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Final report of a coordinated research project 2000–2004

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ISOTOPIC COMPOSITION OF PRECIPITATION IN THE MEDITERRANEAN BASIN
IN RELATION TO AIR CIRCULATION PATTERNS AND CLIMATE

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FOREWORD

The IAEA has operated the Global Network of Isotopes in Precipitation (GNIP) since 1961. There has been an increased need for GNIP data following the recognition of the role of precipitation stable isotopes in better simulating the hydrologic cycle in climate models. The isotopic composition of precipitation is closely related to rain formation conditions, i.e. with the temperature of formation, the origin of air masses, and the degree and mechanism of rainout. Over the last twenty years, use of GNIP data in climate model has indicated a need for a much more refined, process-based understanding of isotope variations in the hydrological cycle. This coordinated research project (CRP) was initiated with the aim of collecting new data on higher spatial density and temporal frequency to improve our knowledge of environmental isotope variations in atmospheric waters.

The Mediterranean region was chosen for this study so that climatic and meteorological conditions, which govern the rain formation process, and their variations along east-west and north-south directions, could be investigated. In addition, the first steps of the hydrological cycle, that is evaporation from seawater and condensation of atmospheric vapour could also be studied.

The IAEA invited scientists from institutes in Mediterranean countries who have already been involved in studies related to the isotopic composition of precipitation to take part in this CRP, which was initiated in 2000.

This publication is a summary of the results achieved in the CRP. The overall achievements are presented as the executive summary, and the detailed findings are presented in each contribution. These results were presented in the final research coordination meeting, held in Vienna from 15 to 19 March 2004.

The results of this CRP are relevant to the Member State scientists conducting hydrological research. In addition, the results would contribute to the IAEA programme on water resources, in particular to its activities related to water resources assessment in Middle East and North African countries, to marine environment studies in the Mediterranean Sea, the Black Sea, the Caspian Sea, and the Red Sea and to the Global Network of Isotopes in Precipitation programme.

The IAEA officer responsible for this publication was L. Gourcy of the Division of Physical and Chemical Sciences.

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SUMMARY

1. INTRODUCTION

The objectives of this Coordinated Research Programme (CRP) were the assessment of the variation of the isotopic values along the main directions west-east and south-north of the Mediterranean basin; the correlation between these variations and the main climatic and meteorological parameters; the determination of physical phenomena in compliant place and the refinement of a process-based understanding to fully realize the value of isotopic data in hydrological and climate studies. The $^{18}O/^{2}H$ analyses of daily precipitation sampling and water vapour give valuable information for climate studies. The conclusions drawn from the regional scale interpretation of data obtained by the scientists is summarized here.

The fourteen Mediterranean countries participating in this research programme carried out the monthly sampling of precipitation at 84 stations from January 2001 to December 2003. Daily or event-based precipitation sampling was also performed at 32 stations (Annex 1). Water vapour sampling was done at eight stations. This sampling was continuously performed during 48 hours starting Monday morning and Wednesday afternoon. The sampling of atmospheric water vapour was performed using similar equipment developed at the IAEA Isotope Hydrology laboratory. Liquid nitrogen cold traps were used when sampling (Annex 2). Stable isotopes analyses (^{18}O and ^{2}H) were carried out for all samples. Tritium analyses were only performed at selected stations on a monthly basis.

In order to reduce the number of isotopes analyses to be done, two sampling periods were chosen for daily/event based and water vapour sampling; October 2001 to March 2002 and October 2002 to March 2003. The minimum information collected at each station is the basic meteorological data (surface air temperature and rain amount). Synoptic weather maps, position of the inversion layer and back-trajectories for specific events were collected in various countries. A common database containing basic meteorological parameters, $\delta^{18}O$ and $\delta^{2}H$ on a monthly and daily-basis was built.

2. UPDATED INFORMATION OBTAINED USING MONTHLY DATA

Previous studies conducted in the Mediterranean basin showed the variability of isotopes content in precipitation. These studies show that the Western part of the Mediterranean basin has a d-excess of 14‰, whereas the Eastern part shows an excess of +22‰. This variation reflects a mixture between the Mediterranean and the Atlantic (d-excess=10‰) air masses. This evolution is not regular from west to east as it also depends on the origin of the air masses. The use of d-excess in addition to absolute values O-18 and H-2 in precipitation is useful for seasonal tracing. The contrast between winter and summer data is very important.

The results obtained under this CRP (Annex 3 and http://isohis.iaea.org) corroborate the global increase of d-excess from the west to the east of the Mediterranean basin. They also show local variations that do not follow this pattern. For example in Greece, very important variations are observed where minimum values are registered for Patras (10.1‰) and maximum for Athens, Pendeli (17.0‰). In Morocco, the local variations are attributed to the topographic effect.

The continental effect can be seen in the d-excess in the Iberian Peninsula and Slovenia. In Spain, d-excess is higher for station located on the eastern coast. These higher values (>10 ‰) were usually attributed to the precipitation coming from the Mediterranean Sea.

The lowest values of tritium in precipitation were observed close to the seacoast. The decrease is a result of the seawater evaporation effect. Lower activities are observed on areas under Atlantic (Slovenia) or Mediterranean (Spain, Italy) influences. In addition, the coastal stations are showing less pronounced seasonal variation of the tritium signal. The ^{3}H data has turned out to be a good tracer for different origins of moisture (e.g. Atlantic, Mediterranean, continentality…). This could be important where the stable isotope signal is masked by other physical parameters.

As a rule, the isotopic composition becomes more depleted in ^{18}O and ^{2}H at higher elevations. The so-called altitude effect is temperature-related and values of ^{18}O effect mentioned in the literature vary between -0.1‰ to -0.6‰. The regular monitoring of stable isotopes during a three-year period allowed the calculation of the altitude effect in different areas of the basin and the evaluation of the spatial variation of this effect in a region under similar climatic characteristics. The altitude effect in Croatia and Slovenia is -0.37‰/100m to -0.26‰/100m for $\delta^{18}O$. The relationship in Morocco is 0.20‰/100m for $\delta^{18}O$. In Italy, the altitude effect was calculated using information collected in small springs and precipitation. Values of -0.19‰ $\delta^{18}O$/100m were found when using precipitation data and -0.18‰ $\delta^{18}O$ when using springs data. The mountain lakes of Central Austria, relatively deep, cold and having a high through flow were considered as good investigation objects. Altitude effect calculated using data obtained from such lakes sampling gives a value of -0.25‰/100m. In Lebanon, the altitude effect was calculated at different periods for selected precipitation events using only two stations. From one period to another, the altitude effect varied from -0.1 to -0.23‰/100m for $\delta^{18}O$. The variations were attributed to air masses of different origin and different degrees of rainout contributing to the formation of precipitation.

The origin of air masses, often influences more the isotopic signals than the well known “altitude effect”. The observed altitude effect depends very much on local orographic condition. The altitude effect can only be calculated if the same air masses are compared. In many cases the monitoring stations are far away one from one another, and the stations are affected by air masses of different origin. Altitude effect cannot then be calculated.

3. ADDITIONAL INFORMATION GIVEN BY DAILY-BASED SAMPLING OF PRECIPITATION

Previous publications were showing that, at a relatively short time scale (1 to 10 days), the factor that controls the isotope variability of rain is the moisture transport system at a large scale. The daily basis sampling allows the study of the evolution of the isotope content in precipitation, depending on the origin and the trajectory of air masses. The d-excess is indicative to the air-sea interaction.

One of the major progresses made during the CRP when using daily information was to understand better the seasonal evolution and to link some very abrupt isotope variations to conditions and parameters governing the rain formation. The seasonal effects are clearly seen when using the daily data information. In general, winter precipitation (December–February) has a more depleted signature while summer precipitation is enriched in $\delta^{18}O$ and $\delta^{2}H$. This could be associated to cold polar air masses.

In Ankara, the annual evolution is following the model described for northern hemisphere stations. Major isotope variations are linked to air temperature changes, but rapid changes, not linked to air temperature, are also observed from one day to another. Most of the depleted values in the heavy isotopes are associated to cold polar air masses. In Spain, the more negative $\delta^{18}O$ and $\delta^{2}H$ values were found for air masses coming from Russia. In Morocco, the d-excess is showing well-defined seasonal variations with maxima during winter months. The minima observed in summer are due to the intense precipitation. In Alexandria, the daily variations are showing very sharp changes in $\delta^{18}O$ and $\delta^{2}H$ from one day to the other. Some of these sharp positive variations have been attributed to the effect of tropical water vapour that has caused the rainfall event. Deep depletions were attributed to the temperature effect. The warming-up of boundary layers modifies the falling rainwater by evaporating rainfall drops before reaching the rain gauge. This phenomena leads to a decrease of the values of d-excess.

In Israel, case studies at different synoptic situations allowed the linking of the daily variation of the d-excess to rapid variation of the position of the inversion layer. Rapid increase of the deuterium excess was linked to the existence of blocking situations. This may due to low temperature associated with severe instability that mixes sea-spray, which is lifted to higher layers by wind shear and stress, with falling rainfall before reaching the ground especially near coastal stations.

Changes in both air trajectory and stability of the air masses are involved in determining the isotopic composition of the precipitation. This can only be observed on a daily or event-based sampling as changes are quite fast (1 to some days).

4. RELATED STABLE ISOTOPES VARIATIONS WITH ORIGIN AND TRAJECTORIES OF AIR MASSES

It is known from past studies, that the isotope content in precipitation depends on the history of the precipitating air masses. The d-excess factor is considered a good indicator of the water vapour origin or the source of precipitation. In Western and Central Europe, $\delta^{18}O$ and $\delta^{2}H$ values of rain and vapour are controlled in first instance by the degree of rainout of the precipitating air mass. This parameter is a function of regional scale processes such as evaporation conditions in the source region, vapour flux variations in the atmosphere and the precipitation-evaporation rates over the whole distance from the source region to the sampling point more than surface and/or cloud base temperature or the amount of precipitation.

Some attempts to correlate the origin and trajectories of air masses with the isotope variation were made in the past. The correlation between isotope composition of precipitation and atmospheric water vapour and origin and trajectories of air masses was calculated in the countries during the CRP. Stable isotopes variations during selected events were correlated to the origin of the depression that produces the specific rainfall. Therefore, the synoptic surface weather maps (500, 700 or 1000hPa) furnished by the Meteorological Services and backtracks of the air mass calculated using a Lagrangian dispersion model (HYSPLIT transport and dispersion model) were used. The origin and trajectory of air masses can be better-assessed using data from daily basis sampling.

For Morocco, three main distinct meteorological situations could be schematised. Precipitation originating from air masses crossing Africa and the Mediterranean Sea has a high d-excess value (20 to 22‰). A clear distinction could be made in terms of isotope composition depending on the origin of the precipitation and can be seen in the $\delta^{18}O$/ $\delta^{2}H$ plot. Precipitation coming from the Atlantic Ocean and having intense interaction with the Mediterranean Sea during their travelling trajectory are plotted along an evaporation line. In Greece, it has been determined that the only precipitation having a d-excess close to 10 are due to warm front occurring mainly in July. The highest d-excess is observed from precipitation formed in Sahara and crossing the Mediterranean Sea before reaching Greece. In Turkey, the higher d-excess values are a result of intense air-sea interaction in the eastern part of the Mediterranean Sea. The lower d-excess observed when the air masses enter the Mediterranean Sea from over Italy or West of Italy, may be attributed to the longer over sea path and thus closer to isotope equilibrium during air sea interaction, mostly with the western part of Mediterranean and Black Sea. The daily precipitations, which have most depleted heavy stable isotopes, are associated with cold polar air masses.

In some cases, Austria for example, the important variation of d-excess values is attributed to local conditions more than the origin of air masses. D-excess value is, therefore, not a valuable tool to trace origin of air masses in this country.

Looking at specific backtracking trajectories including data on the vertical stability, it appears that changes in both the air trajectory and stability of the air masses are involved in determining the isotopic composition of precipitation. In Israel, the lower d-excess values were associated with air masses with a continental trajectory over the North African Continent or over the eastern Levant, whereas the classical routes over the eastern Mediterranean resulted in higher d-excess values under relatively high stability of the air masses.

Generally, the $^{18}O/^{2}H$ values according to the back-trajectory classification are showing some patterns. However, for all countries, the correlation is far to be perfect due to other parameters and the importance of the transport and mixing of air masses with different isotopic concentrations. A rain-to-rain study is not showing a significant difference in the isotope signal, as there is large variation within

each defined category. In addition, a precipitation event can be related to various air masses at different altitude having different origin and trajectory.

5. ATMOSPHERIC WATER VAPOUR AND DAILY PRECIPITATION

The isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) of water vapour and precipitation at a daily or event-basis was measured at six stations. At Ankara, Rehovot, Madrid, and Lisbon, the difference in $\delta^{18}O$ values between vapour and rain is close to the equilibrium value for the prevailing temperature. This was underlined in the past for temperate and humid region. There is a good connection between isotope ratios in water vapour and precipitation samples collected at the same time. This allows the study of the condensation and/or evaporation processes.

The atmospheric vapour is always much more depleted in the heavy isotopic species as precipitation makes the vapour increasingly depleted in heavy isotopes according to the Rayleigh-type process. Annual variation of stable isotopes in water vapour is following the pattern of the precipitation and similar conclusions in term of relation with origin and trajectories of the air masses can be drawn. The strong short-term variations, which are superimposed on the seasonal variation, reflect the varying contribution of tropical and polar, marine and continental air masses to the mid-latitude weather conditions. It is, of course, a great advantage to use the water vapour isotope values in order to obtain information on a continuous way, independent of the presence of precipitation events. Isotope precipitation data provide only an episodic picture of the rainy weather conditions, which may turn out to be insufficient for reliable conclusions on changes in the atmospheric water vapour circulation.

6. CONCLUSIONS

At a monthly-based sampling, comparison with data obtained by the various countries, allows the improvement of the understanding of local and regional isotope hydrological features. The CRP provided for the first time a good coverage to assess better the variations of stable isotopes within the Mediterranean basin. The stable isotopes variations in precipitation are a consequence of the air temperature variations (related to continental and altitude effects), seasonal variations, variations of the origin of the air masses and rain formation mechanisms. A long-term trend in the isotope content of precipitation at some stations were observed and attributed to changes in the synoptic patterns. This hypothesis should be further studied. Stable isotope composition of precipitation may be an additional parameter to monitor changes in circulation patterns.

At a daily-based sampling, the studies being carried out since 2001 allowed to better define the relation between stable isotopes variations and climate patterns. Not only the historical air mass characteristics that lead to rainy cloud formation affect the fractionation processes, but also the characteristics of the underlying air mass beneath rainy cloud play an important role in modification of fractionation ratios of stable isotopes in rainwater. During the CRP, a good relation between isotope signature of each of the air masses and air trajectories and stability of the air masses was established. Variations in space and time of the isotope composition of precipitation are well related to back-trajectories and synoptic situations when events are well defined (no mixture between different air masses). Surface weather systems and air masses trajectories including rainout history along the path that define the history of the water vapour that forms the rain, explained well the isotopic characteristics of the precipitation events. Stable isotopes measurements of rainfall combined with climate and meteorological data enable us to clearly characterize the main isotopic trends in the Mediterranean region. This opportunity to anticipate the isotopic composition of typical rains based on meteorological prediction make easier the use of isotopes for hydrological studies and open perspectives for further use of stable isotopes in climate studies.

ISOTOPIC COMPOSITION OF PRECIPITATION FROM ALGIERS AND ASSEKREM

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Abstract. Two stations of rainfall sampling and measurements of meteorological parameters were used in this study. The first one, located in Algiers, is under Mediterranean climatic influence. The second one, located in the Ahaggar massif, in the middle of Sahara desert, is subject to the extreme inflow of African western monsoon. In Algiers, the mean isotopic contents of precipitation [$\delta^{18}O$= -5‰; $\delta^{2}H$= -28‰ vs VSMOW], define a meteoric water line of slope 7.1, in conformity with what is known in similar climatic situation. The deuterium excess is 11.4‰. In Assekrem, the isotopic results of period 2000/2004, indicate relatively enriched values $\delta^{18}O$=-0.2‰; $\delta^{2}H$= +8‰), compared to the normal. This is due to the preponderance of the summer rains (hot season) compared to the rains of the fresh season (autumn and winter). The oxygen / deuterium relationship presents a slope of 5.05, typical of evaporating line. The mean value of deuterium excess is 1.6‰. The strong isotopic signal in precipitation associated with Inter Tropical Convergence Zone (ITCZ) displacement represents an excellent methodology for a correct reconstruction of the current atmospheric circulation and climatic changes suffered by the region.

1. Introduction

Two stations of precipitation sampling are currently functioning: The University of Algiers station, and the Assekrem station in the central part of Ahaggar massif (Fig. 1)

1.1. Algiers station

Algiers station located on the Mediterranean coast (X=3°11; Y=36°43; Z=18m), is installed inside the USTHB University in Bab-Ezzouar. The water sampling and the meteorological measurements started in October 2000. Measurements in Algiers airport station [1], located near the University, were initiated one hundred years ago.

1.2. Assekrem station

Located in the central part of Ahaggar massif, in the middle of the Sahara desert, the sampling of precipitation at Assekrem is made since 1992. The meteorological parameters are measured in the same place. This meteorological station (X = 5°38; Y=23°16; Z=2726 m) was brought into service in 1955. The meteorological parameters regularly mesured are rainfall amount, temperature, relative humidity and evaporation. In 1992, this traditional station was coupled with an automatic one. Then started, within the framework of the WMO-Global Atmosphere Watch programme the measurement of ozone, gases in traces, carbon monoxide and the aerosols [1].

Now, we have for this site, 225 isotopic analyses of rainfall, which correspond approximately to 30 rainy events per year.

FIG. 1. Location map.

2. Regional climatic conditions

2.1. In Algiers

Located at about 3 km from the sea side, the station of the University is under a Mediterranean climate influence:

- The relative humidity of the atmosphere is high (on average 77% in winter and 70% in summer)
- The average potential evaporation varies between 55 mm/month in winter and 130mm/month in summer, with a total of 1062 mm/year,
- The average monthly temperature varies between 11°C in January and 25°C in July. The annual average value is of 17°C (Fig. 2).

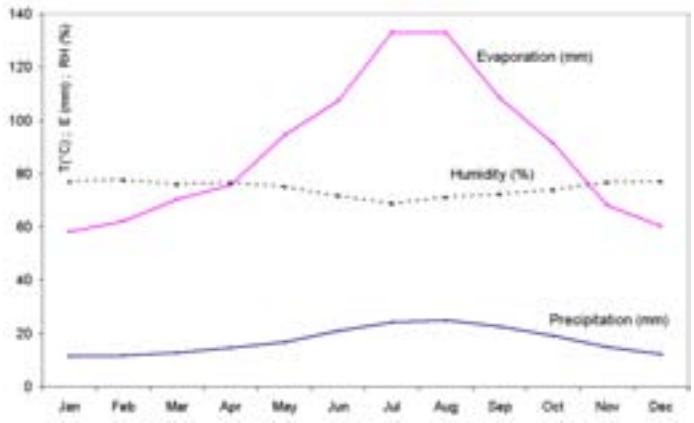

FIG. 2. Mean variation distribution of temperature, relative humidity, and evaporation in Algiers (1956–-2003).

The rainy season goes from October to May, with a maximum in December and an average annual value of 670 mm (Fig. 3).

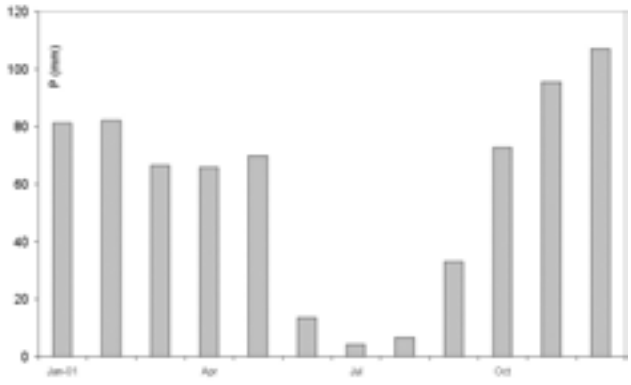

FIG. 3. Monthly precipitation distribution in Algiers (1956-2003).

The interannual variation of precipitations shows a high irregularity (Fig. 4) and a tendency to dryness, in the last 20 years.

FIG. 4. Index of annual rainfall irregularity (Xi-X)/S); Algiers:56-03) Xi= annual precipitation, X= mean value, S = Standard deviation.

2.2. In Assekrem

The meteorological data shows that precipitation generally occurs in summer [2], simultaneously with the intrusion, in the subtropical zone, of the West African Monsoon phenomena. Migration towards the North of Inter Tropical Front (ITF), the generator of Monsoon phenomena [3], reaches its most septentrional position (20° N) at the beginning of August [4]. Consequently, 70% of annual precipitations in this area occur between September and May (Fig. 5). In addition to these hot season rains exist winter and spring sporadic rains.

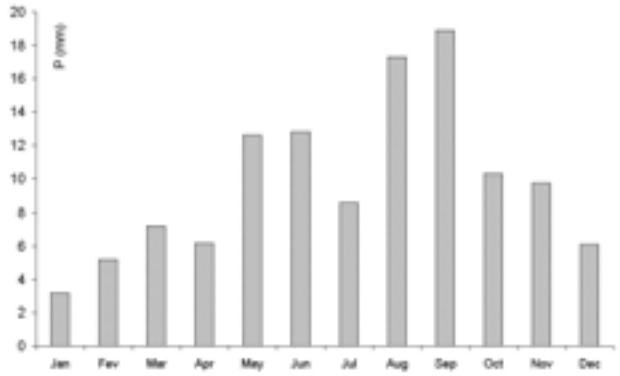

FIG. 5. Monthly precipitation distribution in Assekrem (1955-2003).

The average of rainfall amount reaches 118 mm/an. This value is characterized by a high interannual irregularity (Fig. 6).

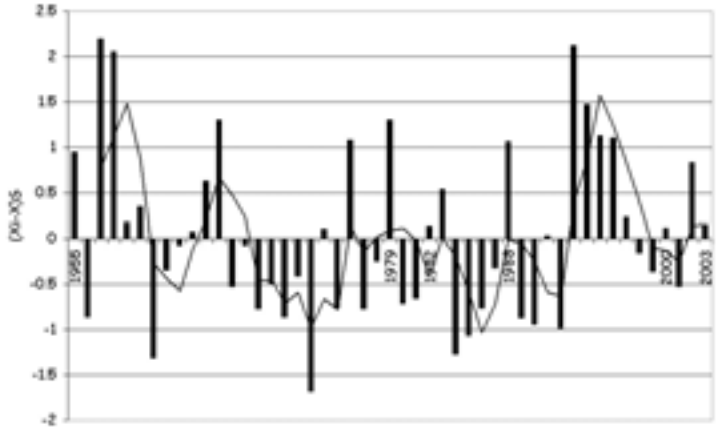

FIG. 6. Index of annual rainfall anomaly (xi-x)/s)- Assekrem:55-03 (Xi= annual precipitation, X= mean value, S = Standard deviation).

Because of high altitude effects (2918 m in Tahat mountain), the annual temperature average in Assekrem is 12 °C [2], varying from 6.5 °C in January to 20 °C in July (Fig. 7).

The relative humidity varies opposite to temperature, with maximum in winter (40 %), and minimum values in summer (28%). This fact seems to be paradoxical since the manifestations of the West African Monsoon phenomenon occur in the summer season.

The average evaporation is 1400 mm/year, and ranges between 85 mm in January and 160 mm in July.

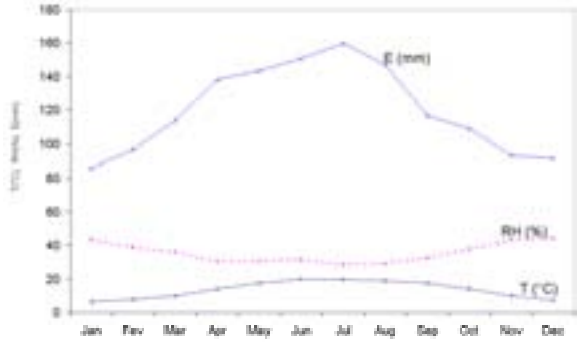

FIG. 7. Monthly variation of temperature, relative humidity, and evaporation in Assekrem (1955–2003).

The monthly distribution in Algiers is in opposition, comparing to the one in the Assekrem (Fig. 8). It shows the existence of two distinct climatic domains: the Mediterranean one in the North and the Monsoon one in the South. The transition between these two climates seems to take place above the Ahaggar massif. Figure 8 illustrates this transition using histograms of monthly precipitation distributions of two Saharian stations (In Salah and El Ménia) located between Assekrem and Algiers according to a North-South transect, on 2 000 km distance.

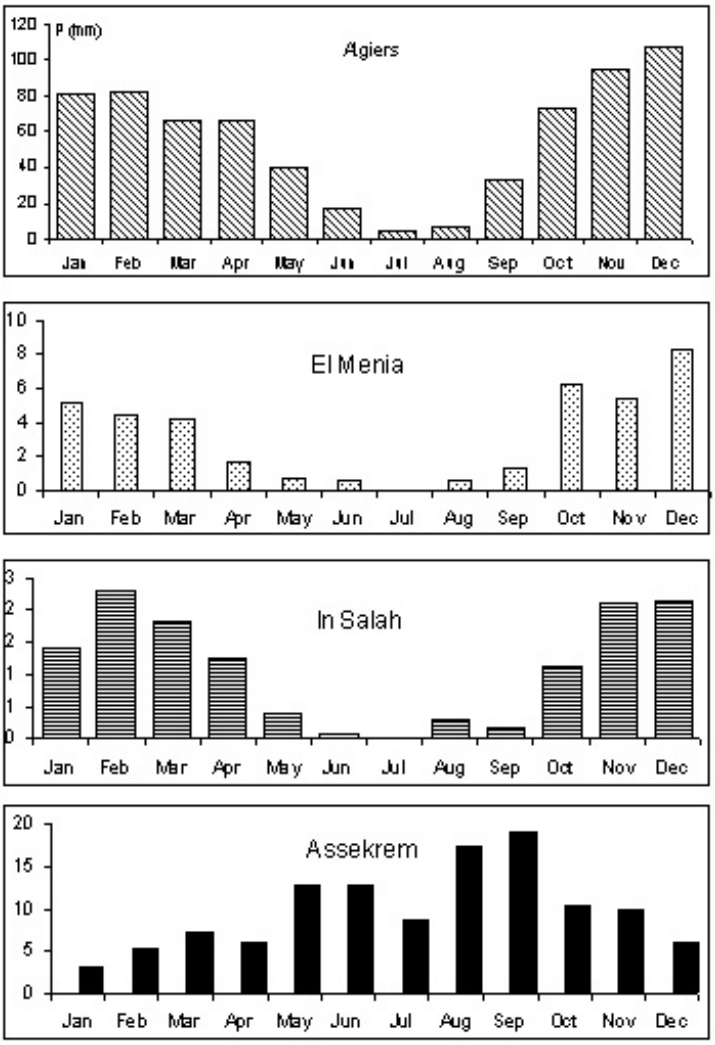

FIG. 8. Meridian evolution of monthly precipitations through the Sahara.

3. Sampling and monitoring network

3.1. Sampling and meteorological measurements

3.1.1. In Algiers

The collection of rain samples started in October 2000. It is a daily sampling. Within four years, 140 samples were taken. In parallel, measurements of daily precipitated amount, temperatures and moisture, are carried out.

These weather statements reveal that:

— Rainfall amount was particularly weak (300 mm) the first two years of study (2001 and 2002), and did not reach even half of the average value (670 mm). On the other hand, 2003 had a particularly hot summer (Figs.9 and 10).

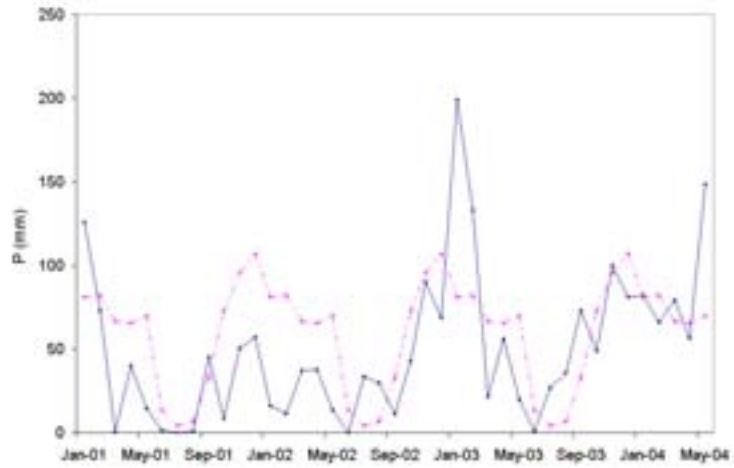

FIG. 9. Monthly precipitation distribution at Algiers-University, [- - - -] Mean value of period 1956/2003.

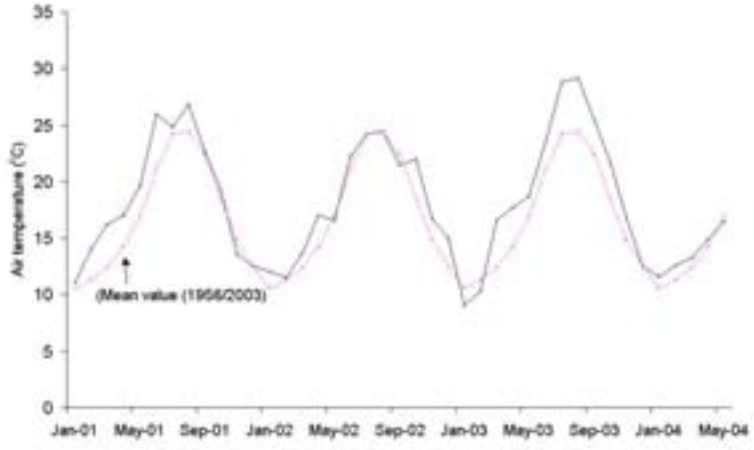

FIG. 10. Mean monthly distribution of temperatures in Algiers-University (01-03).

3.1.2. In Assekrem

Sampling of precipitations is carried out since 1992. Sampling is performed on an event-based. Up 79 samples were taken since October 2000. Rainfall amount was relatively high during these last four years (Fig. 11), in particular during 2002 (172 mm/an) when the value of 118 mm, representing the annual average, was exceeded.

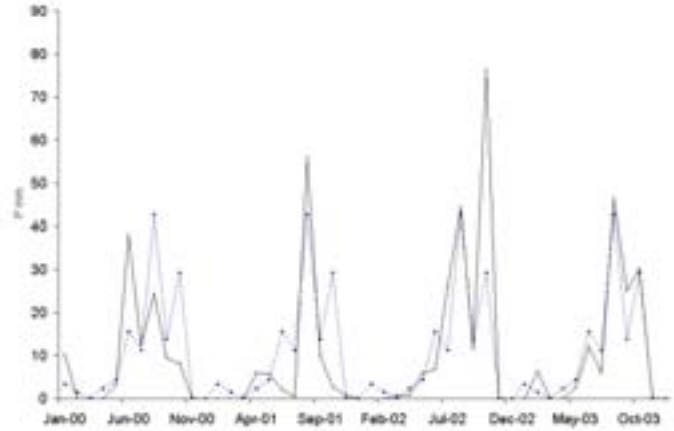

FIG. 11. Monthly precipitation distribution in Assekrem:[------] period 2000/2003 and (- - - -) average of 1955/2003 period.

3.2. Physico-chemical and chemical measurements and their interpretation

The measurements of pH and electric conductivity were carried out for all samples collected in Algiers and for some samples from Assekrem.

Hydrochemical analyses of the major ions were carried out with ionic chromatography, in the Geological Institute of Zurich. Strontium, lithium, fluorine, brominates, phosphates and NH_4, were also carried out on some samples.

3.2.1. pH

It varies from 6.8 to 8.3 and its maximum of frequency is 7.3. This value characterizes the abundant winter rains. Acid rains are rare and those with a slightly basic pH, can sometimes occur in autumn.

3.2.2. Electric conductivities

Even if it varies between 20 and 300 $\mu S.cm^{-1}$, conductivity is generally lower than 100 $\mu S.cm^{-1}$. The maximum of frequencies is between 25 and 50 $\mu S.cm^{-1}$ and reflects abundant rains in the depth of winter season. Only rains occuring during "Sirroco" winds (sand wind), or those which occur after a long dry period, indicate electric conductivity of 300 $\mu S.cm^{-1}$.

The Saharan dust, transported by the wind, constitutes a source of dissolved chemical elements, in meteoric water.

3.2.3. Ionic contents

In general, the total dissolved ions in precipitation varies from 20 to 50 $mg.l^{-1}$. Nevertheless, higher concentrations exist also. In Algiers as well as in Assekrem, the hydrochemical analyses show that chlorine (8 to 14 $mg.l^{-1}$), calcium and sodium (~10 $mg.l^{-1}$) are the dominant ions.

In Algiers, the prevalence of chlorides is characteristic of the coastal station.

In Assekrem, the relatively high chlorine concentrations (15 $mg.l^{-1}$) can be related to small rains affected by "re-evaporation" process during fall.

The trace elements, such as phosphate and bromine, is present in very small quantity in the meteoric water. Fluorine, strontium, lithium, nitrites and ammonium are encountered cloe to the detection limit of the measrurement method.

4. Isotopic results

During the last four years, 140 samples were collected in Algiers, and 79 in Assekrem. The isotopic analyses were carried out at the IAEA laboratory.

4.1. In Algiers

- The oxygen-18 contents vary between -11 to + 6‰ vs SMOW, although the major part of the values gather in a more limited range, between -7 and -1‰. The arithmetic average is 5‰ with a standard deviation of 3‰.
- The deuterium contents vary between -76 and +22‰ vs SMOW, but 90% of the values are comprised between -40 and -10‰. The average is -28‰ with a standard deviation of 21‰.

The histogram of the stable isotopes distribution contents presents one maximum (Fig. 12) which is [-5.5‰; -4.5‰] for oxygen-18, and [-35‰; -25‰] for deuterium.

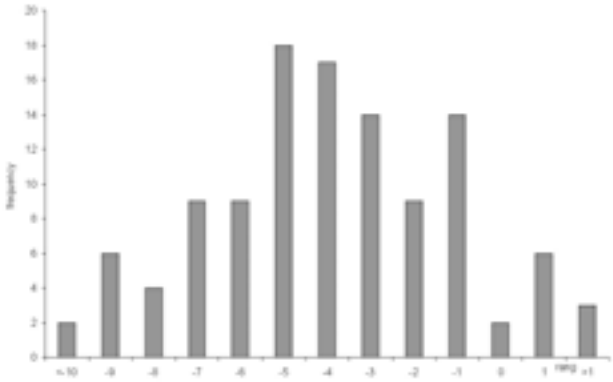

FIG. 12. Frequency distribution of oxygen-18 contents for daily events from Algiers (2000/2004; n= 113 samples.

4.2. In Assekrem

Although we have a much longer set of data [6], we take into account here only the results obtained during the period 2000-2004. The rainfall amount over this period was essentially characterized by hot season rains (principal rainy season). So we could expect that their isotopic contents would be relatively enriched, compared to past results obtained in this area.

Oxygen-18 vary from -9 to + 7.4‰ (Fig. 13) with an arithmetic average of -0.02‰ and a standard deviation of 3.7‰. The isotopic contents higher than +4‰ are exceptional.

Deuterium distribution is very dispersed, varying from -60 to +40‰, with an average of +3‰ and a standard deviation of 20‰.

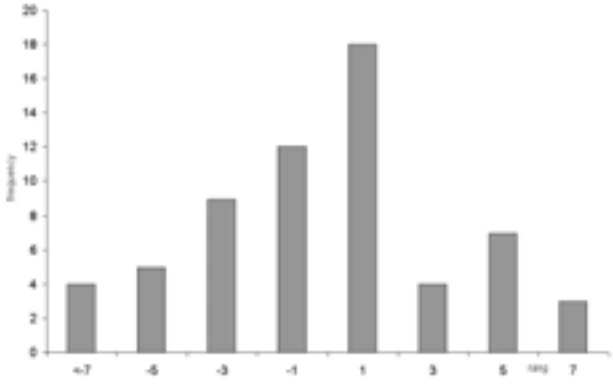

FIG. 13. Frequency distribution of oxygen-18 contents for rainfall events from Assekrem (2000/2004; n=79 samples).

Usually, the main characteristic of the isotopic contents of the Ahaggar rains lies in a bimodal configuration of the frequency distribution histogram, according to the seasons. The first maximum, which is the main one, corresponds to summer rains (^{18}O‰; -1.5‰) and the other is corresponding to the winter rains (^{18}O; -5.5‰) [6]. However, for the period 2000/2004, the secondary maximum is not well marked because the cold seson rains, characterized by oxygen-18 values lower than -10‰, were not very frequent. During the recent observation period, there were summer rains very evaporated and enriched.

5. The δ^2H vs $\delta^{18}O$ relationship

5.1. In Algiers

The local meteoric water line (Fig. 14) admits an adjustment according to the equation :

$\delta^2H = 7.15\ \delta^{18}O + 7.92$ (R^2=0.92; n=113).

The slope, close to 7, is in conformity to precipitation of the southern side of the Mediterranean sea [7; 8]. The intersection point between the local meteoric water line with the Global Meteoric Water Line of Craig [9] is located at $\delta^{18}O$=-2.4‰; δ^2H = -5‰.

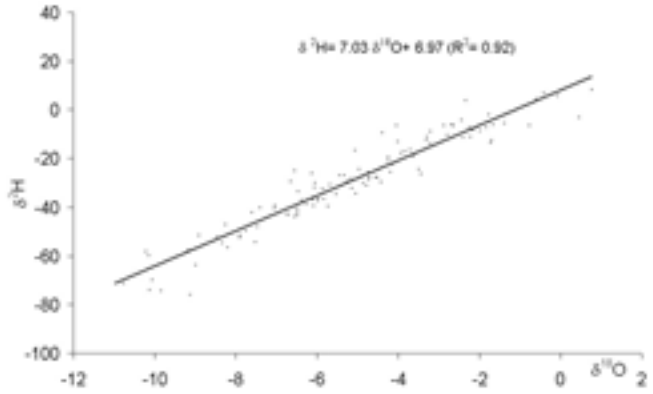

FIG. 14. Oxygen-18 / deuterium relationship of rainfall from Algiers (2000/2004).

5.2. In Assekrem

For the period 00/04, the local meteoric water line admits as equation: $\delta^2H = 5.05\ \delta^{18}O + 1.9$ (R^2=0.86; n=79)

This slope,5, is typical of an evaporating line [10]. If we take into account all the available data in this site (period 1992-2004), the equation is [6]: $\delta^2H = 5.38\ \delta^{18}O + 1$ (R^2=0.89; n=225).

In this case, it is possible to distinguish summer rains and winter rains

$\delta^2H = 5.08\ \delta^{18}O - 0.207.92$ (R^2=0.88; n=114), (summer)

$\delta^2H = 7.29\ \delta^{18}O + 12.23$ (R^2=0.93; n=77), (winter)

6. Deuterium excess

The deuterium excess is a typical characteristic showing the origin of air masses from which precipitation is formed [11]. Values much higher than +10‰ indicate the importance of recycled continental vapour [12].

6.1. In Algiers station

The deuterium excess values vary between 0 and +28‰ (Fig. 15) with an average of 11.4‰, and a standard deviation of 7.4‰. There are some negative values which cannot be explained. The global mode is at +11.4 ‰, indicating that the most important rainfalls are not evaporated.

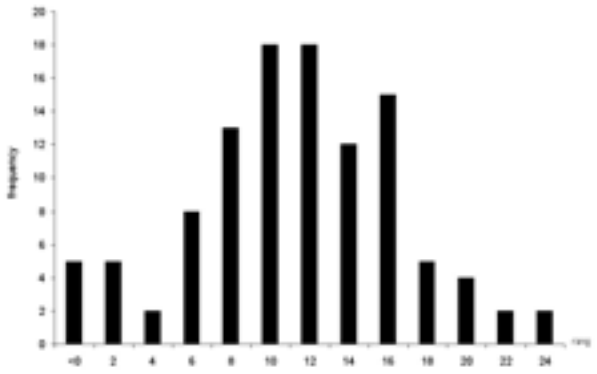

FIG. 15. Frequency distribution of deuterium excess contents of rainfall from Algiers.

6.2. In Assekrem station

Deuterium excess shows some scattered results (Fig. 16) varying between -23‰ and +35‰, but the population is asymmetric developed towards negative values. These negative values show that the rains are evaporated. Thus, the data posterior to October 2000 appears to some extent modified by the intense evaporation phenomena of rain drops during the fall, in an overheated summer atmosphere. The histogram of distribution is very spread out and does not show any particular tendency.

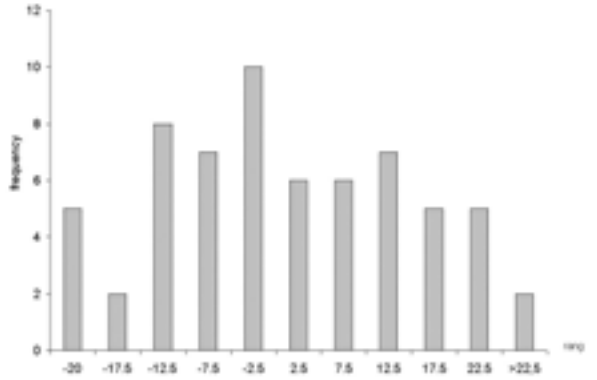

FIG. 16. Frequency distribution of deuterium excess of rainfall from Assekrem.

At a yearly scale, the seasonal distribution of d-excess presents summer rains, isotopically enriched, and with low d values [-12‰; -2‰]. This results of non-equilibrium conditions either during condensation or during the fall. On the contrary, winter rains show the highest values of deuterium excess, with a mean value of +12.5‰, suggesting precipitation originated for a large part, from recycled air moisture.

Table I. Isotopic contents of rainfall from Algiers and Assekrem for the period 2000/2004

		Min	Max	Mode	Average	σ
Algiers	$\delta^{18}O$ (‰)	-11	+5.9	-4.5	-4.9	3
	$\delta^{2}H$ (‰)	-76	+22	-30	-28	21
	d-excess (‰)	0	+28	11.5	11.4	7.4
Assekrem	$\delta^{18}O$ (‰)	-9	+7.4	0.5	0.02	3.7
	$\delta^{2}H$ (‰)	-60	+40	8	3	20
	d-excess (‰)	-23	+35	1	1.6	13

7. Impact of the climatic parameters on the isotopic contents

Event precipitation amount is generally weak. Indeed, 50% of the rainy events are lower than 10 mm in Algiers, and 5 mm in Assekrem. The correlations between the isotopic contents and the climatic factors appear not very significant.

7.1. The $\delta^{18}O = F(P)$ relationship (amount effect)

The relationships are defined by the following equations:

- In Algiers (Fig. 17): $\delta^{18}O = -1.25 \ln(P) - 2.2$; ($R^2 = 0.137$, n = 113)
- In Assekrem: $\delta^{18}O = -2.14 \ln(P) + 22.6$; ($R^2 = 0.29$, n = 78)

The relatively low correlation coefficient is due to the fact that the isotope content of precipitation is not completely controlled by precipitation amount. Thus, the amount effect appears slightly occulted, by the combined effects of other climatic factors, such as temperature and moisture.

