# JOURNAL OF ENVIRONMENTAL HYDROLOGY

The Electronic Journal of the International Association for Environmental Hydrology On the World Wide Web at http://www.hydroweb.com

VOLUME 15

2007

## SEASONAL EFFECT ON THE ISOTOPIC PATTERN OF **RAINWATER IN LEBANON**

Zeinab Saad<sup>1,2</sup><sup>1</sup>Lebanese University, Faculty of Sciences, Hadath, LebanonVéronique Kazpard<sup>1,2</sup><sup>2</sup>Lebanese Atomic Energy Commission, Beirut, Lebanon

Rainwater chemistry and isotopic parameters were studied over a four year period at representative coastal and highland sites in Lebanon. Major inorganic ion composition showed that calcium and sulfate in rainwater had a crustal origin, while potassium, sodium and chlorine had a marine sea spray origin. All rain samples had an average pH varving between 5.6 and 6.8, showing that precipitation tends to be alkaline. Environmental isotopes provide a local meteoric water line in Lebanon that is close to the Mediterranean line, showing that local precipitation is affected by the humid Mediterranean climate. Isotopic characterization of rainwater showed a depletion in both  $\delta^{18}O$  and  $\delta D$  values in highland stations compared to coastal stations. Season, temperature and rainfall amount strongly influence the depletion in isotopic parameters at continental stations. An evaporative enrichment in rainwater occurs during warm months (November) when rain amounts are small. The seasonal effect is pronounced in both coastal and continental sites in December and January. Tritium data of monthly precipitation from all sites within Lebanon show that there are no significant differences in seasonal effect between stations.

Journal of Environmental Hydrology

#### **INTRODUCTION**

Rainfall in Lebanon is influenced by the topography of the country that consists of two parallel mountain chains called the Lebanon and Anti-Lebanon Mountains that are separated by the Bekaa plain (Dubertret, 1948). The Lebanon mountains which face the Mediterranean sea are characterized by a humid maritime climate, whereas the Anti-Lebanon chain, situated inland, has a humid to semiarid more continental climate. These topographic features influence both the chemical and isotopic composition of rainwater.

Previous chemical and isotopic studies of rainwater in Lebanon confirmed the topographic and orographic influence on rainwater quality. Chemical rainwater composition showed large variations between low and high altitude sites, and this was explained by either proximity to the Mediterranean Sea or local agricultural input sources (Saad et al., 2000).

To improve the understanding of rainwater differentiation in Lebanon, isotopic techniques were applied at different rain sites by Saad et al. (2005). They defined the Lebanese Meteoric Water Line (LMWL) by the following equation:  $\delta D = 7.13 \ \delta^{18}O + 15.98$  as compared to the Global Meteoric Water Line (GMWL) (Craig, 1961; Dansgaard, 1964). This relation is close to the Regional Meteoric Water Line (RMWL) in the East Mediterranean with a lower d-excess compared to the region. Values of deuterium excess as determined by Kattan (1997) are 19‰ in Syria and 14‰ in south Turkey; this parameter was found to depend on the humidity and the temperature conditions in the region.

It was also found that the altitude effect, reflecting topographic variation, influences the isotopic fractionation in precipitation, including depletion in both  $\delta^{18}$ O and  $\delta$ D in stations at high altitude (Saad et al., 2005). In fact, as a rule the isotopic composition of precipitation changes with altitude and becomes more and more depleted in <sup>18</sup>O and <sup>2</sup>H at higher elevations. This enables the identification of the elevation at which groundwater recharge takes place.

The current study is conducted in order to evaluate long-term variation (4 years) of isotopic composition of rainwater according to the following factors: Seasonal change, temperature variation and rainfall amount. The stable isotope characteristics of rainfall is investigated from 2003 to 2006 to establish a general hypothesis about how these factors influence rainwater composition. Rainfall was collected from both coastal and highland stations to understand the influence of topographic features (altitude, temperature effects and rainwater amount) on isotope signature drift over these years.

#### **MATERIALS AND METHODS**

Sampling of rainwater was conducted on a monthly basis, during the rainy season extending from November through March and for a period of four years (2003-2006). Stations were chosen in different geographic locations to accurately represent the spatial and temporal distribution of precipitation in the country.

The locations of these sampling sites are:

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

-Three continental stations located at different altitudes (Bhamdoun, 900 m a.s.l in Mount Lebanon; Nabatiyeh 450 m a.s.l, in Anti-Lebanon; and Bekaa, 1050 m a.s.l) influenced partly by internal air masses and a semiarid climate.

Table 1 shows the monthly variation of averaged temperature and rainfall amount in typical coastal and highland stations as furnished by specified official authorities at Beirut International Airport.

The total rainfall amounts vary from year to year; for example total precipitation collected in Beirut city for the years 2003, 2004 and 2005 is respectively 1009 mm, 681 mm and 886 mm.

