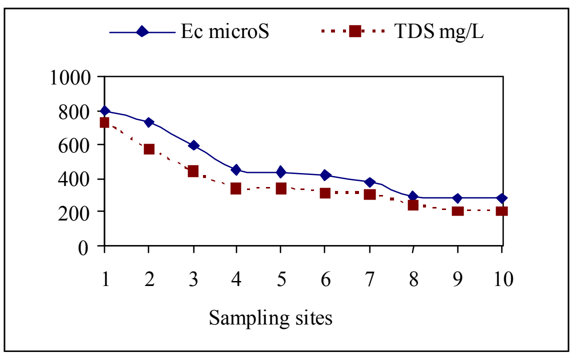

Figure 3. Variation of Total Dissolved Solid and Electrical Conductivity along Litani river from its mouth (site 10) to its estuary (site 1).

and lowest range of mean river composition that is influenced by several factors from the source to the sea (Dojlido, 1993).

Chlorine concentration along the river is shown in Figure 4. This element is often studied because it is extremely mobile, very soluble and chemically non-reactive (Berner, 1987). Values show a gradual increase of chlorine from the source to the coastal sites. Low concentrations (10 mg/L) are found in headwaters. In the mid course of the river, the mean concentration of chlorine is 2.5 times higher than at the sources. The load of chlorine in this part of the river probably originates from runoff carried by various tributaries. The highest concentrations of 90 mg/L near the estuary is an increase by a factor of 9 from the headwaters. An additional input of chlorine is attributed to marine aerosols.

To explain the origin of chlorine in river water, the variation of solutes to chlorine concentration was plotted in Figure 5. If samples are low in both solutes and chlorine concentration, they represent a low dilution of marine aerosols with surface water. Water samples with high concentration contents indicate a potential solute source contributing to the chemistry of water. These sources could be an additional subsurface reaction with bedrock including the aquifer materials and a high influence of sea spray (Struchio et al., 1996; Saad et al., 2004a).