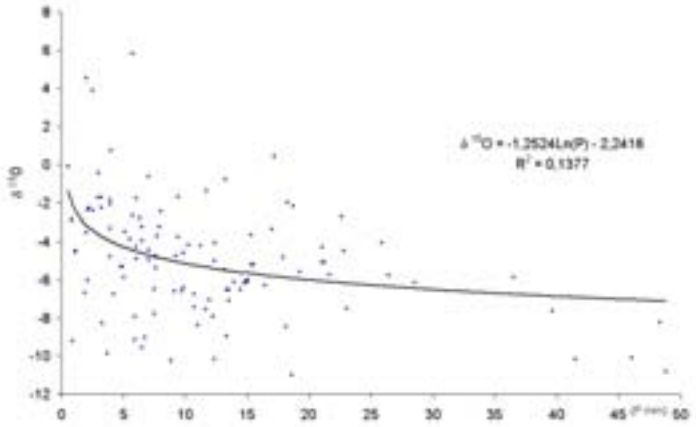

FIG. 17. Oxygen-18 vs. precipitation amount relationship in Algiers station.

7.2. The $\delta^{18}O = F(T)$ relationship

- In Algiers (Fig. 18): $\delta^{18}O = 0.137\ (T) - 8.4$; ($R^2$=0.113; n=113)
  (T being the temperature during the rain).

- In Assekrem $\delta^{18}O = 0.137\ (T) - 8.4$; ($R^2$=0.1; n=61)
  (T being the temperature measured at the time the the sample was taken, i.e. a few moments or a few hours after the rainy event.

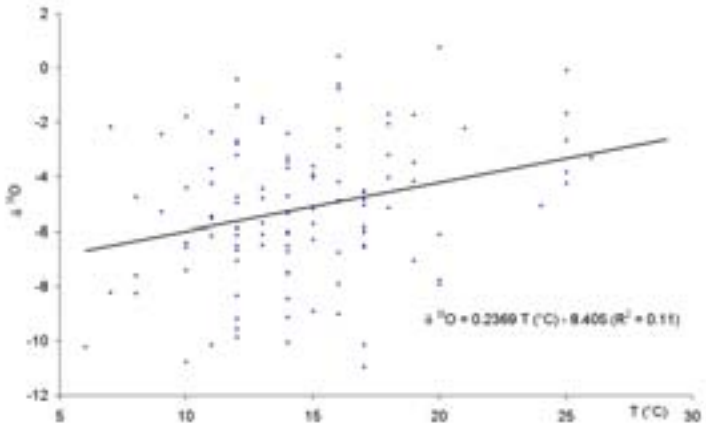

FIG. 18. Oxygen-18 vs. temperature relationship in Algiers.

The seasonal effect clearly appears, showing highest heavy isotope contents that correspond to the warmest months**.** On the contrary, rainfalls of the cold season are depleted in heavy isotopes, with $\delta^{18}O$ values as low as -11.9 ‰, and generally located above the GMWL.

The very bad adequacy obtained in Assekrem station, can be explained by the fact that the temperature varies considerably during the rainy event. The thermal effect, which appears dominant, explains the highest isotopic contents during the hottest months, and vice versa. The highest values are observed for August and July precipitation, which coincide with optimum of the monsoon. During this season, the high temperatures reigning in Ahaggar mountain, maintain the moisture at its lowest middle levels of the year, in spite of arrival of the Monsoon air masses. The rainy events, not frequent and of small amount, do not allow a durable cooling of the atmosphere which, after the rain, very quickly present a severe dryness profile.

- In summer, the temperatures exceed 30°C at midday, and can fall abruptly after a storm. This temporary cooling, translates the intensity of the evaporation responsible for calorific consumption of energy. It is accompanied of an increase of moisture, which generates isotopic contents more impoverished at the end of the rain.
- In winter, the cooling of atmosphere and a higher moisture level explianed lower isotopic contents of precipitation.

7.3. The oxygen-18 vs relative humidity

The relationship appears not very significant. During rainy events, more especially in Assekrem, the moisture fluctuates quickly and very largely. The first drops which fall within a particularly dry atmosphere, are enriched in heavy isotopes. When the atmosphere temporaly saturated, precipitation is very impoverished.

8. Conclusion

The isotopic data obtained for Algiers and Assekrem precipitation permit, conjointly to the meteorological data, to obtain information on circulations of the air masses.

The station of Assekrem is located in a strategic position for the study of circulation of air masses as it is influenced by two different climatic regimes:

- In the North, the polar climatic regime covers the south side of Mediterranean and the north of Africa.

— In the south, and precisely in the Ahaggar massif (to 2000 km from Algiers), the monsoon regime prevails.

The limit between the two regimes may be located between Algiers and Assekrem, our two observation sites.

The influence of the polar climate reaches the Sahara, and even the Ahaggar massif. The influence of the Monsoon climate reaches only the Ahaggar massif. This flux from Guinea Gulf is observed at the tropical latitude, extending northward up to 3° to 4° more than the limit fixed up to present and that is 20° N.

The indices suggesting that the influence of the Monsoon could be extended up to the Ahaggar is the presence of summer precipitation, thermodynamically in non-equilibrium, and evaporated. Influence of Guinean air moisture must be taken in account to explain August precipitation in mountainous regions of Central Sahara. The low $\delta^{18}O$ values of precipitation in winter indicate the influence of the Atlantic Ocean.

In summer, during the incursions of Monsoon air masses, the negatives values of deuterium excess confirm the evaporated character of rain. During the rainy season in winter, the deuterium excess values higher than 10 ‰ indicate processes of recycling of air masses under the polar climatic regime.

ACKNOWLEDGEMENTS

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REFERENCES

[1] Office National de la Météorologie, Bureau régional Sud, Tamanrasset. Répertoire des données ONM (2002).
[2] SAIGHI, O., Thèse de Doc. Etat, USTHB, Alger (2002) 278.
[3] DUBIEF, J., Le climat du Sahara. Mémoire hors série, Institut de recherches sahariennes, Alger, 2 tomes (1960).
[4] CITEAU, J., CAMMAS, J.P., GOURIOU, Y., GUILLOT, B., Remarques sur la migration de la zone intertropicale de convergence en Atlantique, les températures de surface du Golfe de Guinée et la pluviométrie en Afrique de l'Ouest sahélienne et au Nord-Est du Brésil. In "Changements globaux en Afrique durant le Quaternaire, passé, présent et futur", INQUA-ASEQUA, Symposium International Dakar, Ed. ORSTOM, 197 (1996) 67–75.
[5] DORIZE, L., L'oscillation climatique actuelle au Sahara. Rev. Géogr. Phys. Et Géol. Dyn., 18, (2-3) (1976) 217–228.
[6] SAIGHI O. et al, Isotopic composition of precipitation in Ahaggar massif (Central Sahara, South of Algeria), in preparation.
[7] IAEA, Statistical Treatment of Data on Environmental Isotopes in Precipitation. Technical Reports Series No. 331, IAEA, Vienna (1992).
[8] GAT, J.R., CARMI, I., Effect of climate changes on the precipitations patterns and isotopic composition of water in a climate transition zone: case of Easter Mediterranean Sea area. In « The influence of climatic variability on the hydrological regime and water resources ». IAHS, Publ. 168 (1997) 513–523.
[9] CRAIG, H., Isotopic variations in meteoric waters. Science, 133 (1996) 1702–1703.

[10] FONTES, J.C., GONFIANTINI, R., Comportment isotopique au cours de l'évaporation de deux bassins sahariens. Earth Planet. Sc. Lett., 3 (1967) 258–266.
[11] MERLIVAT, L., JOUZEL, J., Global climatic interpretation of the deuterium -oxygen 18 relationship in precipitation. J. Geophys. Research, 84-C8 (1979) 5029–5033.
[12] DANSGAARD, W., Stable isotopes in precipitation. Tellus, 16 (1965) 436–468.

ISOTOPIC COMPOSITION OF PRECIPITATION IN AUSTRIA IN RELATION TO AIR CIRCULATION PATTERNS AND CLIMATE

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Abstract. The isotope records from the Austrian Network for Isotopes in Precipitation (ANIP) show significant but not uniform long-term trends. While the 10-year running means of some mountain stations exhibit a pronounced increase in $\delta^{18}O$ of about 1‰ since 1975, the change of $\delta^{18}O$ at the valley stations is much lower. There are also differences in the temporal pattern. The difference in the $\delta^{18}O$-values of sampling stations at similar altitudes can be explained by different origins of the air moisture (Atlantic or Mediterranean influence). Furthermore, a significant difference in the behaviour of the deuterium excess at neighbouring mountain and valley stations has been observed. There is a slight increase of the yearly mean of the deuterium excess with increasing altitude of the sampling station. But moreover, the seasonal pattern of the deuterium excess is quite different. While the valley stations exhibit the expected minimum in summer, the mountain stations show a distinct maximum between June and October. These variations of the deuterium excess are "homemade" (secondary fractionating processes like re-evaporation) and not the result of a different origin of the air masses transported into the mountainous region. Therefore the deuterium excess seems not to be a reliable tool to trace the origin of air masses and moisture coming from farer away into the Alpine region. The interpretation of data from daily precipitation samples could not be satisfactorily concluded during the CRP period. Collision and mixture of air masses and moisture of different origin in the Alpine region are probably responsible for these difficulties. The only clear finding is that Mediterranean influence is indicated by lower tritium content.

1. Introduction

The Austrian Network for Isotopes in Precipitation (ANIP) started in 1972. At some stations samples have already been taken since the 1960s. 71 stations ranging from 120 to 2250 m in altitude are presently in operation all over Austria with some preference given to the Karst areas north and south of the Alpine mountain range (Fig. 1 shows a map of the stations mentioned in this paper). Precipitation water is collected on a daily basis in ombrometers (500 cm^2) and mixed to monthly samples. All samples not measured immediately have been stored in 1 L bottles in especially dedicated cellar rooms in Vienna and are available for analysis in the future. The aim of ANIP is to provide input data for hydrological and hydrogeological investigations and a data-base for climatologic research.

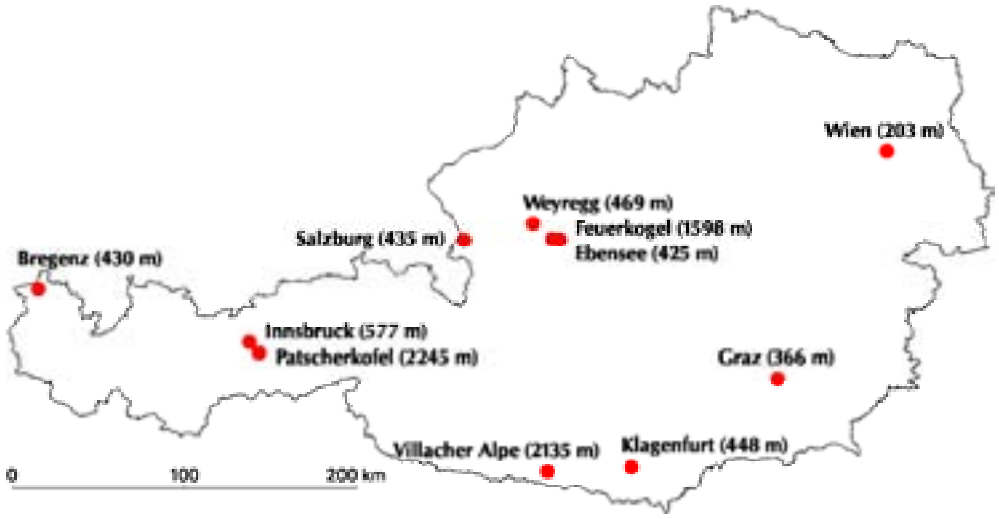


FIG. 1. Selected sampling stations of the Austrian precipitation network.

The amount of precipitation in Austria is highly influenced by the Alpine mountain range (400–3000 mm/a). The amount of annual precipitation increases towards the mountain ranges. However, strong regional differences exist between the windward and the lee side of the Alpine ranges. Precipitation time series from 1901 to 1990 show no continuous trend. Periods of precipitation above and below the long-term trend are recorded with peculiarities in some geographical regions. Wet periods are supposed to represent maritime phases, but there are so far no detailed studies about the origin of the precipitating air masses in Austria. However, the Alps as a weather divide sharply distinguish precipitation events caused by different airflow directions. They are therefore a unique platform to study the origin of precipitating air masses and possible trends in air flow and precipitation patterns.

2. Long-term records

The isotope time series of the stations of the Austrian precipitation network show significant but not uniform long-term trends. While the 10–year running mean of some mountain stations exhibits a pronounced increase in $\delta^{18}O$ of about 1 ‰ since 1975, the change of $\delta^{18}O$ at the valley stations is much lower (Fig. 2). There are also differences in the temporal pattern. The differences in the $\delta^{18}O$-values of sampling stations at similar altitudes can be explained by the origin of the air moisture. An Atlantic influence (moisture from NW) causes lower $\delta^{18}O$-values (e.g. Patscherkofel and Bregenz) than a Mediterranean one (e.g. Villacher Alpe and Graz). The main reason for this different ^{18}O-content is the longer way of the Atlantic air masses over the continent along which the moisture becomes stepwise depleted in heavy isotopes by successive rainout (continental effect).

The stable isotope variations in precipitation are a consequence of the isotope effects accompanying each step of the water cycle. Temperature is the most influencing parameter (Fig. 3), but there are also other influences like changes in the origin of air masses or in rain formation mechanisms [2], [3], [4]. The fluctuations of the ^{18}O-content of precipitation correlate also to a large extent with those of the North Atlantic Oscillation (NAO) index, except during some years where the influence of the amount of precipitation probably dominates in rain formation mechanisms [6].

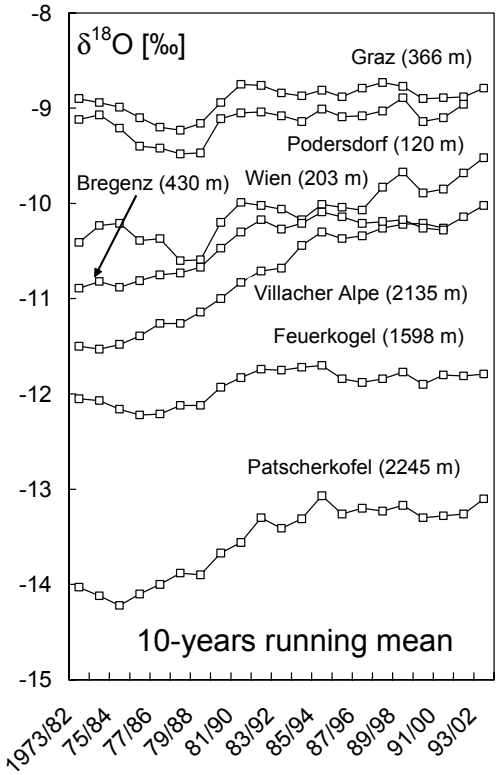


FIG. 2. Long-term $\delta^{18}O$ variations (10–year running means) at several stations of the Austrian precipitation network [1][2] (updated).

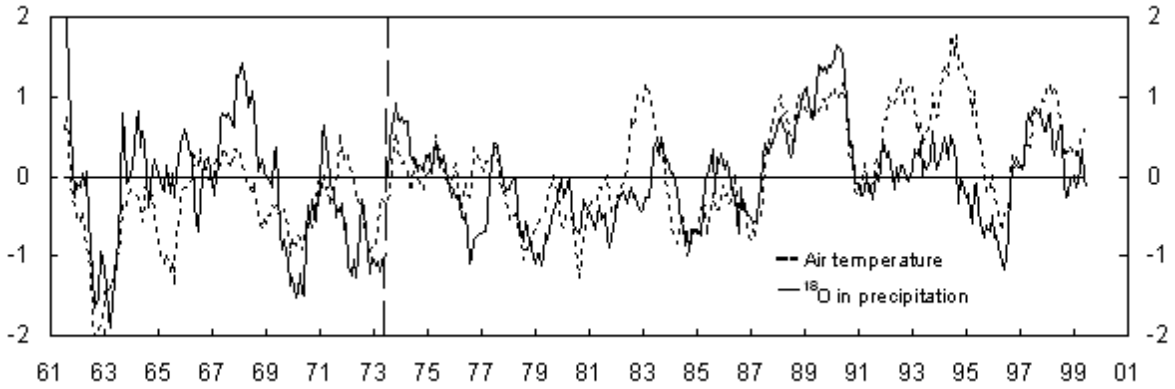


FIG. 3. Long-term fluctuations of isotopic composition of precipitation ($\Delta\delta^{18}O$ [‰]) and surface air temperature (ΔT [°C]) in Austria. Running 12–month mean of seven meteorological stations ($\delta^{18}O$ up to 1973: data of Vienna) [2][5][6].

Fig. 4 shows the time series of tritium content in precipitation and in the Danube at Vienna. The tritium content in precipitation has decreased to about 10 TU during the last years. The influence of air moisture coming from the Mediterranean causes lower tritium contents in precipitation in the southern parts of Austria because of the shorter travel time of these air masses over the continent. The tritium content at Villacher Alpe for instance is about 30 % lower than at Feuerkogel (northern Alpine region, Fig. 5).

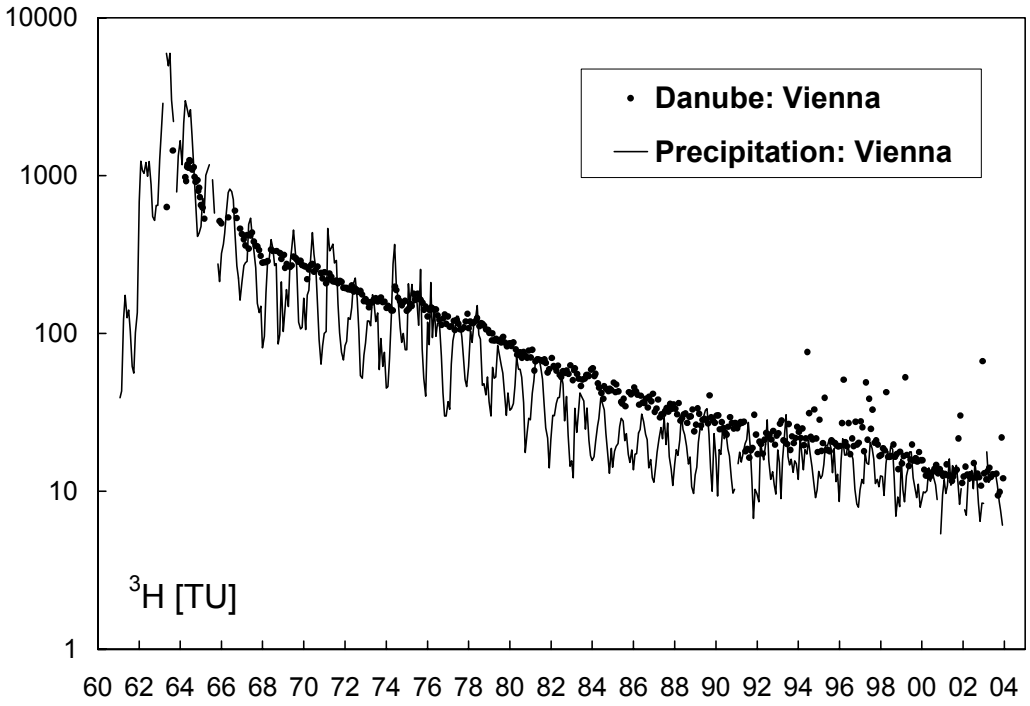


FIG. 4. Time series of tritium content in precipitation and surface water (Danube) at Vienna (precipitation: monthly average samples, Danube: monthly grab samples) [7] (updated).

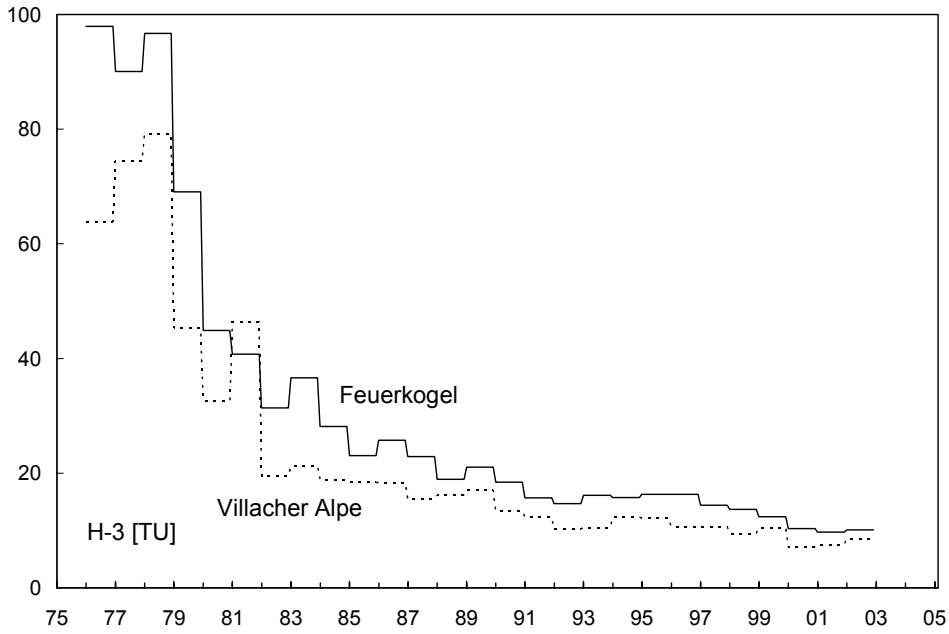


FIG. 5. Long-term trend of tritium content in precipitation in the northern (Feuerkogel) and southern (Villacher Alpe) Alpine ranges (yearly mean values). The tritium content at Villacher Alpe is about 30 % lower than at Feuerkogel and indicates clearly the Mediterranean influence.

3. Results obtained from daily and monthly precipitation sampling

Daily sampling has been performed at three stations: Vienna Arsenal (at 203 m a.s.l.), Feuerkogel (at 1618 m a.s.l. in the northern Alps) and Villacher Alpe (at 2135 m a.s.l. in the southern Alps). The collection of monthly samples at about 70 stations of the Austrian network has been continued.The samples of about 20 of them are routinely analysed. The data base of this CRP summarizes all information available about the samples taken during the CRP activities (e.g. amount of precipitation).

The monthly ^{18}O data show the expected seasonal variations with a minimum in winter and a maximum in summer (Fig. 6). As mentioned before, Villacher Alpe is significantly influenced by Mediterranean air masses, thus the relatively high $\delta^{18}O$ values at an altitude of more than 2000 m are explainable. No major changes could be observed during the last three years regarding the long-term trends of isotopes in precipitation (Fig. 2). The tritium content of precipitation has still decreased a bit during the last three years; the yearly mean value in Austria is now (2003) about 10 TU.

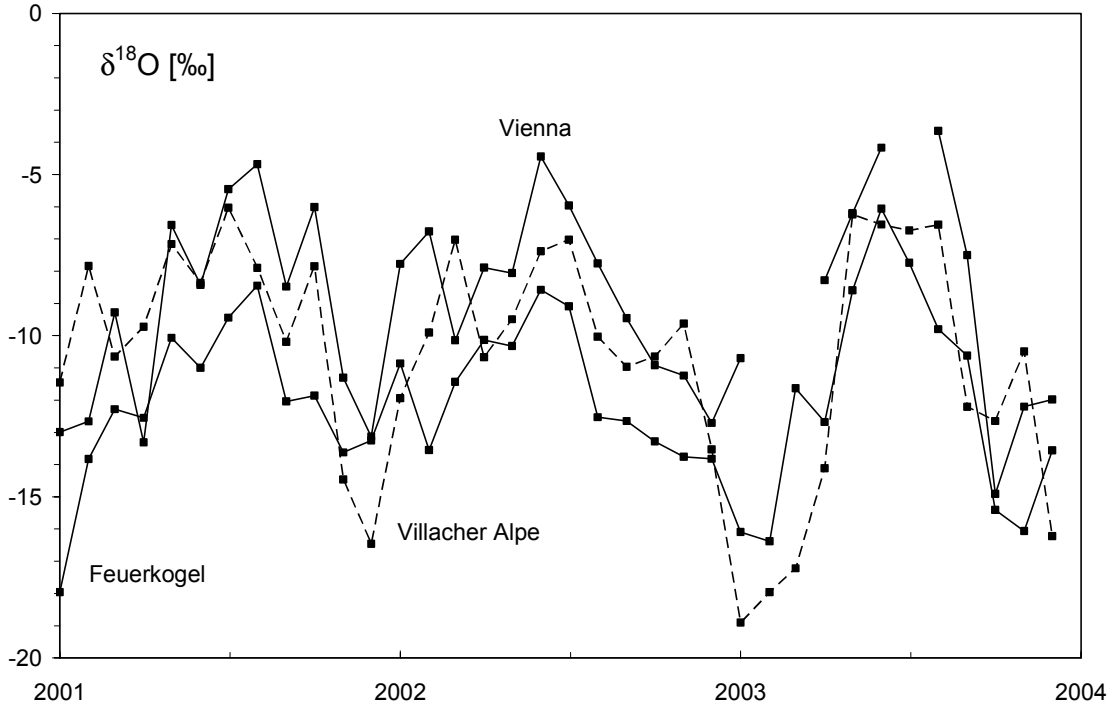
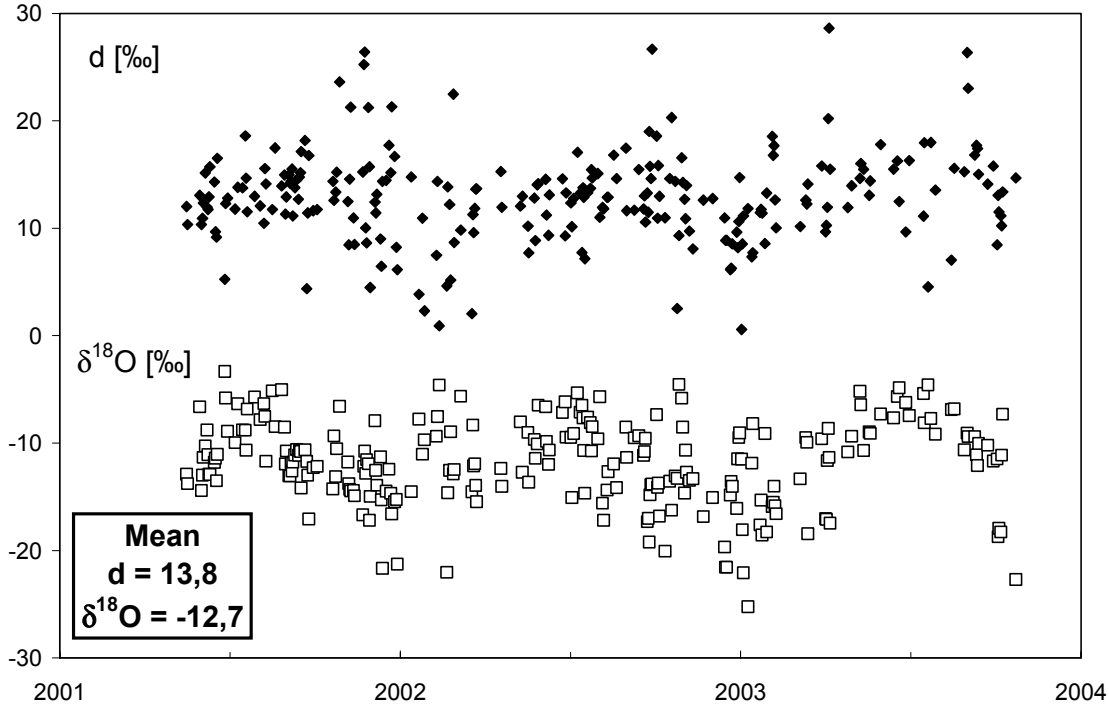


FIG. 6. Seasonal variations of $\delta^{18}O$ in precipitation at the sampling stations Feuerkogel, Villlacher Alpe and Vienna during the CRP-period 2000–2003 (monthly average samples).

Stable isotope ratios (Figs. 7, 8, 9) and tritium content (Fig. 10) of daily precipitation samples from the three stations exhibit a wide variation with the expected seasonal influence (lower values in winter). The calculated mean values in the diagrams are not representative values for these stations, because the sampling period does not cover full years. The daily values do not show any significant correlation with the amount of precipitation. We did also not succeed in establishing simple correlations between isotope ratios in precipitation and weather situations. The only clear finding is that Mediterranean influence can mainly be identified by a lower ^{3}H content in precipitation. The deuterium excess values — similar at the two mountain stations and significantly lower in Vienna — are treated in the following chapter.



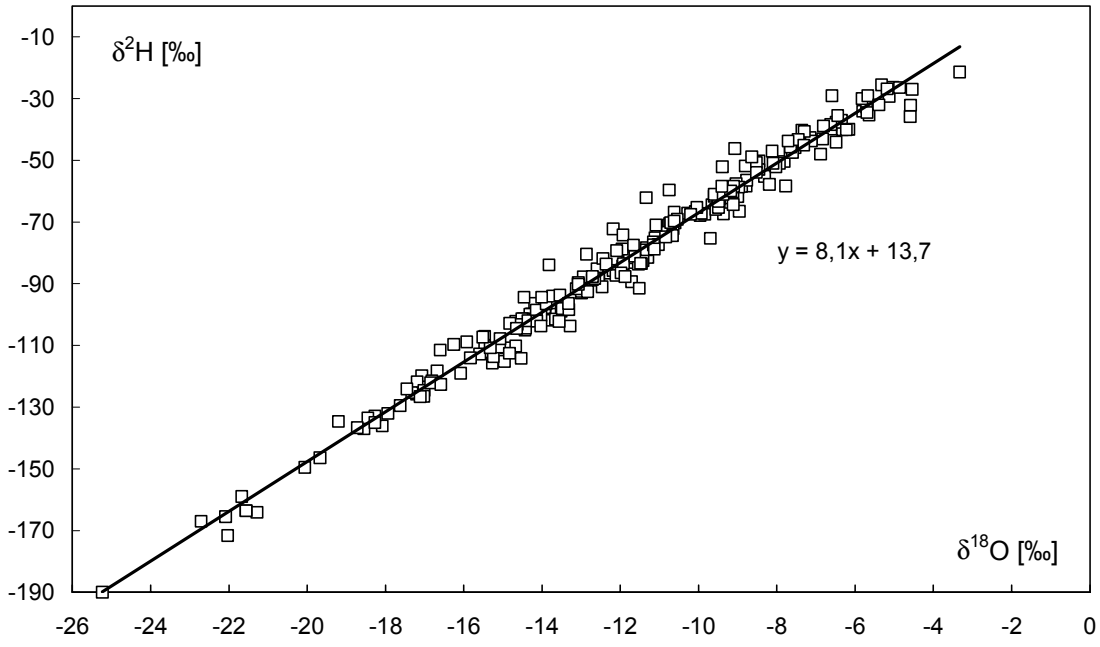
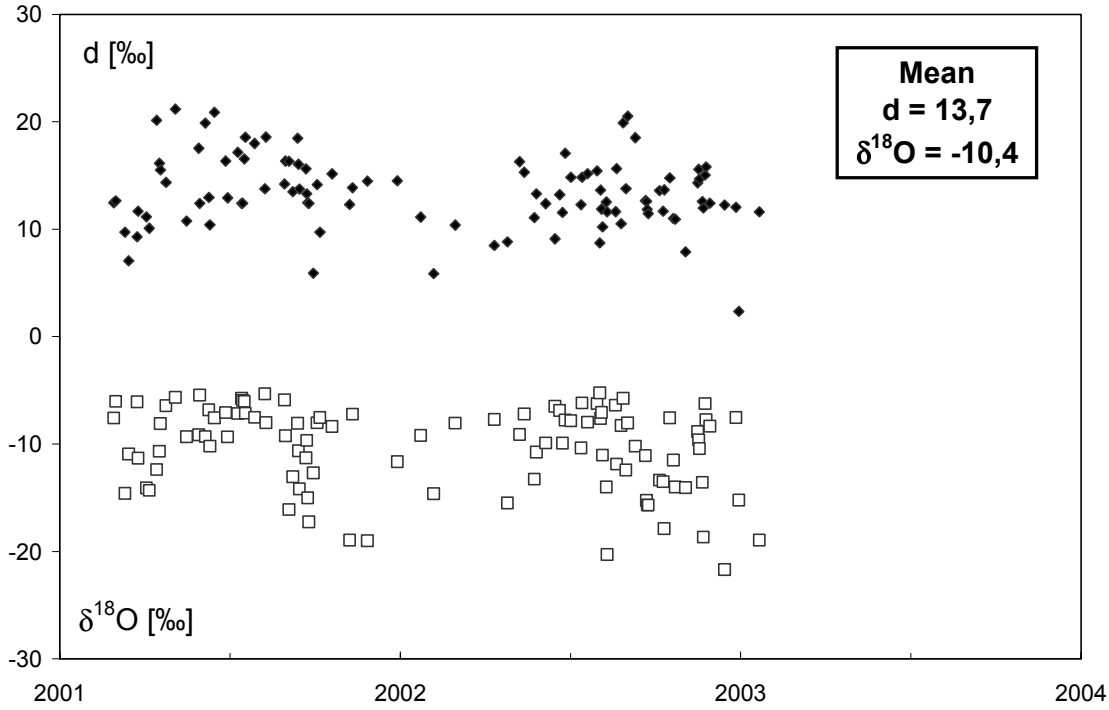


FIG. 7. Feuerkogel (1598 m): a) $\delta^{18}O$ and deuterium excess in daily precipitation; b) $\delta^{2}H$ - $\delta^{18}O$ relation in daily precipitation (precipitation depth >5 mm).



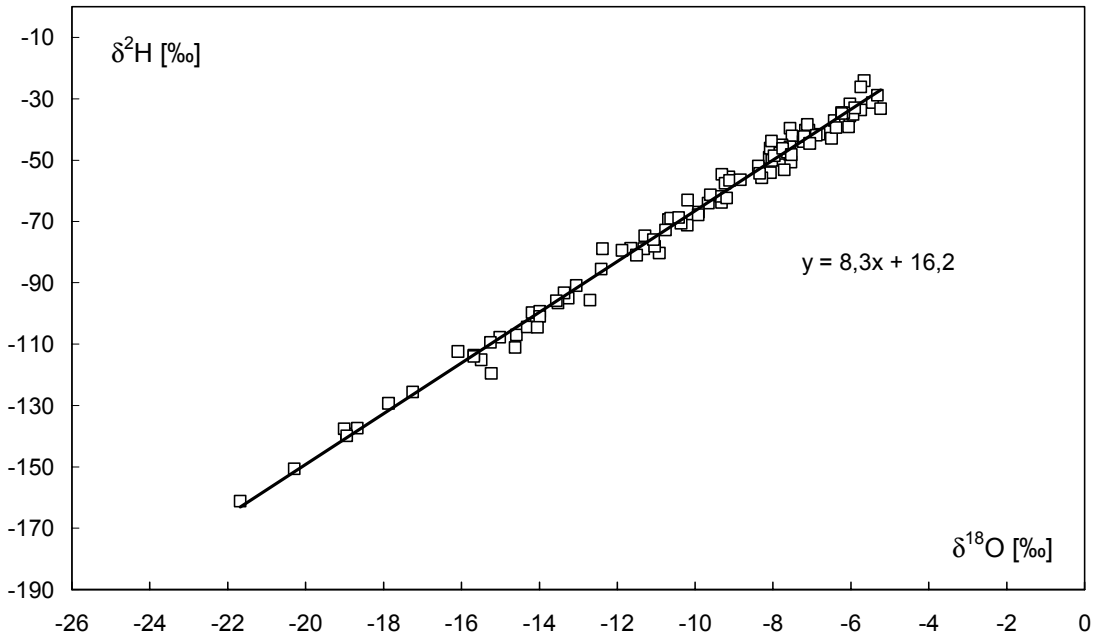


FIG. 8. Villacher Alpe (2135 m): a) $\delta^{18}O$ and deuterium excess in daily precipitation; b) $\delta^{2}H$ - $\delta^{18}O$ relation in daily precipitation (precipitation depth >5 mm).

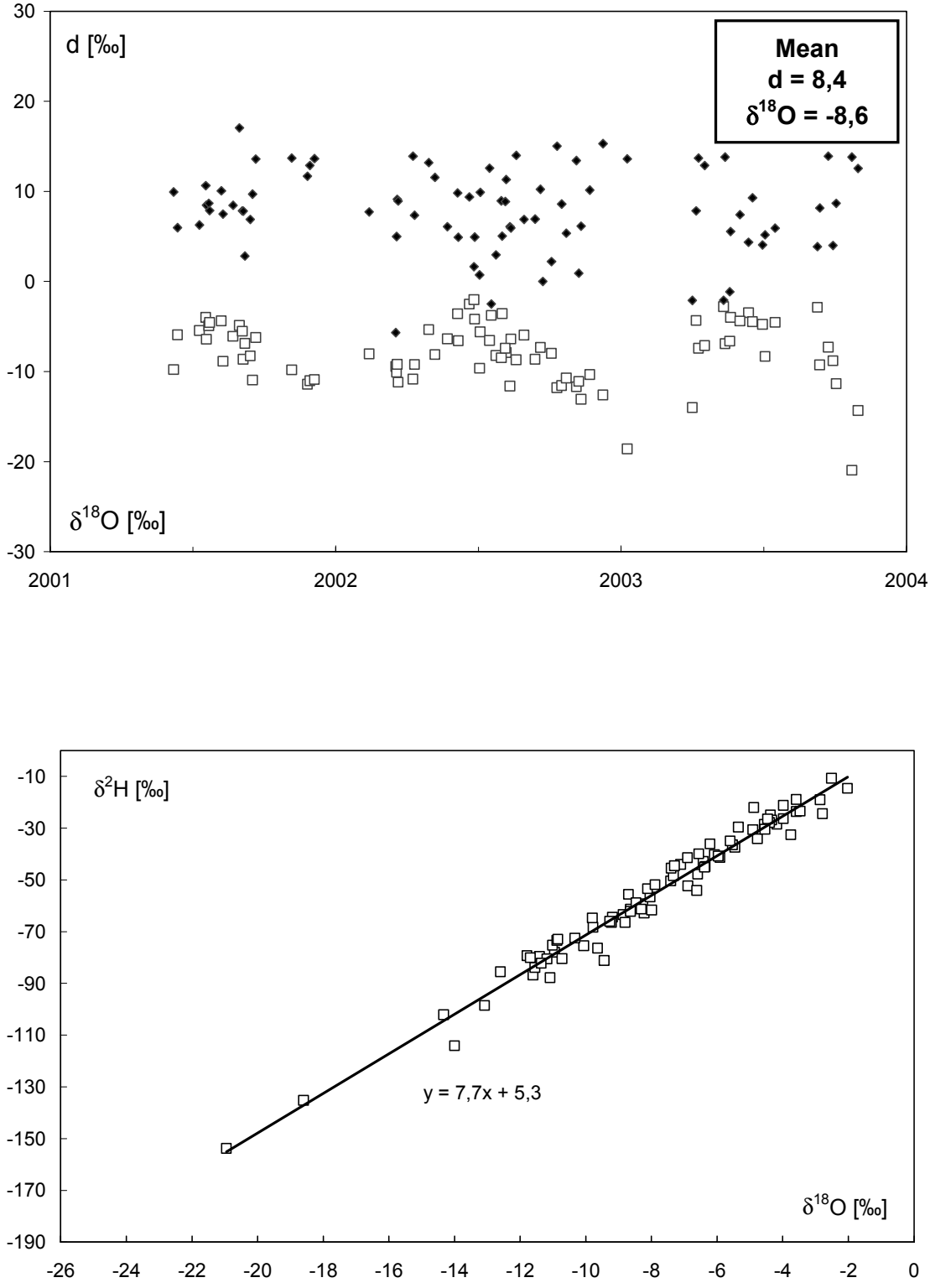


FIG. 9. Vienna (203 m): a) $\delta^{18}O$ and deuterium excess in daily precipitation; b) $\delta^{2}H$ - $\delta^{18}O$ relation in daily precipitation (precipitation depth >5 mm).

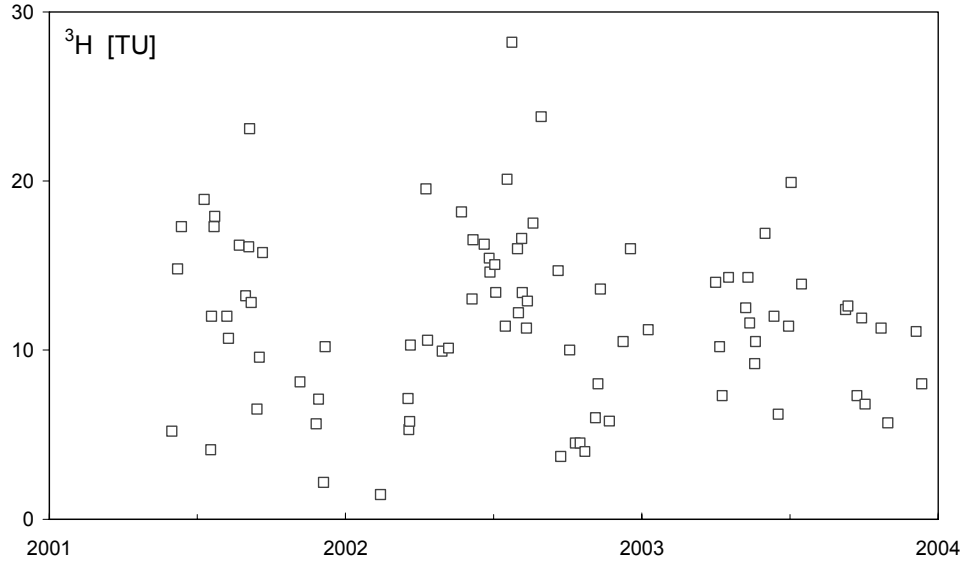


FIG. 10. Vienna (203 m): Tritium content in daily precipitation (precipitation depth >5 mm).

One reason for these difficulties in the interpretation of the data may be that precipitation events in the Alpine region are often a consequence of the collision of air masses of different origin (Atlantic, Mediterranean, continental, influence of local evaporation). The isotopic composition of precipitation can also change significantly during such an event, not only by isotopic effects (e.g. amount effect) but also by a change in the origin of the moisture (see example in Fig. 11). So these events cannot be described as easily as the rainout from a passing cloud. The interpretation of the daily-precipitation data set cannot yet be considered as concluded. For a satisfactory interpretation of the daily data it will probably be necessary to analyze the meteorological conditions during several days before the precipitation event, also including backward-trajectory calculations.

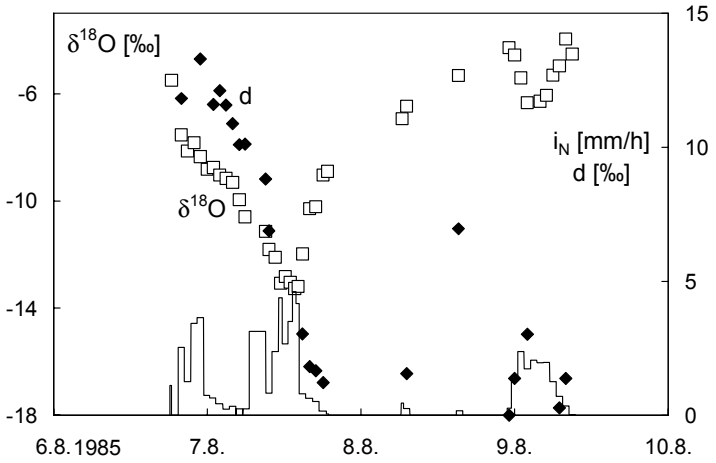


FIG. 11. Variations of $\delta^{18}O$ and deuterium excess in precipitation during a rain event in Vienna (Arsenal) Aug. 6 – 9, 1985 [8].

