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CHEMICAL AND ISOTOPIC COMPOSITION OF RAINWATER IN COASTAL AND HIGHLAND REGIONS IN LEBANON

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Rainwater samples were collected from six stations at coastal and highland regions in Lebanon and analyzed for the major species Ca^{2+}, K^{+}, Na^{+}, Mg^{2+}, NO_3^{-}, NH_4^{+}, pH, Cl^{-}, and SO_4^{2-}. Absolute concentrations and element-to-sodium ratios show clear variations with higher levels found in coastal stations and lower levels found in continental sites for most of the species. Levels of major species from coastal areas can be twice as high as those of the highlands, in terms of both absolute concentration and element-to-sodium ratio. The contrast between low and high altitudes can be explained by proximity to the Mediterranean Sea and local agricultural pollution sources. Isotopic composition of rainwater in coastal sites presents high values of $\delta^{18}O$ and δD, whereas rainwater in continental areas is characterized by low values of $\delta^{18}O$ and δD. The altitude effect influences the isotopic fractionation in precipitation, including depletion in both $\delta^{18}O$ and δD, especially in stations at high elevation. The Lebanese Meteoric Water Line was defined as $\delta D = 7.13\ \delta^{18}O + 15.98$. This relation is close to the Regional Meteoric Water Line in the eastern Mediterranean with a lower d-excess indicating a relatively less pronounced secondary evaporation effect in Lebanon. From a series of ^{3}H data of monthly precipitation from six stations within the small country of Lebanon, we concluded that between the stations there are no significant differences in altitude effect. However, a small continental effect is apparent at the Baalbak station.

INTRODUCTION

Changes in air pollutants in the lower atmosphere have important implications for the environment. Factors that influence the concentrations of these pollutants are important for understanding the interactions between tropospheric composition and rainwater quality. The air mass trajectories with local-scale atmospheric measurements like wind direction and dust load give an insight to the chemical composition of precipitation. A majority of the anthropogenic and natural material that is loaded to the atmosphere is washed out by rainwater (Basak and Alagha, 2004; Charlson and Rodhe, 1982). Many of the trace elements found in the atmosphere are the result of combustion of fossil fuels, including such additives as the lead in gasoline, processing of earth materials for manufacturing cements, and burning of waste materials (Al-Momani, 2003).

In Lebanon, rainfall chemistry is influenced by many factors. Rainwater can be affected either by the Mediterranean Sea in the coastal areas or by continental sources in the internal regions of the country (Al-Momani et al., 1995; Saad et al., 2000). Also formation of smog in major cities such as Beirut, which includes air pollution caused by fossil fuel combustion, affects the precipitation chemistry in these regions. In other parts of the country, the atmosphere is loaded by dust particles originating from agricultural activities, other terrestrial activities, and livestock emissions, which influence rainwater quality. Many studies have shown the differences of precipitation chemistry between urban and continental sites and between low and high altitude zones (Zhang et al., 1999; Loye-Pilot and Morelli, 1988; Mosello and Marchetto, 1996).

Rainwater quality can be characterized by the use of isotopic means. The use of D/H ratios as a proxy for the $\delta^{18}O$ of water is based on the well-known correlation of these isotopic systems for meteoric waters. Worldwide, this is represented by the global meteoric water line (MWL) relationship (Craig, 1961): $\delta D=8\delta^{18}O+10$. However, the intercept in the MWL may vary in a local or regional situation. For example, in the Eastern Mediterranean, the intercept or deuterium excess parameter (d-excess; defined as the difference $\delta D-8\delta^{18}O$) is higher than 10 because evaporation processes at the sea-surface occur into low-humidity air masses of continental origin. Here, the oxygen–hydrogen isotope relationship is better expressed by the Mediterranean meteoric water line (MMWL): $\delta D= 8\delta^{18}O+22$ (Gat, 1980; Gat and Carmi, 1987; 1970).

The topography of Lebanon, dominated by the presence of two main parallel series of mountains oriented from the southwest to the northeast, influences the isotopic composition of precipitation across the country (Saad et al., 2000). The Lebanon Mountains, bordering the Mediterranean Sea, are characterized by a humid Mediterranean climate whereas the Anti-Lebanon Mountains, located inland, are characterized by a humid to a semiarid climate. Due to this topographic effect, the isotopic composition in rainwater is expected to evolve rapidly. Coastal precipitation is isotopically enriched, while the colder inner continental regions receive isotopically depleted precipitation with seasonal differences. This altitude effect is useful in hydrogeological studies, as it distinguishes groundwaters recharged at high altitudes from those recharged at low altitude.