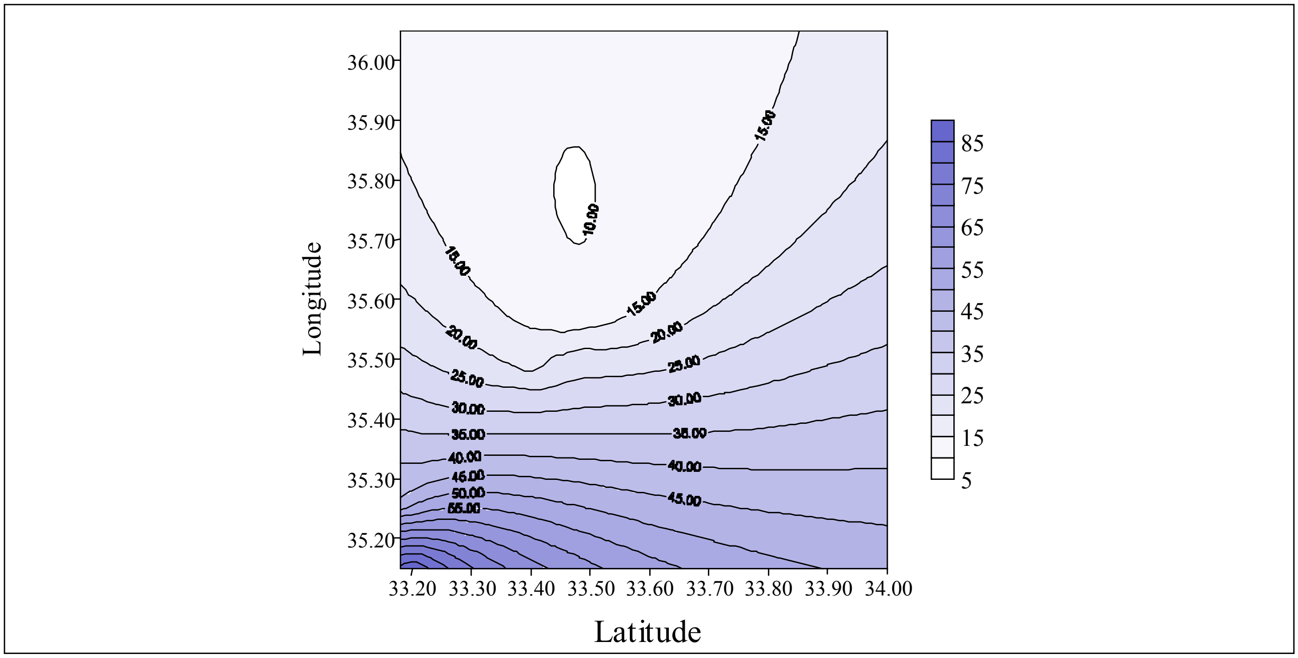

Figure 4. Distribution of chlorine concentration (mg/L) along Litani river.

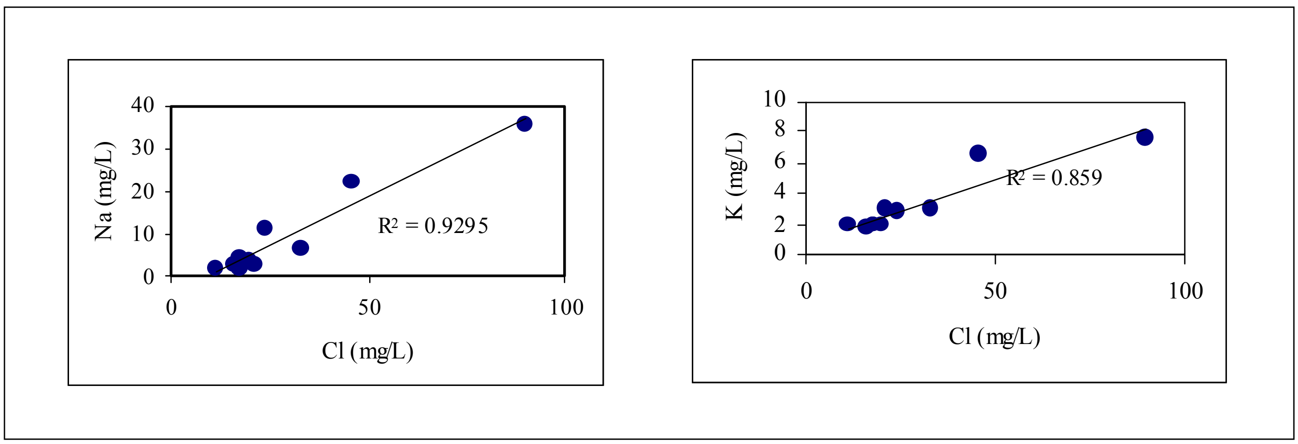

Figure 5. Variation of Na and K (mg/L) versus Cl concentrations in Litani surface water.

Figure 5 shows that high sodium, potassium and chlorine concentrations are found in water samples near the estuary indicating the high influence of marine aerosols. Low contents of sodium, potassium and chlorine in continental water samples nearby the sources of the Litani is related to the small influence of sea spray. The potential point source of these elements is crustal and primarily influenced by the nature of bedrock

The assessment of water quality variation along the course of the Litani was evaluated by nitrate and sulfate parameters (Figure 6). Variation of sulfate shows no obvious trends between sites. It does not increase with increasing distance from the headwaters. The origin of sulfate is probably crustal from dissolution of naturally occurring minerals. The small fluctuation in the mid course of the river is attributed to runoff from agriculture in the Bekaa Plain. High agricultural activity is reflected by a high nitrate level in the mid course of the river. A peak in nitrate is pronounced in the estuary sites due to a larger input of fertilizers in this area drained by additional tributaries to the river. It reaches a concentration of 110 mg/L, which exceeds the permissible range in water. Upstream samples show low nitrate content corresponding to non polluted water (Saad et al., 2005c).