4. Deuterium excess in precipitation in the Eastern Alps

Deuterium excess has widely been used as an additional parameter to identify the source region of water vapour. However, it turns out that a simple relationship cannot be established due to secondary fractionation processes, like snow formation or partial evaporation of raindrops below the cloud base. From the long-term time series a significant difference in the behaviour of the deuterium excess at mountain (Patscherkofel, Villacher Alpe) and valley stations has been observed (Fig. 12) [2]. There is a slight increase of the yearly mean of the deuterium excess with increasing altitude of the sampling station (Fig. 13), an effect, which has been observed by several authors, e.g. [9], [10], [11]. But moreover, the seasonal pattern of the deuterium excess is quite different. While the valley stations (e.g. Innsbruck) exhibit the expected minimum in summer, the mountain stations show a distinct maximum (ca. 15 ‰) between June and October. This is also the period with the seasonal maximum of precipitation. An unexpected result is that no significant differences occur between northern and southern stations, stations with Mediterranean influence like Villacher Alpe and Graz show more or less the same deuterium excess pattern as the northern stations.

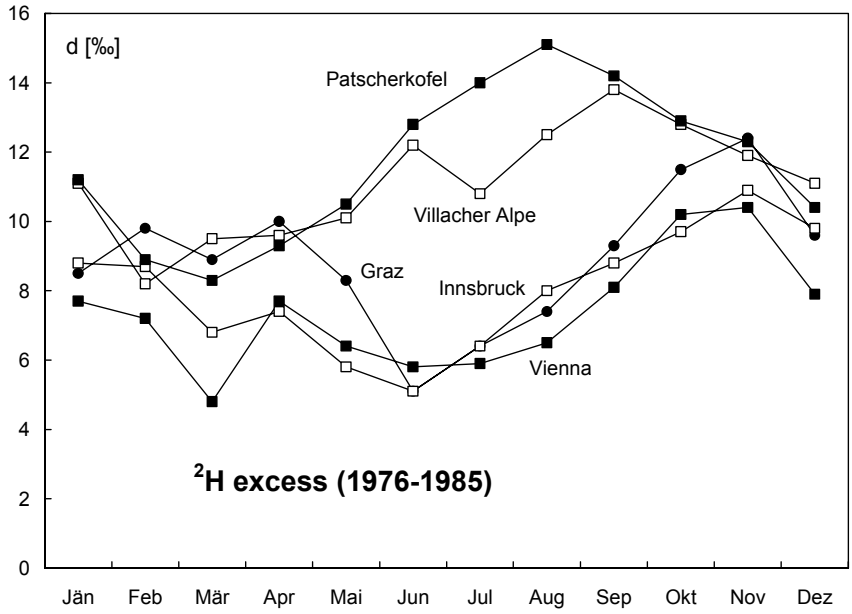


FIG. 12. Seasonal variations of deuterium excess in precipitation at different locations and altitudes in Austria (north: Patscherkofel, Innsbruck, south: Villacher Alpe, Graz).

These differences occur even if the horizontal distance between mountain and valley-station is only a few kilometers (Fig. 1: Patscherkofel and Innsbruck, Fig. 14a). From this we concluded, that the reason for the differences in deuterium excess is obviously evaporation and/or isotopic exchange with air moisture during the falling of the raindrops.

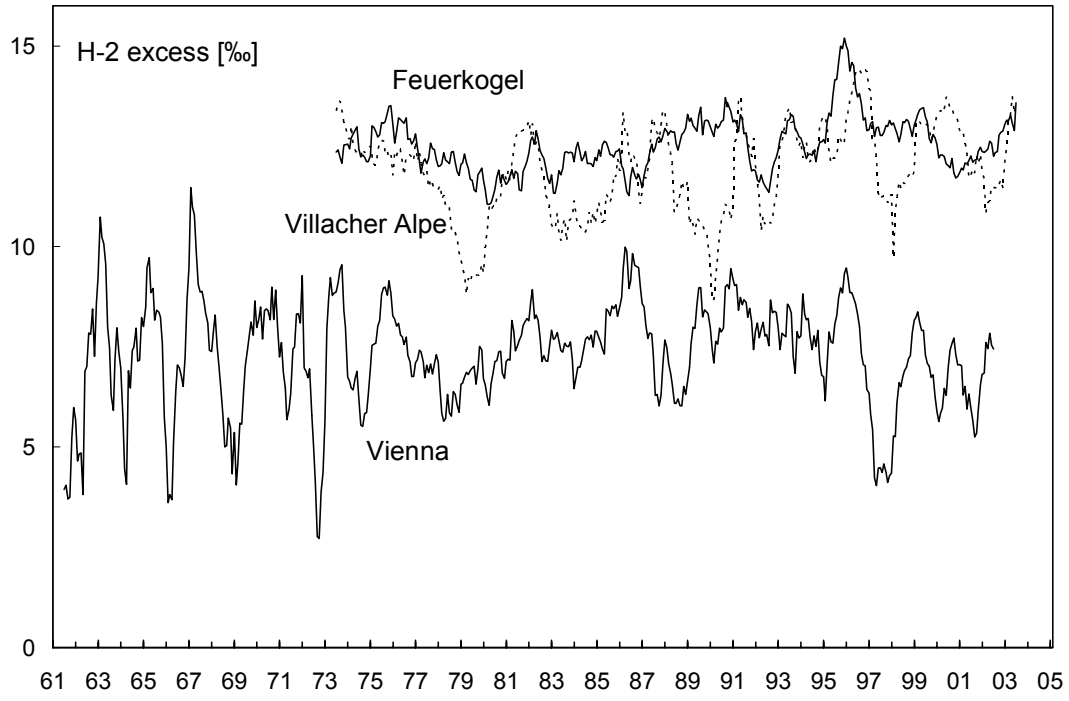


FIG. 13. Long-term variations of deuterium excess in precipitation at Feuerkogel, Villacher Alpe and Vienna (12–month running mean).

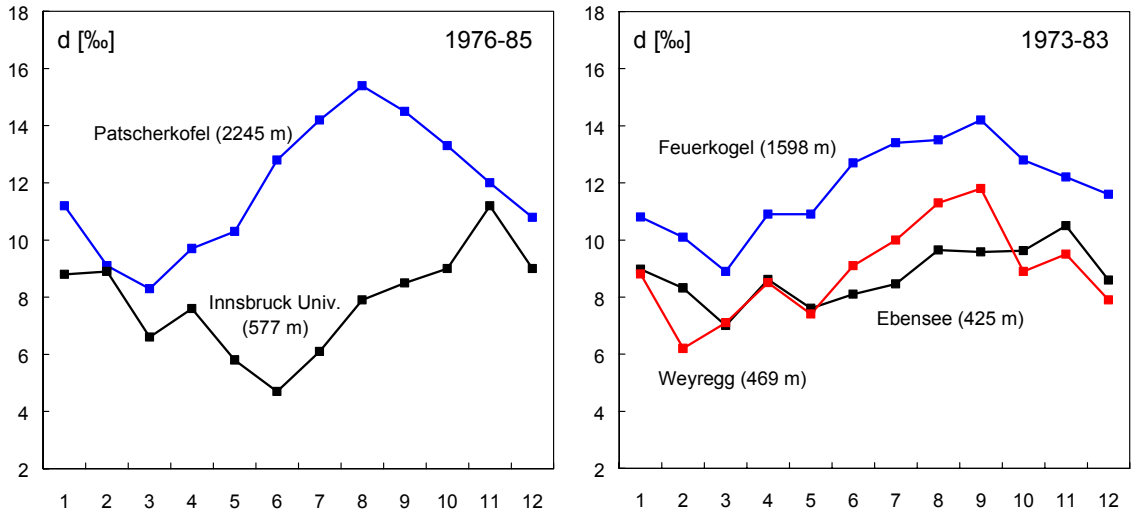


FIG. 14. Seasonal variations of deuterium excess in precipitation at mountain and valley stations nearby in the Eastern Alps [2][6]: a) Patscherkofel (2245 m) and Innsbruck (577 m), b) Feuerkogel (1598 m), Weyregg (469 m) and Ebensee (425 m) (see profile Fig. 15).

In contradiction to these findings, the deuterium excess at a valley station at the northern border of the Alps showed similar time dependence like that of the mountain stations (d-maximum in late summer), but at a lower level (Fig. 14b, Weyregg and Feuerkogel). From this it was supposed that there might be a difference in the d-excess between the weather and the lee side of mountains. To prove this, stored old samples from a former observation station nearby on the lee side of Feuerkogel were analyzed (Ebensee, Fig. 15). The values differ significantly from those of Feuerkogel and Weyregg, there is no summer maximum (Fig. 14b). There is a difference of about 3‰ between the average d-

excess at Feuerkogel and at Ebensee, although the horizontal distance between these two stations is only three kilometers. Evaporation and isotopic exchange during the falling of the raindrops has obviously an important influence on the d-excess. Whereas the transport of air moisture on the weather side of the mountains takes place also in lower air layers, the humid air masses ascend when reaching the foot hills of the mountains (Fig. 15). On the lee side of the mountains, the humid air masses proceed in a higher altitude. Obviously both, the ascent of the moisture at the slope of the mountains as well as the bigger falling height of the raindrops on the lee side of the mountains are connected with secondary fractionation processes that lead to an "altitude" effect of the deuterium excess. Investigations of single events by sequential sampling will probably help to understand better the observed variability.

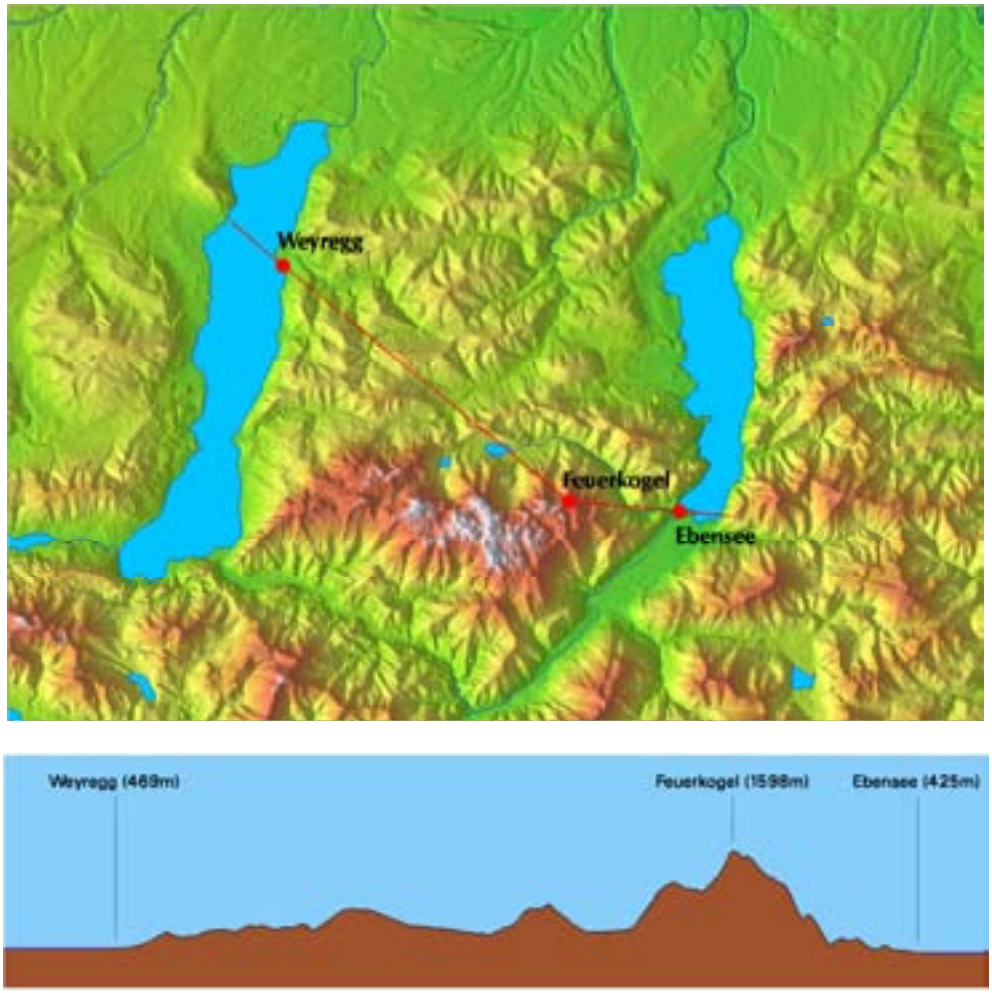


FIG. 15. Orographic position of the sampling stations Weyregg, Feuerkogel and Ebensee (profile NW-SE).

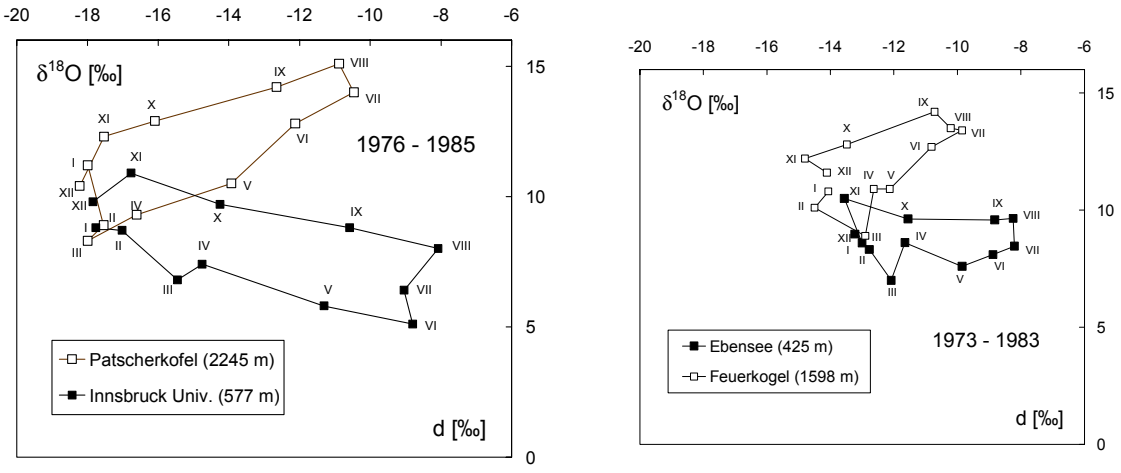


FIG. 16. Deuterium excess vs. $\delta^{18}O$ of monthly precipitation at mountain and valley stations. The Roman numerals indicate the seasonal cycle (January to December).

The deuterium-excess versus $\delta^{18}O$ plots show also impressively the different behaviour of mountain and valley stations (Fig. 16). These hysteresis curves can better demonstrate phase shifts between the seasonal variation of the deuterium excess and $\delta^{18}O$ and other climatic variables.

Backward trajectory calculations seemed then to be a suitable instrument to confirm the finding that high deuterium excess in precipitation at mountain stations is not necessarily a consequence of Mediterranean influence. As a first step into a comprehensive analysis of the meteorological effects on the isotope patterns, the differences in the isotope content of precipitation water during July and August 1998 between the stations Patscherkofel and Villacher Alpe were studied with help of trajectory statistics. This time period was selected because of the high deuterium excess values at these stations in summer and the isotopically different/similar behaviour in July/August. While in July the $\delta^{2}H$- and $\delta^{18}O$-values at Villacher Alpe are much higher than at Patscherkofel, in August both stations show similar values (Table 1). The high $\delta^{2}H$- and $\delta^{18}O$-values at Villacher Alpe in July are attributed to a strong Mediterranean influence. This interpretation is also supported by the low ^{3}H-content. Both sites are elevated points in the Alps. Patscherkofel is north of the main Alpine ridge and Villacher Alpe south of it (Fig. 1).

Table 1. Isotopic composition of precipitation water at Patscherkofel and Villacher Alpe, summer 1998.

	Precipitation sum [mm]	$\delta^{2}H$ [‰]	$\delta^{18}O$ [‰]	d [‰]	^{3}H [TU]
Villacher Alpe, July	171	-14.8	-2.30	3.6	9.7
Villacher Alpe, August	132	-51.9	-8.25	14.1	15.3
Patscherkofel, July	116	-59.7	-9.11	13.2	19.3
Patscherkofel, August	116	-54.3	-8.41	13.0	18.0

Table 2 gives an overview about some precipitation characteristics for July and August 1998. These simple parameters provide a first idea concerning the possible causes of the differences in isotope ratios: During both months precipitation amounts and intensities are higher at Villacher Alpe, but the differences between the two stations are much more pronounced in July. In July, hourly precipitation sums less than 1 mm are observed at Patscherkofel in 85 hours, at Villacher Alpe only in 44 hours, but

strong precipitation events are found more often at Villacher Alpe. The strong differences of the precipitation characteristics between the two stations in July are due to a high portion of convective precipitation events at Villacher Alpe, e.g. thunderstorms, connected with strong upward motion of air. At Patscherkofel, convective precipitation events are much less dominant. In August, precipitation sums, intensities and frequency distributions are much more similar at both stations.

Table 2. Precipitation characteristics for Patscherkofel and Villacher Alpe, summer 1998.

	Precipitation sum [mm]	Hours of precipitation	Precipitation intensity [mm/h]
Villacher Alpe, July	171	87	1.96
Villacher Alpe, August	132	75	1.76
Patscherkofel, July	116	128	0.90
Patscherkofel, August	116	102	1.14

The backward-trajectory calculation was discussed in detail elsewhere [6]. To give an overview, we summarized the residence times of the trajectories for two regions of origin, the Atlantic and Mediterranean (Fig. 17). In both months, only 10%–14% of the air masses connected with precipitation at Patscherkofel originate in the Mediterranean. The remaining precipitation events arrive at Patscherkofel from west or north, originating over the Atlantic. In general, the portion of precipitation events with origin in the Mediterranean is higher at Villacher Alpe compared to Patscherkofel, but note the strong differences between July and August due to strong influence from the Mediterranean in July at Villacher Alpe. An important conclusion from these results is for isotope-hydrological applications that Mediterranean influence cannot be the reason for the high deuterium excess at Patscherkofel and at other mountain stations in the northern Alps.

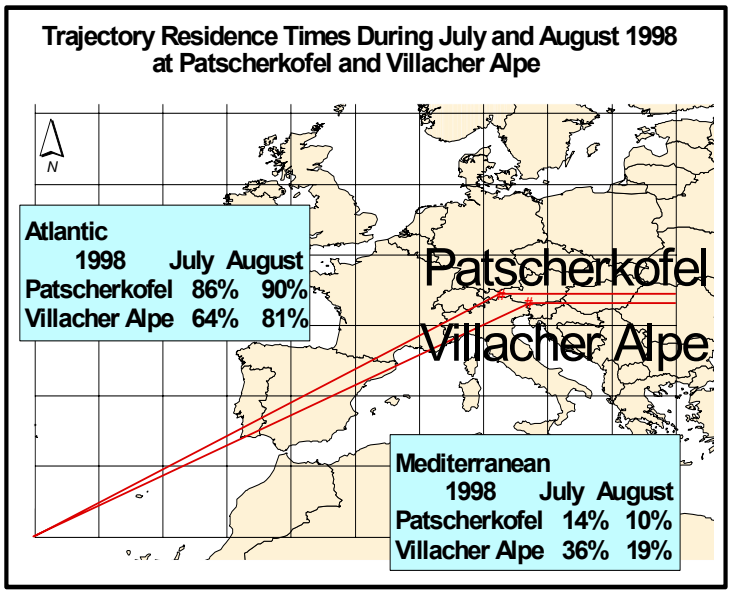


FIG. 17. Residence times of 700 hPa back trajectories ending at Patscherkofel and Villacher Alpe during July and August 1998 added up over the 'Mediterranean' and the 'Atlantic'. The lines separate both subregions [6].

The next step was to look for the response to these deuterium excess variations in surface and ground waters. For this, mountain lakes ("Salzkammergut") seemed to be good investigation objects (Fig. 18). They are relatively deep, cold and have a high flow through (mean residence time of a few years), so

evaporation influence is negligible in most cases. These lakes become well mixed in late winter, so samples from the outflow of the lakes taken at this time deliver more or less yearly mean isotopic values. The measured data showed a clear correlation between $\delta^{18}O$ values and deuterium excess (varies between 7 and 13‰). This result was confirmed by the data from a second sampling campaign in 2003 (Fig. 19). From this an altitude effect of about 0.43 ‰ per 100 m can be calculated for the deuterium excess (taking into account an altitude effect of -0.25 ‰ per 100 m for $\delta^{18}O$).

Referring to the interpretation of deuterium excess data in isotope-hydrological applications, the most important conclusions from these investigations are:

- The relatively big variations of the deuterium excess in precipitation in the Alps (higher values at the mountains, lower values in the valleys and forelands) is mainly "home-made" and not the result of a different origin of the air masses transported into the mountainous region.
- Therefore the deuterium excess is probably no reliable tool to trace the origin of air masses and moisture coming from farer away in the Alps. For this purpose – to distinguish between Atlantic and Mediterranean origin – $\delta^{18}O$ (or $\delta^{2}H$) values and especially ^{3}H data are a suitable instrument.
- The water of the rivers coming from mountainous regions is a mixture of mountain and valley precipitation, so that the resulting deuterium excess is more or less "normal", when the river leaves the mountainous region.

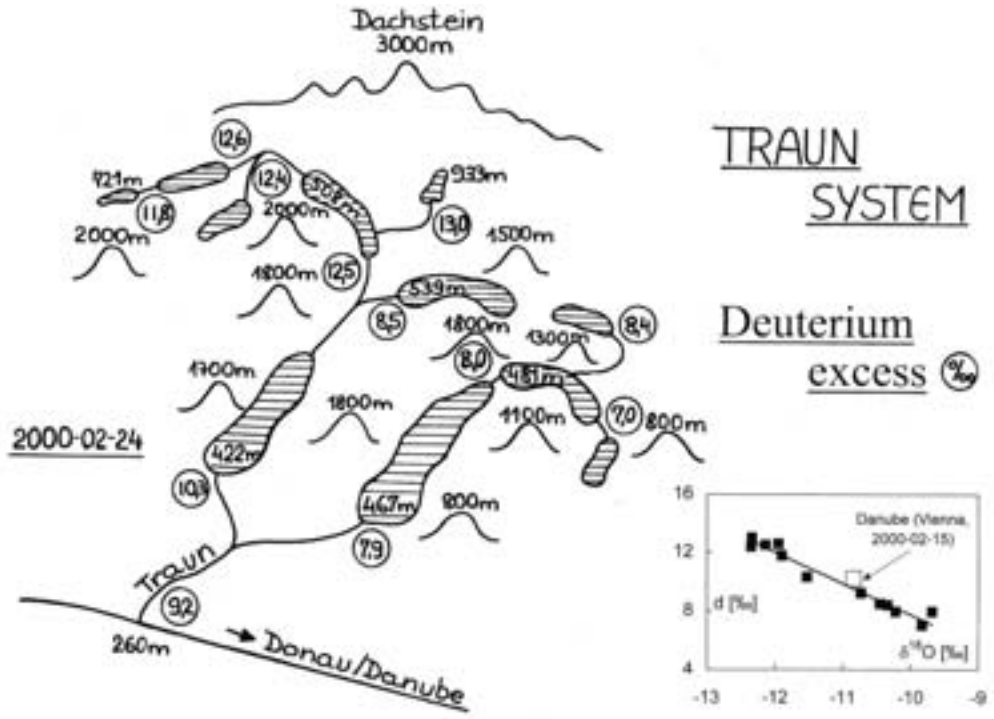


FIG. 18. Deuterium excess in lake water at the outlet of alpine lakes at different elevations in the River Traun system. Insert: deuterium excess vs. $\delta^{18}O$.

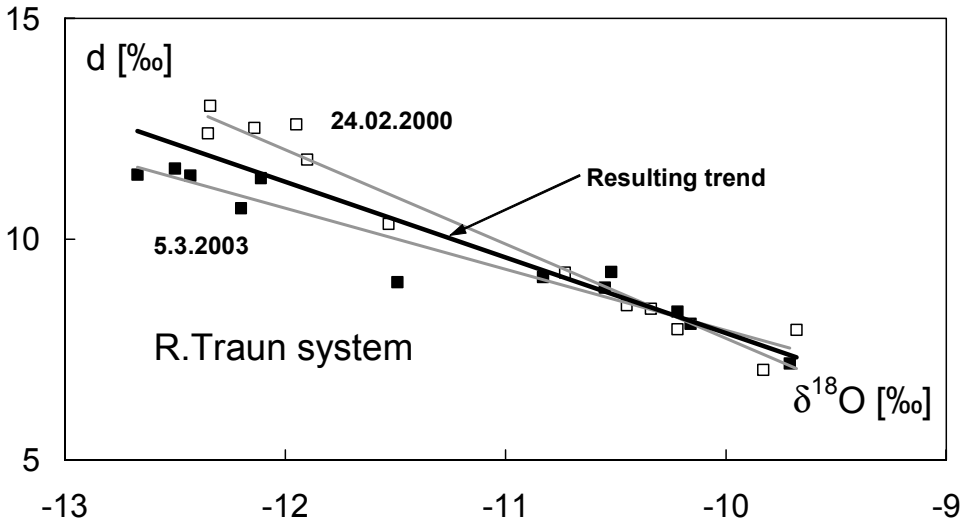


FIG. 19. Deuterium excess vs. $\delta^{18}O$ of lake water at the outlets of the lakes in the River Traun system. Results from two sampling campaigns (2000 and 2003).

Some questions still remain. The mechanism for the higher deuterium excess in mountain precipitation is not yet clear (influence of re-evaporation?). Perhaps more detailed investigation of single precipitation events — sequential sampling — may help to get more insight. The second question is, can these findings in the Eastern Alps be transferred to other mountain regions?

5. Conclusions

(a) The stored samples of the close-meshed Austrian Network for Isotopes in Precipitation turned out to be an excellent material for isotope-climatologic investigations. This applies for long-term trends as well as for local variations of isotope parameters.
(b) The long-term records show a good correlation between fluctuations of isotope ratios in precipitation and surface air temperature, but also other influences like changes in precipitation mechanisms are reflected. This finding applies also for the correlation with the NAO index.
(c) Local variations of the deuterium excess were found in the Alpine region, obviously a consequence of secondary fractionation processes and depending on the morphology of the investigation area. Therefore the deuterium excess is probably no reliable tool to trace the origin of air masses and moisture coming from farer away into mountainous regions.
(d) The interpretation of isotope data from daily precipitation samples could not be satisfactorily concluded until the end of the CRP period. The only clear finding is that Mediterranean influence is indicated by lower tritium content. Due to collisions and mixtures of different air masses in the Alpine region, it will be necessary in order to improve the interpretation to investigate precipitation events by sequential sampling and to analyse the meteorological conditions not only for the event duration, but also for several days before.
(e) The statistical analysis of backward trajectories promises to become a valuable instrument to trace the path and the isotopic evolution of a humid air mass. Precipitation sampling for isotope measurements on a monthly base will not be sufficient for such work; the samples should be taken on an event base.

REFERENCES

[1] RANK, D., Das österreichische Niederschlagsisotopenmeßnetz, Mitteilungsblatt des Hydrographischen Dienstes in Österreich, Heft 70, Wien (1993) 72–76.

[2] RANK, D., PAPESCH, W., Isotopenverhältnisse im natürlichen Wasserkreislauf – Indikatoren für Klimaänderungen, Barbara-Gespräche Payerbach 1998, Geoschule Payerbach, Wien (2001) 241–255.

[3] ROZANSKI, K., GONFIANTINI, R., Isotopes in climatological studies, IAEA Bulletin 32, No. 4, Vienna (1990) 9–15.

[4] IAEA/WMO, The Global Network of Isotopes in Precipitation database available at isohis.iaea.org (2003).

[5] AUER, I., BÖHM, R., SCHÖNER, W., Austrian long-term climate: Multiple instrumental climate time series in central Europe (1767–2000), Österreichische Beiträge zu Meteorologie und Geophysik, Wien (2001).

[6] KAISER, A., SCHEIFINGER, H., KRALIK, M., PAPESCH, W., RANK, D., STICHLER, W., Links between meteorological conditions and spatial/temporal variations in long-term isotope records from the Austrian precipitation network (Proceedings of a symposium on Study of Environmental Change using Isotope Techniques), C&S Papers Series 13/P, IAEA, Vienna (2001).

[7] RANK, D., ADLER, A., ARAGUÁS ARAGUÁS, L., FROEHLICH, K., ROZANSKI, K., STICHLER, W., Hydrological parameters and climatic signals derived from long-term tritium and stable isotope time series of the River Danube (Proceedings of a Symposium on Isotope Techniques in the Study of Environmental Change), STI/PUB/1024, IAEA, Vienna (1998) 191–205.

[8] RANK, D., "Umweltisotope" – Fortschritte in Forschung und Anwendung, Mitt. österr. Geol. Ges. 83**,** Wien (1990) 91–108.

[9] SCHOTTERER, U., FRÖHLICH, K., STICHLER, W., TRIMBORN, P., Temporal variation of ^{18}O and deuterium excess in precipitation, river and spring waters in Alpine regions of Switzerland (Proceedings of a Symposium on Isotope Techniques in the Study of Past and Current Environmental Changes in the Hydrosphere and the Atmosphere) STI/PUB/908, IAEA, Vienna (1993) 53–64.

[10] HOLKO, L., Use of environmental isotopes in hydrological research of a mountain catchment, Final report, IAEA research contract SLR. 7271/RB (1994) Unpublished.

[11] GONFIANTINI, R., ROCHE M.-A., OLIVRY, J.-C., FONTES, J.-C., ZUPPI G. M., The altitude effect on the isotopic composition of tropical rains, Chemical Geology 181 (2001) 147–167.

TRITIUM AND STABLE ISOTOPE DISTRIBUTION IN THE ATMOSPHERE AT THE COASTAL REGION OF CROATIA

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Abstract. Isotope composition of monthly precipitation (^{3}H, δ^2H, δ^{18}O) during the three-year period (Sept. 2000 – Dec. 2003) was monitored at 6 stations in Croatia, 4 maritime and 2 continental stations. Seasonal variations of tritium at maritime stations (mid and south Adriatic coast) are less pronounced and the mean yearly activities are lower than those at the continental stations. δ^2H and δ^{18}O values of monthly precipitation for all stations are compared with the Global Meteoric Water Line. The temperature gradient (δ^{18}O – temperature correlation) for different stations and the altitute effect are discussed. Influence of different climate to the isotope composition of precipitation is also discussed. The results of stable isotope compositions in daily precipitation at the Zagreb station in a six-month period are also presented, as well as ^{14}C activity of atmospheric CO_2 in the Zagreb area.

1. Introduction

A worldwide survey of oxygen (^{18}O/^{16}O) and hydrogen isotope (^{3}H, ^{2}H/^{1}H) content in precipitation has been conducted by IAEA in co-operation with the World Meteorological Organization (WMO) since 1961. The main initial objective was the systematic collection of basic data on isotope content of precipitation on a global scale to determine temporal and spatial variations of environmental isotopes in precipitation. In Croatia the basic isotope data of monthly precipitation (^{3}H, ^{2}H, ^{18}O) have been collected since 1976 at the continental station in Zagreb. The data have been included in the Global Network of Isotopes in Precipitation (GNIP) [1], [2], [3]. Within the present CRP the network has been extended to five stations along the Adriatic coast of Croatia.

The aim of this research was to determine natural variations of background environmental ^{3}H level, as well as distribution of stable isotopes in precipitation over a relatively small area with different climate and geographical characteristics. The obtained isotope data of precipitation gives new information about the influence of different types of climate on isotope content and about air mass movement. Basic isotope data of precipitation will provide more accurate use of environmental isotopes in hydrological investigations in different areas of Croatia. Additionally, the known distribution of ^{3}H in the atmosphere and its natural variation may help in quick recognition of any contamination caused by a nuclear accident or any other release of ^{3}H into the atmosphere by various nuclear facilities.

Here we present the ^{3}H, ^{2}H/^{1}H and ^{18}O/^{16}O composition of monthly precipitation at marine stations at the coastal region of Croatia for the period September 2000 – December 2003 and compare the results with the long-term data for the continental station in Zagreb. The stable isotope composition of daily precipitation collected at the Zagreb station in a six-month period is also presented, as well as ^{14}C activity of atmospheric CO_2 collected in the Zagreb area.

2. Sampling and measurements

2.1. Sampling stations

Croatia, with relative small area of 56 542 km^2, is characterized by three different types of climate: (i) continental climate prevails in the northern part, (ii) colder climate (mountain-type of continental climate) dominates in the mountaneous middle part, mostly karst area, and (iii) the area along the Adriatic coast, also karst area, is controlled by the Mediterranean climate. For this project we selected sampling sites, e.g. meteorological stations for monthly precipitation, mostly at the Adriatic coast area distributed from the north to south part of the coast. Locations of sampling stations in Croatia are

presented in Figure 1. Two stations are situated at the continental coast (Zadar and Dubrovnik) and two at the island coast (Malinska on Krk Island and Komiža on Vis Island). All these stations have Mediterranean climate and are situated at the low altitude (from 1 to 52 m, see Table 1). Zavižan station is situated at the Velebit Mt. at the altitude of 1594 m, above the mid-Adriatic coast. At this station the two types of climate, the Mediterranean and the continental, are mixing. Station Zagreb, N Croatia, has typical continental climate and at this station isotope data of precipitation has been collected since 1976 (GNIP station) [2]. Sampling of monthly precipitation for other stations has been performed since September 2000 and stopped in December 2003. Sampling at Malinska station was performed from December 2000 to November 2001 and then stopped because this station is not involved in the regular meteorological network.

The basic information about sampling stations (coordinates, altitude, period of sampling) and the corresponding meteorological data are presented in Table 1. Precipitation amounts and mean yearly temperatures are shown for each year in the sampling period 2000–2003, as well as the thirty-year mean values (1961–1990).

At all meteorological stations from Figure 1 and Table 1 we collected monthly precipitation samples. We also collected daily precipitation samples in Zagreb in the period 1.10.2002–1.04.2003. Additionally, we collected monthly samples of atmospheric CO_2 for ^{14}C activity measurement at the Zagreb area.

FIG. 1. Map of stations for precipitation sampling in Croatia.

Table 1. Data for sampling stations of monthly precipitation for isotope measurements (^{3}H, ^{2}H, ^{18}O). Maritime stations: Malinska, north Adriatic; Zadar, mid Adriatic; Dubrovnik and Komiža, south Adriatic. Continental stations: Zagreb-Grič, Zavižan.

Station		Zagreb-Grič	Malinska, Krk Island	Zavižan, Mt. Velebit	Zadar	Komiža, Vis Island	Dubrovnik
Coordinates		45º49'N 15º59'E	45º01'N 14º37'E	44º49'N 14º59'E	44º08'N 15º13'E	43º03'N 16º42'E	42º39'N 18º05'E
Altitude (m asl)		157	1	1594	5	6	52
Sampling period		since 1976	Dec. 00– Nov. 01	Sept. 00– Sept. 03	Sept. 00- Dec. 03	Sept. 00- Dec. 03	Sept. 00– Dec. 03
Precipitation amount (mm/yr)	1961 – 1990	882.8		1898.8	914.7	814.7	1203.4
	2000	842	933	2148	826	632	984
	2001	724	1267	1918	782	555	935
	2002	1064	1719	2275	1204	930	1359
	2003	623		1453	587	600	873
Temperature (yearly mean) (°C)	1961 – 1990	11.4		3.5	14.7	16.3	16.3
	2000	13.8		5.1	16.3	17.9	17.2
	2001	12.7		3.8	15.7	17.4	17.0
	2002	13.2	14.8	4.5	15.8	17.5	17.4
	2003	12.9		4.1	15.9	17.7	17.4

2.2. Measurement technique

Tritium activity in monthly precipitations was measured at the Radiocarbon and Tritium Laboratory at the Rudjer Bošković Institute by a gas proportional counter (GPC) technique. From water sample (50 ml), CH_4 is obtained by reaction of water with aluminium carbide at 150°C [4], purified and used as a counting gas in a multi-wire GPC. The counting energy window is set to energies between 1 keV and 10 keV to obtain the best figure of merit. Gas quality control has been performed by simultaneous monitoring of the count rate above the tritium channel, i.e. above 20 keV [5]. The lowest tritium activity that can be distinguished from the background, i.e., the limit of detection is 0.2 Bq/L.

Stable isotope compositions of hydrogen, $\delta^{2}H$, and oxygen, $\delta^{18}O$, were measured in monthly and daily precipitation. The measurements were performed on mass spectrometer at the Department of Environmental Sciences of the Jožef Stefan Institute in Ljubljana (monthly samples) and at the Isotope Hydrology Section at the IAEA in Vienna (daily samples).

Samples of atmospheric CO_2 were collected by absorption of CO_2 in the saturated carbonate-free sodium hydroxide solution. CO_2 was then released by dissolving with HCl and catalytically converted to CH_4 by hydrogenation over a Ru catalyst. ^{14}C activity was measured by GPC using CH_4 as a filling gas.

3. Results and discussion

3.1. Meteorological data

The meteorological data including mean monthly temperature and monthly amount of precipitation were collected at all 6 stations for the period 2000–2003. The data are presented in Fig. 2 and Fig. 3, respectively. All numerical values are presented in tables in Annex 3.

Typical seasonal variation of temperature with winter minima and summer maxima is characteristic for all 6 stations. Maritime stations at southern Adriatic show higher mean temperatures (15.9°C, 17.6°C and 17.2°C at Zadar, Komiža and Dubrovnik, respectively) than the continental stations (13.1°C and 4.4°C at Zagreb and Zavižan, respectively). The mean temperature at the North Adriatic lies between the continental and maritime values (15.6°C at Malinska). The lowest mean temperature (4.4°C) and highest mean yearly amount of precipitation (2275 mm) in the period 2000–2003 have been recorded at Zavižan. In this period, in year 2002 the amount of precipitation at all stations was much higher (about 20%) than the long-term average, while in year 2003 it was lower about 30% than the average. Mean temperatures for each of the year 2000–2003 are higher than the long-term averages at all stations (1°C or more), and summer 2003 was specially warm and dry (Table 1, Fig. 2).

3.2. Monthly precipitation

3.2.1. Tritium

Long-term tritium record for continental station Zagreb (Fig. 4) shows that in the past mean yearly tritium activity in precipitation continuously decreased after reaching a global atmospheric maximum in 1963 due to thermonuclear bomb-tests in the 1950s and 1960s [3]. The results are compared with tritium activity of precipitation in Ljubljana, Slovenia; the data for both stations have been included in GNIP [1][2]. The observed seasonal variations were typical for the continental stations of the Northern Hemisphere. Minima have been observed during winter, from December to March, depending on the specific year.

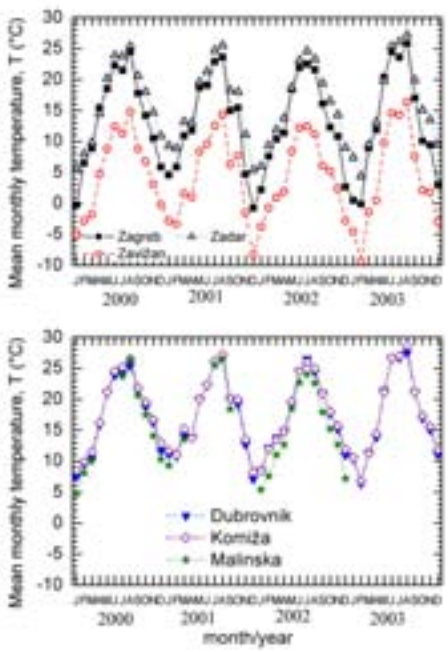

FIG. 2. Mean monthly temperatures for sampling stations for period 2000–2003.

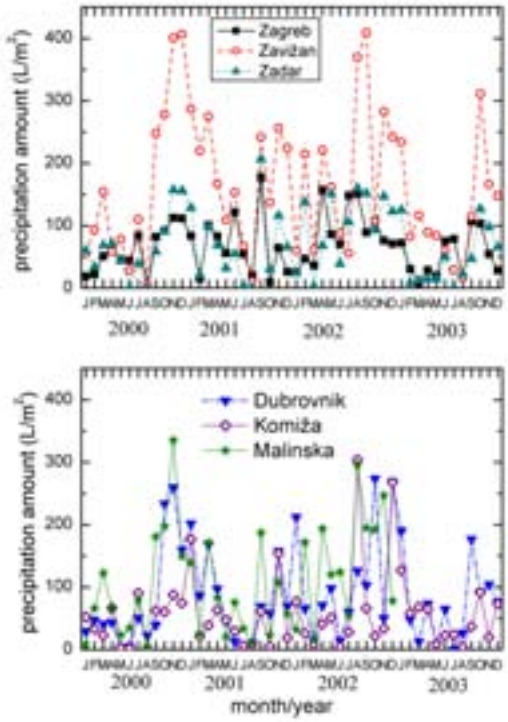

FIG. 3. Monthly amount of precipitation for sampling stations for period 2000–2003.

Seasonal variations in the last decade were less pronounced than in the period 1976–1990. Tritium activity in monthly precipitation for period 1996-2004 in Zagreb and Ljubljana is presented in Fig. 5. The minimal activities in winter approach in the last years the natural pre-bomb tritium level (≤0.4 Bq/L). Maxima are observed in early summer, usually in June or July, and reach presently up to 2.1 Bq/L. Mean yearly tritium activity in Zagreb precipitation during the last decade does not vary considerably, and it is equal to 1.1 Bq/L. For the last three-year period the mean tritium activity is equal to 1.0 Bq/L.

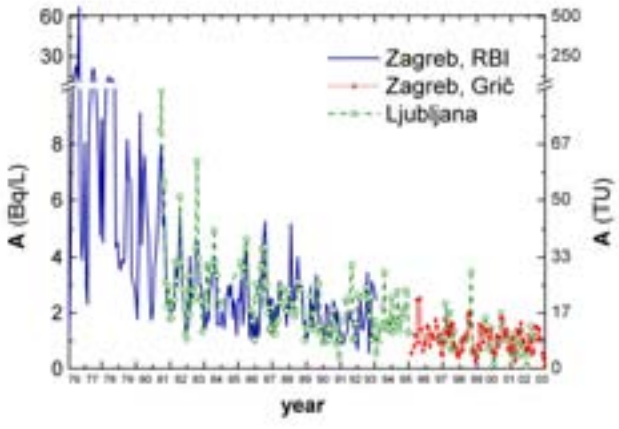

FIG. 4. Long-term record of tritium in precipitation at Zagreb and comparison with the long-term record of tritium in precipitation at Ljubljana, Slovenia. In Zagreb, samples were collected at two stations: 1976-1993 at the Rudjer Bošković Institute (RBI), 1995-2003 at the Grič meteorological station.