Combining the two approaches of chemical and isotopic characterization of rainwater in Lebanon, we will show the influence of topography, natural and anthropogenic sources on the precipitation quality. The study relies on three years of data that allows the definition of the trend of the Lebanese Meteoric water line in comparison with the MMWL and the MWL. Also, data will be compared with the characteristic meteoric water lines in the surrounding eastern Mediterranean area.

MATERIALS AND METHODS

Sampling of rainwater was performed on a monthly basis, during the rainy season extending from November till March and for a period of three years (2003-2005). Stations were chosen in different geographic locations to accurately represent the spatial and temporal distribution of precipitation in the country (Figure 1). The details of these sampling sites are described below:

Figure 1. Location of sampling sites (indicated by triangles).

- Three coastal stations located from the north to the south, Tripoli, Beirut, and Tyr, which are influenced mainly by the Mediterranean maritime winds.

Three other continental stations located at different altitudes, Bhamdoun (850 m in the Lebanon Mountains); Majdelselm (650 m in the Anti-Lebanon Mountains); and Baalbak (1050 m in the Bekaa plain), which are influenced partly by internal air masses and a semiarid climate.

All rainwater samples were collected twice a day by means of a rain gauge. The open precipitation collector was a 22 cm diameter polyethylene funnel. The collector was positioned about 1.5 m above the ground. The gauges were rinsed with bidistilled water every day at the time of sample collection and transferred to a tightly stoppered container large enough to accommodate the monthly amount of precipitation.

Each sample was divided into two small bottles. The first was used for the analysis of major anions. The second bottle was acidified with hydrochloric acid (0.1%), refrigerated at 4°C, and used for the analysis of major cations. All bottles used for sample storage were cleaned by rinsing repeatedly with double distilled water. The pH was measured using a HANNA HI8314 model instrument with a combination calomel glass electrode.

Following the determination of bicarbonate (by acid-base titration), all samples were filtered through a 0.45-µm filter. Calcium, magnesium, sodium and potassium were measured using AA (Perkin Elmer analyst 100 Model A.A.S) using air-acetylene flame after addition of lanthanum chloride to minimize the interference phenomena. Chloride, sulfate, nitrate and ammonium were measured using IC (Dionex). Each sample was analyzed for $\delta^{18}O$, $\delta^{2}H$ and ^{3}H in the Isotope Laboratories of Damascus (Syrian Atomic Energy Commission). 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 ($\delta^{18}O$, $\delta^{2}H$), relative to the Vienna Standard Mean of Ocean Water (VSMOW).

RESULTS AND DISCUSSION

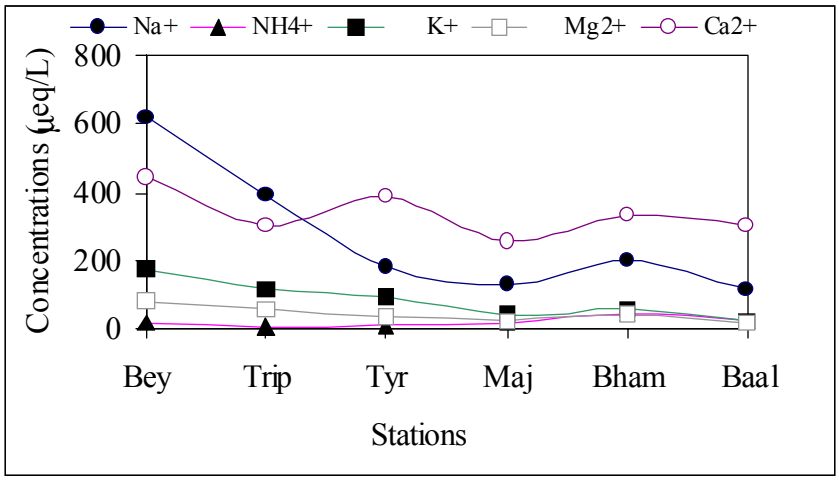
Rainwater chemistry

In this paper, average concentrations and average element-to-sodium ratios are rainwater-volume-weighted. Concentrations of chemical species (K^+, Ca^{2+}, Na^+, Mg^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-}) are shown in Figure 2 to compare the six stations. As shown in Figure 2, concentrations of rain samples are highly variable, depending upon the sample location and the species of interest. In fact, most of the rain constituents have higher levels at coastal sites (i.e., Beirut) relative to continental locations (i.e., Baalbak), especially elements sensitive to sea-salt fraction. For example, concentrations of Na^+ and Cl^- at coastal sites can be fourfold higher than at stations located at higher altitudes.