Analysis of environmental isotopes

Different factors influence the isotopic composition of surface and groundwater systems. Monitoring $\delta^{18}O$ and $\delta^{2}H$ is a fundamental means to determine the origin and mixing of ground and surface waters in water-supply aquifer basins (Gat and Tzur, 1967).

Figure 7 shows the variation of $\delta^{18}O$ in the course of Litani river from the headwaters to the estuary. Tηε $\delta^{18}O$ values decrease with altitude. Litani surface waters are enriched in $\delta^{18}O$ in the lower reaches of the river relative to the headwaters, and mean values are observed in the mid course of the river. This result suggests a hydrograph separation where contributions of precipitation runoff and additional stream inputs in the Litani catchment area could be determined. The combined hydrochemical and isotopic data are used to delineate three main parts of the Litani river with different elementary composition, the headwaters, the mid course of the river, and the estuary.

In order to define the origin of surface water in the course of the river, combined analysis of $\delta^{2}H$ and $\delta^{18}O$ is plotted in Figure 8. Additional data for rainwater was added to define the Lebanese

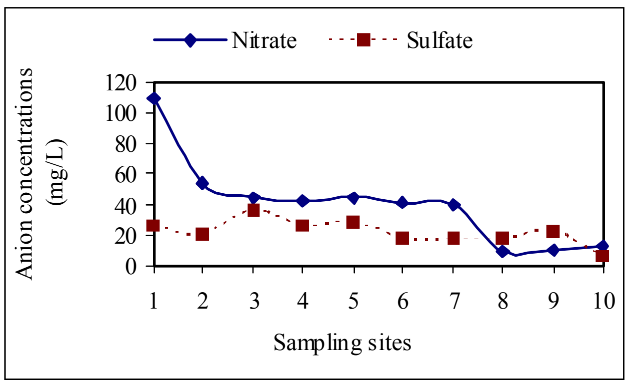

Figure 6. Variation of sulfate and nitrate in Litani river water.

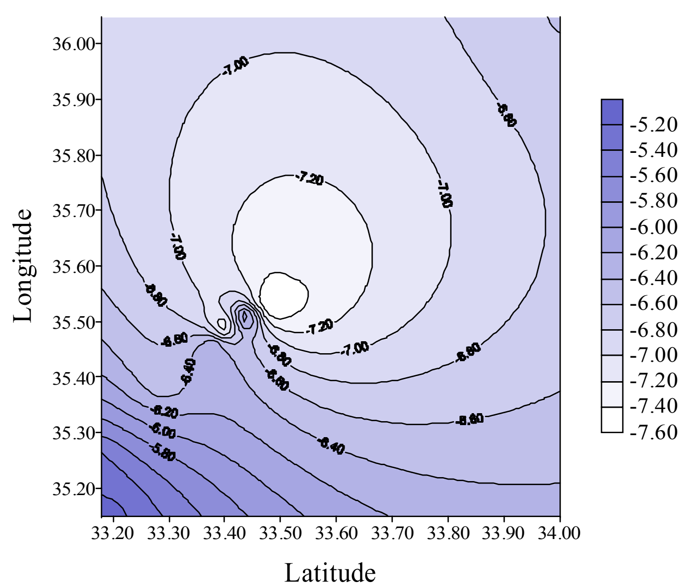

Figure 7. Distribution of $\delta^{18}O$ along Litani river from the headwaters to the estuary.

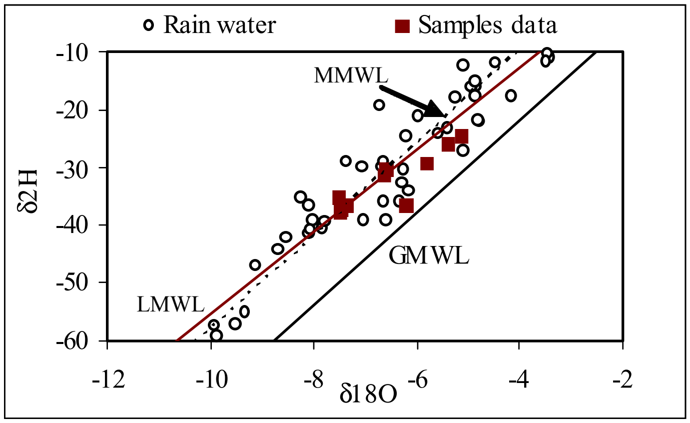

Figure 8. Isotopic data of Litani surface water and precipitation samples. GMWL: Global Meteoric Water Line; MMWL: Mediterranean Meteoric Water Line.