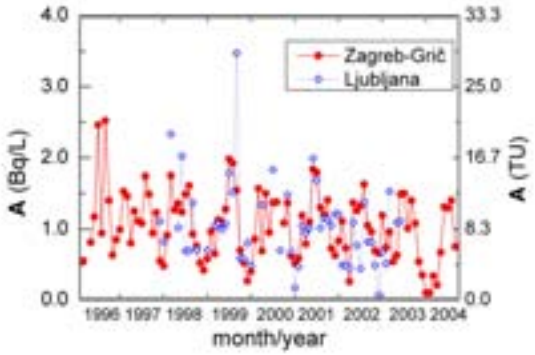

FIG. 5. Tritium activity in monthly precipitation at Zagreb and Ljubljana for the period 1996-2004.

Tritium activity in monthly precipitation at 6 sampling stations for period September 2000–December 2003 is presented in Fig. 6. Tritium activity distribution at the north Adriatic coast (Fig. 6a) is similar to that at the continental stations, showing just slightly lower mean values (0.83 Bq/L at Malinska, 1.04 Bq/L at Portorož, 0.92 Bq/L at Kozina, last two stations are in Slovenia, N. Adriatic, see Fig. 1 [6]). Seasonal variations at maritime stations of mid-Adriatic (Fig. 6b) and especially of south-Adriatic (Fig. 6c) are less pronounced (summer maxima reach 1.4 Bq/L) and the mean yearly activities are lower than those at the continental and north-Adriatic stations due to sea-water evaporation influence. Thus, mean tritium activities in precipitation in Zadar, Komiža and Dubrovnik are equal to 0.75 Bq/L, 0.60 Bq/L and 0.46 Bq/L, respectively. Although station Zavižan is a high-altitude station with a typical cold continental climate, tritium distribution pattern (mean value 0.78 Bq/L, Fig. 6b) is closer to that of the Mediterranean stations in the vicinity than to the pattern of continental stations.

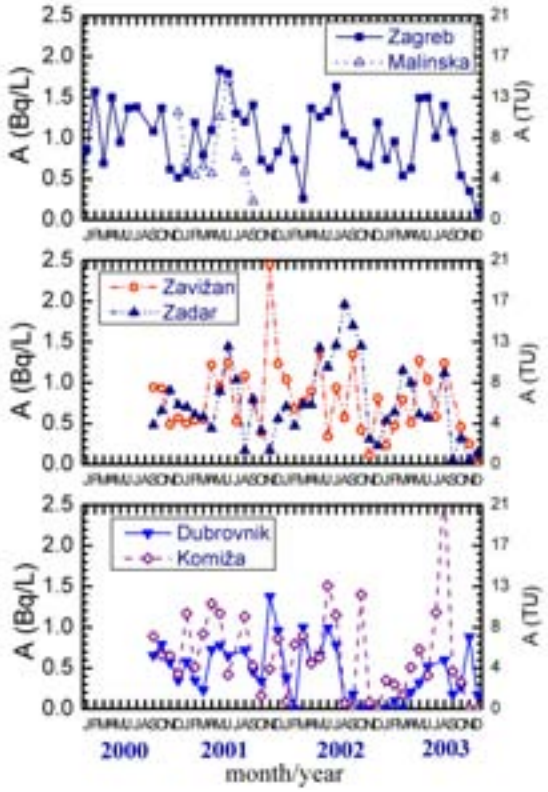

FIG. 6. Tritium activity in monthly precipitation for the period 2000-2003 for six sampling stations: (a) continental and north Adriatic stations, (b) mid-Adriatic stations, (c) south Adriatic stations.

3.2.2. Stable isotopes

$\delta^{18}O$ values and d-excess values of monthly precipitation from 6 stations for period September 2000 – December 2003 are shown in Fig. 7 and Fig. 8, respectively, and the mean values are presented in Table 2. The stable isotope composition of precipitation shows different patterns of seasonal variations at continental and maritime stations. The continental stations show larger seasonal variations in the stable isotope content (e.g. seasonal variations equal to 13‰ and 8‰ in $\delta^{18}O$ at stations Zagreb and Dubrovnik, respectively) due to larger temperature variations. At the high-altitude station Zavižan on Mt. Velebit the two types of climate, the Mediterranean and the continental, are mixing. The isotope pattern of precipitation reflects such a mixing: tritium distribution is close to the nearest maritime station Zadar, while the seasonal variations in stable isotopes are close to the continental pattern. On the other hand, the mean value of d-excess is highest at Zavižan (14.4‰), then follow maritime stations Malinska (13.1‰), Dubrovnik (12.0‰) and Komiža (10.1‰), while Zagreb as the continental station, and Zadar as the mid-Adriatic station, have similar d-excess value, 8.4 and 8.9, respectively.

Table 2. Isotope values of precipitation for period Sept. 2000–Dec. 2003 for six sampling stations in Croatia

Station	Tritium activity (Bq/L)		$\delta^{8}O$ (‰)			LMWL	d-excess (‰)	Temp. gradient (‰/°C)
	Mean value	Maximal monthly	Mean	Min.	Max.	slope	Mean	
Zagreb	0.99	1.8	-8.2	-16.5	-3.5	7.2	8.4	0.33
Malinska*	0.83	1.7	-6.6	-9.3	-3.3	6.5	13.1	-
Zavižan	0.78	2.4	-9.3	-16.5	-2.8	7.2	14.4	0.40
Zadar	0.75	2.0	-5.1	-13.4	+2.1	6.6	8.9	0.24
Komiža	0.60	1.5	-5.4	-12.9	-1.2	6.8	10.1	0.15
Dubrovnik	0.46	1.4	-5.1	-10.3	-2.4	6.1	12.0	0.14

* only one season, period Dec. 2000 – Nov. 2001

The correlation between $\delta^{18}O$ and $\delta^{2}H$ is very good for each station (Fig. 9) and obtained data fit well to the Global Meteoric Water Line (GMWL), $\delta^{2}H = 8\ \delta^{18}O + 10$. Local meteoric water line (LMWL) for Zagreb based on long-term measurements [3] is also very close to GMWL and its equation is $\delta^{2}H = (8.1 \pm 0.2)\ \delta^{18}O + (9.1 \pm 1.9)$. Detailed inspection of all stations for the studied period shows that the slope of the LMWL is higher for Zagreb and Zavižan (7.2) (continental climate) than for the maritime stations: Malinska 6.5, Zadar 6.6, Komiža 6.8, and Dubrovnik 6.1 (Table 2). Smaller slope for these stations, which are also warmer, may indicate some evaporation of summer rain events. The intercept is also smaller for the maritime stations (between 3 and 7) than for the continental stations and Zavižan (about 14).

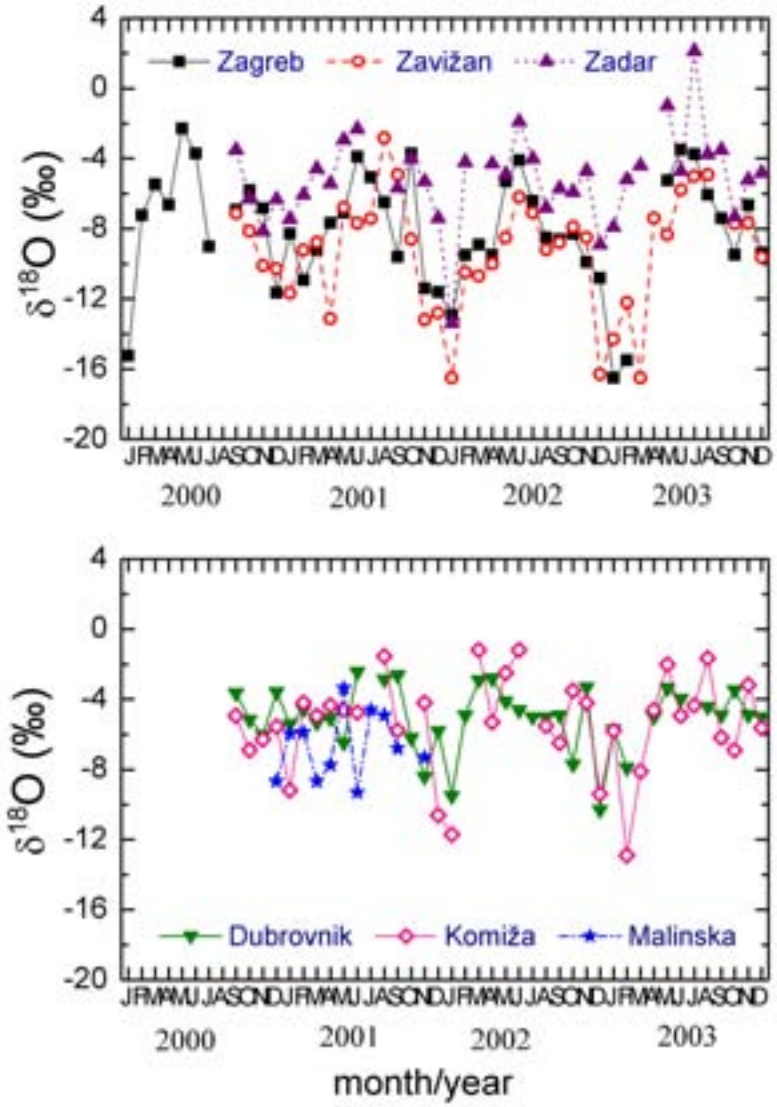

FIG. 7. $\delta^{18}O$ in monthly precipitation at 6 stations, Sept. 2000 – Dec. 2003.

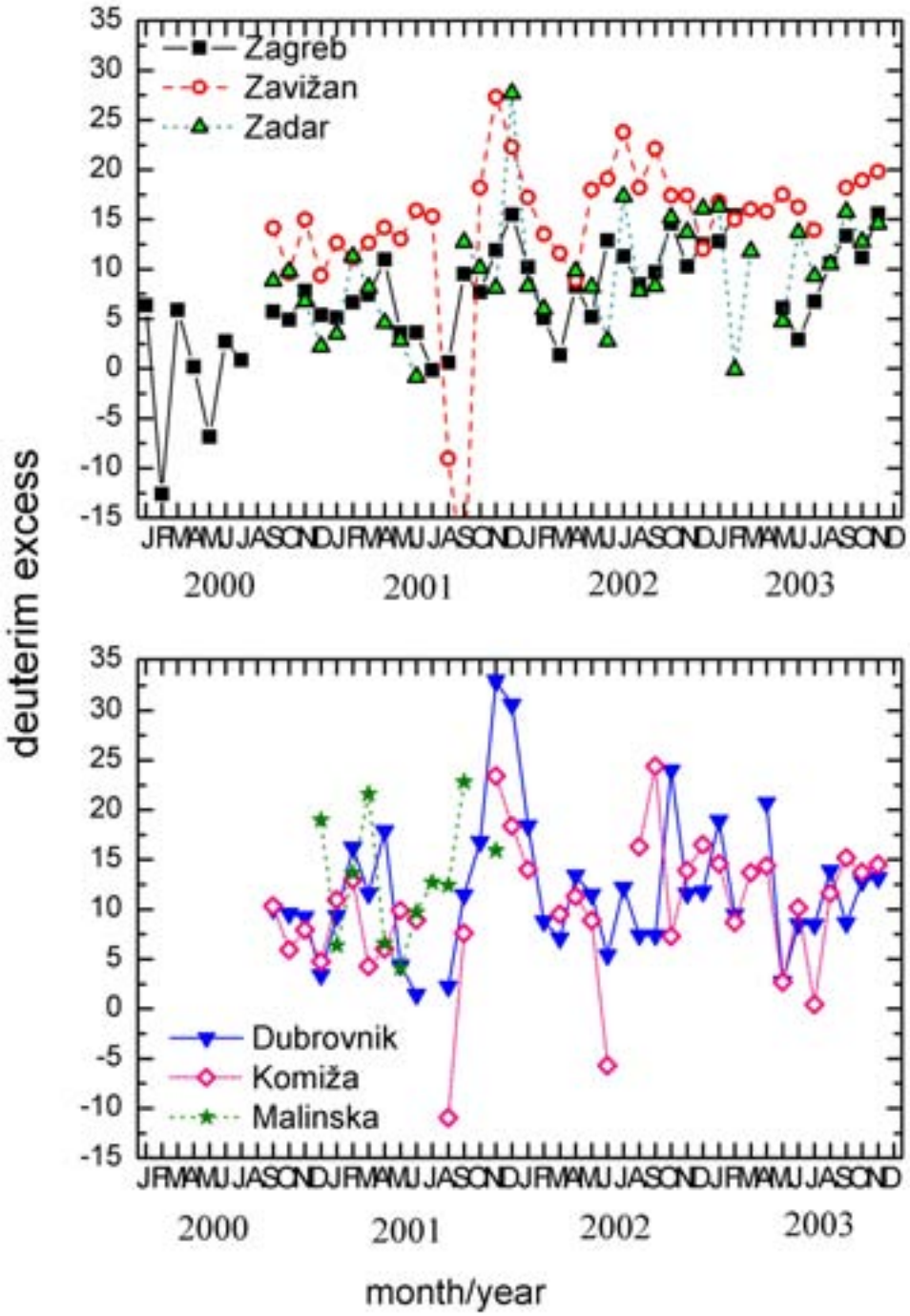

FIG. 8. Deuterium excess in monthly precipitation at 6 stations, Sept. 2000 to Dec. 2003.

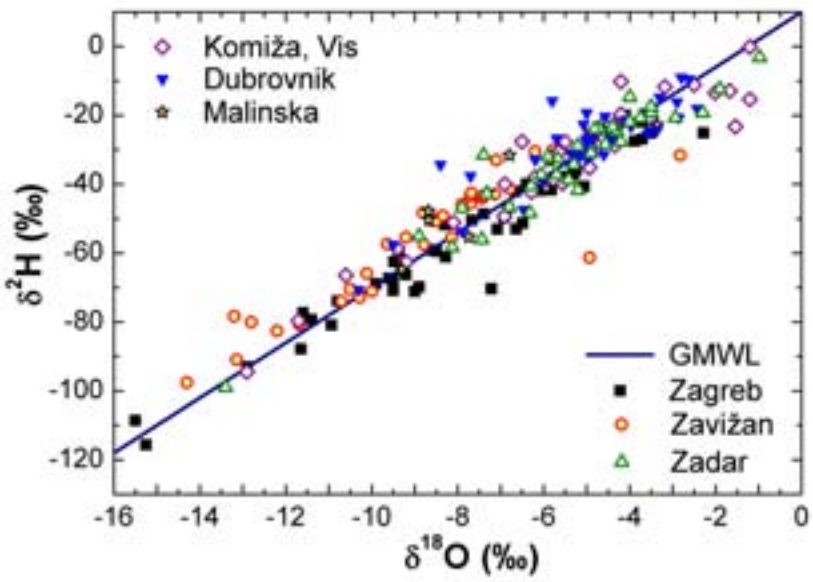

FIG. 9. Relation between $\delta^{18}O$ and $\delta^{2}H$ in monthly precipitation at 6 sampling stations. Global Meteoric Water Line = GMWL.

The correlation between $\delta^{18}O$ values of precipitation and mean monthly air temperature for 6 stations (Fig. 10) showed slightly different temperature gradients (different slopes) for each station. The obtained temperature gradient can be correlated with the mean annual temperature at the particular station: the higher the mean temperature, the lower the gradient. For example, the highest temperature gradient (0.40‰/°C) is obtained for Zavižan (4.4°C mean temperature), followed by 0.33‰/°C for Zagreb (13.1°C), 0.24‰/°C for Zadar (15.9°C), and the lowest gradients are ~0.15‰/°C for Dubrovnik and Komiža (17.2°C and 17.6°C, respectively). Those values are in concordance with the variable temperature gradient for station within the global GNIP database [7][8], as well as with the long-term temperature gradient for Zagreb (0.32‰/°C) [3].

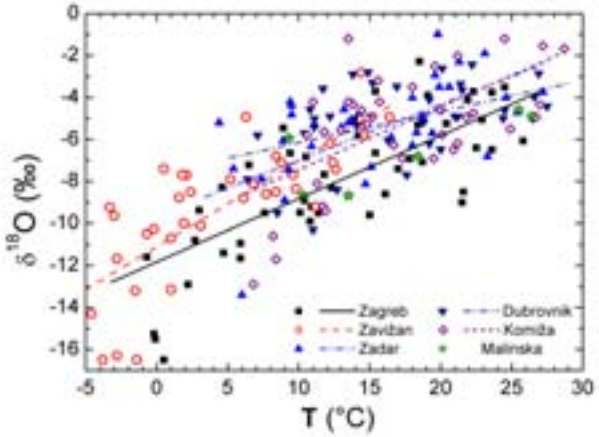

FIG. 10. Relation between $\delta^{18}O$ and mean monthly temperatures at 6 sampling station. Lines represent linear fits to the data for each station.

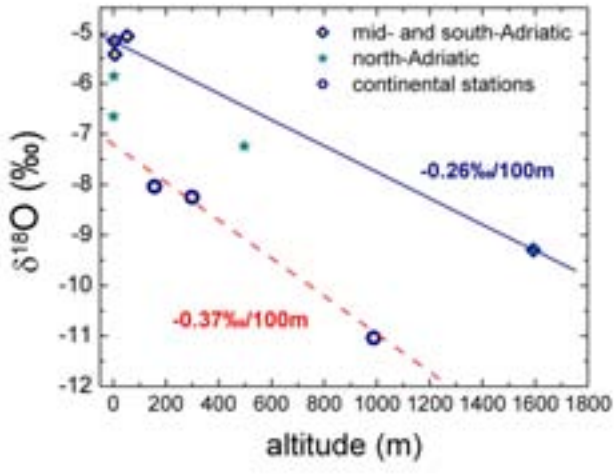

FIG. 11. Altitude effect for stations in Croatia and Slovenia. Diamonds: maritime stations of mid-and south-Adriatic (Zadar, Zavižan, Dubrovnik, Komiža); circles: continental stations (Zagreb, Ljubljana, Puntijarka [3]); stars: maritime stations of North Adriatic (Portorož, Malinska, Kozina).

In Fig. 11 we show the relation of mean $\delta^{18}O$ in precipitation (2000-2003) and the altitude of the sampling station. For comparison, data for Slovenian stations [6] and high-altitude (988 m) station Puntijarka near Zagreb [3] are also shown. The presented data can be grouped into 3 groups: continental stations, north-Adriatic stations, and mid- and south-Adriatic. The typical continetal stations (Zagreb, Ljubljana, Puntijarka) result in an altitude effect of 0.37‰ decrease in $\delta^{18}O$ per 100 m altitude increase. High-altitude station Zavižan, having cold continental climate, shows $\delta^{18}O$ too high for the continental relation. It can be well related to typical maritime stations of mid- and south-Adriatic (Zadar, Dubrovnik, Komiža) resulting in a $\delta^{18}O$ decrease of 0.26‰ per 100 m altitude difference. Three stations at the north-Adriatic coast (Malinska, and Portorož and Kozina in Slovenia) can not be related to any of the two relations, indicating mixing of continental and Mediterranean air masses.

3.3. Daily precipitation

Daily precipitation samples were collected in the period from October 1, 2002 to April 1, 2003 at the Rudjer Bošković Institute, Zagreb. The results of stable isotope compositions as well as daily temperature and daily precipitation amount are presented in Table 2. Good correlations between $\delta^{18}O$ and $\delta^{2}H$ values with daily temperature are shown in Fig. 12. Temperature gradient obtained for this period is 0.65‰/°C for the mean temperature 6°C. The LMWL obtained for daily samples collected in the 6 month period (Fig. 13) fits well to the GMWL, as well as to the long-term LMWL for Zagreb. Daily amount of precipitation and d-excess (mean value 8.7) of daily precipitation (Fig. 14) do not show any particular correlation. There is also no correlation between $\delta^{18}O$ and the amount of precipitation, as it was the case with the monthly data.

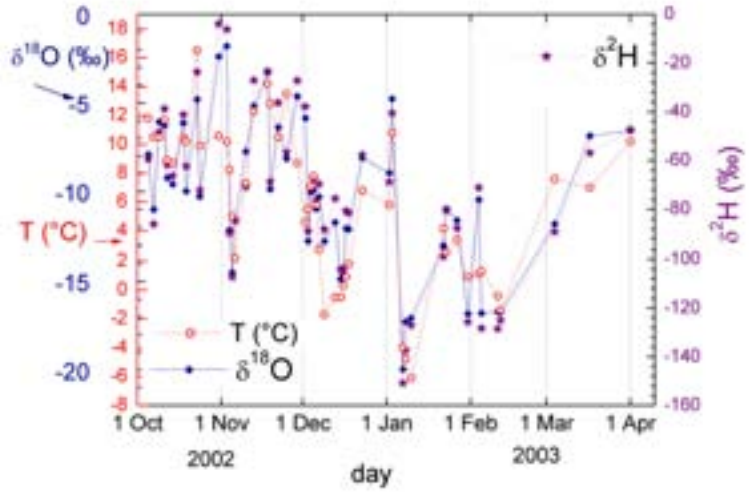

FIG. 12. Comparison of daily air temperature and stables isotopes composition of daily precipitation in Zagreb for Oct. 2002 – March 2002.

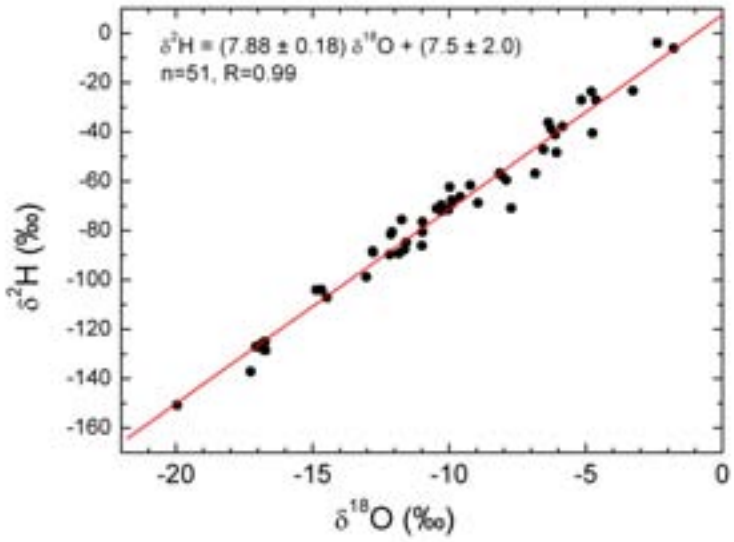

FIG. 13. Correlation between δ^2H and $\delta^{18}O$ for daily precipitation collected in period Oct. 2002 – March 2003 in Zagreb.

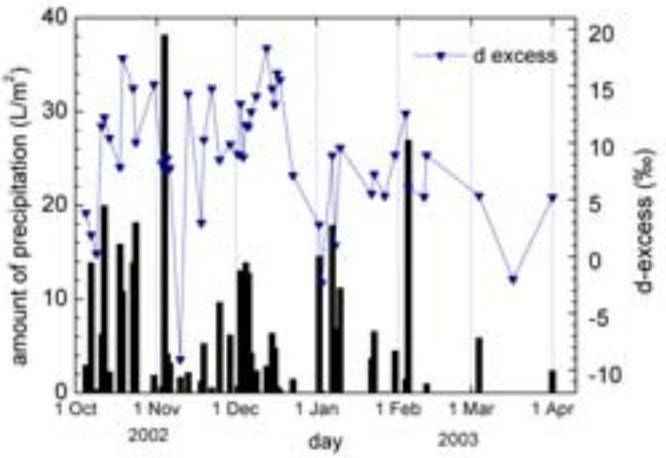

FIG. 14. Comparison of amount and d-excess of daily precipitation in Zagreb for period Oct. 2002 – March 2003.

3.4. ^{14}C in atmospheric CO_2

^{14}C activity of monthly samples of atmospheric CO_2 collected at the Rudjer Bošković Institute during the period 2000–2003 are shown in Fig. 15. Variations of ^{14}C activity with lower values in winter months (lowest $\Delta^{14}C$ = 22‰) and higher in summer (highest $\Delta^{14}C$ = +92‰) are caused mostly by fossil fuel combustion in winter time. Mean $\Delta^{14}C$ for winter months (Oct. – March) in period 2000 – 2003 is 24‰, and that for summer months is 53‰, while the mean value for the whole period is 40‰.

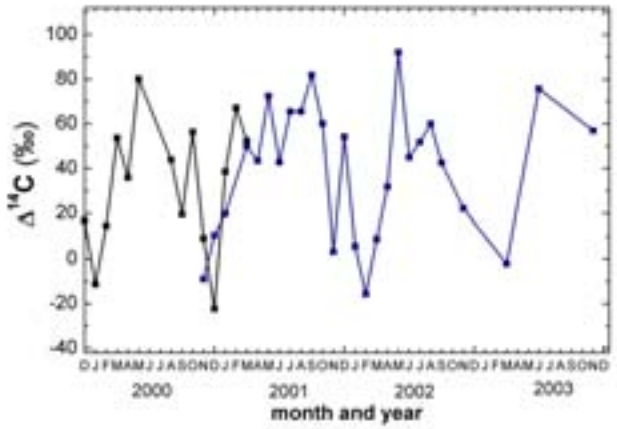

FIG. 15. ^{14}C in the monthly atmospheric CO_2 samples at the Zagreb station for the period 2000–2003.

4. Conclusion

According to the characteristics of isotopic composition of precipitation collected at 6 stations in Croatia we can conclude the following:

(a) Seasonal variations of tritium at maritime stations (mid- and south-Adriatic coast) are less pronounced and the mean yearly activities are lower than those at the continental stations. The difference in tritium activity between the continental precipitation and the maritime ones can be used as a tracer for different origins of precipitation, e.g. relative influence of different air masses can be determined. Additionally, a decrease in tritium activity along the Adriatic coast, from the north (0.83 Bq/L) to the south (0.48 Bq/L) as a consequence of sea-water evaporation effect, is observed.

(b) Stable isotope composition of precipitation (δ^2H and $\delta^{18}O$) for all 6 stations fit well to the GMWL. Slight difference in the slopes of the LMWLs between continental and maritime stations may indicate some evaporation of summer rain events at the coastal area. The obtained LMWL for each station can be used as a basic input data in hydrological investigation in the Adriatic coast area.

(c) Data of stable isotope composition at different stations (with different climate and at different altitude) is used for determination of the temperature gradient and altitude effect (see Table 2). The d-excess is in principal higher for maritime stations than for the continental ones. However, the highest d-excess is observed for the continental station Zavižan (14.4). This station at high altitude (1594 m) and very close to the Adriatic sea (Fig. 1) has extreme conditions of continental climate, but according to the stable isotope composition of precipitation the influence of Mediterranean climate is also present.

(d) The collected data of isotope composition (^3H, δ^2H, $\delta^{18}O$) of monthly (6 stations) and daily (1 station) precipitation during the 3-year period gives database for studing different influences to the isotope composition of precipitation. These data can be applied in studying of air mass movement (circulation pattern), climate variability/change, local and regional hydrological features, etc.

ACKNOWLEDGEMENTS

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REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Statistical Treatment of Data on Environmental Isotopes in Precipitation. Technical Reports Series No. 331, IAEA, Vienna (1992).
[2] INTERNATIONAL ATOMIC ENERGY AGENCY, *Isotope Hydrology Information System. The ISOHIS Database.* Accessible at: http://isohis.iaea.org/. Accessed Feb 23, 2004.
[3] KRAJCAR BRONIĆ, I., HORVATINČIĆ, N., OBELIĆ, B., Two decades of environmental isotope record in Croatia: Reconstruction of the past and prediction of future levels. Radiocarbon **40** (1998) 399–416.
[4] HORVATINČIĆ N., Radiocarbon and tritium measurements in water samples and application of isotopic analyses in hydrology. Fizika **12** (S2) (1980) 201–218.
[5] KRAJCAR BRONIĆ, I., OBELIĆ, B., SRDOČ, D., The simultaneous measurement of tritium activity and the background count rate in a proportional counter by the Povinec method: Three years experience at the Ruđer Bošković Institute. Nuclear Instrum. Meth. in Physics Research **B17** (1986) 498–500.
[6] VREČA, P., KANDUČ, T., ŽIGON, S., TRKOV, Z., Isotopic composition of precipitation in Slovenia. this issue.
[7] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R., Isotopic patterns in modern global precipitation. Geophysical Monograph **78** (1993) 1–36.
[8] SCHOTTERER, U., OLDFIELD, F., FROELICH, K., GNIP – Global Network for Isotopes in Precipitation (1996) 45.

EFFECT OF SYNOPTIC AND CLIMATIC SITUATIONS ON FRACTIONATION OF STABLE ISOTOPES IN RAINWATER OVER EGYPT AND EAST MEDITERRANEAN

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Abstract. Fractionation ratios $\delta^{18}O$, $\delta^{2}H$ of deuterium, and deuterium excess in daily rainfall samples and their corresponding climatic variables have been used by the Egyptian work team in this study. The samples were taken from 1/10/2000 to 29/5/2003. Egypt has shared by more than 160 daily samples in this data set. Besides, due high temperature and dryness of air in the region, seven samples for water vapour have been only collected at Cairo main Analysis Center.

The variation of fractionation ratios has been investigated in different pressure distributions such as inverted V-shaped, blocking and wide spread synoptic situations. In addition, relationship among fractionation ratios and their corresponding climatic elements of simulated vertical-soundings in the Planetary Boundary layer (PBL) above Alexandria has been also investigated.

The main findings of the study have indicated that most coastal Egyptian stations have a quasi similar fingerprint to those of Mediterranean basin for stable isotopes in rainwater. In addition, wind direction plays an important role in change the values of fractionation ratios and deuterium excess such that high values of deuterium excess are attained in low wind persistence. Also, it was found that the characteristics of a thermal field that exist beneath rainy clouds play an important role in fractionation processes such that warm boundary layer makes rainfall samples be characterized by small positive values of deuterium excess, which become negative at PBL of mean temperature 23^{o}C. In case of blocking situation that lasts for many days, fractionation ratios of $\delta^{18}O$ and $\delta^{2}H$ as well deuterium excess tends to decrease gradually by time. On the other hand, in case of wide spread instability over Mediterranean countries, deuterium excess is higher at western stations than at eastern ones in Mediterranean basin.

1. Introduction

Meteorological factors play an important role in fractionation processes of stables isotopes of oxygen-18 and deuterium in rainwater. The associated pressure systems to rainfall events determine the sources and sinks of air masses that define weather condition at a specified area. Because the climate of Egypt is affected by the climate of north coast of Africa and semi arid zone in the north of the Sahara, we will depict the climate of north coast of Africa and Egypt as well as the main characteristics of pressure system in each season. In additions, the variability of fractionation ratios and associated meteorological elements will also be investigated.

1.1. Climate and orographic features of the area

The general features of climate systems that prevail in the rainy seasons over Egypt are similar to those prevail in the Middle East and North Africa. However, this climate could be classified into two main zones; the coastal zone, which is quasi similar to those of the Mediterranean climate and the semi arid zone, which includes the north part of the Sahara.

The main orographic features of African North Coast are including the Atlas mountain range of a peak that rises above 4000 m. in the northwest part and the Red sea mountains (2500 m) to the east. The vast area between the far west and the far east of the African Coast is broken by a few plateaus of which the important ones are Ahaggar and Tibesti. In the western desert of Egypt, Qattara Depression is situated. This land depression is the deepest point in Africa, where the depth is much deep as 132 m below the mean sea level.

In cool season, the eastward moving cyclones crossing Europe bring outbreaks of cold northwest air. This air is faced by the warmer air to the south. When humidity exists, vertical instability arises. Then

active depressions are formed and relatively heavy rainfall and frequent gales on the coastal areas are experienced. In most cases, the precipitation is associated with northerly and westerly winds. Some rain is related to the northeast flow over the Mediterranean Sea in late winter especially in Tunisia. However, the rainiest region of the north coast of Africa is extending from near Algiers to the west of Bizerta in Tunisia, where annual mean is amounted to 800 mm.

During the spring, this zone is also affected by traveling troughs over Europe. This period could be called the windy time of the year on the northern coast. But these moving troughs, by this time, give little rainfall compared to that of the winter time. This transitional season is characterized by the Khamsin hot depressions, which are normally associated with sandstorms over most parts of the north coast of Africa, including Egypt. On other hand, during the autumn time, the situation is similar to that of spring, but the intensity of thermal depressions and wind speed are dramatically decreased.

In summer, the Azores high pressure shifts to the west and, in the same time, the Indian Monsoon thermal-low extends to the west. As a result, of this situation, north coast of Africa is covered by northeast trade winds and stable weather dominates, especially over Egypt.

Because local characteristics of climate have a large effect on the fractionation processes of stable isotopes in rainwater, we will also give the outstanding features of pressure distribution, associated weather phenomena, and prevailing air masses over the southern coast of Mediterranean Sea and Egypt in the following section.

1.2. Outstanding features of pressure systems in rainy season

The whole area, including Egypt, is situated in the subtropical zone. The zone is semi arid in most places, so there is no source of water vapour to make instability arise inspite of the existence of warm air in the boundary layer. The area could be regarded as a sink of the water vapour that must be brought by the air flow from the boundaries. To attain instable weather conditions in the zone, water vapour, topographic effect and frontal activity would be required. To know the different air masses that invade the area, we will display the important features of pressure distribution that play the major role in the weather situation in each season.

1.2.1. Outstanding pressure features in winter season

There are four main features in the winter season. They are explained briefly in the following items.

(a) The Sahara high pressure

It is the extension of the Azores anticyclone that belongs to the so called subtropical high belt around the globe at about 30^{o} N. This high is associated with a major subsidence, which leads to a local dynamical heating of the air and drying it up. This situation leads to absolute stability in most places.

(b) Traveling depressions over Mediterranean

Instability arises only when a moving low pressure system invades the Mediterranean. In front of these depressions, the surface wind are south to southwesterly. These lows cause rain, showers, and sometimes thunderstorms along the African coast. But in some cases, when a low reaches Egypt the polar air associated with it is modified and becomes dry. When the low becomes already in East Mediterranean, the orography around east Mediterranean and the warm air flow from the south reinforce the depression and instability arises again.

(c) The Balkan High

It belongs to the well established very cold anticyclone over central Asia. When this high extends to the west, extreme cold air invades east Mediterranean. A worse weather is attained

when upper trough is associated. This situation is normally associated with a barometric minimum at Cyprus Island in East Mediterranean.

(d) The formation of Cyprus Low

When this low is formed, successive cold fronts are remarkable on the weather charts. According to El-Fandy [1] and our daily experience at Cairo Main Analysis Center, the associated weather is generally analogous to squall phenomena rather than to the development of a depression. However, there are two main currents, which accompanied this low. The first is the relatively warm southeast currents over Iraq, which takes the form of the orography to the east and north of Iraq. The second current is the polar current from Balkan in the rear of the low (Fig. 1). Besides to these two currents, an upper trough is also necessary to make the low persist.

Due to the polar air mass in the rear of the low, successive cold fronts travel from north to south over the Mediterranean and then from west to east over land. Such cold fronts lead to the coldest weather in the Middle East area. As a result of blocking situation, the low may persist for a week.

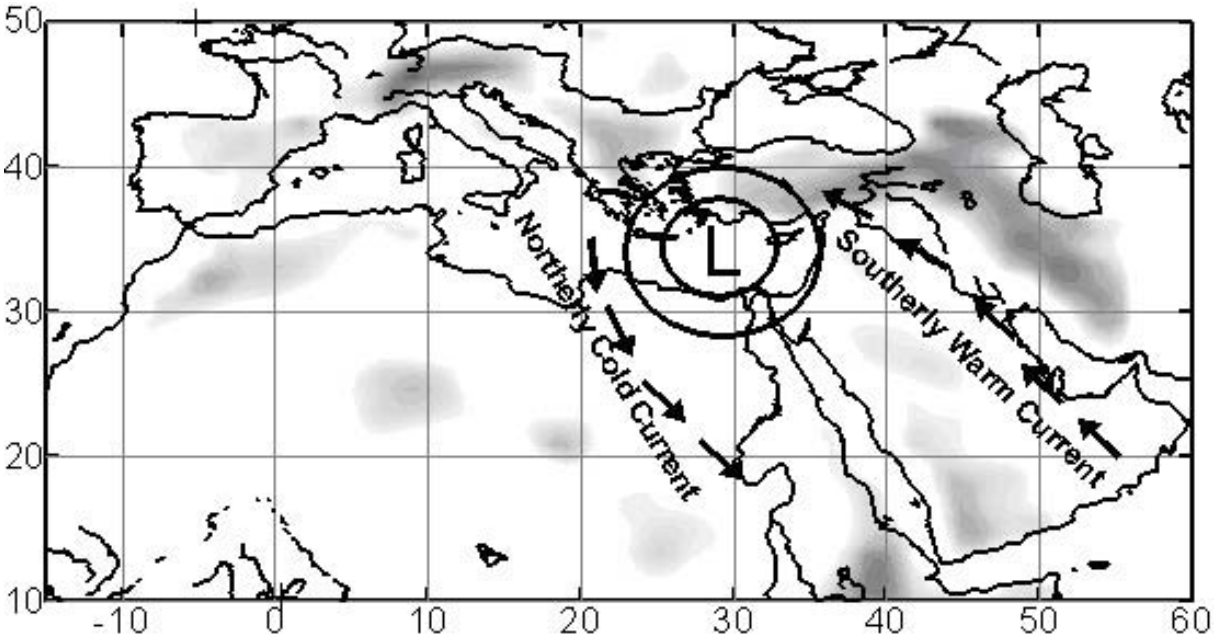

FIG. 1. Warm and cold currents associating the formation of Cyprus depression, which is reinforced by terrain feature in eastern and northern parts of east Mediterranean.

1.2.2. Outstanding features in spring season

The whole pressure system begins to move northward associated with decreasing of the intensity of the Sahara high pressure. A new inverted trough is developed as an extension to the Sudan Monsoon thermal low. This inverted trough may extend to the south of Balkan. The air mass, which is dominant in this period, is the tropical continental air mass from easterly and southerly regions. However, the most important weather phenomena over north coast of Africa, including Egypt, are the Khamsin depressions which will be explained in the following item.

(a) Khamsin depressions

Khamsin depressions are the most frequent phenomena in spring season. They are normally associated with strong southerly winds that are very hot, very dry and dusty. When a Khamsin

depression attacks Egypt, dust storms or sandstorms occur. The wind associated with Khamsin depression takes different names in different countries of North Africa. For example, it is called Chili in Tunisia, and Gibli in Libya. In most cases after passing Khamsin depression, small amounts of rainfall are experienced. The small amounts of associated rainfall may be due to the evaporation of rainfall drops in the vicinity of warm boundary layer in the area. Such evaporation and isotopic exchange with the atmospheric moisture below the base of rainy cloud affects fractionation ratios of stable isotopes in rainwater [2], [3], [4], [5]. However, according climatic studies of [6], [7], [8], [9], Khamsin Depressions can be classified into two main types, which will be explained briefly in the following sections.

(b) Winter-like depressions

These depressions are similar to those attack south Mediterranean. They may be independent of well developed secondaries, coming from the Atlantic or forming in the Mediterranean. The most favorable part is that in which the depressions are formed in Gulf of Genoa on one of the lagging cold fronts, or when strong northeast winds blow around the southern end of the Alps to the Gulf of Lyons. Scherhag [10] has attributed the formation of such depression to topographic nature of this part of Mediterranean basin. However, this type of Khamsin depressions is formed in late winter and early spring.

(c) Desert depressions

They form in the lee side of Atlas Mountains or over the desert of Libya. These depressions are mostly fast and vigorous. However, rainfall is rarely associated with this type of depressions. Sometimes, this type continues moving for seven days along its track from the point of formation at the lee side of Atlas Mountains up to north Iraq (Fig. 2). However, the depression during its motion at the surface is associated with an upper air cold trough, which is bounded from south by the subtropical jet stream in upper layer of the atmosphere.

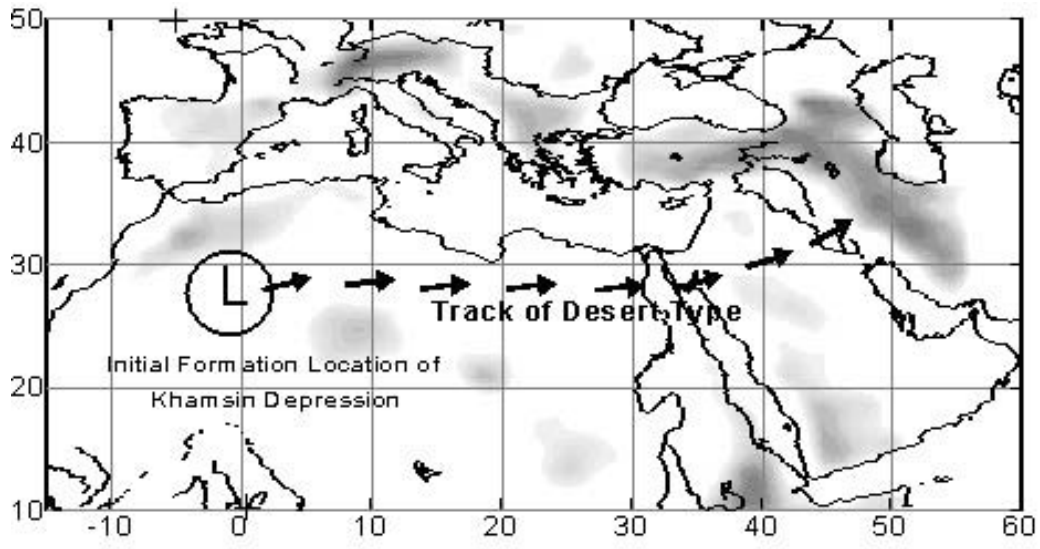

FIG. 2. Mean Track of Khamsin depressions that are frequently formed at the lee side of Atlas Mountains in spring.

1.2.3. Outstanding features in autumn season

The pressure distribution is nearly similar to that of spring. The similarity of pressure distribution in autumn and spring leads to the formation of Khamsin-like depressions in autumn as those in spring.

But, they are weak and slower in their eastward motion than those of the spring season. Also, the humidity in this season is higher than that of spring, which leads to higher frequency of rain and thunder storm, a fact that is especially true in November [11]. Flash floods and thunderstorms may happen over the eastern parts of Egypt especially in the months of October and November. This happens when a cooled upper air trough are superimposed over an inverted surface trough, which is associated with southerly surface winds along the Red Sea.

2. Seasonal variations of stable isotopes and associated meteorological elements at Alexandria

Before we study different fractionation processes associating different synoptic situations, it is logic to give an idea about seasonal variations of deuterium fractionation ratio δ^2H, oxygen fractionation ratio $\delta^{18}O$, deuterium excess (d), and some meteorological elements. To do so, we have used the Alexandria data available in WMO/IAEA GNIP. Some of the analysis of recent rainwater monthly-samples have been supplied by IAEA.

2.1. Monthly variation of δ^2H, $\delta^{18}O$, and d-excess

Figure 3 depicts monthly variations of deuterium fractionation ratio δ^2H, oxygen fractionation ratio $\delta^{18}O$, and deuterium excess, d at Alexandria. From the figure, it can be seen that δ^2H, $\delta^{18}O$, and d are generally increasing gradually in spring and decreasing gradually from early autumn to early winter. In the same time, there are two minima in March and September during these two periods respectively, especially for δ^2H. Also, the variation in $\delta^{18}O$ is generally in parallel with the variation of monthly temperature March.