To determine the relative contribution of marine and other sources to the precipitation, the species-to-Na^+ ratios are presented in Figure 3. Using Na^+ as a marine tracer, the contribution of sea salts to rainwater composition is higher for K^+ in coastal sites than continental sites. Samples collected from Tyr and other continental stations have M/Na ratios for NO_3^-, NH_4^+, Ca^{2+}, SO_4^{2-} up to a factor of two higher than those from other coastal sites for some species. Other species like Mg^{2+} show less difference in Mg/Na between coastal and continental sites. Higher Ca^{2+}/Na^+ values at highland stations reflect a continental origin for Ca^{2+} originating from abundant terrestrial minerals like carbonates in these regions (Basak and Alagha, 2004).

In order to evaluate the origin of different species in the rain chemistry, we calculated the excess of some elements using Na^+ as a reference metal. The non-sea-salt source contribution of sulfate and calcium was estimated by the following equation:

$$\text{Excess M (\%)} = [1-(Na/M)_{rain}*(M/Na)_{sea}] \text{ (Zhang et al., 1999)} \quad (1)$$



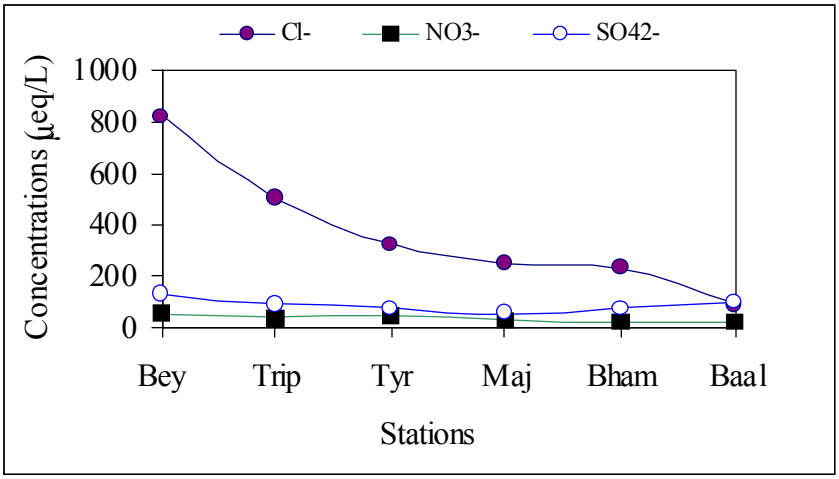


Figure 2. Volume weighted mean ion concentration in rainwater samples at coastal (Bey:Beyrouth, Trip:Tripoli, Tyr) and continental stations (Maj:Majdelselm, Bham:Bhamdoun, Baal:Baalbak) from November 2003 to March 2005.

where $(Na/M)_{rain}$ represents sodium to species in rainwater, and $(M/Na)_{sea}$ is species to sodium in seawater.

In this study, the excess Ca^{2+} varied from 93% at Beirut to 98% at Baalbak. This weak excess variation reflects the dissolution of carbonate minerals from crustal rocks throughout the different sample locations. The dissolution of carbonate, due to the predominance of limestone formations in Lebanon, releases up to 450meq/L to the atmosphere. The high Ca excess in the rainwater chemistry induces high pH values that reach 6.5 in almost all stations. The carbonate dissolution in rainwater provides this elevated buffering capacity in wet deposition.

For anions the excess SO_4^{2-} is at 41% at coastal stations, whereas at continental sites excess SO_4^{2-} increased to 86 %. Such a difference in excess should provide a first estimate for the impact of local anthropogenic emissions on regional rainwater chemistry. Similarly elevated ratios of NO_3^-/Na^+ and NH_4^+/Na^+ in Tyr and continental stations reflects anthropogenic emissions such as combustion of fossil fuels and fertilizer applications in these agricultural areas (Zhang et al., 1999; Elagha et al., 2001).