Meteoric Water Line LMWL (Saad et al., 2005a). In a previous study, the Lebanese Meteoric Water line LMWL was defined by the following equation:

$$\delta D = 7.13\ \delta^{18}O + 15.98 \qquad (1)$$

According to this line, isotopic data of surface water either plot close to LMWL or lie under the line. Samples in the headwaters are very close to LMWL. The local precipitation is an important component of Litani river water in this part. Compared to world rivers, the Litani is a small river and responds faster to changes in the isotopic composition of precipitation than do large rivers, because the surface-runoff component of the discharge is more direct and pronounced (Saad et al., 2004a).

In the lower reaches, samples are enriched in both $\delta^{18}O$ and δ^2H relative to upstream. In this part, local additions of precipitation are of minor importance, and the evaporation process relative to the Rayleigh fractionation model is a major influence on the water quality. In these coastal areas, water surface area is greater in the wider course of the river promoting the evaporation process.

Surface-groundwater interaction

The isotopic method can be used to quantify any groundwater mixing of different recharge origins such as precipitation and direct infiltration from surface waters. For this purpose, additional surface and groundwater samples are taken: Four surface water sites in Karaoun Reservoir (K1-K4), four surface sites in the river before and after the dam (S1- S4), and six groundwater sites surrounding the dam (W1-W6). Figure 9 shows the isotopic data of surface and groundwater in Litani basin. The data points in the $\delta^{18}O$ /δ^2H fall in between the global (GMWL) and the Mediterranean meteoric water lines (MMWL).

This method of determining the water balance of reservoirs is based on the fact that the evaporation process leads to a measurable increase of δ^2H and $\delta^{18}O$ of the reservoir water (Imboden and Wüest, 1995). The deviation from the LMWL is very clear for the isotopic data of the Karaoun reservoir. There is an isotope enrichment of the Karaoun water with respect to the Litani river inflow, by more than 3‰ in $\delta^{18}O$ and 10‰ in δ^2H. The degree of evaporative enrichment is controlled by meteorological variables such as the atmospheric relative humidity over the reservoir and the surface water temperature, and is correlated with the reservoir water balance (Fontes et al., 1979).

The regression line of the diagram of ^{18}O and deuterium of the wells surrounding the reservoir including reservoir waters and Litani surface water has a high correlation coefficient that is represented by the following equation (Figure 10):

$$\delta^2H = 5.39\ \delta^{18}O - 0.67 \qquad r^2=0.91 \tag{2}$$

This high correlation indicates a mixing of the origin of groundwater between the natural recharge from river infiltration and the artificial induced recharge from the reservoir.

Karaoun reservoir water - groundwater interactions

The extent of interaction between a reservoir and the adjacent groundwater can be shown through delineation of the mixing zone down gradient from the reservoir reflecting the mixing of local recharge and the reservoir water outflow. Adequate characterization of the mixing zone is of particular importance for aquifers being exploited for water supply (Fontes et al., 1979). In such cases the vulnerability of the wells to accidental pollution originating in the reservoir needs to be assessed. The physicochemical parameters of reservoir water (e.g. conductivity, temperature) cannot be used as the only tools for this purpose, as they are usually not sufficiently well preserved in the downstream aquifer. Heavy isotope buildup in reservoirs can be substantial, depending on climatic parameters and hydrology of the system. In our case the difference between the isotopic composition of groundwater and the reservoir water reaches 3‰ for $\delta^{18}O$. In this case the reservoir water entering adjacent groundwater systems can easily be distinguished from local river infiltration. Knowing the isotopic composition of the two end-members (reservoir water and local