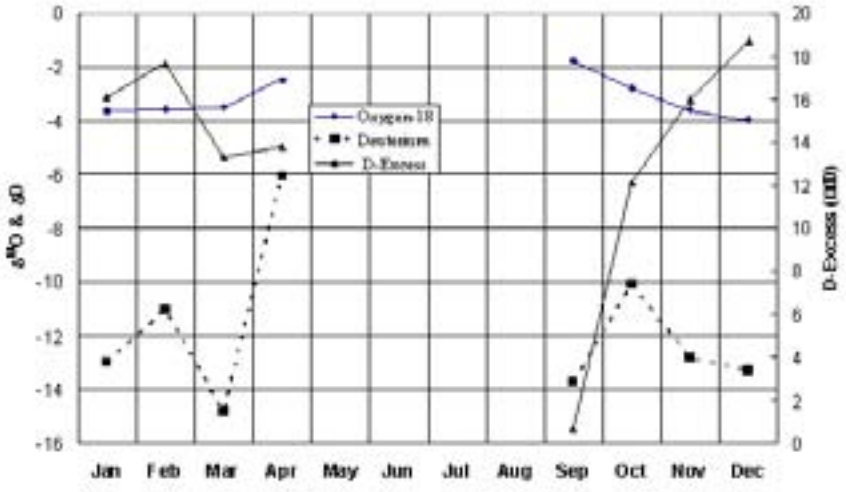

FIG. 3. Monthly variation of $\delta^{18}O$, δ^2H and d-excess deduced from daily samples in the period from 3/12/2000 to 25/3/2003 at Alexandria.

In spite of monotonic increasing or decreasing of $\delta^{18}O$ in the two mentioned periods respectively, the two absolute minima of δ^2H and d-excess during the two periods in March and September may refer to other dynamical effects in cloud formation in addition to temperature effect in spring and autumn. However, the monthly values of $\delta^{18}O$ ranges from -4‰ to -1.8‰, while δ^2H ranges from -15‰ to -6.03‰. On other hand, deuterium excess ranges from 0.7‰ to 19‰ with two maxima in February and December.

2.2. Monthly variation of deuterium excess with pressure and wind persistence

Figure (4) depicts monthly variation of d-excess along with surface pressure л and wind persistence P. However, P is the ratio between the magnitude of mean resultant of wind-vector and mean wind-speed. The values of P may take any value in the range: $0 \leq P \leq 1$ and is determined from relation (1), which takes the form:

$$P = \frac{\left| \sum_{j=1}^{n} \overrightarrow{V_j} \right|}{\sum_{j=1}^{n} S_j} \qquad (1)$$

Where $\overrightarrow{V}_j$ wind vector at observation j, Sj is wind speed at observation j, and n the total number of observations in a specified period. The small values of P means that wind direction is likely to be variable and is likely to be steady in case of high values of P in the specified climatic period. However, when P equals 0, the wind is equally comes from all directions and when P equals 1, the wind blows from one direction all the time.

It can be seen that the monthly values of d-excess increase as the monthly values of surface pressure л increase. This is due to the eastward extension of the Azores high pressure in winter and westward extension of the Indian Monsoon thermal low in summer.

The values of P are higher in summer than in winter and in transitional seasons. That is because the direction of northeast trade wind is steady in summer, while major wind in winter and in transitional seasons is interrupted by southwest winds, which associate moving depressions frequently. As a result, the correlation coefficients between d-excess and P and between d-excess and л are -0.949 and 0.803 respectively (Table 1). This may give an explanation of high values of d-excess in winter and in transitional seasons, which are associated with high values of surface pressure л and lower values of wind persistence P.

Table 1. Correlation Matrix among Monthly d-excess, Surface Pressure, and Wind persistence P at Alexandria

Variables	d-excess	Pressure л	Persistence P
d-excess	1	+ 0.803	- 0.949
Pressure л	-	1	- 0.914
Persistence P	-	-	1

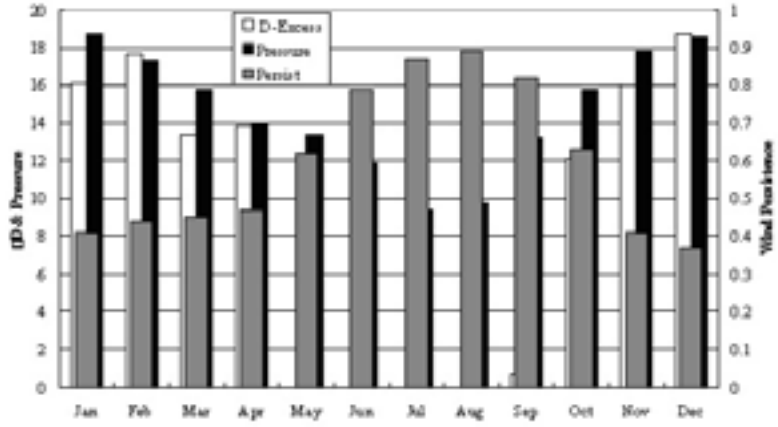

FIG. 4. Monthly variations of d- excess, surface pressure π, and wind persistence P deduced from daily data in the period from 3/12/2000 to 25/3/2003 at Alexandria site.

3. Variation of fractionations ratios in daily rainfall events

In this section, we will depict daily variations of fractionation ratios δ^2H, $\delta^{18}O$ of stable isotopes of deuterium and oxygen at Alexandria as well as variation of their associated d-excess with meteorological elements. These daily values of δ^2H and $\delta^{18}O$ are obtained from analyzing 107 daily rainfall samples in the period from 3/12/2000 to 25/3/2003.

The analysis of rainwater samples has been made by the Isotope Hydrology Section of the IAEA in Vienna and by other laboratory of some European countries. More than 20 stations in different Mediterranean countries have participated in the experiment during the period from 1/10/2000 to 29/5/2003. The results of the analysis in the mentioned period were collected at IAEA and have been sent to all countries that participated in the experiment. Over 600 daily rainfall samples and over 300 water vapor samples have been analyzed. Figure 5 depicts variations of means of d-excess latitude and longitude.

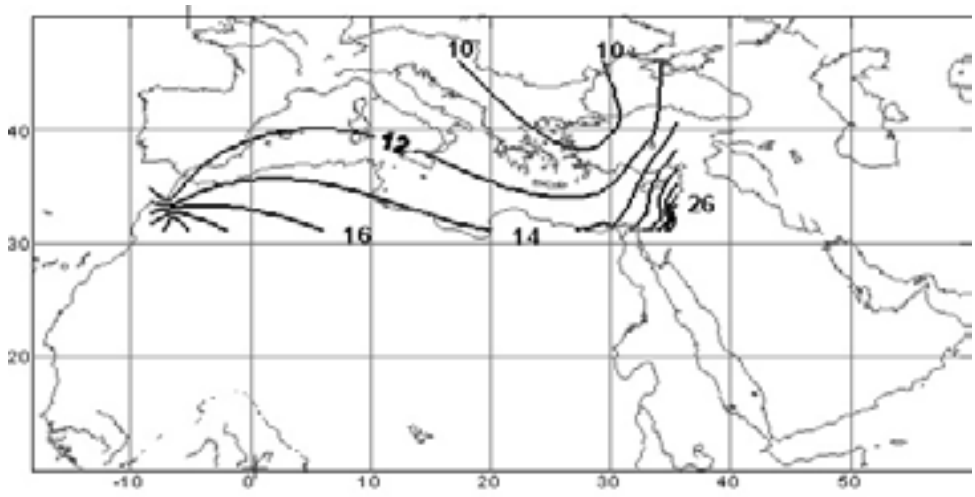

FIG. 5. Mean daily distribution of d- excess deduced from daily samples at 15 stations in the period from 1/10/2000 to 29/5/2003.

From the figure, it can be seen that there is slight gradual decrease in the means from south to north. Also, d-excess attains high values at coastal areas in east Mediterranean and at northwest of Morocco.

This type of variation may be referred to the effect of topographic as well as to the interaction between tropical air mass and that of middle latitudes at the north coast of Africa. To study temporal variation, we will study variations in the whole period as well as variations associated with some synoptic situations, especially over Egypt.

3.1. Daily variations of δ^2H, and $\delta^{18}O$ in the whole period at Alexandria

The daily results of this analysis in the whole period at Alexandria are depicted in Figure 6. From the figure, it can be seen that the values of δ^2H and $\delta^{18}O$ are varying in parallel manner, since a significant correlation coefficient of 0.953 has been found between them. Also, deep depletions are observed in early winter, while small and even positive ones are observed in late winter, spring and autumn. For example, in rainwater event on 10/2/2002, the values of $\delta^{18}O$ and δ^2H are 2.17‰ and 33.25‰ respectively. This may be due to the effect of tropical water vapour that has caused this rainfall event.

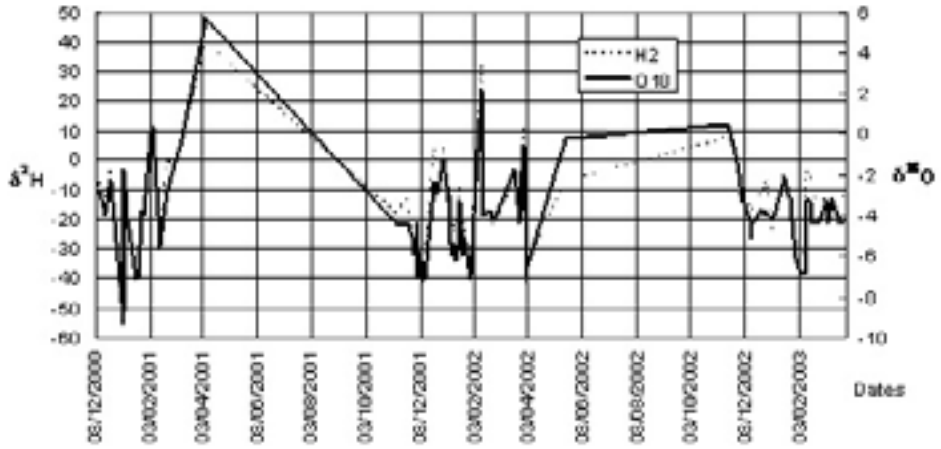

FIG. 6. Variation of δ^2H and $\delta^{18}O$ in daily rainfall samples in the period from 3/12/2000 to 25/3/2003 at Alexandria.

On the other hand, deep depletions took place in January, where values of δ^2H and $\delta^{18}O$ reached -9.32‰ and -54.8‰ on 2/1/2001 respectively. This may refer to the temperature effect, where the absolute minimum of temperature at Alexandria takes place normally in January. The meteoric lines at Alexandria and Sidi Barrani, by using the daily samples, are shown in Figure 7. From the figure, one can see that the relationships between δ^2H and $\delta^{18}O$ are linear and take the forms.

$$\delta\ ^2H = 6.56\ \delta\ ^{18}O + 11.14 \quad (2)$$

$$\delta\ ^2H = 5.83\ \delta\ ^{18}O + 10.10 \quad (3)$$

With R^2 equals 0.90 at Alexandria, which is significant at 0.01 probability level and R^2=.77 at Sidi Barrani. These meteoric lines in equations (2) and (3) are quasi-parallel to meteoric line of monthly values at Alexandria. In the same time, they have been different in the intercepts when compared with intercept of monthly meteoric line. The intercept based on monthly values was found to be 7.9‰ [12]. These differences may refer to changes of air mass characteristic in a given month, since many different air masses may cause multiple rainfall events in the same month. Also, local features of station may have minor effects on the inclination of meteoric line and its corresponding intercept.

Daily variations of d-excess are depicted in figure 8. High values are observed in winter and small ones in late spring or early autumn. For example, in rainfall event on 6/1/2002 d-excess culminated to 27.29‰ and on 9/3/2001 it was lowered to 5.01‰. In late spring, d-excess dropped to -5.42‰ on 5/4/2002 especially at Ras-Benas.

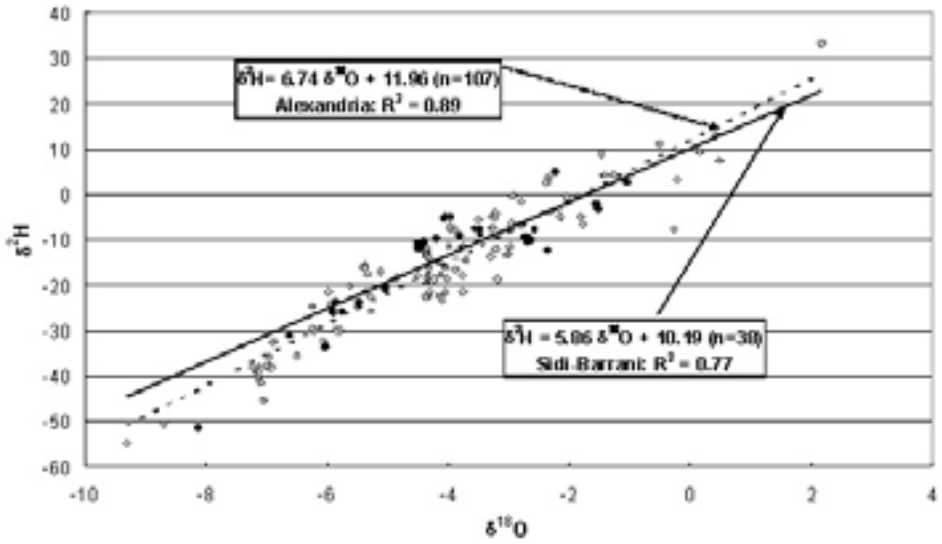

FIG. 7. Meteoric Line deduced from 107 daily rainfall samples at Alexandria and 38 daily samples at Sidi-Barrani in the period from 3/12/2000 to 25/3/2003.

As in the monthly variations, the warming up of boundary layer leads to cease the values of d-excess, where the values of δ^2H rise and those of $\delta^{18}O$ are become near to zero. The warming up of the boundary layer by that time modifies the falling rainwater by evaporating rainfall drops before reaching the rain gauge at the earth's surface.

In addition to compare monthly variations with daily variations, type and trend of variations among fractionations ratios of $\delta^{18}O$, δ^2H, d-excess and means of meteorological elements at the hours of daily rainfall events have been made. For this purpose, correlation matrix among mean surface temperature T, relative humidity H%, rainfall amounts R, fractionation ratio of O-18, fractionation ratio of H-2, and d-excess at rainfall hours for 71 daily rainfall events at Alexandria has been computed. If the rainfall event in a day lasted for n hours, we would regard the means of surface temperature and humidity during these n hours as the corresponding meteorological elements to the given daily rainfall sample. The resulted correlation matrix is shown in Table 2.

Table 2. Correlation coefficients among mean surface temperature T, relative humidity H%, rainfall amounts R, fractionation ratio of $\delta^{18}O$, fractionation ratio of $\delta^{2}H$, and d-excess at rainfall hours for 71 daily rainfall events at Alexandria

		T	H%	R	$\delta^{18}O$	$\delta^{2}H$	d-excess
T	Pearson Correlation	1	**-0.495****	-0.084	**0.443****	**0.332****	**-0.531****
	Sig. (2-tailed)		0	0.484	0	0.005	0
	No. of observations	71	71	71	71	71	71
H%	Pearson Correlation	**-0.495****	1	0.194	**-0.347****	**-0.3***	**0.298***
	Sig. (2-tailed)	0		0.104	0.003	0.011	0.011
	No. of observations	71	71	71	71	71	71
R	Pearson Correlation	-0.084	0.194	1	**-0.263***	-0.207	**0.287***
	Sig. (2-tailed)	0.484	0.104		0.027	0.083	0.015
	No. of observations	71	71	71	71	71	71
$\delta^{18}O$	Pearson Correlation	**0.443****	**-0.347****	**-0.263***	1	**0.961****	**-0.579****
	Sig. (2-tailed)	0	0.003	0.027		0	0
	No. of observations	71	71	71	71	71	71
$\delta^{2}H$	Pearson Correlation	**0.332****	**-0.3***	-0.207	**0.961****	1	**-0.329***
	Sig. (2-tailed)	0.005	0.011	0.083	0		0.005
	No. of observations	71	71	71	71	71	71
ΔD	Pearson Correlation	**-0.531****	**0.298***	**0.287***	**-0.579****	**-0.329****	1
	Sig. (2-tailed)	0	0.011	0.015	0	0.005	
	No. of observations	71	71	71	71	71	71

* Correlation is significant at 0.015 level (2-tailed)

** Correlation is significant at 0.01 level (2-tailed)

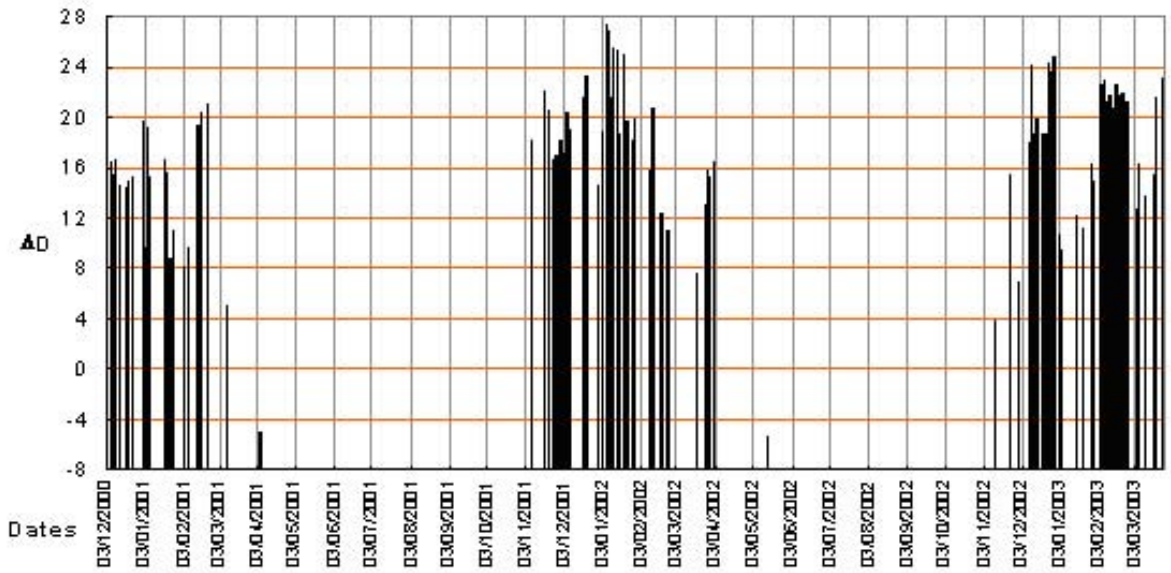

FIG. 8. Variation of d-excess deduced from 107 daily rainfall samples in the period from 3/12/2000 to 25/3/2003 at Alexandria.

From the table, it can be seen that negative significant correlation coefficient at the 0.01 level is found between surface temperature and humidity or deuterium excess. Contrary, a positive significant correlation coefficient at 0.01 level is found between temperature and $\delta^{18}O$ or $\delta^{2}H$. On the other, the correlations coefficients between relative humidity and $\delta^{18}O$ or $\delta^{2}H$ are negative and significant at 0.01 level, while the correlation coefficient with d-excess is positive and significant at 0.05 level. Also, the values of correlation coefficients among d-excess, $\delta^{18}O$, and $\delta^{2}H$ indicate that the change in deuterium excess is more sensitive to the change in $\delta^{18}O$ than to the change in $\delta^{2}H$. Theoretically, the range of d-excess can be derived from equations (4) and (5) that describe the relationship of d-excess with $\delta^{18}O$ and $\delta^{2}H$ and the equation of local meteoric line at Alexandria.

$$\Delta D = \delta^{2}H - 8 * \delta^{18}O \qquad (4)$$

By substituting for $\delta^{2}H$ into (4) from the local meteoric line that has been deduced from daily sample in equation (2), equation (4) takes the form:

$$\Delta D = 6.56\,\delta^{18}O + 11.14 - 8 * \delta^{18}O \Rightarrow$$
$$\Delta D = 11.14 - 1.44\,\delta^{18}O \qquad (5)$$

As the absolute minimum of $\delta^{18}O$ was -9.32‰ on 2/1/2001 and the absolute maximum was 2.17‰ on 10/2/2002 at Alexandria, the mean of least upper bound and the mean of highest lower bound of d-excess by using equation (5) may be determined from inequality (6).

$$24.56 \geq \Delta D \geq 8.02 \qquad (6)$$

This range agrees with the computed monthly values of d-excess, where high values were observed in winter and small ones were observed in spring and autumn. Also, formula (5) can be used to compute d-excess either at Alexandria or at Sidi-Barrani.

From the above results, one can conclude that changes in deuterium excess at the coastal stations of Alexandria and Sidi-Barrani are sensitive not only to the changes in temperature but also to the changes in humidity and $\delta^{18}O$.

3.2. Case studies in different synoptic situations

To distinguish the effect of pressure distribution in daily rainfall events in the period from 3/12/2000 to 25/3/2003, three synoptic situations will be selected. The synoptic situations have been selected such that they could represent different history of air masses that bring water vapour from different sources at the boundaries of the area in different seasons of the year. These three synoptic situations represent rainfall events during inverted V-shape situation in late winter from 10/2/2002 to 12/2/2002, during blocking situation from 6/1/2002 to 10/1/2002 and during wide spread instability on 30/11/2002. Besides, we will explain an abnormal event during Khamsin situation, which took place on 5/4/2001 at Ras-Benas.

3.2.1. Variation during an inverted V-Shape Situation

During the successive three days of this synoptic situation in the period from 10/2/2002 to 12/2/2002, the rainfall amounts have decreased gradually from 24.4 mm on the first day to 6.3 mm on the third day. The general distribution of geopotential heights at 1000 hPa level is depicted in Figure 9. It can be seen that there is an arm of equatorial trough extending along the Red Sea in a form of an inverted V-shape. The low pressure in the area of this inverted V-shape brings warm and humid air mass in lower layers from the Indian Ocean and Red Sea to the convergence zone over East Mediterranean and Egypt. Also, the existence of cold upper air trough in the middle troposphere at 500 hPa level (Fig. 10) caused severe instability at the first day on10/2/2002.

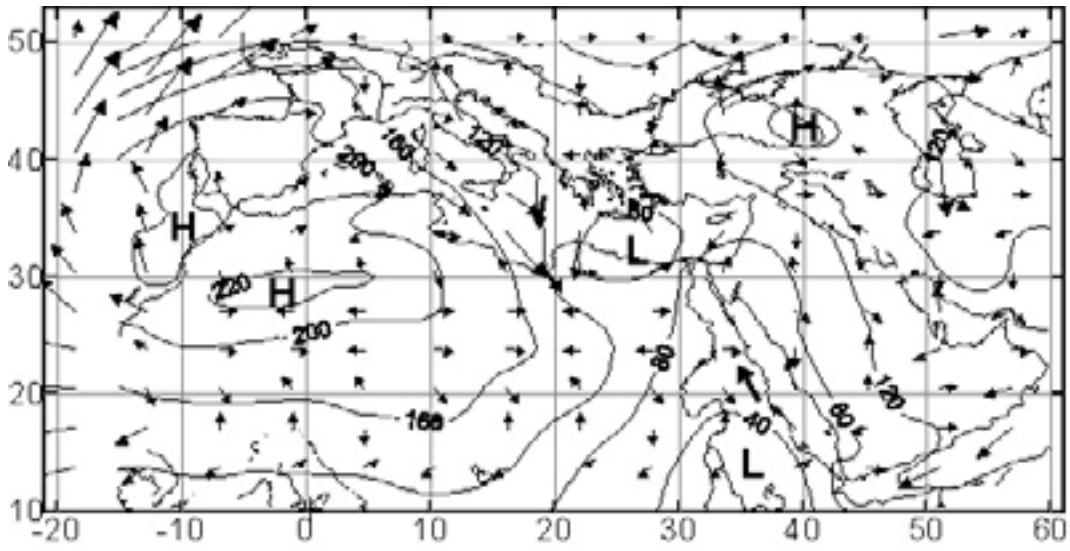

FIG. 9. Contour lines and field of wind vector at 1000 hPa associated with Inverted V-shape trough at surface layers and rainfall event on 10/2/2002 at Alexandria.

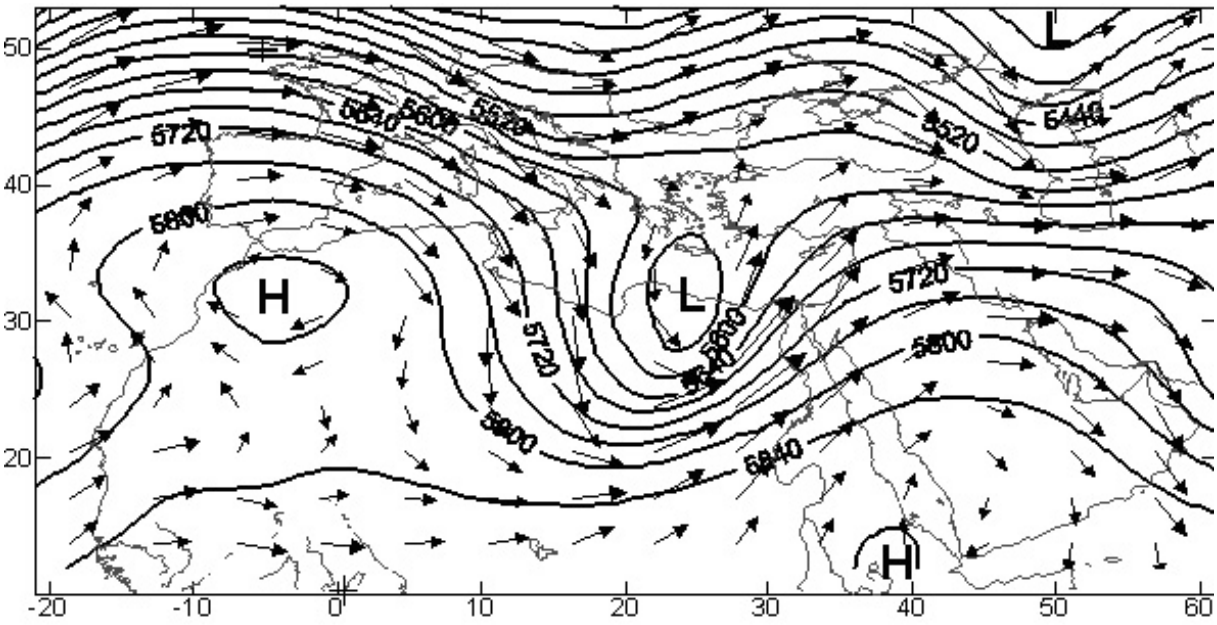

FIG. 10. Contour lines and field of wind vector at 500 hPa associated with Inverted V-shape trough at surface layers and rainfall event on 10/2/2002 at Alexandria.

The backward trajectories BA, CA, and DA on three levels at Alexandria are depicted in Figure 11. The route BA indicates the backward trajectory at 1000 hPa level, which may represent the trajectory at surface in the period from 8/2/2002 to 12/2/2002. The route CA at the 850 hPa level in the same period may represent the trajectory near the top of Planetary Boundary Layer (PBL). The route DA may represent trajectory at the base of the free atmosphere.

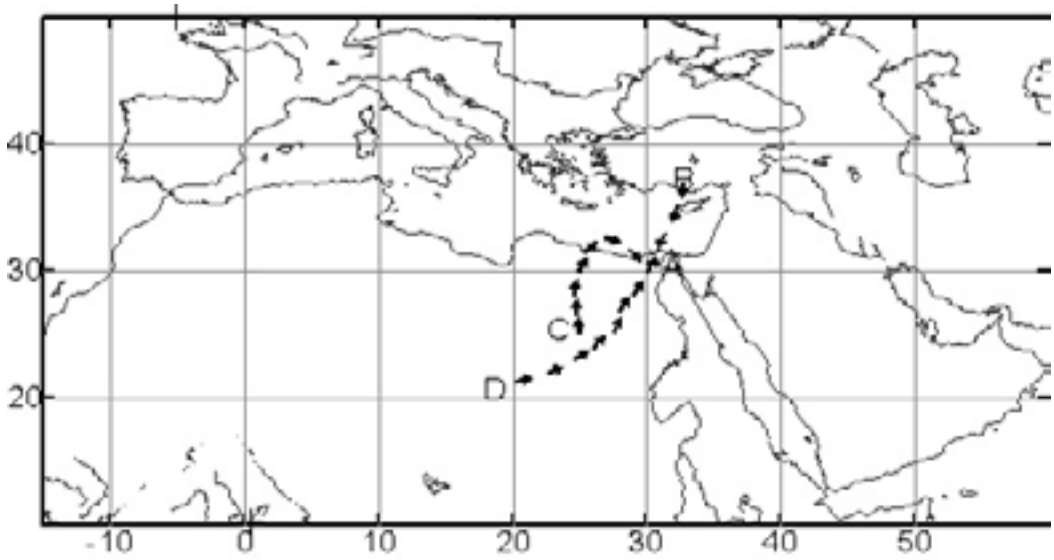

FIG. 11. Backward trajectory during foregoing 72 hours from Alexandria at 1200 UT on 10/2/2002 at 1000, 850, and 700 hPa levels represented by routes BA, CA and DA on the figure respectively.

From Figure 11, it can be seen that the route BA at 1000 hPa level leads to bring humid-air from east Mediterranean area. In the same time, the surface currents bring humid-air from subtropical region along the Red Sea, which is mainly originated from Indian Ocean. Also, the routes of air parcel CA at 850 hPa and roué DA at 700 hPa lead to bring hot air mass from subtropical regions. In addition, the domes of cold air from middle atmosphere are mixed with these types of different air masses in the

PBL. Such situation causes severe instability and leads of falling of 24.4 mm of rainwater in one day at Alexandria. Also, it gave an explanation of the abnormal positive fractionation ratios of 2.17‰ and 33.25‰, which were found for $\delta^{18}O$ and $\delta^{2}H$ on 10/2/2002 respectively.

From the foregoing results, one can conclude that abnormal high positive values of fractionation ratios of $\delta^{18}O$ and $\delta^{2}H$ in rainwater over Egypt in late winter may be as result of evaporation of falling rainfall-drops during its course in the PBL. This evaporation increases the ratios of $\delta^{18}O$ and $\delta^{2}H$ dramatically, especially when the rainy cloud is a result of combing domes of cold air at upper layer with tropical air mass in the PBL that is originated from the Red Sea and Indian Ocean.

3.2.2. Rainfall events during a blocking situation

The blocking synoptic situation that has lasted for five days from 6/1/2002 to 10/1/2002 leaded to high values of d-excess in most days with absolute maximum of 27.29‰ on the first day of blocking followed by gradual decrease and ends by isotopic inverted V-shaped trend with its minimum value on 9/1/2002 where it ceased to 21.61‰ (Fig. 12). These relatively high values of deuterium excess may be referred to the existence of severe instability in air column in the vicinity of deep depression in east Mediterranean by that time at 500 hPa level (Fig. 13). In addition, high wind stress and shear near sea surface leads to lift sea spray upward and increase its concentration in lower parts of the PBL of the atmosphere. These high values of deuterium excess and isotopic trend are normally experienced in east and west Mediterranean in winter [13], [14]. Also, high values of Deuterium excess were found in daily water vapor samples from air aloft Mediterranean Sea surface in January [15].

The fields of wind vector at 500 hPa (Fig. 13) and at 1000 hPa (Fig. 14) indicate clearly that the associated air mass is of European source which, is remarked in such blocking situation. Form the above; one can conclude that blocking situations in winter are characterized by high deuterium excess associated with a V-shape trend and non significant changes in $\delta^{18}O$. This may due to low temperature associated with severe instability that mixes sea-spray, which is lifted to higher layers by wind shear and stress, with falling rainfall before reaching the ground especially near coastal stations.

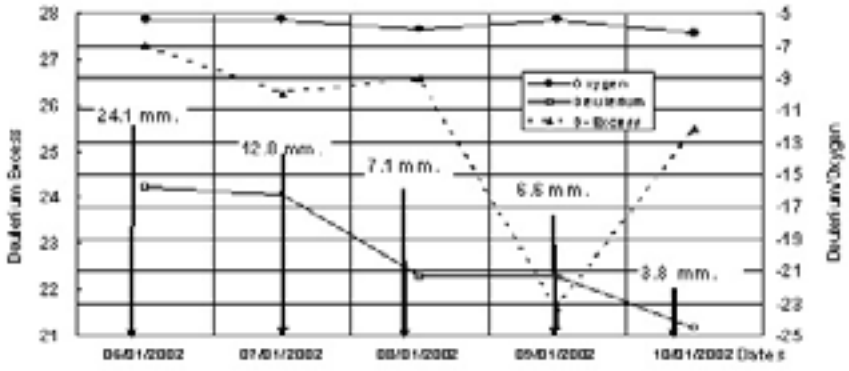

FIG. 12. Variation of $\delta^{18}O$, $\delta^{2}H$ and d-excess during blocking situation in the period from 6 to 10/1/2002 at Alexandria with daily rainfall amounts written on the upper ends of vertical arrows.

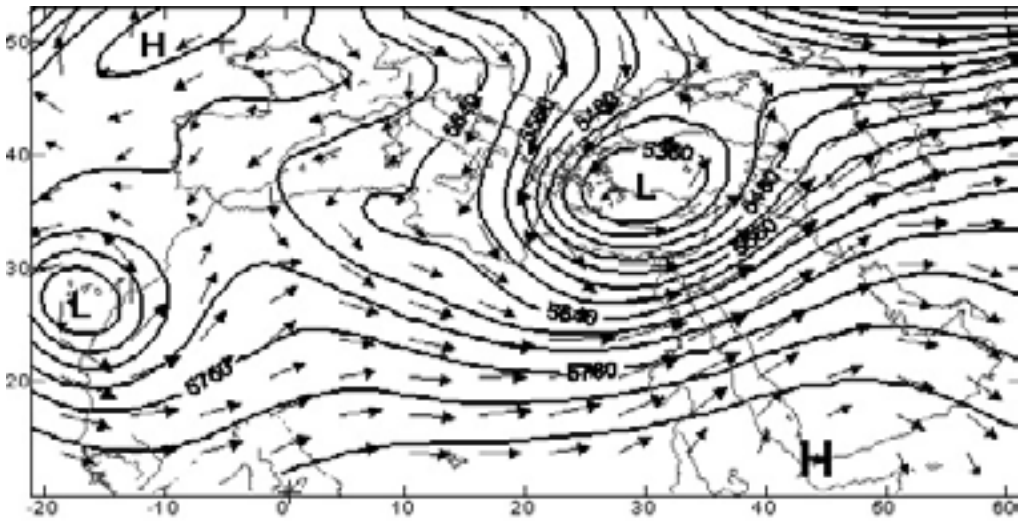

FIG. 13. Contour lines and field of wind vector at 500 hPa level on 6/1/2002 during the blocking situation lasting for successive days in the period from 6 to 10/1/2002 associated with 24.1 mm of rainfall and d- excess value of 27.29‰ at Alexandria.

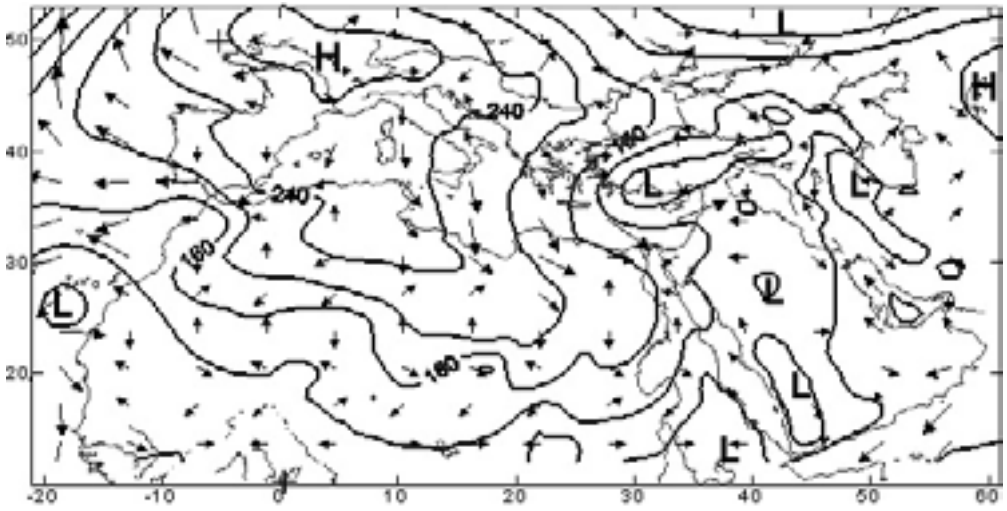

FIG. 14. Contour lines and field of wind vector at 1000 hPa level on 6/1/2002 during the blocking situation lasting for successive days in the period from 6 to 10/1/2002 associated with 24.1 mm of rainfall and d-excess value of 27.29‰ at Alexandria.

3.2.3. Wide spread instability synoptic situation in autumn

Synoptic situation sometimes leads to unstable weather condition on west and east Mediterranean at the same time. Such situation occurred on 30/11/2002. This synoptic situation can be seen in the two maps of Fig. 15, which represent levels 500 hPa (15-a) and 700 hPa (15-b). On the same day, rainfall took place at Alexandria in Egypt and at Alger in Algeria and at other different stations in the Mediterranean basin.

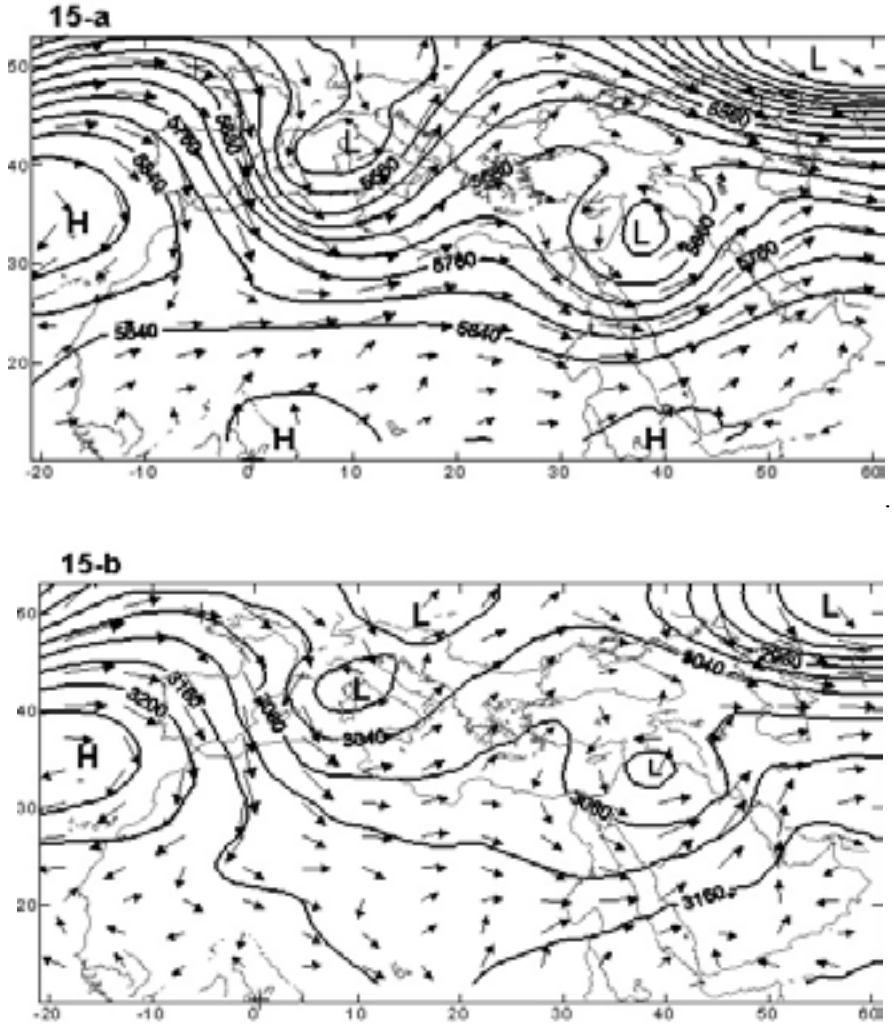

FIG. 15. Contour lines and vector wind fields at 500 hPa (15-a) and 700 hPa (15-b Levels on 30/11/2002 where instability occurred simultaneously in east and west Mediterranean Basin associated with 8.7 mm of rainfall and d-excess of 6.96‰ at Alexandria (29.95^o E, 31.18^o N) that coincide with 13.9 mm of rainfall and ratio of 16.9‰ for deuterium excess at Alger (3.1^o E, 36.77^o N).

These two stations are apart from each other by about 26 degrees of longitudes. From the two maps in Figure 15, one can see that most parts of Mediterranean basin were affected by the same synoptic pattern on the same date. It is clear that the air mass that leads to develop rainfall events at different sites of the basin was originally from the same source, which was the Atlantic Ocean. The big difference between value of deuterium excess at Alexandria (6.96‰) and that at Alger (16.9‰) may refer to the successive changes in synoptic history of the precipitating air masses associated with the route of weather system from west to east Mediterranean. Such synoptic situation of the precipitating air masses was found to behave as if it were a fingerprint of the predominant factor, which controls the isotopic composition in precipitation [16], [17], [18].

3.2.4. The effect of spring situation on fractionation at Ras-Benas station

As stated in the introduction of this work, warming up of boundary layer in spring season may lead sometimes to formation of Khamsin depressions over north coast of Africa. After passing one of these thermal depressions, rainfall occurs with relatively warm boundary layer in the lower layers beneath cloud base. Evaporation from the falling rain-drops changes the isotopic fractionation ratios of oxygen and deuterium and in turn d-excess. The synoptic situation that took place on 5/4/2001 represents rainfall event that is similar to Khamsin condition. The synoptic situation at 1000 hPa and 700 hPa levels are depicted in Figures 16 and 17 respectively. On that day, there was only 12.7 mm of rainfall

over Ras-Benas. The associated values of fractionation ratios of $\delta^{18}O$ and $\delta^{2}H$ were found to be 5.66‰ and 40.2‰ respectively. For this reason, the estimated d-excess equals -5.08‰. These abnormal values may be explained from the distribution of thermal and wind field at 700 hPa level as shown in figures 17. At 700 hPa level, which is situated directly above the top of boundary layer of the atmosphere; the thermal field is quasi barotropic (the isotherms are quasi parallel to the contour lines and wind vectors at the level). This means that the advected cold air has not yet reached the ground surface and the boundary layer has been still warm during rainfall event. This leads to successive evaporation of falling rain drops, which change the fractionation rations markedly. Also, this explains the small amount of rain in the rainfall sample on 5/4/2001 at Ras-Benas.