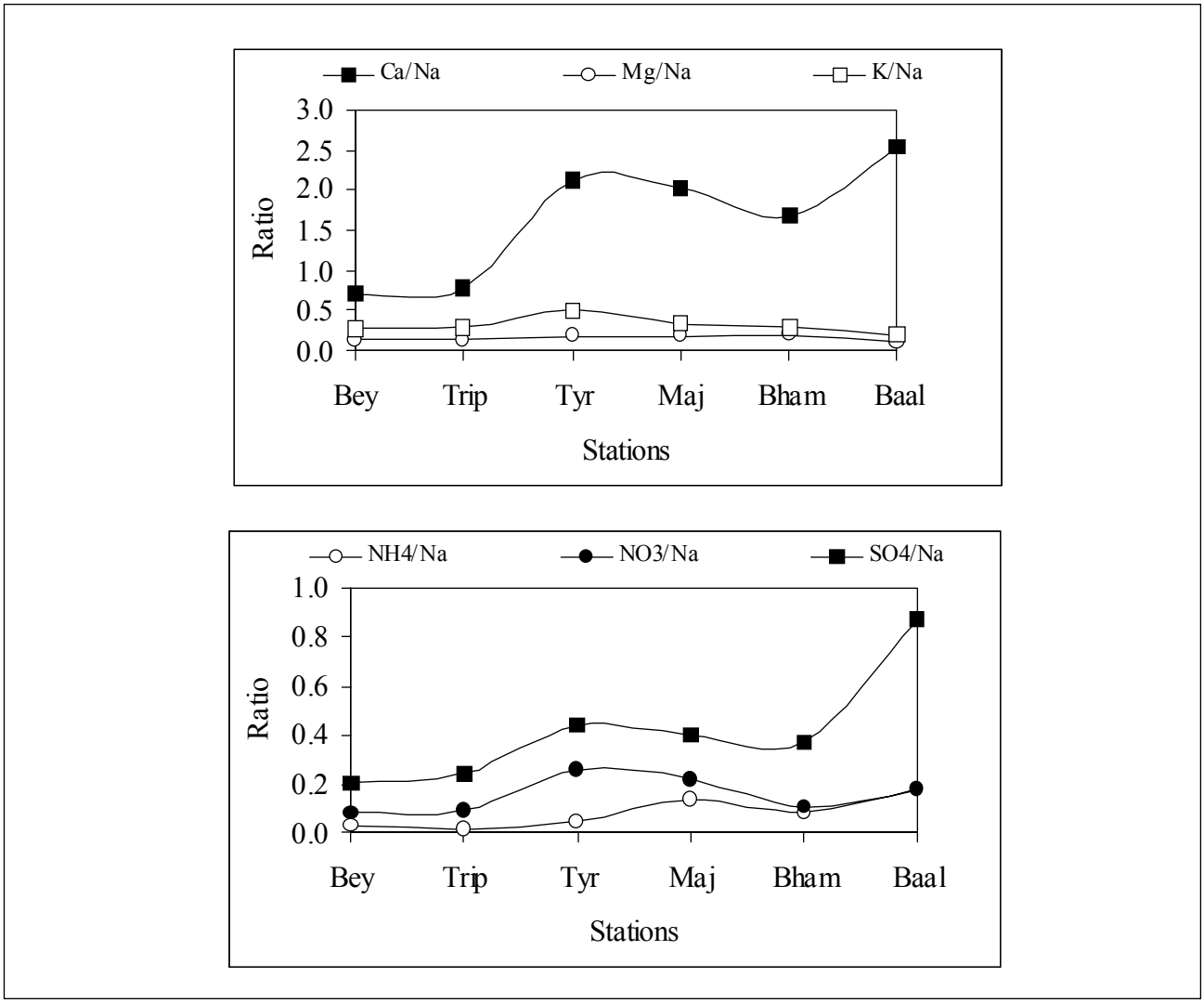


Figure 3. Average element-to-Na ratios in rainwater samples at coastal (Bey:Beyrouth, Trip:Tripoli, Tyr) and continental stations (Maj:Majdelselm, Bham:Bhamdoun, Baal:Baalbak).

Rainwater isotopic composition

It should be emphasized that measuring the oxygen as well as hydrogen isotopes in precipitation often presents additional information for rainwater characterization. Stable isotopic composition of precipitation is explained by applying the Rayleigh model including the progressive condensation of the vapor during transport to higher latitudes with lower temperatures. In addition, the local meteoric water line provides a baseline for tracing groundwater recharge (Barnes and Allison, 1988). The position of meteoric waters on this line is controlled by a series of temperature-based mechanisms that drive the rainout process. These include vapor mass trajectories over the country, rising over topographic features, moving to high altitudes and seasonal effects. Each has a characteristic effect on the stable isotopic composition of precipitation (Clark and Fritz, 1997).