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 located at approximately 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%) and then refrigerated at 4°C, and used for the analysis of major cations. All samples were filtered through a 0.45-µm filter. Cations were measured using AAS (Perkin Elmer analyst 100 Model A.A.S) using air-acetylene flame. Anions were measured using IC (Dionex). Each sample was analyzed for  $\delta^{18}$ O,  $\delta^{2}$ H in the Isotope Laboratories of Damascus (Syrian Atomic Energy Commission) using the method according to Epstein and Mayeda (1953).

	Coastal stations (Beirut)		Highland stations (Zahle)	
Month	Mean Temperature(℃)	Mean rainfall (mm)	Mean Temperature(°C)	Mean rainfall (mm)
November	19	78	13.9	91
December	14	105	9.3	102
January	12	113	5.6	189
February	15	80	7.3	176

Table 1. Monthly variation of average temperature and rainfall.

### **RESULTS AND DISCUSSION**

Chemical and physical characteristics of rainwater were studied from 2003 to 2006 for coastal and highland stations. Figure 1 presents mean yearly pH variation in rainwater for different sites for four years progressively. Values were found to be rather alkaline (higher than 5.7). This result is due to the loading of atmosphere by carbonate, to the alkaline nature of the soil, and the predominance of limestone formations in Lebanon (Dubertret, 1975).

Chemical variation was found for some species between coastal and continental sites. The contribution of sea salts to rainwater composition is higher for K<sup>+</sup>, Cl<sup>-</sup> and Na<sup>+</sup> in coastal sites compared to continental sites (Figure 2). Both continental and coastal stations have almost comparable  $Ca^{2+}$  and  $SO_4^{2-}$  variation. These elements are likely originating from abundant terrestrial minerals like calcite and dolomite that are predominant in the region (Basak and Alagha, 2004).

The chemical differentiation of rainwater between the different sites is also studied using isotopic methods to highlight the influence of topography, temperature, season and rainwater amounts on isotope composition.



Figure 1. Mean yearly variation of pH in rainwater in different sites.



Figure 2. Chemical variation in rainwater collected from coastal and continental stations.

### Isotopic characterization of rainwater in Lebanon

In Lebanon, the topography induces a high altitude effect on the isotopic fractionation in rainwater. In fact, at highland stations, where the average temperatures are lower than the coastal areas, precipitation will be isotopically depleted. This altitude effect is useful to distinguish groundwaters recharged at high altitudes from those recharged at low altitude.

The stable isotope composition of precipitation in Lebanon (Figure 3) shows the LMWL defined by the following equation (Saad et al., 2005):

$$\delta D = 7.13 \ \delta^{18}O + 15.98$$

(1)

The slope of this line (7.13) is different from the slope of the GMWL estimated by Craig (1961). But the overall average of these data is close to the Mediterranean Meteoric Water Line



Figure 3.  $\delta D$ - $\delta^{18}O$  relationships of the rain water in Lebanon. The Lebanese Meteoric Water Line is labeled as LMWL.

(MMWL). The deviation of the slope from the MMWL is influenced by a secondary evaporation during rainfall. The LMWL was found to be close to the RMWL as estimated for data collected from Syria and Jordan in the following equation:

$$\delta dD = 7.8 \,\,\delta^{18}O + 19.25 \,\,(\text{Kattan}, \,1997) \tag{2}$$

The calculated d-excess for the LMWL (15.98) was found to be lower than the d-excess for the 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.

#### Altitude effect on rainwater

The altitude effect on the fractionation of isotopic composition of rainwater was extensively determined over 4 years (2003 - 2006). Figure 4 shows typical isotopic variation against altitude for the last two years.

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

### Seasonal variation of isotopic composition of rain water

Figures 5 and 6 show the seasonal variations in  $\delta^{18}$ O shown by weighted averages of monthly precipitation samples collected in typical coastal and highland stations.

Coastal and highland stations from the north to the south show a seasonal change in the isotopic composition ( $\delta^2$ H and  $\delta^{18}$ O) of the precipitation. These variations are correlated with the temperature.

The most pronounced factors which determine the offset of monthly data at the stations are:

1) different source characteristics of the moisture, either due to the seasonal change of the





meteorological conditions, or different location of the source regions. This basically fixes a series of parallel meteoric water lines, for each of the seasons.

2) evaporative enrichment in the falling droplets beneath the cloud base, effective during warm and dry months when rain amounts are small. This partially evaporated rain is characterised by relatively higher  $\delta^{18}$ O values and small to negative d-excess values (Dansgaard, 1964; Rozanski et al., 1993).

3) high values of the d-excess parameter associated with snow or hail. These events are also associated with very depleted isotopic values. (Jouzel and Merlivat, 1984)



Figure 5. Monthly mean variation of  $\delta^{18}$ O and  $\delta^{2}$ H of rainwater in coastal stations (a) and highland stations (b) in relation with temperature change.

Journal of Environmental Hydrology



Figure 6. Monthly mean variation of d<sup>18</sup>O of rainwater in all studied sites.