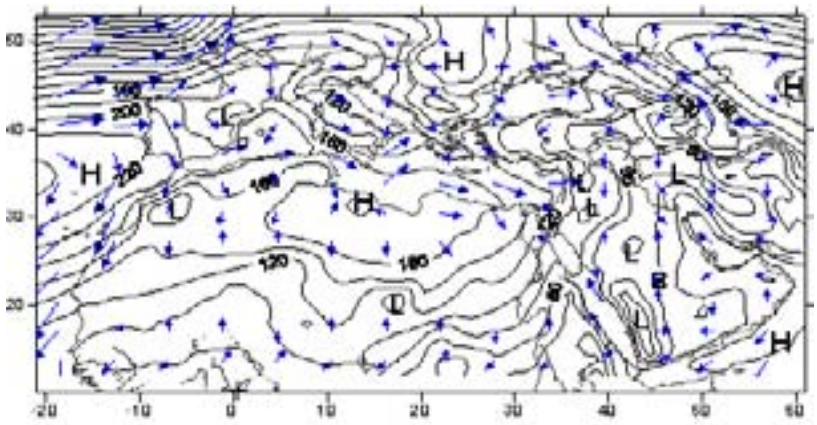

FIG. 16. Contour lines and field of wind vectors at 1000 hPa level on 5/4/2001 associated with 12.7 mm of rainfall and abnormal values of d-excess=-5.08‰, $\delta^{18}O$ =5.66, and $\delta^{2}H$=40.2‰, which were found as a result of relatively warm boundary layer at Ras-Benas and its surroundings.

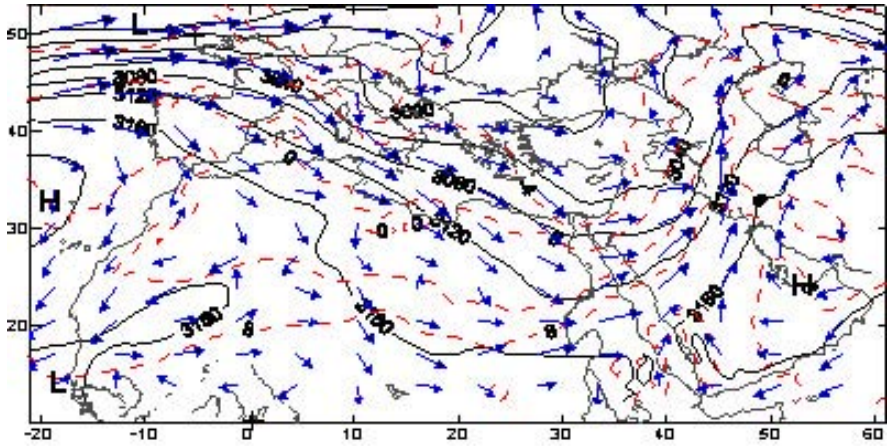

FIG. 17. Contour Lines, thermal field and field of wind vectors at 700 hPa level on 5/4/2001 associated with 12.7 mm of rainfall and abnormal values of d-excess=-5.08‰, $\delta^{18}O$ =5.66, and $\delta^{2}H$=40.2‰, which were found as a result of relatively warm boundary layer at Ras-Benas and its surroundings.

4. Variation in simultaneous daily samples over Egypt

In the period of daily experiment, there were 107 daily rainfall samples at Alexandria, 38 events at Sidi-Barrani, 10 events at Ras-Eltine, and only one event at Ras-Benas. The abnormal event in spring

at Ras-Benas was explained in the foregoing section. Among these samples there are 21 daily rainfall samples, which have taken place on the same dates at Alexandria and Sidi-Barrani. Table 3 depicts these samples and the associated results of the analysis. From the table, one can see that values of $\delta^{18}O$, $\delta^{2}H$ and deuterium excess are similar except on some dates. For example, on 23/12/2002 the difference between $\delta^{2}H$ at the two stations makes deuterium excess be 18.9‰ at Alexandria and 27.7‰ at Sidi-Barrani. This difference may be due to the difference in thermal structure in the boundary layers at the two sites. The values of deuterium excess were reversed on 6/3/2003, where deuterium excess at Alexandria was 16.8‰ and 9.8‰ at Sidi-Barrani. The associated synoptic situation at 700 hPa with the last case is depicted in Figure 18. In spite of the two sites were affected by the same source of air mass, this difference in values of d-excess may refer to modification made by PBL on falling drops of rain. Since, The Planetary Boundary Layer (PBL) is very complex by that time of year, especially during Khamsin situations in spring season.

Table 3. Fractionation ratios of 21 synchronized daily samples at Alexandria and Sidi-Barrani stations in Egypt

Date	$\delta^{18}O$(‰)		$\delta^{2}H$(‰)		d-excess(‰)	
	Alexandria	Sidi-Barrani	Alexandria	Sidi-Barrani	Alexandria	Sidi-Barrani
30/11/2002	-3.2	-2.6	-18.6	-10.1	7.00	10.70
10/12/2002	-5.1	-6.6	-16.9	-31.1	23.90	21.70
11/12/2002	-4.3	-5.5	-16.0	-23.8	18.40	20.20
20/12/2002	-3.8	-2.7	-11.4	-9.4	19.00	12.20
23/12/2002	-3.8	-4.1	-11.5	-5.1	18.90	27.70
24/12/2002	-4.0	-4.0	-7.5	-5.0	24.50	27.00
25/12/2002	-3.9	-4.1	-7.6	-5.3	23.60	27.50
27/12/2002	-3.7	-3.8	-14.4	-9.1	15.20	21.30
02/01/2003	-4.1	-5.0	-22.4	-20.8	10.40	19.20
20/01/2003	-3.0	-3.5	-13.0	-7.7	11.00	20.30
28/01/2003	-6.1	-8.1	-32.2	-51.4	16.60	13.40
29/01/2003	-6.0	-4.5	-33.3	-11.6	14.70	24.40
07/02/2003	-6.9	-4.4	-32.2	-11.1	23.00	24.10
19/02/2003	-4.4	-4.4	-13.1	-10.7	22.10	24.50
24/02/2003	-4.4	-3.5	-13.7	-8.8	21.50	19.20
03/03/2003	-3.3	-1.6	-13.6	-2.0	12.80	10.80
06/03/2003	-4.4	-1.5	-18.4	-2.2	16.80	9.80
11/03/2003	-3.2	-1.6	-11.9	-2.0	13.70	10.80
18/03/2003	-4.4	-3.6	-19.4	-7.5	15.80	21.30
24/03/2003	-4.4	-2.7	-11.8	-10.4	23.40	11.20
15/04/2003	-4.3	-2.7	-14.0	-9.3	20.40	12.30

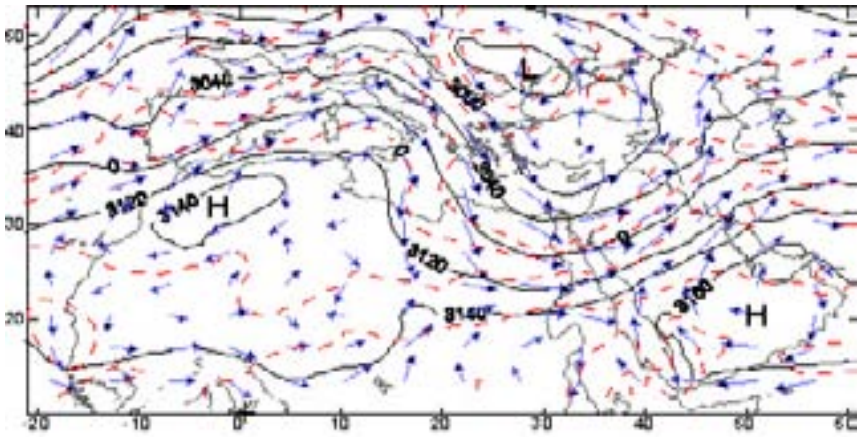

FIG. 18. Contour, thermal and wind fields at 700 hPa level associated with synchronized rainfall events at Alexandria and Sidi-Barrani on 6/3/2003 giving 16.8‰ and 9.8‰ of deuterium excess at the two sites respectively.

5. Variations of fractionation ratios with climatic variables in upper layers above Alexandria

By using successive runs of numerical ETA model on days of rainfall events, simulations of vertical soundings have been made every six hours interval. Each vertical sounding was made every 50 hPa step from 1000 hPa level up to 100 hPa level. As a result, the atmosphere was divided into 19 levels. Height in meters, temperature, dew point, relative humidity, and lapse rate of dry bulb temperatures were computed at each level of the simulated sounding at rainfall time as shown in Table 4 at Alexandria during rainfall event on 6/1/2002. The elements of dry bulb temperature, dew point, relative humidity and lapse rate/100 m. in each layer along with their corresponding fractionation ratios have been grouped for all daily rainfall events. As a result, 18 matrices were obtained. One matrix is devoted for each one of the levels 1000 hPa, 950 hPa, 900 hPa, ……., 200 hPa, and 150 hPa. One of these matrices can be shown in Table 5 below, which represents the layer 900 hPa with the corresponding lapse rates.

Table 4. Simulated sounding at Alexandria (29.95^{o} E, 31.20^{o} N) during rainfall event at 0600 UT on 6/1/2002 associated with 24.1 mm of rainfall

Level (hPa)	Height (m.)	Dry Temp	Dew Point	Humidity %	Lapse/100 m.
100	16126.03	-58.69	-72.70	-	-
150	13558.34	-52.88	-91.50	0.25	-0.23
200	11685.96	-49.01	-83.84	0.62	-0.21
250	10223.07	-47.32	-77.38	1.50	-0.12
300	9012.49	-44.20	-71.46	2.60	-0.26
350	7969.91	-38.90	-64.45	3.95	-0.51
400	7045.11	-33.99	-56.54	6.75	-0.53
450	6213.44	-29.60	-51.31	8.41	-0.53
500	5456.03	-25.29	-47.10	9.17	-0.57
550	4759.94	-22.23	-33.91	31.01	-0.44
600	4118.13	-20.11	-24.41	67.52	-0.33
650	3521.99	-17.05	-17.95	93.65	-0.52
700	2962.00	-13.15	-13.75	84.36	-0.70
750	2432.40	-9.47	-10.26	86.56	-0.70
800	1930.61	-6.06	-8.03	87.27	-0.68
850	1452.77	-2.82	-4.79	87.20	-0.68
900	996.86	0.28	-1.69	87.49	-0.68
950	560.73	3.36	1.30	87.61	-0.71
1000	141.93	6.73	4.80	88.55	-0.81

The variations, relationship and correlation coefficients among variables in matrices similar to that in Table 5 were investigated. It was found that there is correlation coefficient of -0.551 between $\delta^{18}O$ and relative and humidity, which is significant at .05 level. In the same time, a negative correlation of -0.682 was found between dew point and deuterium excess, which is significant at 0.01 level. However, the climatic elements in PBL beneath cloud base are highly correlated with fractionation ratios in daily rainfall samples. Also, significant linear relationship was found between temperature in the layers beneath cloud base and deuterium excess. Figure 19 depicts the relationship between series of dry bulb temperature T at 900 hPa level and series of d-excess of daily samples. The linear relationship between temperature T and d-excess is depicted in equation 7. It was found for this relation that $R^2 = 0.67$, which is significant at .05 probability level. However, the correlation coefficient between T and d-excess equals -0.818, which is significant at 0.01 level.

$$\Delta D = -1.1834 T + 27.14 \quad (7)$$

From equation 4, when T is greater than 23° C, deuterium excess is turned negative. This case was observed on 5/4/2001 at Ras-Benas Station in Egypt where deuterium excess lowered to -5.08‰ as depicted before in Figures, 16 and 17.

Table 5. Variables of simulated soundings at 900 hPa level with relevant fractionation ratios $\delta^{18}O$, $\delta^{2}H$ and d-excess at Alexandria associated with 21 daily rainfall events

Date	Dry Temp.	Dew Point	Humidity %	Lapse rate	O-18 (‰)	H-2 (‰)	d-excess (‰)
02/01/2001	6.88	4.95	88.58	-0.57	-9.32	-54.80	19.76
03/01/2001	8.45	3.23	70.54	-0.68	-1.81	-4.80	9.68
04/01/2001	9.55	-3.71	39.34	-0.70	-8.71	-50.50	19.18
03/12/2001	7.31	4.53	83.74	-0.82	-6.93	-38.20	17.24
04/12/2001	7.05	4.08	82.60	-0.63	-6.23	-30.00	19.84
05/12/2001	7.05	4.39	84.10	-0.62	-6.24	-29.60	20.33
06/01/2002	0.09	-1.85	88.15	-0.65	-5.38	-15.75	27.29
07/01/2002	-0.33	-1.63	92.00	-0.67	-5.38	-16.20	26.84
07/01/2002	0.87	-1.64	84.54	-0.79	-5.38	-16.20	26.84
08/01/2002	3.33	0.85	85.19	-0.93	-5.99	-21.35	26.57
09/01/2002	4.23	2.17	87.62	-0.86	-5.37	-21.35	21.61
10/01/2002	2.21	-0.33	84.19	-1.01	-6.25	-24.50	25.50
27/01/2002	7.84	6.14	90.38	-0.84	-7.14	-38.90	18.22
28/01/2002	7.11	1.14	66.61	-0.51	-6.97	-35.85	19.91
10/02/2002	11.07	1.92	53.86	-0.62	2.17	33.25	15.89
11/02/2002	8.27	1.99	65.28	-0.84	-1.47	8.95	20.71
12/02/2002	5.08	2.62	85.51	-0.62	-4.05	-15.95	16.45
19/02/2003	5.92	1.33	73.66	-0.96	-4.40	-13.10	21.78
23/11/2002	13.11	8.43	74.32	-0.74	-1.40	4.20	15.56
30/11/2002	12.34	10.19	88.32	-0.71	-3.20	-18.60	6.96
06/03/2003	5.61	2.43	81.34	-0.66	-4.40	-18.40	16.40

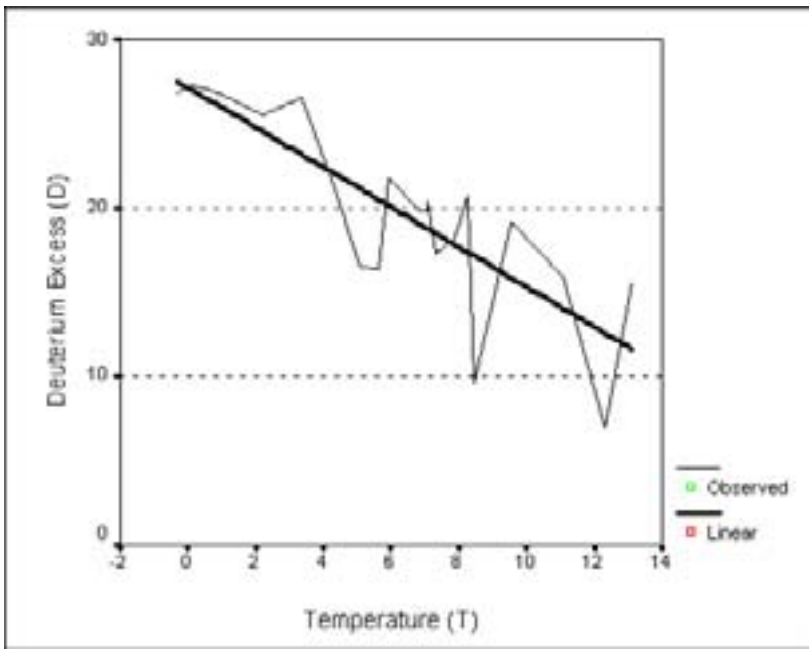

FIG. 19. Variation of d-excess in daily rainfall samples with temperatures (T^o C) using simulated soundings associated with 21 daily rainfall samples at Alexandria.

From the above results, one can conclude that not only the history air mass characteristics, which lead to rainy cloud formation, affect the fractionation processes, but also the characteristics of the underlying air mass beneath rainy cloud play an important role in modification of fractionation ratios of stable isotopes in rainwater.

6. Conclusion

From the foregoing results and discussions, one can conclude that the fractionation ratios of $\delta^{18}O$, $\delta^{2}H$ and d-excess in daily rainwater samples over Egypt have the following features and characteristics;

(a) The fractions ratios in rainwater over coastal stations in Egypt have a quasi similar fingerprint as those in east Mediterranean.

(b) Minimum values of $\delta^{2}H$ and d-excess happened in early spring and early autumn. This may be due to hot and dry winds by that time especially in lower layers of the atmosphere.

(c) The correlation coefficients between monthly d-excess and monthly wind persistence P and between d-excess and surface pressure л are -0.949 and 0.803 respectively. This leads to high values of d-excess in winter, which is associated with high values of surface pressure л and lower values of wind persistence P. Since the wind is variable in winter and in transitional seasons, due to passing troughs and depressions, than in summer and the pressure л is normally higher in winter than in other seasons.

(d) The minor differences in meteoric lines at Alexandria and Sidi-Barrani in Egypt may refer to the absence of dominant effect of a specified air mass in a given month, since many different air masses may cause multiple rainfall events in the same month. Also, local features of station may have minor effects on the inclination of meteoric line and its corresponding intercept.

(e) Blocking synoptic situations over east Mediterranean in winter are characterized by high d-excess associated with slight gradual decrease by time in $\delta^{18}O$, $\delta^{2}H$, and d-excess at Alexandria station during the blocking period. This may be due to severe instability that mixes

sea-spray, which is lifted to higher layers by wind shear and stress, with falling rainfall before reaching the ground especially near coastal stations.

(f) There was slight gradual decrease in the daily means from south to north. Also, d-excess attains high values at coastal areas in east Mediterranean and Morocco.

(g) The warming up of boundary layer leads to ceasing the values of d-excess, where the values of δ^2H rise and those of $\delta^{18}O$ are become near to zero. Also, the warming up of the boundary layer by that time may modify the falling rainwater by evaporating rainfall drops before reaching the rain gauge at the earth's surface.

(h) In case of wide spread atmospheric instability when most parts of Mediterranean basin are affected by the same synoptic pattern on the same date, a big difference in fractionation ratios were found at different sites. For example, on the wide spread case on 30/11/2002, the value of deuterium excess at Alexandria was found to be 6.96‰ and that at Alger was found to be 16.9‰. This may refer to the successive changes in synoptic history of the precipitating air masses associated the journey of weather system from west to east Mediterranean.

(i) The results of simulating vertical soundings above Alexandria, which have been made every six hours interval, indicates that high temperature in the boundary layer beneath rainy cloud may change the value of d-excess markedly especially when mean field of temperature is greater that 23^oC.

(j) Not only the historical air mass characteristics, which lead to rainy cloud formation, affect the fractionation processes, but also the characteristics of the underlying air mass beneath rainy cloud play an important role in modification of fractionation ratios of stable isotopes in rainwater especially at boundary between semi arid zone and middle latitude one.

REFERENCES

[12] EL-ASRAG, A. M., Climatic Study of Khamsin Depressions over North Africa in the last four foregoing decades, SAMS First International Conference on Applied Science, King Saud University, Riyadh, K. S. A., 23–26 April (1993).

[1] EL-FANDY, M. G., Barometric Lows of Cyprus, Q. J. Roy. Meteorological Soc., vol. 72 (1946) 291–326.

[2] MIYAKE, Y., MATUSUBAYA, O., NISHIHARA, C., An isotopic study on meteoric precipitation. Pap. Meteor. Geophys. 19 (1968) 243–266.

[3] MAC DONNELL, J. J., BONELL, M., STEWART, M. K., PEARCE, A. J., Deuterium variations in storm rainfall; implications for stream hydrograph separation. Water resour. Res. 26 (1990) 455–458.

[4] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R., In: Swart, P. K., Lohmann, K. C., McKenzie, J., Savin, S., (Eds.), Isotopic pattern in Modern Global Precipitation Continental Isitope Indicators of Climate, AGU Geophysical Monographs, American Geophysical Union, Washington, D. C. (1993) 1–36.

[5] TAUPIN, J.D., GALLAIRE, R., Variabilité isotopique à l'échelle infra-événement de quelques épisodes pluvieux dans la région de Niamey, Niger. CR Académie des Sciences, Paris, 326, n.7 (1998) 493–498.

[6] SUTTON, L. J., A barometric depressions of Khamsin type. Physics Department, Paper no, 20, Government Press, Cairo, Egypt (1923).

[7] EL-FANDY, M. G., The formation of depression of Khamsin type. *Q. J. Roy. Meteorological Soc.*, vol. 66 (1940) 286.

[8] AHMED, M. M. S., Khamsin and Khamsin conditions, Met. Department, Paper no. 1, Government Press, Cairo, Egypt (1949).

[9] EL-ASRAG, A.M., AL-GAMAL, S.A., YOUSSEF, A., AHMED, D.M., Spatial and temporal variation of rainwater stable isotopes in Egypt and the east Mediterranean, Journal of Theoretical and Applied Climatology, Springer Verlag, Vol. 74 (2003) 191–202.

[10] SCHERHAG, R., Die Genua Und Skagerrak-Zyklonen., Neue Methoden der Wetter und Wetterprognose, Springer Verlag, Berlin/Goettingen/Heidelberg, Deutschland (1948) 213.
[11] SOLIMAN, K. H., The Climate of Egypt. The Egyptian Meteorological Authority, Government Press, Cairo, Egypt (1978).
[12] EL-ASRAG, A. M., Climatic Study of Khamsin Depressions over North Africa in the last four foregoing decades, SAMS First International Conference on Applied Science, King Saud University, Riyadh, K. S. A., 23–26 April (1993).
[13] GAT, J. R., DANSGAARD, W., Stable isotope survey of the fresh water occurrences in Israel and the Jordan Rift Valley, J. Hydrology **16** (1972) 177–211.
[14] CELLE, H. GONFIANTINI, R., TRAVI, Y., SOL, B., Oxygen-18 variations of rainwater during precipitation: application of the Rayleigh model to selected rainfalls in Southern France, journal of Hydrology, Elsevier Pub., 289 (2004) 165–177.
[15] GAT, J. R., KLEIN, B., KUSHNIR, Y., ROETHER, W., WERNLI, H., YAM, R., SHEMESH, A., Isotope composition of air moisture over the Mediterranean Sea: an Index of the air-sea interaction pattern. Tellus 55B (2003) 953–965.
[16] RINDSBERGER, M., MAGARTIZ, M., CARMI, I., GILAD, D., The relation between air mass trajectories and the water isitope composition of rain in the Mediterranean Sea Area. Geophys. Rev. Lett. 10 (1983) 43–46.
[17] LEGUY, C., RINDSBERGER M., ZANGWIL, A., ISSAR, A., GAT, J. R., The relation between oxygen-18 and deuterium contents of rainwater in the Negev Desert and air mass trajectories. Isotope geosciences 1 (1983) 205–218.
[18] RINDSBERGER, M., JAFFE, SH., RAHAMIM, S., GAT, J. R., Patterns of the composition of precipitation in time and space: data from the Israeli storm water collection program. Tellus 42B (1990) 263–271.

OXYGEN-18 AND DEUTERIUM CONTENTS OVER MOUNT LEBANON RELATED TO AIR MASS TRAJECTORIES AND LOCAL PARAMETERS

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Abstract. Stable isotope composition of rainwater has been measured over three years (November 2001 to May 2003) on four stations at different altitude and time scales, in Mt Lebanon. In the same time, the air mass trajectories have been determined using ARPEGE and CEP models as well as radio-soundings and Meteosat imagery. Stable isotope measurements on rainfall at event (or daily) based coupled with air mass trajectory determination enable us to clearly characterize four main isotopic trends in this Eastern Mediterranean region. This opportunity to anticipate the isotopic composition of "typical" rains based on meteorological predictions could make easier isotope hydrological applications. 90% of the isotopic composition of the rain waters are situated above the GMWL and show a d-excess between 10‰ and 30‰. High deuterium excess values are not only encountered along the European coast but also when air masses originate from the Atlantic and cross North Africa.

1. Introduction

This work has been carried out in the frame of the IAEA Coordinated Research programme on the isotope composition of precipitation in the Mediterranean basin in relation to air circulation patterns and climate [1]. One of the specific objectives was to characterize isotopic content of precipitation in relation with air masses origin and meteorological conditions. The main issue of this work is an application to hydrogeological systems, especially those having a rapid response to rain events and to provide informations about the isotopic signal changes that could occur during infiltration.

At the beginning of the programme, studies have been carried out on the western side of the Mediterranean Sea and in Tunisia [2], [3]. On the western side of the Mediterranean Sea the spatial distribution of the monthly isotopic content of precipitation is mainly controlled by the temperature related to continental and altitude effects, and seasonal variations. On a daily basis, the main factor is the origin and the trajectories of air masses. Monthly data allowed to establish the Local Meteoric Water line with a deuterium excess of 14‰ showing the mixed Atlantic and Mediterranean influences. On a daily basis, using origin of air masses, precipitation amount and chemical and isotopic content, the events can be classified as (i) Mediterranean rainfall bringing large volumes of water enriched in oxygen-18 (- 6‰) and in ions from marine or Saharan origin, (ii) Atlantic precipitation of smaller volume of water more depleted in isotope contents and containing mainly anthropogenic elements (NO_3, SO_4).

In Tunisia, although this area is strongly influenced by Mediterranean air masses, due to the seaside locations of Sfax and Tunis, the d-excess of 11‰ is closer to the Atlantic's value (10‰) than Western Mediterranean's one (14 ‰). The global atmospheric circulation, air masses coming from the Western sector, could explain this phenomenon for 30% of the air masses, which directly come from the Atlantic. This could also partially be due to re-evaporation of droplets. But, in Tunisia, the impact of climatic conditions on precipitation isotopic content is confirmed on an event basis sampling. Rains generated by air masses coming from Northern Africa are depleted in oxygen-18 (-6.7‰) whereas Mediterranean ones are enriched (-4.1‰).

The present paper focuses on the second part of the programme and is focusing on the eastern part of the Mediterranean basin. Based on collaboration between the University of Avignon, the CREEN,

University St Joseph of Beirut and the IAEA, this work presents and briefly discusses the isotopic data available, from a sampling programme carried out during 3 years at different time scales and at four different stations of the Mount Lebanon. It tries, mainly at daily or event scales, to characterize the space and time variability of rainfall isotopic signal in relation with origin and trajectories of air masses as well as local meteorological and orographic factors.

2. Scientific background and methodology

Over the Mediterranean sea, the intensive air-sea interaction near the coast under conditions of a large humidity deficit results in labelling atmospheric waters with stable isotopes and particularly with a large d-excess parameters. This parameter is then considered as a good indicator of the water vapour origin or the source of precipitation. The first conceptual model based on both stable isotope and tritium was proposed by Gat and Carmi in 1970 [4].

Some attempts to correlate the origin and trajectories of air masses with isotope variation were already made in eastern Mediterranean [5], [6]. They confirm the model of air-sea interaction mainly along European coast. More recently, both from atmospheric moisture measurements over the sea [7] and from Mount Lebanon [8], such a phenomena (increasing d-excess) have also been observed where the air masses originate from North Africa.

The objective of our investigation is to improve the data set along the air mass paths in order to enable more reliable modelling.

More over if this allows, to some extent, to predict the isotopic behaviour of "typical" rains from the meteorological conditions, this may make easier the hydrological application of isotopes techniques by better planning the fieldwork.

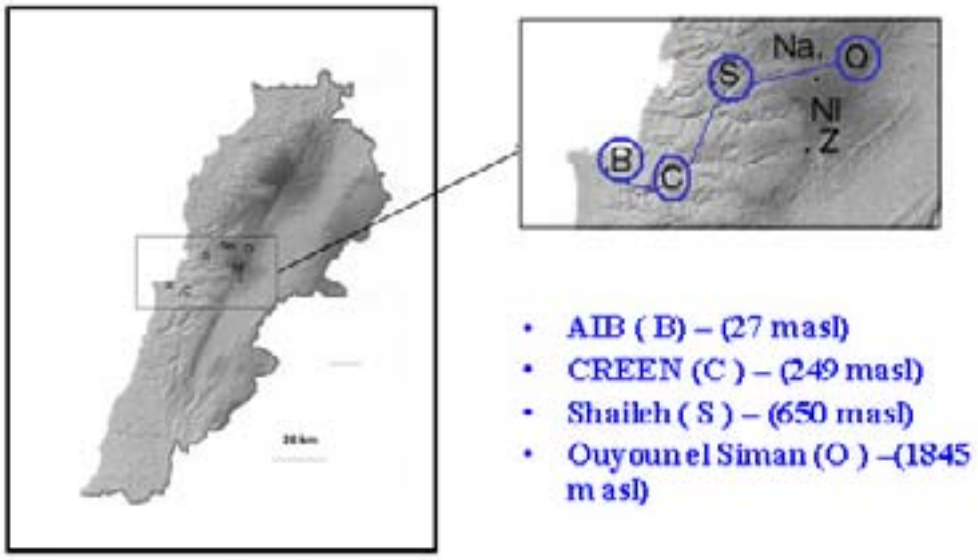

FIG. 1. Sampling location.

2.1. Rain sampling and analyses

During 2001–2003, events, daily and sequential samples have been collected from 4 stations located on Mount Lebanon along a W-NE section, at different altitudes (Fig. 1).

Following is the detail of the sampling:

Year 01–02: sequential event sampling AIB (16), CR (17) and SHA (17) stations; events (23) CREEN station and daily OS (12) station .

Year 02–03: sequential sampling CR (21) station; events AIB (26), CR (27), SHA (27) stations and daily OS (12) station.

Year 02–03: events AIB (15), CR (20), SHA (12) stations and daily OS (14) stations.

In the present paper we consider only the daily and events samples (^{18}O and ^{2}H for CREEN and Shaileh stations in 02–03; ^{18}O on the 4 stations for 2001 to 2003).

The oxygen and deuterium analysis was performed by Hydrogeology Laboratory of the University of Avignon and the IAEA Laboratory.

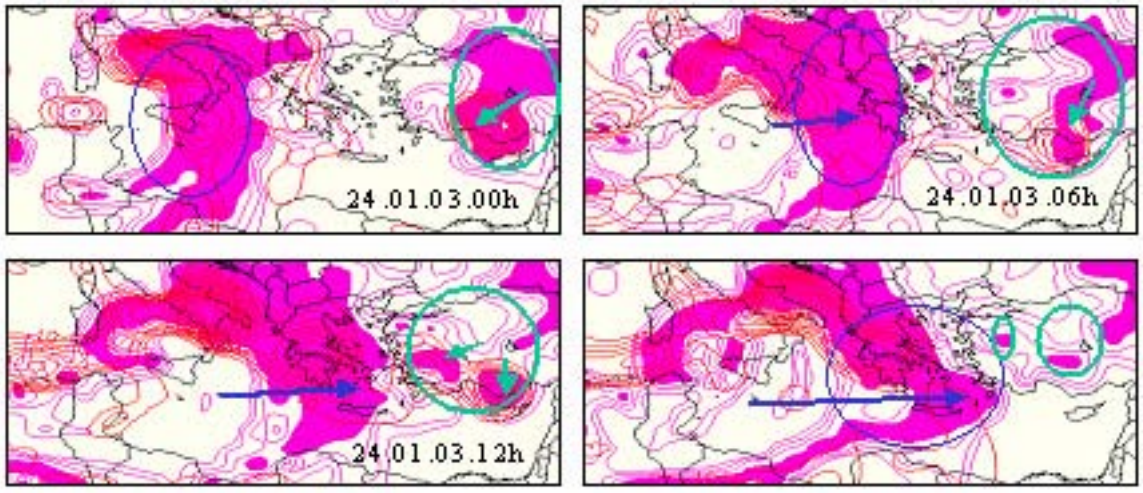

FIG. 2. Example of ARPEGE—Air moisture—700 hPa level, vertical velocity.

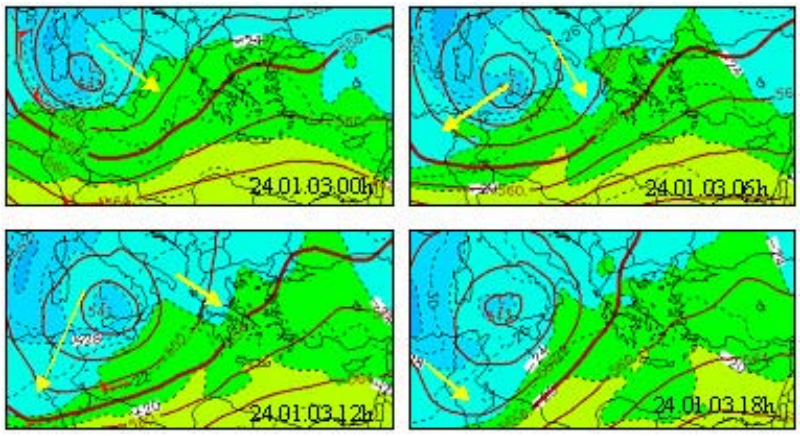

FIG. 3. Example of ARPEGE-Geopotential 500 hPa level, temperature and wind.

2.2. Meteorological parameters

Maps of geopotential height, air temperature, winds at 500 hPa and humidity, vertical velocity at 700 hPa have been prepared using the ARPEGE (Météo France) and CEP (Centre Européen de Prévision) models, respectively. Added informations from Radiosondes and satellite data (Meteosat 7,

channels IR and WV) were used to estimate the circulation of the moisture that will produce rainfall. Examples of such determinations are shown in Figures 2 and 3.

3. Results and discussion

3.1. The air mass trajectories

The air mass trajectories have been determined using ARPEGE and CEP models (6h), as well as radiosondes and remote sensing (Meteosat 7), as indicated above.

Considering the origin of air masses and the region in which they entered the Mediterranean Sea [6] and the flow and the direction of approach to the Lebanese coast, we characterized four groups of trajectories, from North to South (Fig.4).

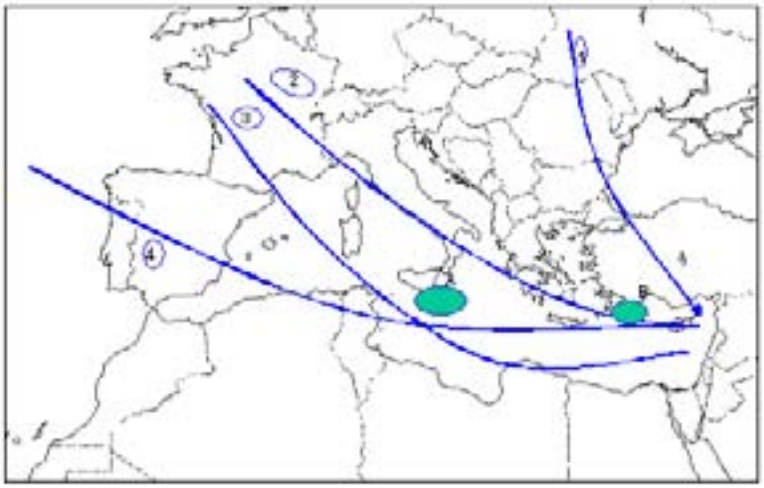

FIG. 4. Origin and air mass trajectories producing rains over Mt Lebanon (meteorological data between October 2001 and April 2003 related to fifty events).

- Trajectory 1: Air masses originating from East Europe reach Lebanon having crossed the "Anatolian Plateau", Turkey, Cyprus and a small distance over the Mediterranean Sea.

- Trajectory 2/3: Air masses coming from West Europe reach Lebanon by travelling across Italy, then the Mediterranean sea (Lebanon coast approach is from West), or by crossing the Mediterranean sea and then travelling along the North African coast (Lebanon coast approach is from South West).

- Trajectory 4: Air masses with an Atlantic origin enter from the West side of the Mediterranean Sea and travel along it before reaching the mount Lebanon. Usually these air masses are subjected to low pressure areas at the feet of Italy (Point A, Fig.4) or over the triangle Turkey, Cyprus and Crete.

3.2. Local factors controlling isotope contents

Despite the synoptic scale history of the air masses seems to be the predominant factor which control the isotopic data [9] the composition of individual rain events from the same group shows significant variations reflecting singular local factors such as precipitation patterns, local temperature and altitude gradient.

3.2.1. Altitude effect

Lowering of temperature with increasing elevations in mountainous regions usually leads to enhance condensation process and to progressive depletion in heavy isotopes of precipitation with altitude. Values of this effect usually vary between –0.1‰ to 0.6‰ [10] [11].

The global data (trajectory, rainfall, relative humidity, temperature, stable isotopes values, d-excess) from November 2002 to April 2003 are summarised for the CREEN (249 m) and SHAILEY (650 m) stations in Table 1.

Using these two stations the altitude effect has been separately calculated for the different air masses trajectories. Based on 18 events, where rains were collected for the both stations at the same time, the altitude effect varies from –0.1‰ to –0.23‰ $\delta^{18}O$/ 100m (Fig. 5, Table 1)

Even if trajectory 4 and trajectory 1 globally seems to be associated with the lower and the higher altitude gradient, respectively, there are no clear relations, on the average, between on one hand trajectories and temperature variations and on the other hand altitude gradient. Nevertheless, higher values (up to 0.4‰) are related to air masses coming from the North (Table 1). This problem should be examined again when the data of the four stations will be completed and available.

Comparing d-excess values from CREEN and Shailey stations (Annex 3), a systematic increase with altitude can be shown. The upper variation values (up to 9) are clearly related to the trajectory 2 and the strongest temperature variations. Such variations were observed in mountainous region, for example, by Rank D, and Papesh W. in Austria (this issue).

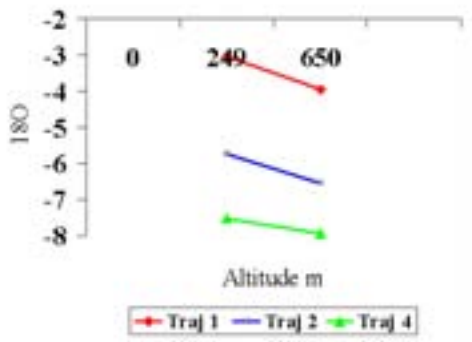

FIG. 5. Altitude effect for ^{18}O including CREEN and Shailey.

Table 1. Altitude effect (CREEN and Shaileh stations) for both stable isotopes and d-excess during 2002–2003

Tmj /number	$\Delta\delta^{18}O$/100m	$\Delta\delta^{2}H$/100m	ΔT/100m	$\Delta\delta^{2}H/\Delta\delta^{18}O$ /100m	Δd-excess /100m
1/8	-0.23	-1.03	-0.54	4.47	0.75
2/6	-0.20	-0.08	-1.08	0.4	1.44
4/4	-0.10	-0.39	-0.55	3.91	0.44

3.2.2. Variation with temperature and rain amount

As usually observed at most of the stations of the Mediterranean Basin, at an event scale one observes a poor correlation between rain amount, air temperature and isotope contents (Fig. 6 and 7). The $\delta^{18}O = f(T)$ relationship, $\delta^{18}O = 0.25T_{\text{(ground level)}} - 7.3$, looks relatively bad, compared to that is usually observed. This could be also due to a wide variability in ground level temperature on Mount Lebanon (- 5.5 to 26°C). If we except some evaporated rains at the beginning and the end of the rainy season, there is no clear seasonal effect, underlining the prominent role of origin and flow direction of air masses.

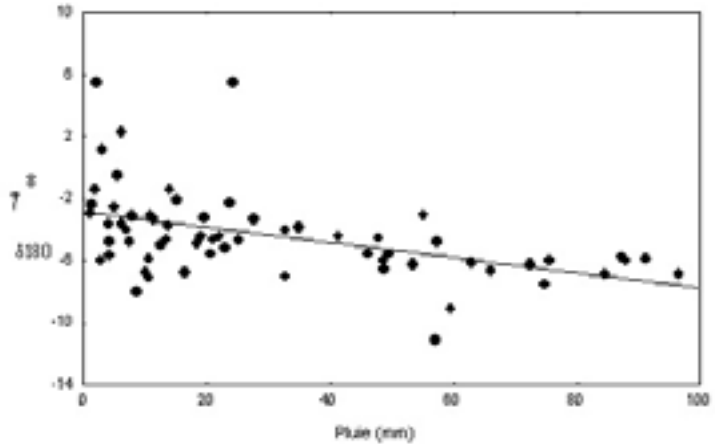

FIG. 6. ^{18}O - rain amount relationship for precipitation from Mt Lebanon.

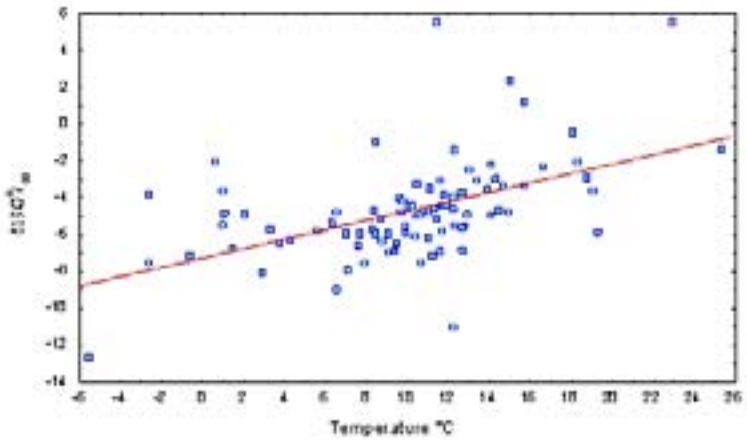

FIG. 7. ^{18}O - ground level temperature relationship for precipitation from Mt Lebanon.

3.3. The δ^2H - $\delta^{18}O$ relationship

The δ^2H - $\delta^{18}O$ relationship for all samples from MT Lebanon (Fig. 8) define a local meteoric water line according to the equation $\delta^2H = 6.3\ \delta^{18}O + 8.2$ with a regression line coefficient r = 0.96.

Globally, 90% of the measured values lie above the Global Meteoric Water Line; 45% have a d-excess between 10‰ and 20‰ and 45% between 20‰ and 30‰.

Points lying under the GMWL show enriched values; they correspond to rainy events isotopically modified by evaporation process, particularly evident at the beginning and the end of the rainy season. If one ignores these points the relation becomes: $\delta^2H = 7.4\ \delta^{18}O + 14.5$ with r = 0.94.

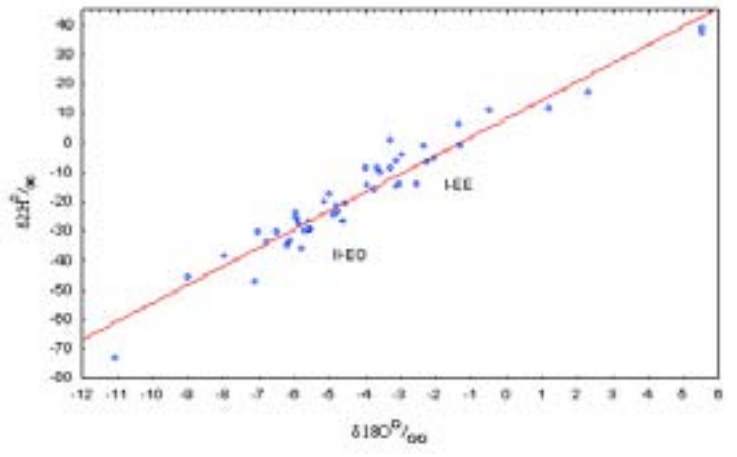

FIG. 8. ^{2}H -^{18}O relationship for precipitation from Mt Lebanon.

3.4. Isotopic data related to air mass origin and trajectories

From October to May 2003, at CREEN station, more than 40 rain events have been collected and analysed for ^{18}O and ^{2}H (table 1 and [8]). Globally the $\delta^{18}O$ vs $\delta^{2}H$ diagram (Fig. 8) provides a good characterization of evaporated rainfalls, air masses coming from East Europe, West Europe and directly from the Atlantic (flow path 4). The high d-excess values related to the classical pattern of air-sea interaction [4], do not clearly show a seasonal or trajectory-inferred variation, even if the higher values could be observed in January 2002, on rainfall originating from the trajectory 4.