In Lebanon, isotopic composition of rainwater is influenced by three main air mass trajectories: one originating from Eastern Europe which is humid and cold, another originating from the Mediterranean Sea that is warm and rainy, and warm winds passing over the Syrian Desert. Also the topographic feature of the country induces a high altitude effect on the isotopic fractionation in precipitation. In fact, in the Lebanon and Anti-Lebanon mountains where the average temperatures

are lower than the coastal areas, precipitation will be isotopically depleted. This altitude effect is useful to distinguish groundwater recharged at high altitudes from that recharged at low altitude. The stable isotope composition of precipitation in Lebanon (Figure 4) shows the Lebanese Meteoric water line LMWL defined by the following equation:

$$\delta D = 7.13\ \delta^{18}O + 15.98 \quad (2)$$

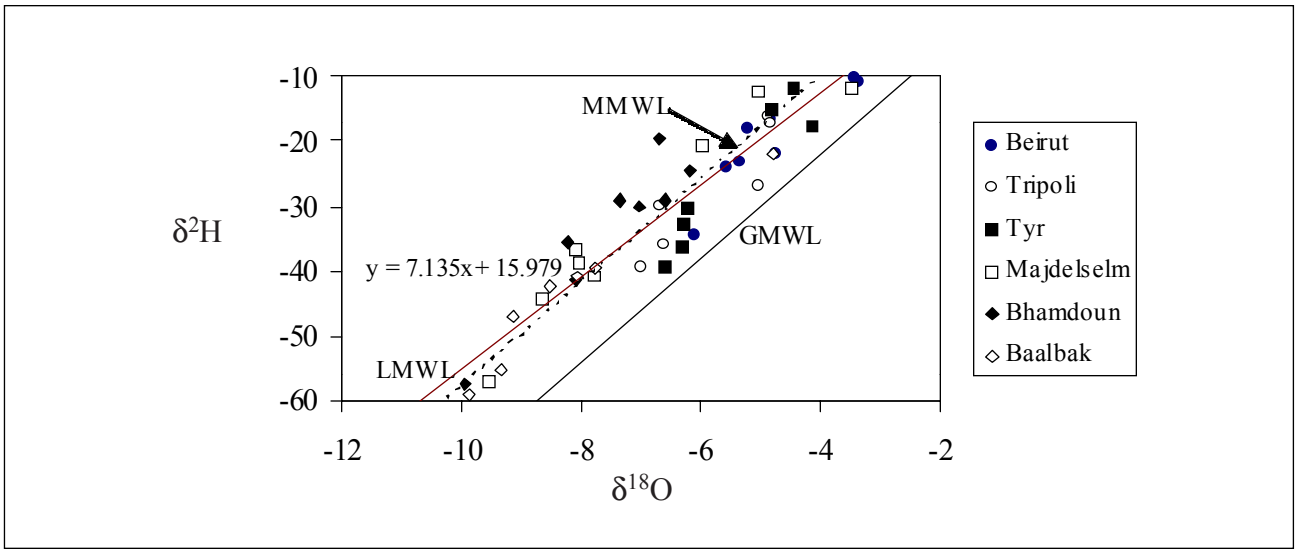


Figure 4. δD-$\delta^{18}O$ relationships plot showing monthly isotopic values of the rain water of coastal and continental stations. The MMWL and GMWL lines are shown for reference. The Lebanese Meteoric Water Line is labeled as LMWL.

The slope of this line (7.13) is different from the slope of GMWL estimated by Craig (1961). But the overall average of these data is close to the MMWL. The deviation of the slope from the MMWL is influenced by a secondary evaporation during rainfall. The LMWL was found close to the Regional Meteoric Water Line RMWL as estimated for data collected from Syria and Jordan in the following equation:

$$\delta D = 7.8\ \delta^{18}O + 19.25 \quad \text{for RMWL (Kattan, 1997)} \quad (3)$$

The calculated d-excess for LMWL (15.98) was found lower than the d excess for RMWL (19.25) indicating a relatively less pronounced evaporation effect in Lebanon. In fact the d-excess varies significantly depending on the temperature and humidity at the vapor source region.

Figure 5 shows the variation of $\delta^{18}O$ against $\delta^{2}H$ for coastal and continental highland stations. Samples located in the highlands (Majdelselm, Bhamdoun, and Baalbak) scatter along the MMWL with d-excess higher than +20 (+23.43). This is characteristic for precipitation in the highlands of the eastern Mediterranean region (Gat and Carmi, 1970; Gat and Dansgaard, 1972; Al-Momani et al., 1995). Samples from the coastal areas of Lebanon (Beirut, Tyr, and Tripoli) scatter slightly below the Mediterranean Meteoric Water line with a slope of 8.7. Note that the samples of Tripoli, Beirut and Tyr, showing deviation from the MMWL, have isotopic composition in precipitation at these stations that is subjected to temperature effects.