Precipitation over the coastal stations has the characteristics of a first condensate of the vapor. The range of most  $\delta^{18}$ O values is relatively smaller than the continental stations. The same is true for the  $\delta^{2}$ H values. The continental effect, also referred to as the distance-from-coast effect (i.e. a progressive  $\delta^{18}$ O depletion in precipitation with increasing distance from the sea) varies considerably from season to season. The amplitude of seasonal variations in temperature increases with the continentality of the site (Figure 6). It is also strongly correlated with the temperature gradient and depends both on the topography and the climate regime. However, the effect of depletion in November (where temperature is still elevated) is smaller than the effect in winter. This was attributed to the re-evaporation of rain water (Rozanski et al. 1982).

#### Effect of temperature and amount of rainwater on isotopic fractionation

Figure 7 shows seasonal correlations between T and  $\delta^{18}$ O for a coastal and continental site.

The rainfall amount effect (i.e. a correlation of the depletion of heavy isotopes with the amount of rain) is explained by the preferential isotopic exchange of the smaller droplets, which are predominant in light rains, with the near-surface moisture. Heavier rains on the other hand maintain the depleted isotopic values from within the clouds. The dip in the  $\delta^{18}$ O curve for seasonal precipitation at coastal and continental stations (Figure 7) in December and January is due to the high rain intensity during these months (Dansgaard, 1964).

#### CONCLUSIONS

The chemical and isotopic composition of precipitation in coastal and highland regions of Lebanon has been investigated for four years (2003-2006). Rainwater affected by the Mediterranean Sea and characterized by a large marine fraction of salts in the coastal sites, has high values of  $\delta^{18}$ O and  $\delta$ D. Rainwater affected by crustal sources in highland stations, has low values of  $\delta^{18}$ O and  $\delta$ D. Isotope fractionation in precipitation, including depletion in both  $\delta^{18}$ O and  $\delta$ D in highland stations, is primarily due to rainout and altitude effects. Coastal and highland sites portray a seasonal change in the isotopic composition of the precipitation where the amplitude of seasonal and temperature variations increases with the continentality of the site. An evaporative enrichment in rainwater is effective during warm months (November) when rain amounts are small. The dip in the  $\delta^{18}$ O curve for seasonal precipitation at coastal and continental stations in December and January is due to the high rain amount during these months. From a series of tritium data of monthly precipitation from



Figure 7. Isotopic variation of  $\delta^{18}$ O in rainwater compared to precipitation amount in coastal site (a) and highland site (b).

all sites within Lebanon we concluded that between the stations there are no significant regular differences in seasonal effect.

#### REFERENCES

- Basak, B., and O. Alagha. 2004. The chemical composition of rainwater over Büyükçekmece Lake, Istanbul. Atmospheric Research, 71, 275-288.
- Craig, H. 1961. Isotopic variations in meteoric waters. Science 133: 1702-1708.

Dansgaard, W. 1964. Stable isotopes in precipitation. Tellus 4, 436–468.

- Dubertret, L. 1948. Apercu de géographie physique du Liban, l'Anti-Liban et la Damascene. Notes et memoires, Beyrouth IV. 191-226.
- Dubertret, L. 1975. Introduction à la carte géologique au 1/50000 du Liban. Notes et Mémoires sur le Moyen-Orient, 23: 345-403.
- Epstein, S., and T. Mayeda. 1953. Variations of O<sup>18</sup> content of waters from natural sources. Geochim. Cosmochim. Acta 4: 213-224.
- Jouzel, J., and L. Merlivat. 1984. Deuterium and oxygen-18 in precipitation: modelling of the isotopic effects during snow formation. J. Geophys. Res. 89: 11749-11757.
- Kattan, Z. 1997. Chemical and environmental isotope study of precipitation in Syria. Journal of Arid Environments, 35,601-615.

Journal of Environmental Hydrology

- Rozanski, K., L. Araguas-Araguas, and R. Gonfiantini. 1993. Isotopic patterns in modern global precipitation, in: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), Climate change in continental isotopic records. Am. Geophys. Union, Washington, DC, pp. 1–37.
- Rozanski, K., Ch. Sonntag, and K.O. Munnich. 1982. Factors controlling stable isotope composition of modern European precipitation. Tellus 34: 142-150.
- Saad, Z., V. Kazpard, A.G. El Samrani, and K. Slim. 2005. Chemical and isotopic composition of rainwater in coastal and highland regions in Lebanon. Journal of Environmental Hydrology, vol 13, 29, 1-11.
- Saad, Z., K. Slim, A. Ghaddar, M. Nasreddine, and Z. Kattan. 2000. Chemical composition of rain water in Lebanon. European Journal of Water Quality, 31, 223-238.

ADDRESS FOR CORRESPONDENCE Zeinab Saad Lebanese Atomic Energy Commission CNRSL PO Box 11-8281 Beirut, Lebanon

Email: zsaad@cnrs.edu.lb