Air masses originating from West Europe (trajectory 1) produce rainfalls with ^{18}O isotopic compositions ranging from -2‰ to -4‰ (CREEN station). This could be interpreted as a signature of a first condensation stage. Frequently occurring at the end and the beginning of the rainy season, the isotopic composition of low intensity rains can also be distorted by the fractionation accompanying the evaporation process on the falling rain drops. This could also lower the d-excess. The later shows sometimes values upper than 25‰.

Trajectories 2 and 3 produce rain with ^{18}O isotopic composition ranging between -4,6‰ and 6,6‰, and d-excess between 15‰ and 24‰ (CREEN station).

The last group (trajectory 4) characterized by a long travel along North Africa, shows the most depleted rain water (-6.1‰ to -11‰) and a very variable d-excess. Comparing with the data obtained in Tunisia, the $\delta^{18}0$ values are in agreement with an oceanic air mass origin; the air-sea interaction process (high d-excess) probably occurs as the air masses flow over the Mediterranean Sea between Tunisia and Lebanon.

4. Conclusions

Stable isotope measurements on rainfall at event (or daily) scale coupled with air mass trajectory determination enable us to clearly characterize at least four main isotopic trends in this Eastern Mediterranean region. This is clearly related with the air mass origin and their synoptic scale history.

The estimated knowledge of the isotopic composition of “typical” rains, based on meteorological predictions could make easier its hydrological applications, especially for spring hydrograph separations on the Mt Lebanon karstic system.

As observed on atmospheric water vapour [7], the high d-excess values are not only encountered along the European coasts where cold and dry air from the continent reach the Mediterranean Sea, but also where the air masses originate from the Atlantic after crossing North Africa. It may be noted that air masses, coming from West Europe and crossing all the Mediterranean Sea sometimes show high

deuterium excess. The lack of relation between ^{18}O and d-excess and the space and time variability of the later suggest that its interpretation is probably complex and need more data including vertical atmospheric profiles.

Finally, the air mass origin and history greatly conceal the local factors; but comparing our results with data obtained southern more [5], [6] Mt Lebanon appears to play a major role on the rainfall isotopic composition, especially those coming from East Europe.

REFERENCES

[1] GOURCY, L., AOUAD-RIZK, A., ARAGUAS, L., ARGIRIOU, A., BONO, P., DIAZ TEIJEIRO, M.F., DIRICAN, A., EL-ASRAG, A.M., GAT, J. GONFIANTINI, R., HORVATINCIC, N., OUDA, B. CARREIRA-PAQUETTE, P., RANK, D., SAIGHI, O., TRAVI, Y., VRECA, P., Isotopic composition of precipitation in relation to air circulation patterns in the Mediterranean basin: preliminary results. Paper presented at the International Workshop on the application of isotope techniques in Hydrological and Environmental studies. UNESCO, Paris, France, September 2004.

[2] CELLE-JEANTON, H., TRAVI, Y., BLAVOUX, B., Isotopic typology of the precipitation in the western Mediterranean region at three different time scales. Geophysical Research Letter, 28 (2001) 1215–1218.

[3] CELLE-JEANTON, H., ZOUARI, K., TRAVI, Y., DAOUD, A., Caractérisation isotopique des pluies en Tunisie. Essai de typologie dans la région de Sfax. C.R. Acad. Sci. Paris, 333 (2001) 625–631.

[4] GAT, J., CARMI, I., Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. J. Geophysical Research. 75 (1970) 3039-3048.

[5] LEGUY, C., RINDSBERGER, M., ZANGWIL, A., ISSAR, A., GAT, J., The relation between the oxygen-18 and deuterium contents of rainwater in the Negev Desert and air mass trajectories. Isotopes geosciences, 1 (1983) 205-218.

[6] RINDSBERGER, M., JAFFE, S., RAHAMIN, S., GAT, J., Patterns of the isotopic composition of precipitation in time and space: data from Israeli storm water collection program. Tellus, 42B (1990) 273–271.

[7] GAT, J., KLEIN, B., KUSHNIR, Y., ROETHER, W. ,WERNLI, H., YAM, R., SHEMESH, A., Isotope composition of air moisture over the Mediterranean Sea: an index of the air-sea interaction pattern. Tellus, 55B (2003) 953–965.

[8] AOUAD, A., TRAVI, Y., BLAVOUX, B., JOB, J.O., NAJEM, W., Etude isotopique de la pluie et de la neige sur le Mont Liban: premier résultats. Journal Hydrological Sciences. 49-3 (2004) 429–441.

[9] YOSHIMURA, K., OKI, T., OHTE, N., KANAE, S., A quantitative analysis of short-term ^{18}O variability with a Rayleigh-type isotope circulation model. Journal of Geophysical Research, 108 (D20), ACL 13 (2003).

[10] VOGEL, J.C., LERMAN, J.C., MOOK, W.G., Natural isotopes in surface and groundwater from Argentina. Hydrological Sciences Bulletin, XX (2) (1975) 203–221.

[11] FONTES J. C., OLIVRY J. C., Gradient isotopique entre 0 et 4000 m dans les précipitations du Mont Cameroun. Comptes Rendus réunion Annuelle Sciences de la Terre, Société Géologique de France (1977) 701.

STABLE ISOTOPES IN RAINFALL OVER GREECE: RESULTS OF THE 2000–2003 MEASUREMENT CAMPAIGN

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Abstract. In the frame of the IAEA CRP "Isotopic Composition of Precipitation in the Mediterranean Basin, in relation to Air Circulation Patterns and Climate" rainfall sampling has been performed during the period August 2000–March 2003 in four Hellenic stations. Simultaneously, the relevant meteorological information has been collected, namely, rainfall height, temperature, relative humidity and also the type of precipitation (water, snow, etc.). The samples were analysed in order to determine the concentration of stable isotopes (^{18}O, ^{2}H) and tritium. This data was processed in order to define local water meteoric lines and other correlations with weather parameters. Previous measurements, starting from 1960, from other Hellenic locations were completed with weather data and analysed, in order to identify possible statistically significant deviations compared to current data. Also the isotopic results were correlated with tracks of rain producing fronts and back trajectories of air masses. It was found that the local meteoric lines present a behaviour between that of the Eastern and Western Mediterranean. No statistically significant differences between the current and older samples were found. The tritium values evolve as expected. Finally, back trajectories can explain in some extend the isotopic characteristics of rainfall, but it appears that further analysis is required.

1. Introduction

This report summarizes the work performed by the Hellenic consortium in the frame of this project. Table I contains detailed information on the location, and the measurements of the Greek isotopic sampling stations, the data of which were used in this work.

Table 1. Hellenic rain sampling network

	Lat. (North)	**Long.** (East)	**Altitude** (m)	**Sampling Frequency**	**(δ^2H, $\delta^{18}O$)** Period	**Tritium** Period
GNIP historical stations						
Athens (Hellinicon)	37.9	23.73	15	Monthly	60–74	61–91
Rhodes (Maritsai)	36.40	28.08	37	Monthly	63–72	63–87
Heraklion	35.33	25.18	39	Monthly	63–74	60–87
Methoni	36.83	21.72	33	Monthly	64–68	63–68
Limnos	39.88	25.07	17	Monthly		
Alexandroupolis	40.85	25.95	4	Monthly		
CRP Stations						
Athens (Pendeli)	38.05	23.86	498	Event Monthly[1]	00–03	
Athens (Thission)	37.97	23.72	107	Monthly	00–03	00–01
Patras	40.62	22.95	32	Monthly	00–02	00–01
Thessaloniki	38.29	21.79	100	Monthly	00–03	00–01

[1] Monthly collection started on April 2003. Before this date samples were collected on an event basis.

2. Data analysis

Stable isotope data (δ^2H, $\delta^{18}O$) are examined in order to establish the local relationships between δ^2H and $\delta^{18}O$, as well as the intensity of the effects of temperature and seasonality, precipitation amount and altitude on the isotopic composition of precipitation. Furthermore the time series are examined for possible trends.

Tritium data are also examined in order to obtain some information on the recovery rate over Greece.

2.1.Stable isotopes

Monthly data are the most commonly available data and most of the aforementioned isotopic effects have been documented on such data. Event-based data, on the other hand, due to their temporal resolution, allows for the better investigation of specific aspects of these effects as well as possible correlation to other environmental parameters such as synoptic weather systems.

2.1.1. Local Water Meteoric Lines — δ^2H, $\delta^{18}O$ relationship

The best fit $\delta^2H = f(\delta^{18}O)$ line for each station — called Local Meteoric Water Line — is presented in Figure 1. The event-based data are grouped per hydrological year (from August to July), each shown with a different mark.

All stations are characterized by water lines with slopes significantly lower than GMWL, except Heraklion, suggesting the influence of local factors on the isotopic composition of the precipitation. Even though some data points from Pendeli, Patras and Thessaloniki have a relatively large spread, the overall correlation between δ^2H and $\delta^{18}O$ is very good.

The Local Meteoric Water lines for Greece (data from all stations grouped in one dataset) are also presented in Figure 1. This figure is derived from all the available monthly data, and using only the GNIP data. The differences are not statistically significant either in terms of slope or intercept.

2.1.2. Temperature effect

Considering the case of atmospheric vapour being formed by evaporation over warm oceans and afterwards being gradually removed by condensation as it is transported to higher latitudes, the isotopic composition of the produced precipitation follows a well documented Rayleigh fractionation process. This, so-called, latitude effect is in the order of 0.6 ‰/ºC for $\delta^{18}O$, referring to annual average temperatures, while seasonal variations are smaller ranging from 0.5 ‰/ºC for northern latitudes to almost 0.0 ‰/ºC at the equator.

GNIP stations, apart from Thission, give slopes in the expected range for mid-latitudes (0.25‰/ºC -0.30 ‰/ºC), as can be seen in Figure 2. Thission and Hellinikon, located within a distance of 5 km, give much smaller slopes just above 0.10 ‰/ºC. This could be partly explained by the fact that Thission is located in the middle of the city therefore it might be affected by the urban heat island, while Hellinikon is almost on the coastline. For the rest of the stations there are significant data gaps that might bias the slope. Despite that Heraklion also presents a plausible slope (0.30 ‰/ºC).

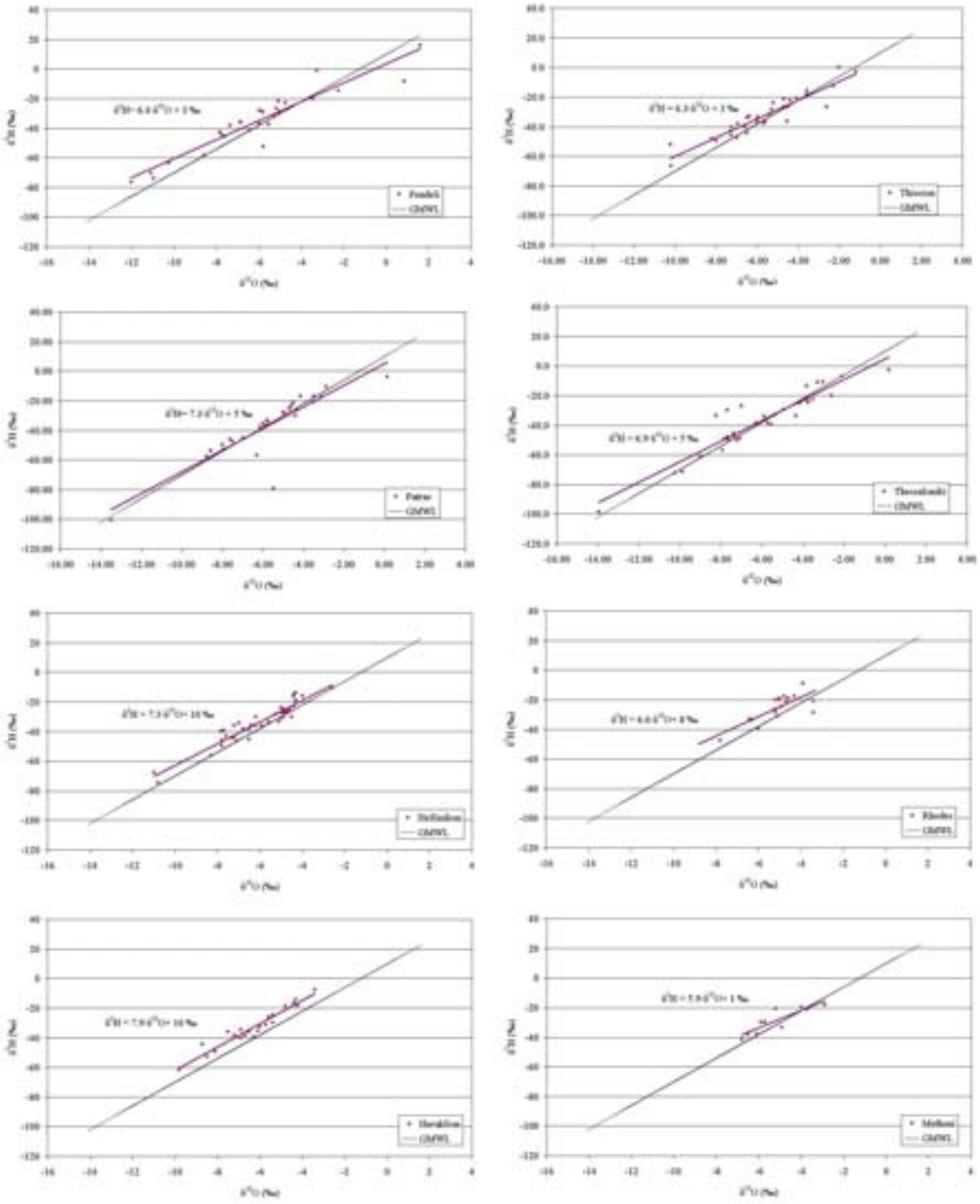


FIG. 1. δ^2H - $\delta^{18}O$ relationship.

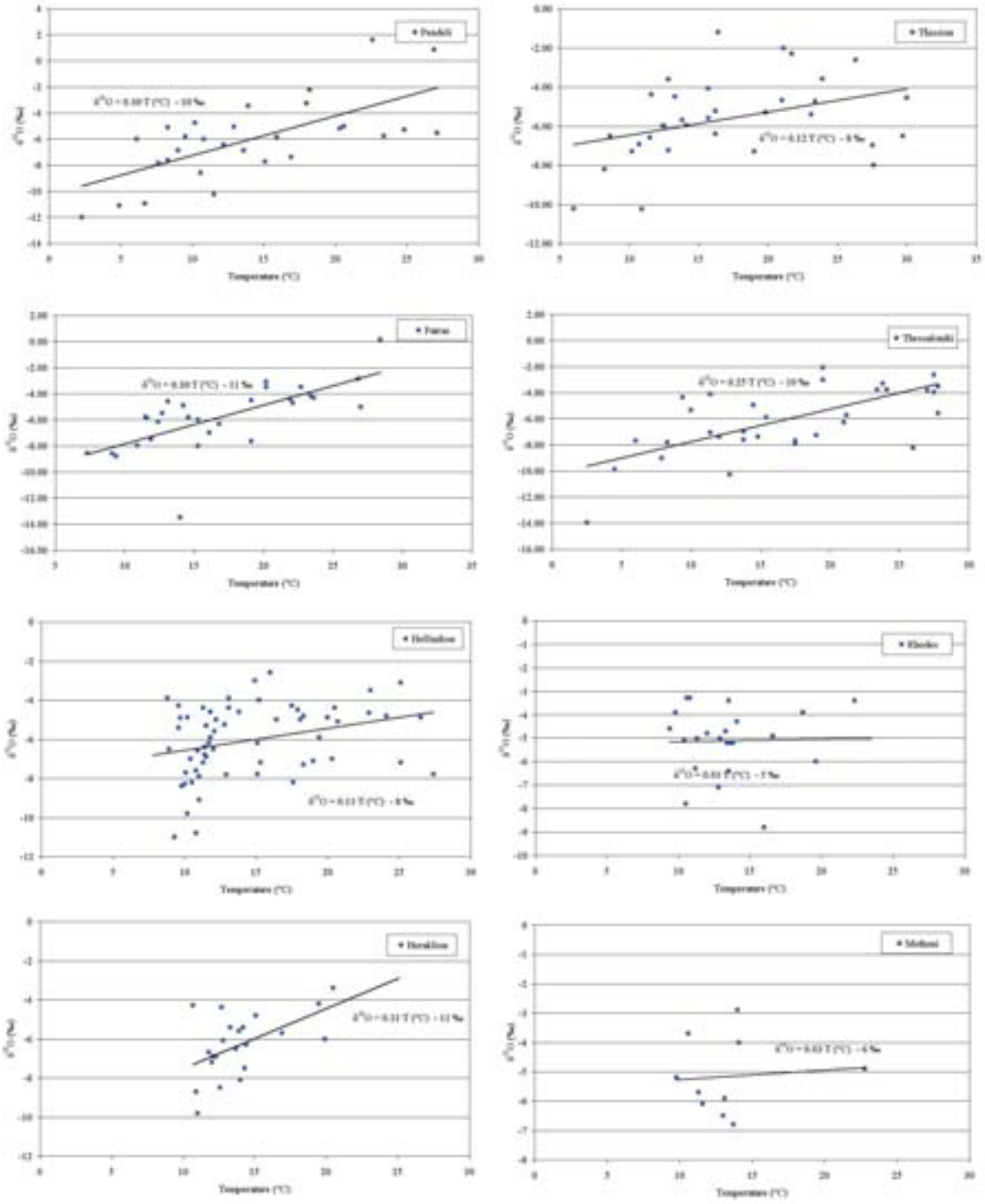


FIG. 2. $\delta^{18}O$ – f (temperature).

The seasonal variation of $\delta^{18}O$ is more or less typical of northern hemisphere mid-latitude stations, with a pronounced minimum during August for the drier stations.

2.1.3. Amount effect

Figure 3 illustrates the variation of $\delta^{18}O$ as a function of the rainfall height. As expected, heavy rains result into depleted samples, especially in stations that are not characterized by long lasting rain events.

Notably during the event of 24–25/03/2002 a sharp drop of $\delta^{18}O$ is observed in time with the intensification of the rain rate from 11:00 to 13:00. The higher $\delta^{18}O$ value of the last sample, is also representative of an intense rainstorm, and is the result of mixing depleted rainwater from the second half of the rainstorm and water from the last part of the rainstorm that is being re-enriched as the drops leaving the base of the cloud travel through a $\delta^{18}O$ rich environment.

2.1.4. Deuterium excess

Linear relationships in the form of $\delta^{2}H = 8 \times \delta^{18}O + d$ are used to calculate the deuterium excess, d, a parameter very useful for the identification of locally induced effects on the isotopic composition of precipitation.

Figure 4 presents the temporal variation of d, in terms of rain episodes from Pendeli, monthly samples from all stations and on a monthly basis using aggregate data. Winter rainfall is less intense therefore less depleted, while summer rains are intense leading to the observed d-excess minima during summer months.

Observing the variations of monthly averages, we can see that those stations located in the middle latitudes of the country present a maximum d-excess value during winter and striking minima during summer, probably due to convective precipitation. The data from Patras, located to the west and Thessaloniki at the north, present somewhat different behaviour with profiles having a secondary minimum during winter and maximums during the mid-season. This indicates that both stations are less susceptible to local high intensity rains. Patras' large minimum on August is due to an intense rain event recorded over the short period of measurements.

Data from the CRP stations present significantly higher temporal variability compared to the older data from GNIP historical stations. On the other hand GNIP data have many gaps, especially during summer months, when extreme d-values are to be expected.

The temporal profiles of d-excess variation do not show any statistically significant trend neither on a monthly nor on an event basis (Figure 3). The only exception is the Hellinicon station, where a negative linear trend is detected over the period 1960 to 1974. This trend is statistically significant over a 95% confidence interval, however we could not confirm this finding using another, non-parametric method, because of the gaps in the time series. Treating the Hellinikon and Thission series as one, since both stations are located in Athens, did not produce any trend.

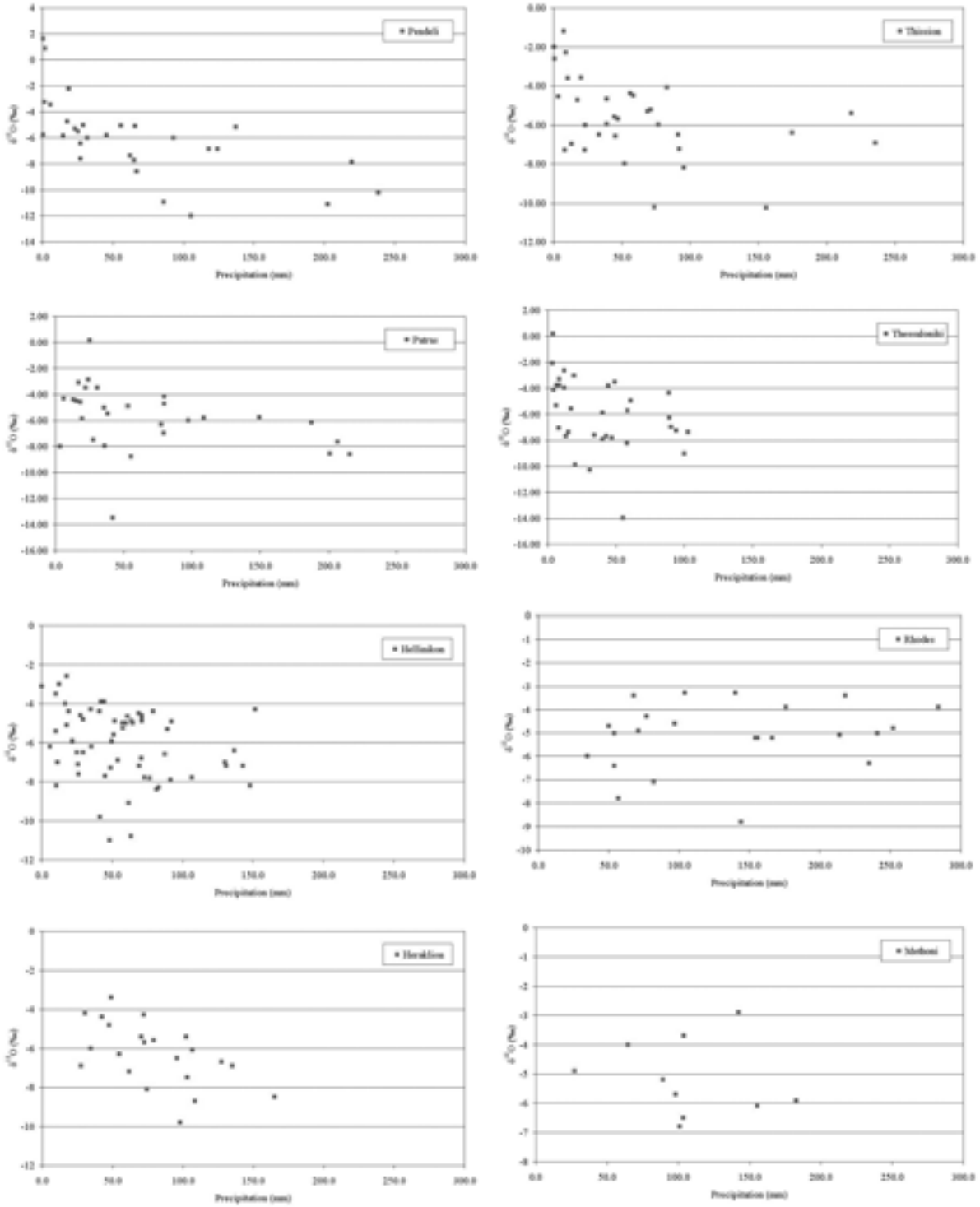


FIG. 3. $\delta^{18}O = f$ (Precipitation).

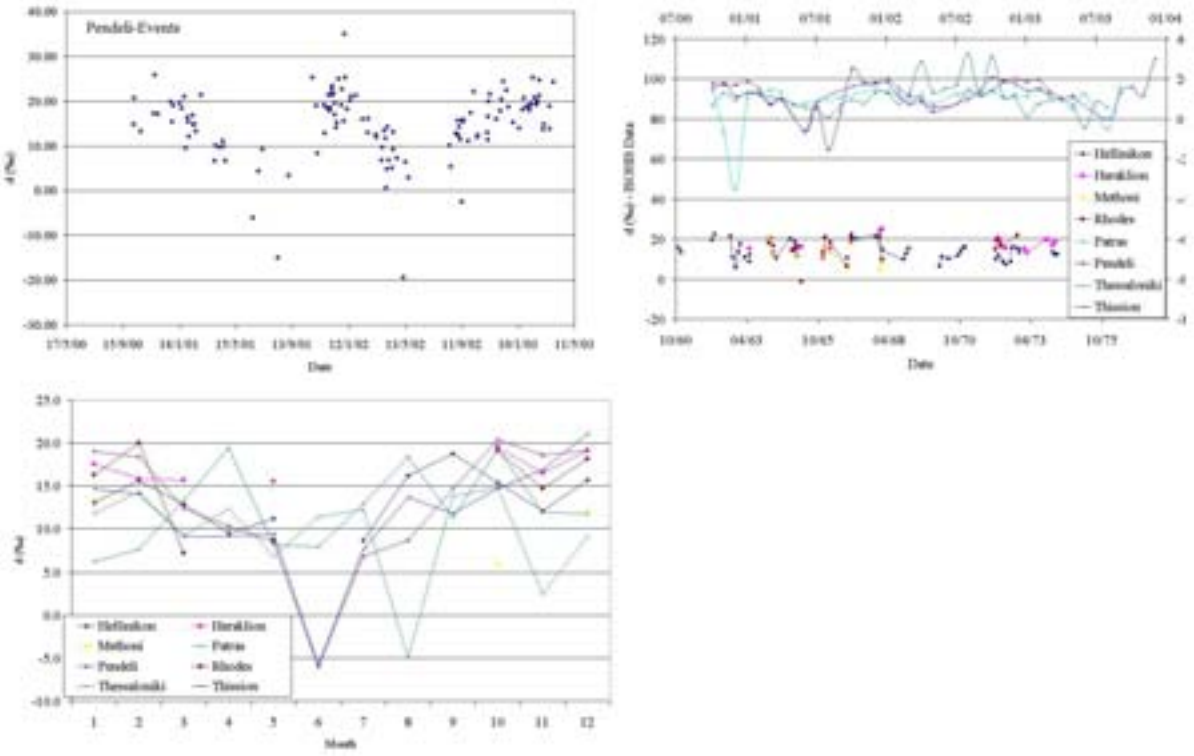


FIG. 4. Temporal variation of deuterium excess, d.

Table 2 contains the calculated d-excess values for the stations and periods listed in Table I.

Table 2. Calculated deuterium excess values for the Greek stations

Location	**d (‰)**	**±σ_d (‰)**
Pendeli	17	4
Thission	15	6
Patras	11	8
Thessaloniki	13	8
Hellinicon	14	4
Rhodes	16	7
Heraklion	17	4
Methoni	13	5
Greece (GNIP series)	14	7
Greece (ISOHIS series)	15	5
Greece (All data)	15	6

We see that, in all cases, the deuterium excess parameter (d) lays between the expected values for the Western (13.7‰) and Eastern Mediterranean (22‰)

The data of Table 2 are illustrated in Figure 5. The lowest d-excess value is observed at Patras and the highest at Heraklion. Pendeli also has a high d-value, probably due to the fact that it has the highest elevation of all stations.

Stations located at the western part of Greece have lower d-excess values possibly as a result of receiving relatively larger amounts of precipitation originating either over the Atlantic or the Western Mediterranean. On the other hand precipitation collected at Rhodes and Heraklion might have formed from evaporation over the Aegean or the Mid-eastern Mediterranean.

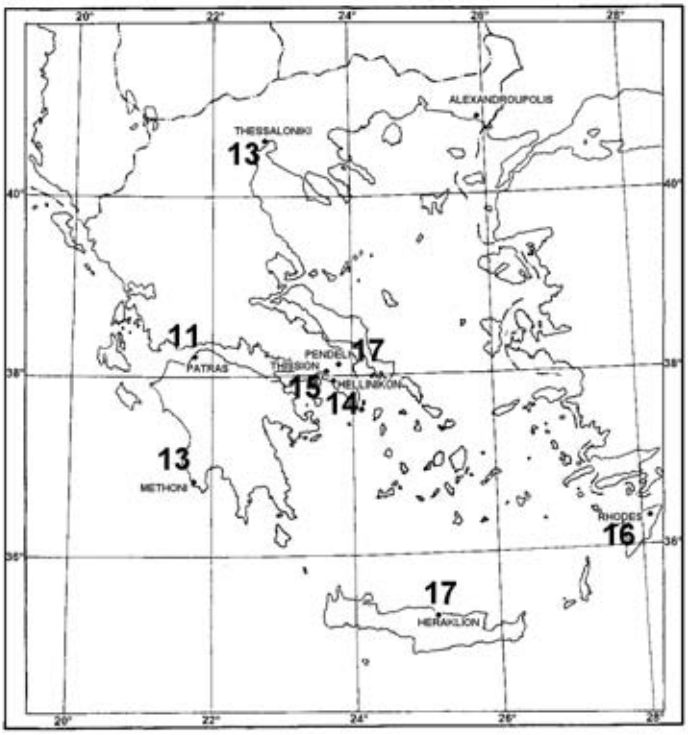


FIG. 5. Spatial distribution of deuterium excess over Greece.

In order to assess whether the average d-excess values differ statistically between stations we applied the t-test[2] for all possible pairs of stations. The results obtained show that there are only two pairs of stations for which the hypothesis of equal mean values can not be rejected at a 95% confidence level. The pairs are Thission –Rhodes and Thessaloniki-Methoni. In both cases no conclusions regarding the close behaviour between the two stations can be drawn, since the paired stations are very different from a physiographic point of view, and on the other hand, the data were collected at periods some 35 years apart.

The variance for the Patras station is particularly important (Coefficient of Relative Variation[3], CV = 1.1). The data from the stations of Pendeli and Thessaloniki show a moderate variance (CV = 0.7) while the remaining stations show a relatively smaller variation (CV = 0.3 to 0.5).

[2]The two-sample unpaired t test is used to test the null hypothesis that the two population means corresponding to the two random samples are equal.

[3]CV is defined as the ratio of standard deviation over the mean value.

2.1.5. Isotopic composition and surface weather systems.

The isotopic composition of rainfall depends largely on the origin of the water vapour that forms it. Therefore an attempt was made to correlate the deuterium excess of each event with the origin of the weather system that produced the specific rainfall.

The surface systems that produced rainfall were: (i) Frontal depressions which are classified in four categories — A, B, C and D — according to the location where they were originally formed [1][2], (ii) Warm or cold fronts moving in the area of interest. These may be related to frontal depressions the centres of which are located far north from Greece [2] and (iii) lows that are created in the area of interest and do not have the characteristics of frontal depressions but are either orographic or thermal.

Figure 6 illustrates the mean and median deuterium excess of each category, while one standard deviation bars indicate the variation observed in each case.

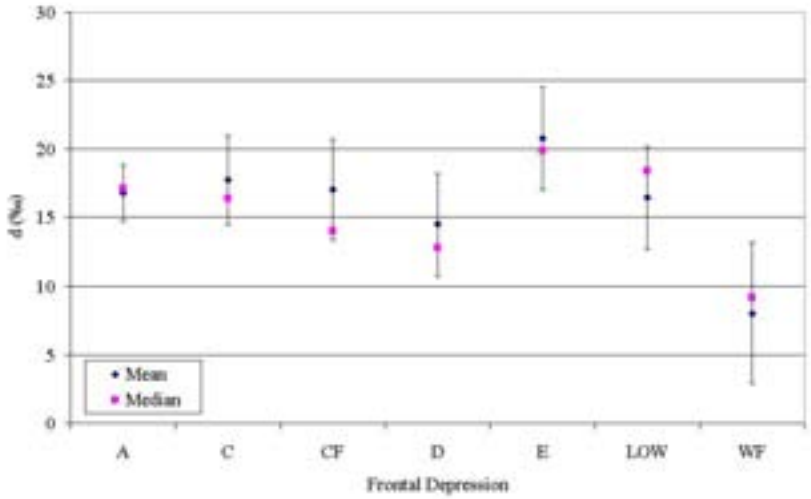


FIG. 6. Relationship between isotopic composition and frontal depressions.

Category A includes those frontal depressions formed over the Biscay Bay that arrive in Greece crossing Central Italy. The d-value of this category is 17 ‰. The frontal depressions formed in the Atlantic, close to the Gibraltar straight belong in category B. During this period no events due to this type of depression occurred. Category C includes frontal depressions formed northern of the Pyrenees. These reach Greece after having crossed the Western Mediterranean, Central Italy and the Southern Adriatic. The d-value is 18 ‰. Frontal depressions formed south of the French Alps, cross the Po valley in Italy, Albania and reach Greece belong to category D. This category presents one of the lowest d-values 14 ‰. Finally, category E includes frontal depressions formed in Sahara that cross the Mediterranean and reach Greece. Since the main source of water vapour in this case is the central Mediterranean, the resulting rain has a d-value 20 ‰, in a way similar to categories A and C. A smaller value (16 ‰) is found for the rain due to non-frontal lows formed over the Libyan Sea (marked as Lows). Rains due to warm fronts have the smallest d-value of all (d=8 ‰). This is due to the fact that this category contains results from rain events that occurred mainly in July, when the deuterium excess is low. Finally a d-value of 17 ‰ is observed for episodes due to cold fronts corresponding to a larger proportion of water vapour originating in the Atlantic, and being depleted through rainout across the European continent.

2.1.6. Isotopic composition and air mass trajectories.

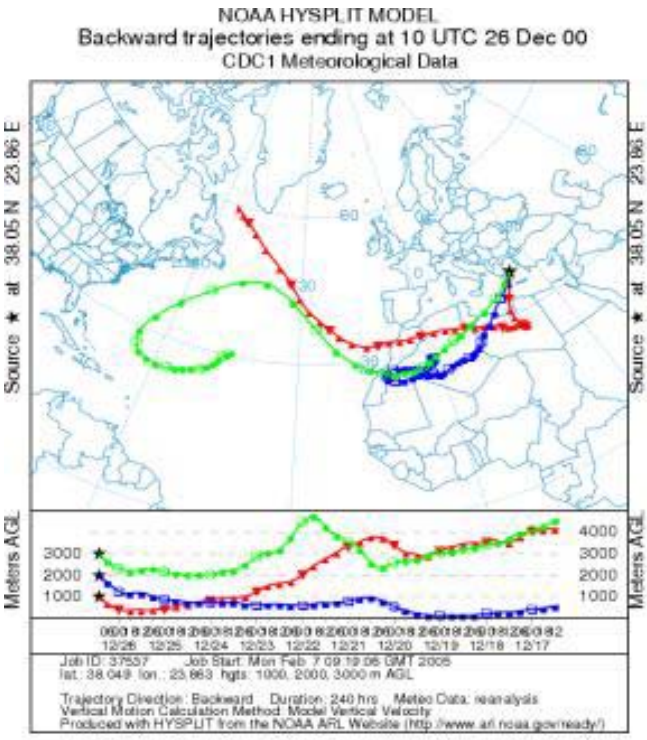
A different approach to investigate the origin of the water vapour that formed a specific precipitation event is by tracking the route of the air mass that delivered this precipitation. This is possible by calculating the back-trajectory of each air mass with a Lagrangian dispersion model. For this purpose we run the HYSPLIT transport and dispersion model from the READY website. We have obtained back trajectories for all episodes of the Pendeli station and classified them into seven categories. Figure 8 presents typical trajectories for each category.

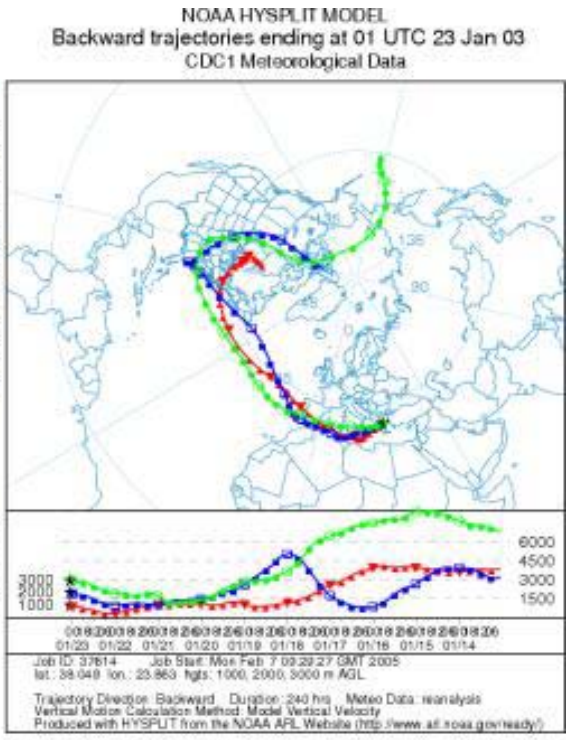
The main characteristics of these categories are:

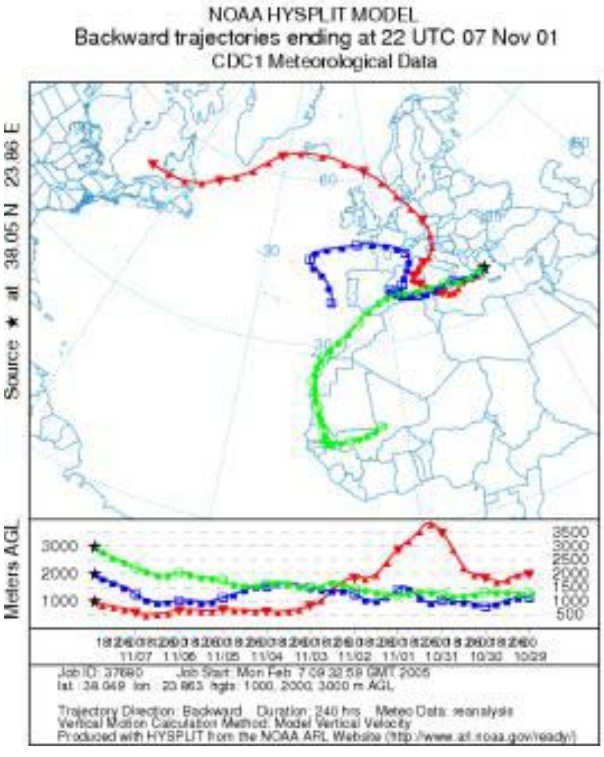
- Air mass formed in the Atlantic mid-latitudes passing below Morocco through Northern Sahara, enters the Mediterranean in the area of the Gulf of Syrti.
- Air mass formed in the Atlantic mid-latitudes passes through Gibraltar, and follows the North-African coastline entering the Mediterranean in the area of Sicily.
- Air mass formed in the Northern Atlantic passing from Southern France, enters the Mediterranean in the area of Marseilles moving southwards and then turns eastwards.
- Air mass formed in the Northern Atlantic/Arctic passing through Great Britain and France enters the Mediterranean in the area of the Gulf of Genoa moving southwards and then turns eastwards.
- Air mass formed in the mid-latitudes/northern Atlantic passing through Germany, over the Alps, enters the Mediterranean in the area of the Gulf of Genoa moving southwards and then turns eastwards.
- Air mass circling around of central and eastern Mediterranean.
- Air mass formed in the Arctic travels south through Northern Europe.

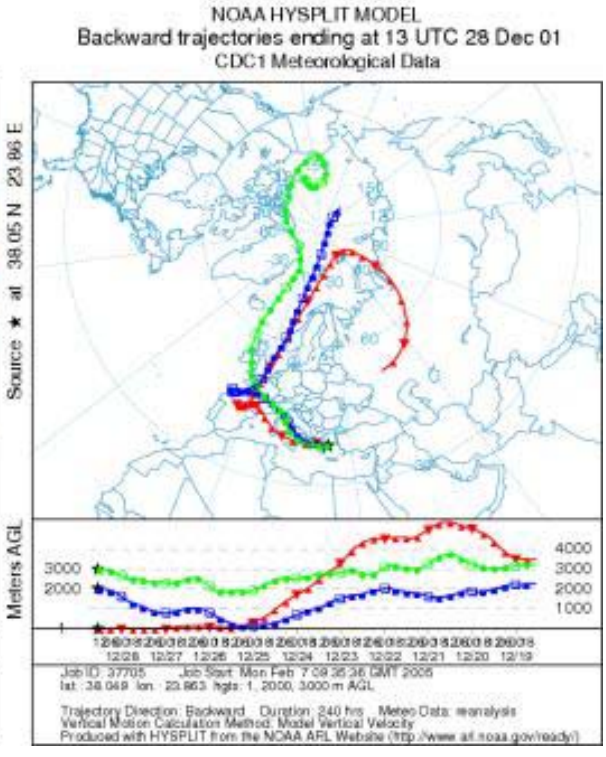
Figure 7 presents the (δ^2H, $\delta^{18}O$) values according to the back–trajectory classification, both on an event basis and on average, as well as the deuterium excess values for each category. It is obvious that adopting an event classification approach based on air mass origin alone is not adequate since there is large variation in all categories. On average though, there are some patterns that can be identified. More specifically, air masses of category 3 present the lowest d-excess value (12 ‰) as a result of their prolonged passage through the Mediterranean. Categories 1 and 7 form the next group with d-values around 15 ‰. Category 7 air masses exhibit a continental type depletion due to their course across Northern Europe. Category 1 has a behaviour similar to that of category 3, but the trajectory over the Saharan desert raises the temperature of the air mass, and allows its enrichment with water vapour of lower d-values upon its entry in the Middle of the Mediterranean. Similarly category 6 has an even higher d-excess value as a result of the circling of the air masses around the central and eastern Mediterranean. Air masses classified as type 4 and 5 have similar origin and the difference in their d-values could reflect the rainout depletion of masses type 5 over the Alps.

Finally, category 2 has the highest d-value (20 ‰), possibly due to the fact that this category is observed during late winter and early spring associated with the passage of cyclonic systems.