Coastal stations are isotopically enriched in heavy isotopes. There is also a tendency that with high altitude the oxygen-18 value of precipitation is more depleted than at a low altitude. This spatial

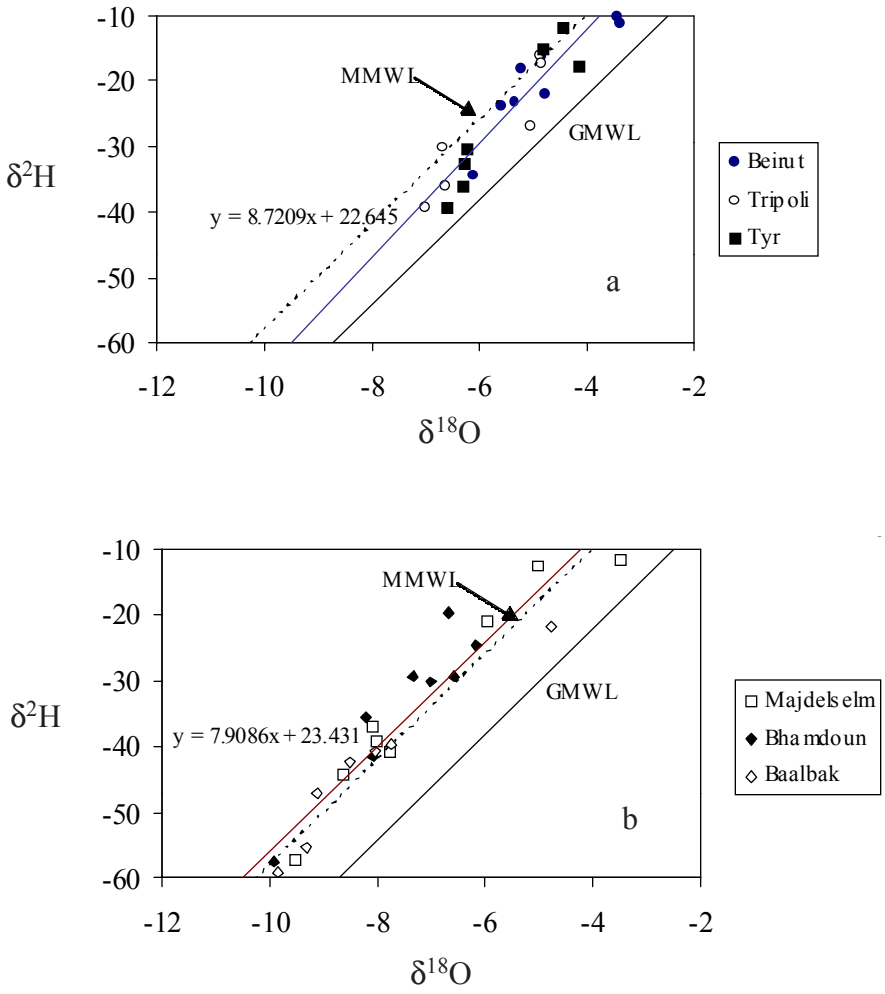


Figure 5. δD-$\delta^{18}O$ relationships plot showing monthly isotopic values of the rain water of either coastal (a) or continental stations (b). The lower line indicates GMWL; the dashed line is the MMWL

variation in the stable isotope composition is also of practical significance for hydrogeological applications. Figure 5 shows the evolution of the isotopic composition of rain with increasing altitude from the coast to the topographic highs to the east along the direction of movement of air mass. The figure shows a continuous depletion in heavy isotopes of the air masses during their ascent and passage over the eastern escarpment of the country (Siegenthaler and Oeschger, 1980). We can conclude that the Mediterranean Sea is the dominant vapor source for the regional Lebanese precipitation. These features of the isotope distribution give rise to a model which is based on the air mass movement into the Mediterranean area during winter, when cold and dry continental air masses come in contact with a relatively warm sea, resulting in rapid evaporation (Rindsberger and Magaritz, 1983).

Altitude effect

When air masses are orographically uplifted they cool and precipitate the heavier isotopes preferentially. Depending on the precipitation history, the topographic situation, the degree of

cooling and the precipitable moisture left, the altitude effect on oxygen-18 generally ranges between -0.15 and -0.50‰ for each 100 m of altitude gained (Clark and Fritz, 1997). A corresponding decrease of about -1 to -4‰ per 100 m rise for ^{2}H is also observed. In applied isotope hydrology, this effect is used to estimate the altitude of groundwater recharge areas. The Lebanon and Anti-Lebanon mountains offer an excellent opportunity to study this effect with an altitude difference of nearly 1000 meters. Figure 6 shows that the long-term average of oxygen-18 decreases from -5.36‰ at 100 m to -8.2‰ at 1000 m.