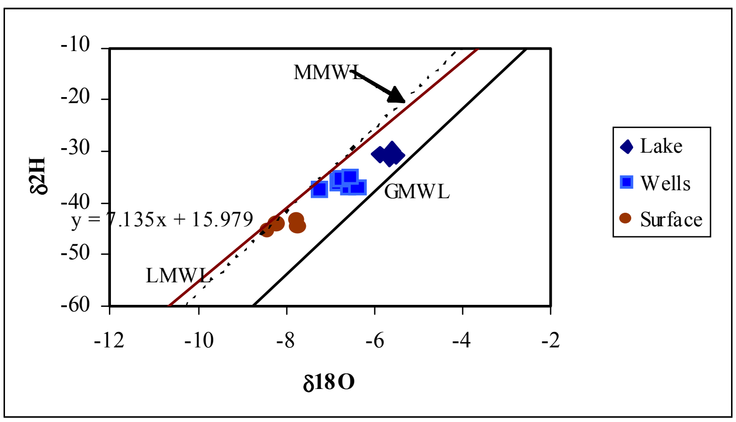

Figure 9. δ^2H versus $\delta^{18}O$ plot of wells, Litani surface water (before and after dam) and karaoun lake.

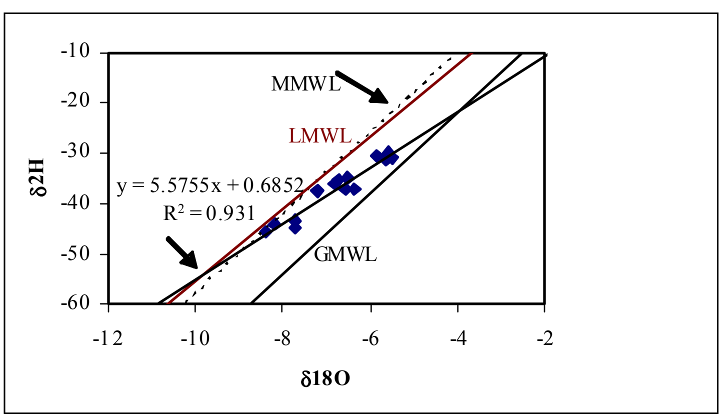

Figure 10. δ^2H versus $\delta^{18}O$ plot showing mixing line between different waters.

groundwater), one can calculate the percentage of reservoir water in the wells located down gradient from the reservoir. In our case, the use of stable isotope enrichment of Karaoun reservoir water shows a percentage of recharge of about 28.5% in the groundwater system at the entrance of the reservoir and about 20.7% near the dam (Yehdegho et al., 1997).

CONCLUSIONS

Evolution of surface water quality was determined along the Litani river from the headwaters to its lower reaches. Combined hydrochemical and isotopic data were used to delineate three main parts in the course of Litani river:

1. Headwaters are directly influenced bycontributions of rain water as the isotopic composition of surface water is close to the Lebanese Meteoric Water Line. In this part of the river, the potential source of solutes is crustal and primarily influenced by the nature of bedrock.

2. In the mid course of the Litani river, high agricultural activity in the Bekaa plain is reflected by a high nitrate level in surface water. Also isotopic analysis showed an additional input of elements from different tributaries in the course of the river, changing the water quality.

3. The lower reaches of the river showed a high element composition indicating the influence of marine aerosols. A peak in nitrate is pronounced in the estuary sites due to a larger input of fertilizers in this area drained by additional tributaries. Enrichment in $\delta^{18}O$ in the lower reaches of the river is found relative to the headwaters due to high evaporation effects.

4. The quantifying of Karaoun reservoir water – groundwater interactions shows a percentage of artificial reservoir recharge of about 28.5% in the groundwater system at the entrance of the reservoir and about 20.7% near the dam.

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