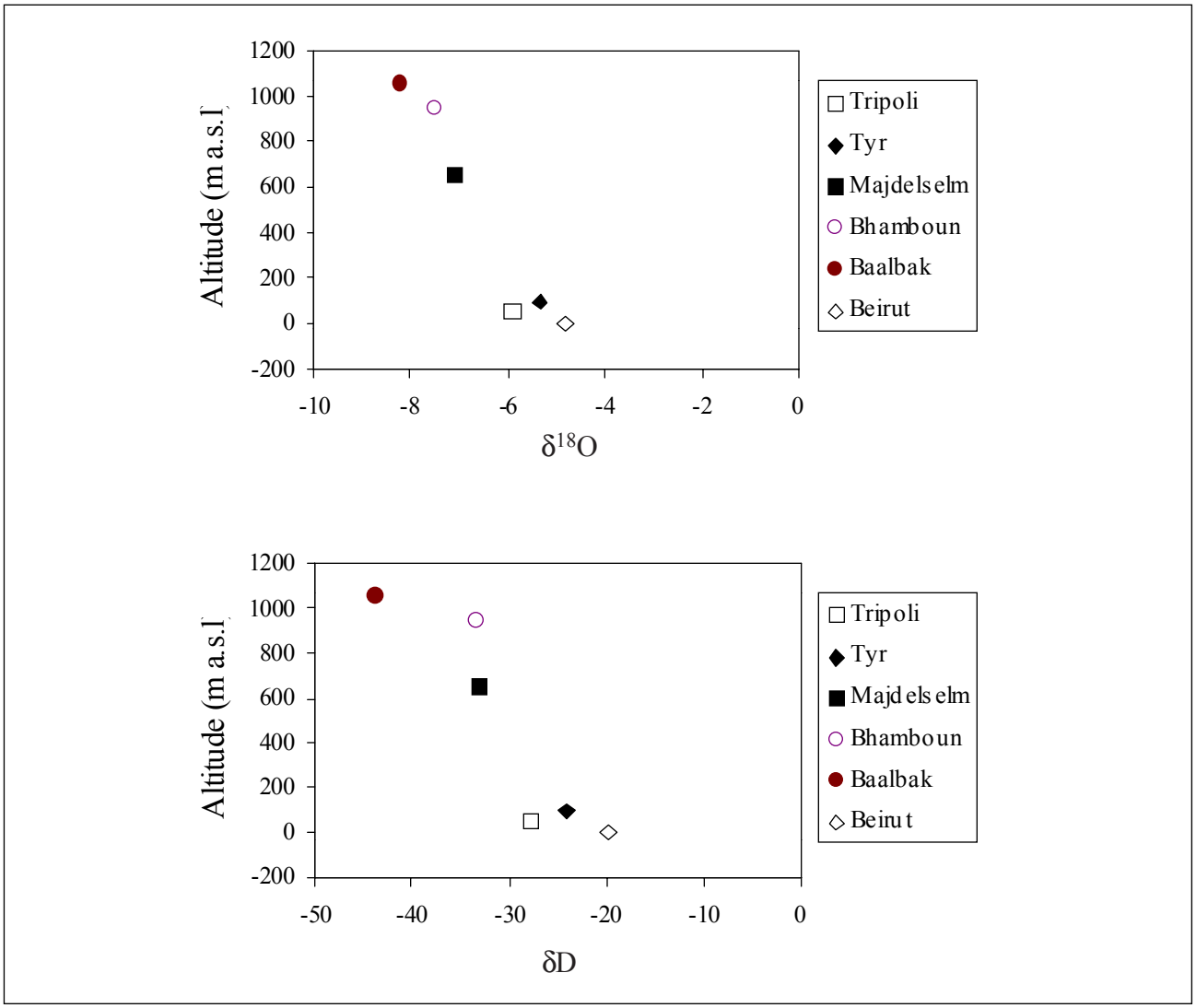


Figure 6. Evolution of $\delta^{18}O$ and δD values of rainwater against altitude in the studied stations.

In the coastal lowlands, $\delta^{18}O$ decrease is -0.53‰ per 100m. From 100 m and up to 800 m rise, the average decrease in oxygen-18 is -0.18‰ per 100 m; above this altitude it falls more rapidly (-0.7‰ per 100 m). The possible explanation may be seen in the forced rainout of already isotopically depleted moisture onto the steep ridges of the Lebanon and Anti-Lebanon mountains.

The variation of δD/altitude reveals a steeper gradient in the coastal lowlands (-4.1 ‰ per 100 m) than in the highlands up to 800 m (-1.1‰ per 100 m). Above this altitude,dD decrease falls drastically to -10.37‰ per 100 m. This trend is similar to the variation of $d^{18}O$ against altitude. This isotopic fractionation seems to be characteristic for the Mediterranean moisture regime across the different features of the country.

Tritium analysis in rainwater

Tritium is the most commonly employed radioisotope used to identify the presence of modern recharge. Tritium, incorporated into the water molecule, is the only radioisotope that actually dates groundwater (Clark and Fritz, 1997).

In Lebanon, the mean Tritium concentration in atmospheric precipitation ranges from 2.8 TU in coastal stations up to 4.3 TU at the Baalbak station (Figure 7). Averaged over the year, a small continental effect is apparent at Baalbak. The local variations are likely to be small, because the ^{3}H content in rain is not influenced by altitude effect (as are ^{18}O and ^{2}H) (Gat et al., 1962). We conclude that these values are close to the ones found for precipitation at low latitudes.

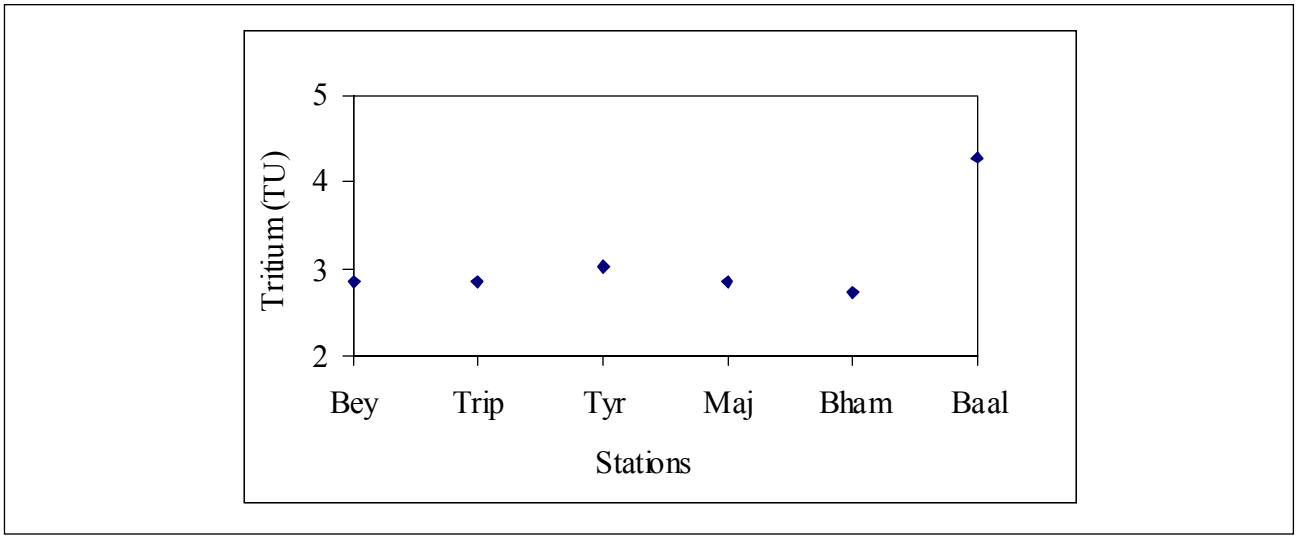


Figure 7. Relationship between the weighted means of tritium values and coastal (Bey:Beyrouth, Trip:Tripoli, Tyr) and continental stations (Maj:Majdelselm, Bham:Bhamdoun, Baal:Baalbak).

CONCLUSIONS

The chemical and isotopic composition of precipitation in coastal and inland regions of Lebanon has been investigated. The chemistry of precipitation in the study area is similar to that of other areas of the Mediterranean basin. The observed pH values of precipitation have an average value of 6.5. The acidity of the rainwater was significantly neutralized by alkaline soil dust, principally calcium. The chemical composition of precipitation in the coastal area is influenced by sea-salt spray of the Mediterranean Sea, whereas anthropogenic activities like agriculture and alkaline soil dust are predominant factors in the continental area. Rainwater affected by the Mediterranean Sea and characterized by a large marine fraction of salts, has high values of $\delta^{18}O$ and δD. Whereas rainwater affected by continental and anthropogenic sources with a relatively small contribution of marine salts, has low values of $\delta^{18}O$ and δD. Isotope fractionation in precipitation, including depletion in both $\delta^{18}O$ and δD in highland stations, is primarily due to the rainout and the altitude effects. The Lebanese Meteoric Water Line was found close to the Regional Meteoric Water Line with a lower d-excess indicating a relatively less pronounced secondary evaporation effect in Lebanon. Averaged over the year, ^{3}H content in rainwater showed a small continental effect at the Baalbak station.

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