NOAA HYSPLIT MODEL
Backward trajectories ending at 10 UTC 26 Dec 00
CDC1 Meteorological Data
Source ★ at 38.05 N 23.86 E
Meters AGL
Job ID: 37537 Job Start: Mon Feb 7 09:19:06 GMT 2005
lat: 38.049 lon: 23.863 hgts: 1000, 2000, 3000 m AGL
Trajectory Direction: Backward Duration: 240 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Backward trajectories ending at 01 UTC 23 Jan 03
CDC1 Meteorological Data
Source ★ at 38.05 N 23.86 E
Meters AGL
Job ID: 37614 Job Start: Mon Feb 7 09:29:27 GMT 2005
lat: 38.049 lon: 23.863 hgts: 1000, 2000, 3000 m AGL
Trajectory Direction: Backward Duration: 240 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Backward trajectories ending at 22 UTC 07 Nov 01
CDC1 Meteorological Data
Source ★ at 38.05 N 23.86 E
Meters AGL
Job ID: 37690 Job Start: Mon Feb 7 09:32:59 GMT 2005
lat: 38.049 lon: 23.863 hgts: 1000, 2000, 3000 m AGL
Trajectory Direction: Backward Duration: 240 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)


NOAA HYSPLIT MODEL
Backward trajectories ending at 13 UTC 28 Dec 01
CDC1 Meteorological Data
Source ★ at 38.05 N 23.86 E
Meters AGL
Job ID: 37705 Job Start: Mon Feb 7 09:35:36 GMT 2005
lat: 38.049 lon: 23.863 hgts: 1, 2000, 3000 m AGL
Trajectory Direction: Backward Duration: 240 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

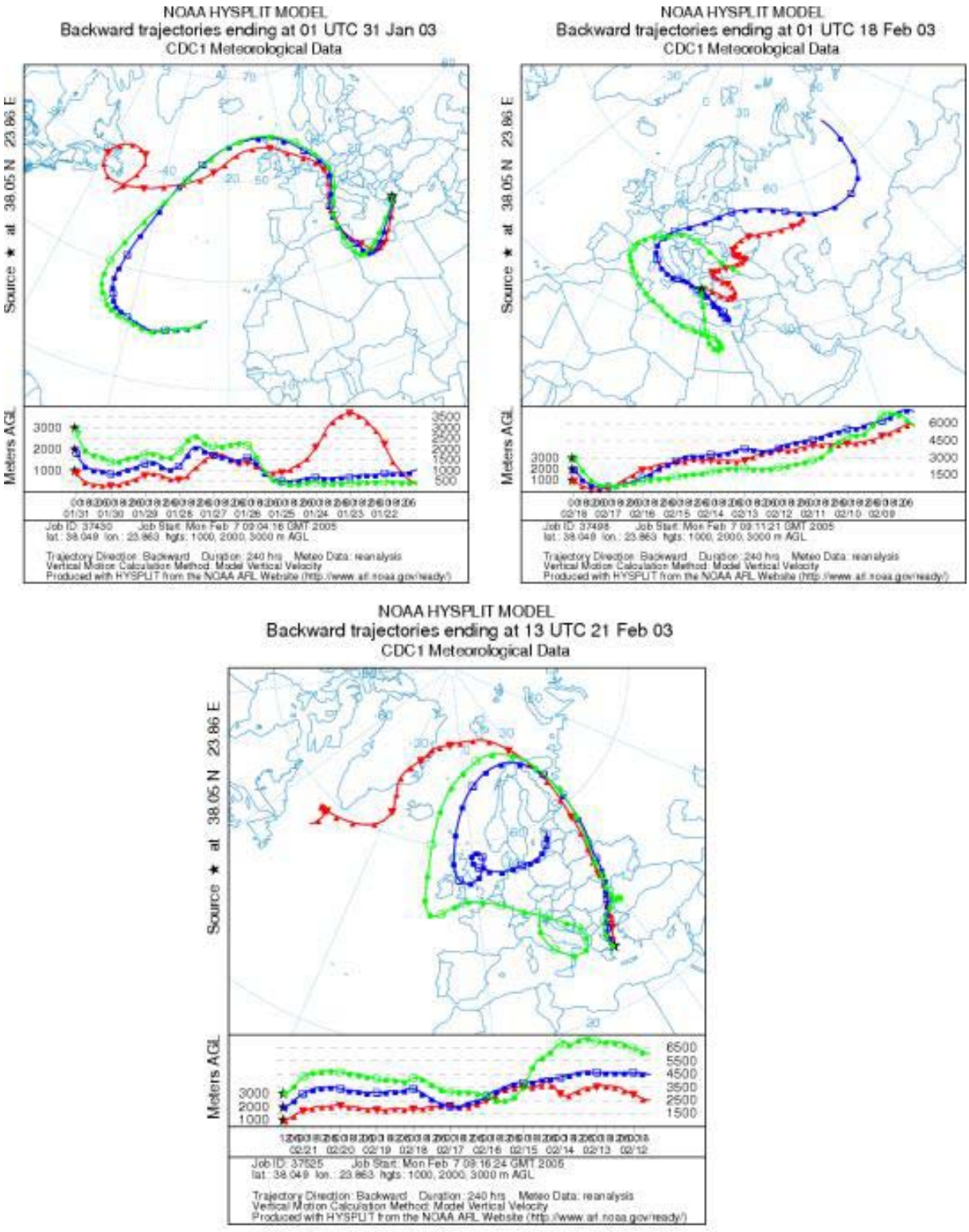


FIG. 7. Typical cases of back-trajectories.

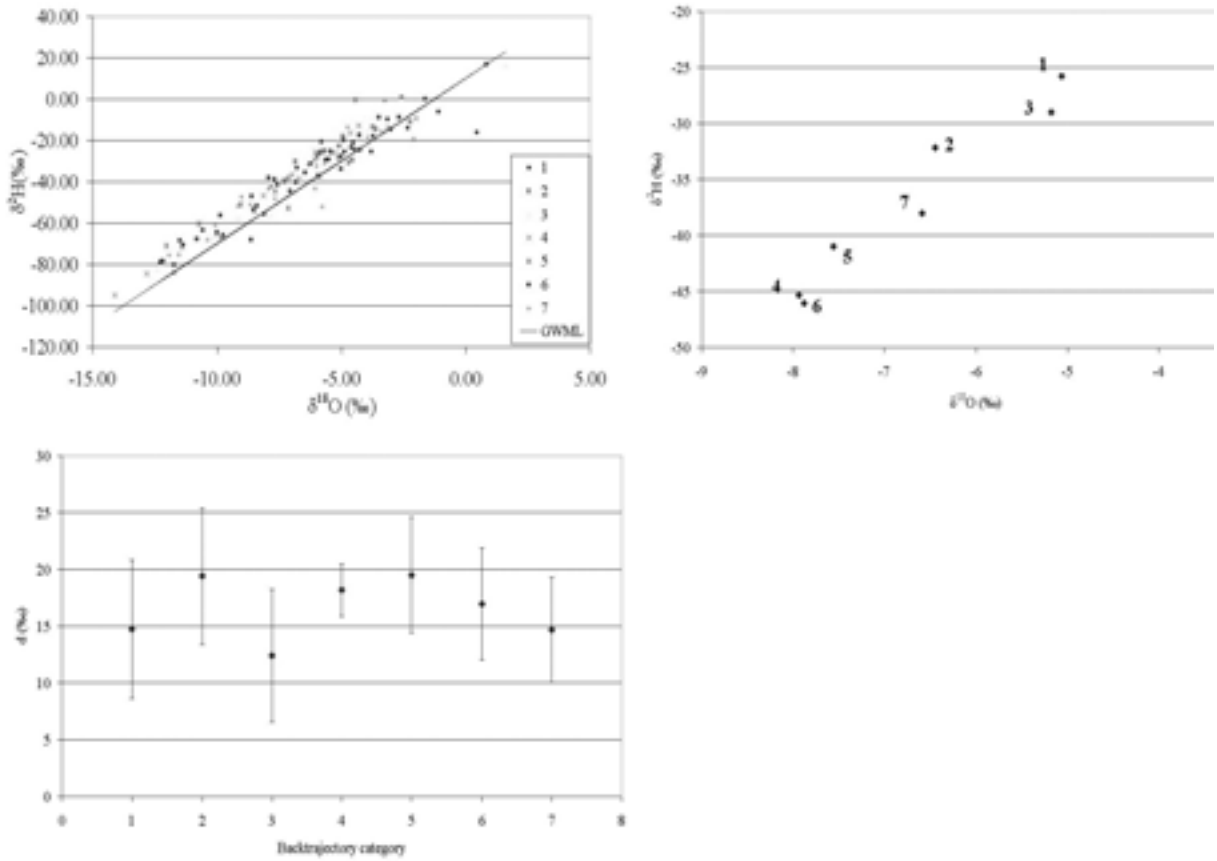


FIG. 8. δ^2H, $\delta^{18}O$ variation according to back-trajectory category.

2.1.7. Isotopic composition and cloud temperature.

Suzuki and Endo [3] studied the isotopic composition of rain in Central Japan during the winters of 1993/1994 and 1994/1995 and found that the $\delta^{18}O$ values correlate poorly with the ambient temperature, but have a satisfactory correlation with the cloud top temperatures as calculated by radiosonde data. The latest correlation improves even more when grouping the rain episodes according to their origin. This type of correlation was attempted for the Pendeli station events. In addition, the $\delta^{18}O$ values were correlated with cloud top temperatures calculated using infrared satellite images from METEOSAT. The obtained results for 15 rain episodes are shown in Figure 9. The obtained correlations are very poor.

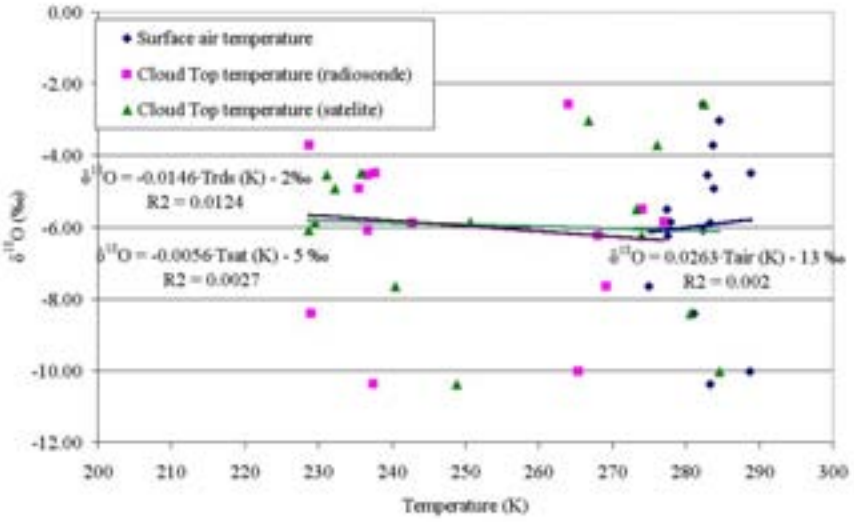


FIG. 9. $\delta^{18}O$= f(Cloud top temperature).

The correlation when grouping the data according to the mechanism of rain formation were also investigated. Figure 10 presents the results of these correlation for rains due to cold fronts. From this figure it is shown that the correlation between $\delta^{18}O$ and ambient temperature is bad (the two parameters are proportional and not inversely proportional) but $\delta^{18}O$ correlates well with the cloud top temperature calculated from the radiosonde data. The corresponding correlation with the cloud top temperature calculated from satellite images is very poor. This is due to the fact that there are significant random differences between the cloud top temperatures calculated by the two methodologies. One example could be that in case of multiple cloud layers, the satellite detects only the temperature of the upper layer, while the rain could have come from another layer. It should be noted however that this last finding is far from being conclusive due to the small number of episodes belonging in this category.

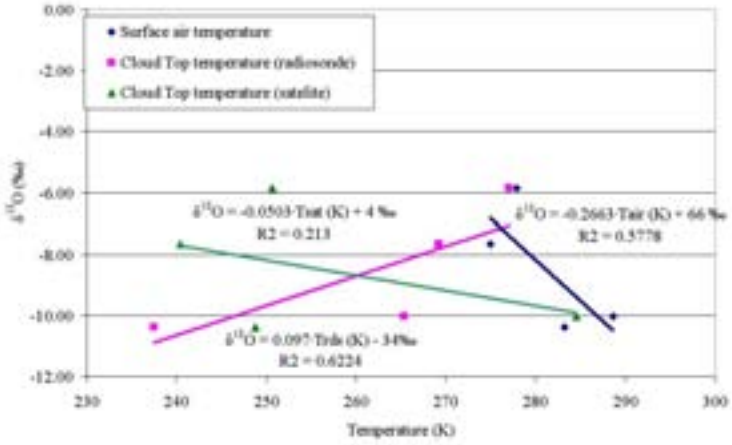


FIG. 10. $\delta^{18}O$ = f(Cloud top temperature) – Episodes due to cold fronts.

2.2. Tritium

The bulk of the tritium data comes from the 1960–1991 period and only a few from the current CRP. All the available results are illustrated in Figure 11.

For each curve of Figure 11, we calculated the slope of the line ln(TU) = a + b (Date) and found that these are not statistically different. Therefore the decrease rate of tritium concentration is practically the same for all the stations.

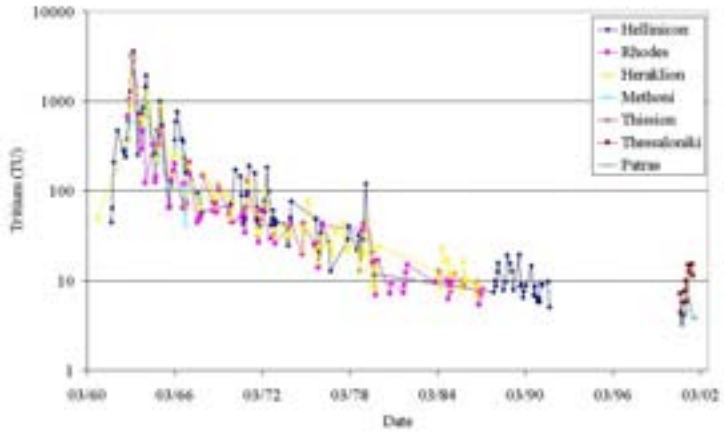


FIG. 11. Tritium profile.

The tritium variation follows the expected trend. The recent values are still too few in order to allow us to draw further conclusions.

3. Conclusions

The main conclusions that can be drawn from this preliminary analysis are:

The isotopic composition both of the monthly samples and of individual rain episodes shows characteristics intermediate of those that characterize the Eastern and Western Mediterranean.

The observed seasonal variations are as expected.

These intermediate characteristics are explained well by the correlation of the isotopic characteristics with the surface weather systems and the air mass trajectories, that define the history of the water vapour that forms the rain.

The $\delta^{18}O$ correlates better with the cloud top temperature as determined by radiosonde measurement rather than with the ambient temperature. This finding however requires further investigation.

Tritium exhibits the expected behaviour that is uniform over Greece.

ACKNOWLEDGEMENTS

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REFERENCES

[1] FLOCAS, A.A., Frontal depressions over the Mediterranean sea and central southern Europe. Mediterranee, 4 (1988) 43–52.
[2] FLOCAS, A.A., GILES, B.D., Distribution and intensity of frontal rainfall over Greece. International Journal of Climatology, 11 (1991) 429–442.
[3] SUZUKI, K., ENDO, Y., Oxygen isotopic composition of winter precipitation in central Japan. J. Geophys. Res., 106-D7 (2001) 7243–7249.

THE ISOTOPE COMPOSITION OF ATMOSPHERIC WATERS IN ISRAEL'S COASTAL PLAIN

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Abstract. During the project years from 2000-2003 the monthly sampling of precipitation at the GNIP - Rehovot station in the southern Israel coastal plain was augmented by weekly vapour sampling and event-based precipitation sampling. The three rainy seasons differed extremely in rain amount and pattern, but the isotope values were not too outstanding considering to the long-term scatter; there was only a weak correlation with the rain amounts, but a shift in the event-based spectral distribution of isotopes was noted, apparently dictated by the synoptic pattern. The isotopic composition of the vapour samples undergoes a marked seasonal cycle, with d-excess values up to +40‰ in winter. The difference in $\delta^{18}O$ between the vapour and rain on the rainy days was usually close to the equilibrium value for the prevailing temperature.

1. Introduction

Precipitation sampling for tritium analysis in the southern coastal plain was started at Rehovot during the 1958/59 rainy season and reported in Ref. [1]. As of the 1960/61 rainy season, stable isotope analyses of monthly-lumped precipitation samples at Bet-Dagan (measured at first in the laboratory of Prof. Dansgaard in Copenhagen and since 1966 at the Rehovot Isotope Laboratory of the Weizmann Institute) were added to the tritium measurements. Bet-Dagan was then incorporated into the GNIP network along with other stations in the eastern Mediterranean area. Results were reported in [2], [3] as well as in publications of the IAEA [4]. Vapor sampling was first performed sporadically at Rehovot in 1963 and 1964 [5] and systematically from Jan. 1969 to the end of October 1970 by Y. Tzur [6].

The routine precipitation sampling was augmented from time to time by more detailed sampling campaigns, both in space and time, including the sampling of individual rain events and fractions of some rain showers. To be especially mentioned is the work of M. Rindsberger [7] and the IAEA-sponsored project 4793/RB on "*The detailed isotope anatomy of a rain shower*" conducted from 1987 to 1991. Both these included sampling of rain events both in the coastal plain and in transects to other areas of the country. Additional data are available in conjunction with hydrological and ecological studies in diverse regions of the country, e.g. in Jerusalem [8] and throughout the Negev Desert area [9–12].

More recently, from the 1990/91 season to the end of 1997, monthly samples of precipitation from Bet-Dagan were analyzed for Oxygen-18, but Deuterium analyses are available for only part of these samples {*Boatto, priv. communication*}. Since 1995 all rainfall events are being sampled in the Judean foothills at Sorek Cave as part of the "Speleothem Project" of the Israel Geological Survey [18] and this has been extended to five additional sites in 1998. Since 1998 event-based sampling of precipitation has also being carried out at Rehovot (about 10 kms south of the GNIP station of Bet-Dagan) by the team of the Weizmann Institute. The coordinates of the Bet-Dagan and Rehovot stations, respectively, are as follows:

Bet-Dagan	32º00'N / 34º49'E with altitude of 30m (asl)
Rehovot	31º54'N / 34º49'E at an altitude about 50m (asl).

Starting from January 1998, vapor collection is being conducted a few times a week at the Weizmann Institute at Rehovot, usually during daytime for a period of about seven hours. More recently, the diurnal change is being explored by occasional round-the-clock vapor sampling.

2. Summary of past findings

Precipitation in Israel occurs primarily during the winter months and is characterized by a d-excess value larger than that of the GMWL, close to d = 20‰ on the average. The average seasonal march is shown in Fig.1.

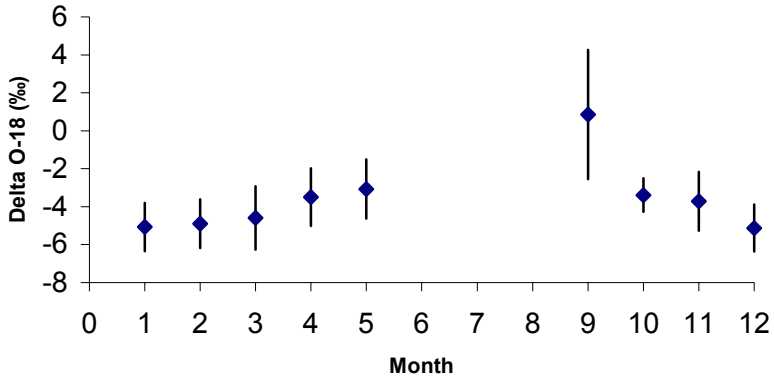


FIG. 1: Average seasonal O-18 values of precipitation in Israel (Bet-Dagan).

The regression line for the monthly composites in δ-space at the GNIP station Bet-Dagan for the period of 1961 to 1987 was:

$$^{2}\delta = 5.48\,^{18}\delta + 6.87(‰) \quad (r^2 = 0.695)$$

with the weighted mean $^{18}\delta = (-5.02 \pm 0.55)‰$ and the d-excess = 18.4 ‰.

In the mountain station of Har-Kna'an (Tirat-Yael) the corresponding value was:

$$^{2}\delta = 5.91\,^{18}\delta + 8.73(‰) \quad (r^2 = 0.71)$$ and d-excess = 23.2 ‰ [4]

Undoubtedly, these trends are strongly biased by the values for the transition months in spring and autumn (which are characterized by relatively enriched isotopic values and low d-excess numbers); the values for November to March form a much tighter cluster.

For the period of 1961-1990, with a seasonal average of (543±164) mm of precipitation, the amount-weighted average of the isotopic composition was

$^{18}\delta = -4.70 \pm 0.60‰$ with $^{18}\delta = -5.15‰$ for the mid-winter months of Dec-March [3]

The apparent slight disparity with the averages reported in [4], probably are due to a re-calibration of the isotopic measurements in the early sixties. Between 1990-1997 the corresponding values were respectively:

$^{18}\delta = (-5.16 \pm 0.58)‰$ and –5.3‰, for rain amounts of (573 ±164) mm.

Whereas there is a residual correlation of the data with the amount of precipitation both for the monthly and annual averages, alas often masked by the large scatter due to other causes, it was found that the overall determining factors for the isotope composition of the precipitation (both the δ-values as well as that of the d-excess) is the synoptic history of the air masses concerned [10], [14], [15]

including the rainout history along the flow path. The local rain intensity is a factor to a lesser degree [16].

3. Precipitation at Rehovot during the years 2000–2003

As shown in Table 1, these three rainy seasons differed widely in their rain yield being 255, 579 and 785 mms, respectively; not only the total yield differed widely but also the distribution of rain amounts throughout the rainy season, notably the late start of the rains during 2000/2001 and very strong rains towards the end of the third season (2002/2003). The weighted mean values of $^{18}\delta$ for all precipitation during these three rainy seasons were $^{18}\delta$ = -4.76‰; -5.61‰ and -5.67‰; the corresponding d-excess values were d = 19.7‰, 19.9‰ and 23.3‰, respectively.

Table 1. Monthly amount weighted averaged isotope data of precipitation at Rehovot, 2000–2003, compared to the long-term average at the Bet-Dagan station

	Bet-Dagan (average)	2000–2001			2001–2002			2002–2003		
Month	$\delta^{18}O$ and rain amount (mm)	Rain amount mm*	$\delta^{18}O$ ‰	d-excess ‰	Rain amount mm*	$\delta^{18}O$ ‰	d-excess ‰	Rain amount mm*	$\delta^{18}O$ ‰	d-excess ‰
Sept.	0.86	-	-	-	-	-	-	-	-	-
Oct.	-3.39 25	-	-	-	29.6 (4)	-2.91	13.4	6.6 (2)	-2.00	17.9
Nov.	-3.72 69	0.9 (2)	-1.66	5.3	51.7 (6)	-2.70	17.6	19.0 (4)	-0.99	15.2
Dec.	-5.13 137	87.6 (10)	-5.30	23.0^	146.6 (7)	-7.11	18.6	176.6 (13)	-5.21	20.3
Jan.	-5.07 142	87.8 (9)	-5.06	18.7^	174.8 (13)	-5.70	23.5^	86.1 (5)	-6.33	17.3
Feb.	-4.90 77	67.1 (10)	-4.08	20.5^	71.4 (4)	-4.88	-	311 (14)	-5.96	27.7
March	-4.59 57	1.7 (1)	-4.85	-	80.15 (5)	-5.64	-	168 (9)	-5.94	23.2
April	-3.50 19	-	-	-	24.7 (2)	-7.84	-	17 (2)	-4.97	12.2
May	-3.07 2	5.7 (1)	-0.19	8.1	-	-	-	-	-	-
Seasonal total		254.7	-4.76	-	578.9	-5.61	-	784.3	-5.67	23.2

* - number of rain events sampled per month are shown in brackets (n).

^ - partial summary, with some missing data.

As shown in Table 2 and Fig.2, the changes are caused by shifts in the spectral distribution of the isotopic values. Such a feature was already seen in previous years [15] and is apparently correlated with changes in the synoptic patterns. This aspect needs further study. Notable are a few rain events during midwinter of 2001/2002 with extremely depleted values of $^{18}\delta \leq$ -8‰.

Table 2. Number of precipitation event with Oxygen-18 in range per season (#)

				Normalized		
≤ δ ≥	#(00/01)	#(01/02)	#(02/03)	# (00/01)	#(01/02)	#(02/03)
-10/-9	-	1	-	0	0.03	0
-9/-8	-	2	-	0	0.05	0
-8/-7	2	3	4	0.075	0.08	0.08
-7/-6	6	3	7	0.22	0.08	0.15
-6/-5	2	3	12	0.075	0.08	0.25
-5/-4	6	5	6	0.22	0.14	0.125
-4/-3	8	8	7	0.3	0.22	0.15
-3/-2	1	8	5	0.04	0.22	0.105
-2/-1	1	3	3	0.04	0.08	0.07
-1/0	1	-	4	0.04	0	0.08

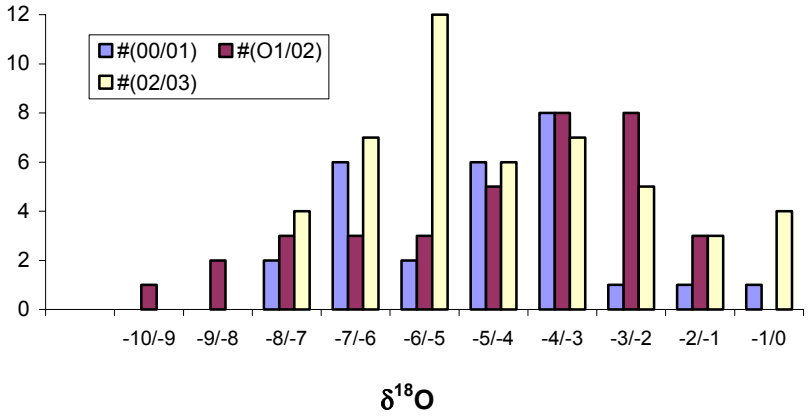


FIG. 2a: Number of weighted mean values of $\delta^{18}O$ of precipitation at Rehovot from 2000 to 2003 for the range indicated.

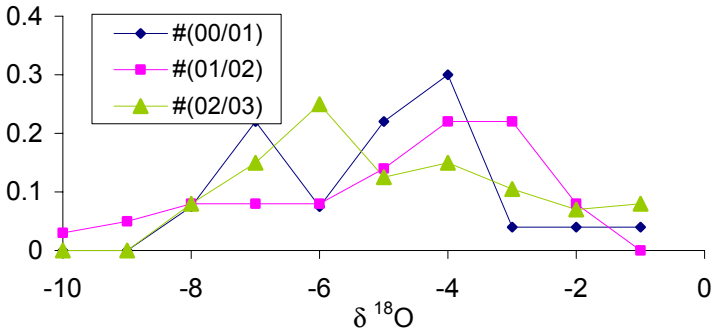


FIG. 2b: Spectral distribution of the $\delta^{18}O$ values of precipitation at Rehovot.

Compared to the average monthly values and their long-term variability, shown in Fig.1, the most outstanding data are for Nov. 2000 and Oct. and Nov. 2002 where the values are enriched, and for Dec. 2001 and April 2002 with very depleted values. Moreover, all data from the second half of the winter are depleted relative to the long-term averages reported in IAEA [4] although within the long-term scatter. There is only a weak correlation of the isotopic values with the measured rain amounts.

4. Atmospheric Moisture (vapor collection) at Rehovot, 2000–2004

The isotopic composition of the vapor samples undergo the marked seasonal cycle noted before [6], with $^{18}\delta$ values between -13‰ and -9‰ and the d-excess of 5‰ ≤ d ≤ 22‰ in summer. Winter values are more scattered ranging between 10‰ ≤ $^{18}\delta$ ≤ -18‰ and with d-excess values up to +40‰. The data from spring and autumn follow a trend line between these two seasonal values. Samples from rain days often show the most extreme values.

The results are summarized on a plot of d-excess vs. $^{18}\delta$ in Figs. 3 to 7 (values are shown in ‰).

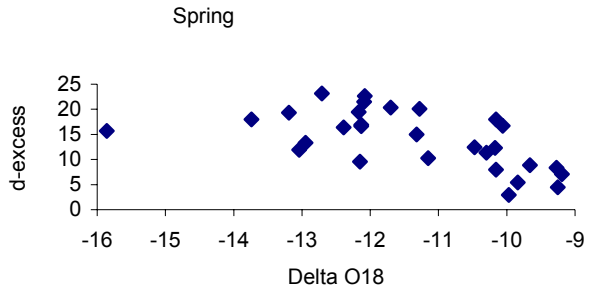


FIG. 3: d-excess vs. $\delta^{18}O$ in water vapour collected at Rehovot during spring periods.

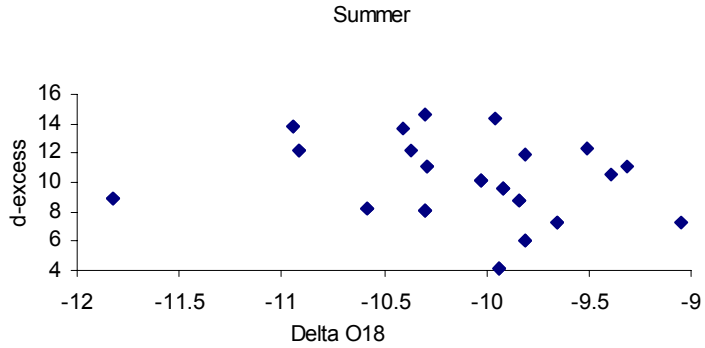


FIG. 4: d-excess vs. $\delta^{18}O$ in water vapour collected at Rehovot during summer periods.

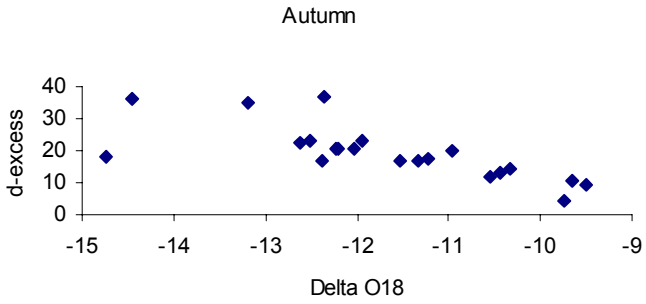


FIG. 5: d-excess vs. $\delta^{18}O$ in water vapour collected at Rehovot during automn periods.

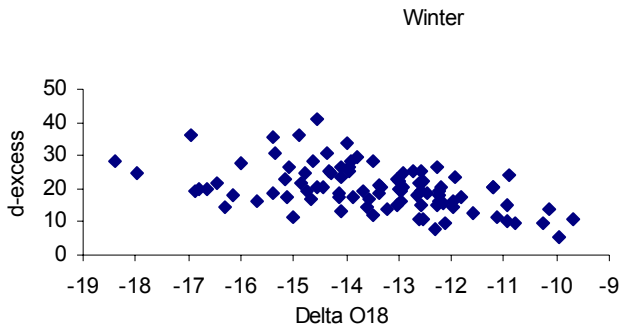


FIG. 6: d-excess vs. $\delta^{18}O$ in water vapour collected at Rehovot during winter periods.

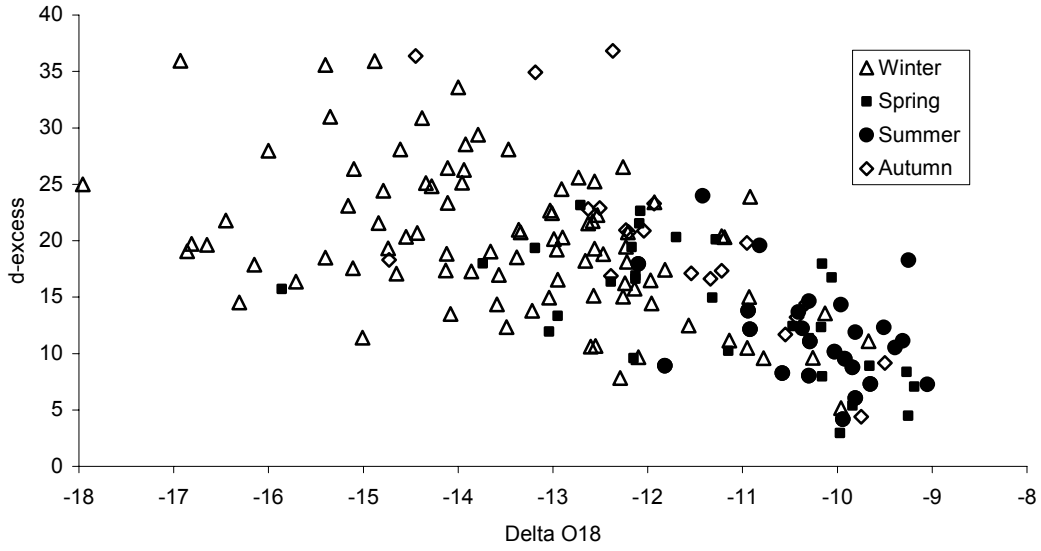


FIG. 7: d-excess vs. $\delta^{18}O$ in all water vapour samples collected at Rehovot during period 2000-2003.

The overall trend line for all samples is given by: $^{2}\delta = 5.^{18}\delta - 18.5(‰)$ [$r^2 = 0.60$], which translates into the correlation: $d = -3.\ ^{18}\delta - 18.5(‰)$.

A weak temperature dependence of the data [$r^2 = 0.34$] is obviously a reflection of the seasonal pattern rather than pertaining to the individual samples.

On 21 occasions where vapor data on rainy days were available (Table 3), the difference in $^{18}\delta$ between the vapor and rain was usually close to the equilibrium value for the prevailing temperature. With the exception of two cases in late autumn of 2001, the difference in the value of the d-excess was within the large analytical error for such a comparison, which is estimated to be ± 5 ‰. One needs to consider, however, that the time span for the vapor and precipitation sampling is not the same in most instances.

Table 3. Comparison of isotope data of vapour and precipitation at Rehovot (all given in ‰)

Date	Rain amount mm	$\delta^{18}O$ (‰)	d-excess (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	$\Delta\delta$ (^{18}O) (‰)	Δd (‰)
		Rain		Vapor			
03.12.00	4.35	-6.88	15.2	-16.81	19.7	9.9	+4.5
10.12.00	5.8	-6.78	15.9	-15.16	23.1	9.4	+7.2
13.12.00	0.8	-6.23	20.0	-16.0	28	9.7	+8.0
23.01.01	4.7	-4.48	20.6	-14.74	19.3	10.3	-1.3
25.01.01	27	-5.26	19.7	-14.65	19.7	9.4	0
04.02.01	10.7	-3.18	20.7	-10.93	15	7.75	-5.7
15.02.01	12.7	-3.76	20.85	-11.82	17.4	8.1	-3.4
28.10.01	12.9	-3.45	15.7	-13.81	39	10.4	+23.3
18.11.01	27.6	-3.70	18.1	-14.56	41	10.9	+22.9
03.01.02	9.7	-3.84	21.85	-13.94	26.3	10.1	+4.4
16.12.02	3.4	-2.63	21.35	-13.04	14.9	10.4	-6.5
19.12.02	3.5	-2.68	22.85	-12.24	16.25	13.6	-6.6
23.12.02	2.3	-0.76	21.2	-12.26	26.5	11.5	+5.3
26.12.02	4.8	-4.02	17.9	-13.59	14.35	9.6	+0.3
20.01.03	7.2	-5.59	13.5	-15.71	16.3	10.1	+2.8
10.02.03	12.6	-3.54	28.25	-13.01	22.45	9.5	+0.2
20.02.03	16.3	-6.95	22.8	-12.56	19.3	5.6	-3.5
24.02.03	2.5	-4.11	24.45	-14.61	28.05	10.5	+3.6
13.03.03	12.1	-5.16	18.1	-12.14	15.75	7.0	-2.3
20.03.03	3.6	-3.31	18.1	-13.36	20.95	10.05	+2.8
28.04.03	10.9	-5.62	12.85	-12.95	13.35	7.3	+0.5

It is of interest to note that the isotope composition of vapor samples collected all over the Mediterranean during the cruise of the Research Vessel "Meteor" in January 1995 [17] fall inside the field of the Rehovot data set, which indicates that some of the air masses that penetrate to our shores maintain their marine characteristics.

The general validity of these observations, using the data from previous years within their meteorological and synoptic context is now being examined. One salient feature already detected is exemplified by the case of the period of May 17 to May 23, 2001 where a drop of the *d-excess* value from 23,15 to 5.4 is on record with a commensurate change of the δ values, It appears that in this case the vertical mixing of the air column above the sea was an important factor; during these days the height of the inversion layer above the coastline dropped from more than 1000 m to less than 500 m {*Information provided by P. Alpert of Tel-Aviv University}*.

A detailed (backtracking) trajectory analysis was performed by H. Wernli for the periods of May 13-24, 2001; August 9–23, 2001 and March 31–May 5, 2003, including data on the vertical stability of the air masses concerned. Singling out the May 2001 and April 2003 periods (see Table 4 and Figs 8 and 9) it appears, however, that changes in both the air trajectory and stability of the air masses are

involved in determining the isotopic composition. Thus during May 2001 (Fig. 8) the prolonged sojourn of the air-masses over the Mediterranean prior to May 22 enabled the establishment of marine characteristics with a low d-excess value at that time. In contrast, as shown in Fig.9 during the period from March 31 to May 5, 2003, the lower d-excess values ranging from d=8‰ to d=10.25‰ were associated with air-masses with a continental trajectory over the north African continent (April 3 and 7) or over the eastern Levant (May 4 and 5), whereas the classical routes over the eastern Mediterranean resulted in higher d-excess values, e.g. for March 31, April 10 and April 24 under relatively high stability of the air-masses. Evidently the role of stability all along the trajectory needs to be carefully investigated for these varying synoptic situations.

It is to be further noticed that on a few occasions when the vapor sampling was extended to 24 hours, specifically on the Nov. 20 and Nov. 27, 2001 and Febr. 3, 2002, the $^{18}\delta$ values were more enriched by 2.5‰ on the average when compared to the daytime samples, presumably due to the more stable air column at night.

Table 4. Selected vapour data from Rehovot

Date	$^{18}\delta$(‰)	$^{2}\delta$(‰)	d-excess(‰)	Stab-1	Traj#
13/05/2001	-11.32	-75.6	+14.95	5.31	1b
15/05/2001	-12.63			4.65	1a
17/05/2001	-12.71	-78.5	+23.15	6.75	1a
20/05/2001	-9.89			3.54	5
22/05/2001	-9.84	-73.3	+5.42	3.37	6
24/05/2001	-10.47	-71.3	+12.46	3.00	6?
09/08/2001	-9.65	-69.9	+7.3	6.91	1
12/08/2001	-9.30			2.00	1
14/08/2001	-10.29	-7.3	+11.05	4.41	3, 1
19/08/2001	-11.38			2.13	1
31/03/2003	-12.66	-8.1	+18.2	4.45	5
03/04/2003	-10.16	-73.3	+8.0	2.34	7
07/04/2003(24 hrs)	-12.15	-86.6	+9.6	1.67	3, 4
10/04/2003	-12.39	-82.7	+16.4	6.19	1a,3
14/04/2003	-11.15	-79.0	+10.25	4.42	6
24/04/2003	-15.86	-111.2	+15.7	6.67	1a,4
28/04/2003	-12.95	-90.3	+13.5	4.99	2
05/05/2003	-9.66	-68.4	+8.9	4.26	5

* Stab-1 is the averaged value of the vertical the difference between (lon,lat,p+50hPa) and (lon,lat,p-50hPa) calculated for every trajectory at the closest position to Rehovot where ECMWF data were available, subject to the limitation that these are available only every six hours.

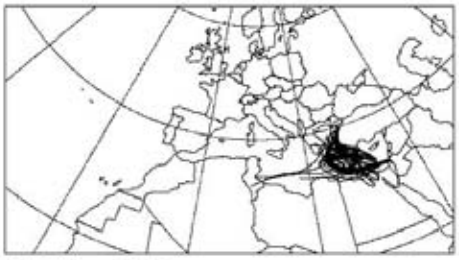
Classification of trajectory backtracks:

#1a - classical from Europe through Aegean and north-eastern Mediterranean
#1b – from Europe through Aegean and south-eastern Mediterranean
#2 – over eastern Med. from Eastern Europe via Turkey
#3 - from Western Europe along axis of central and eastern Mediterranean
#4 – from the west over North Africa
#5 – from the north over lands of the Levant (no contact with Mediterranean)
#6 – local, from eastern Mediterranean
#7 – from south, Red-Sea area

All trajectories for one day started every 2 hours between 06 and 18 UTC at Rehovot. Trajectories have been started on model levels 1,3,5 and 7, 96 hours backward in time.

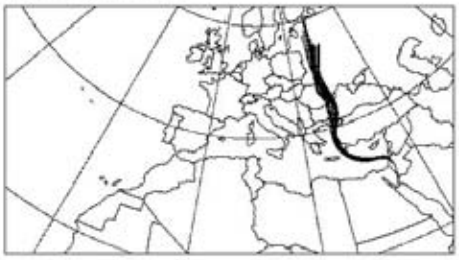
13 May 2001

14 May 2001



15 May 2001

16 May 2001



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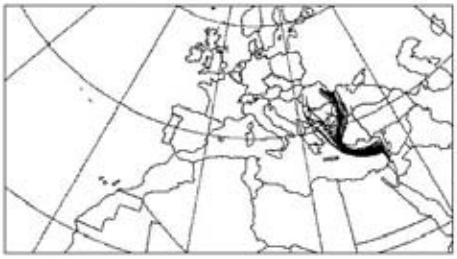


18 May 2001

19 May 2001

20 May 2001

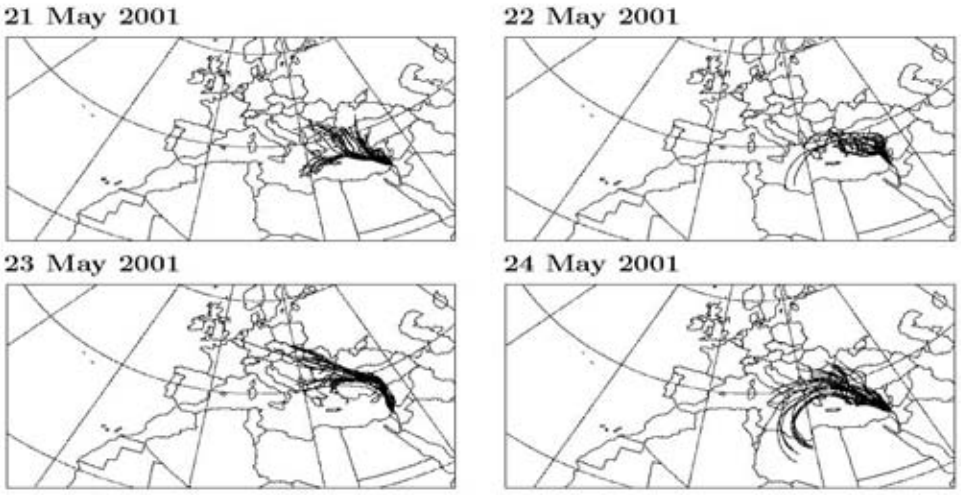


FIG. 8. Backtracking trajectory analysis in May 2001.

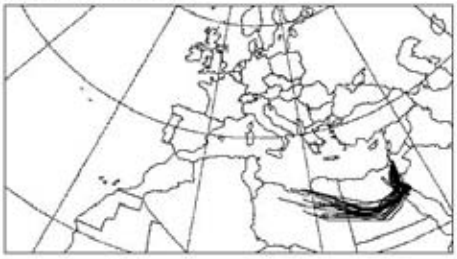
31 March 2003

01 April 2003

02 April 2003

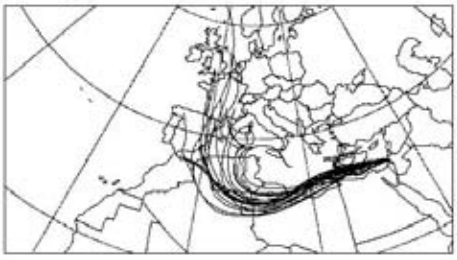
03 April 2003

04 April 2003

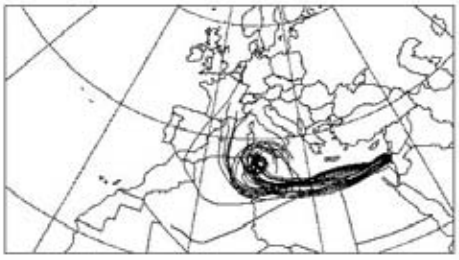


05 April 2003

06 April 2003



07 April 2003



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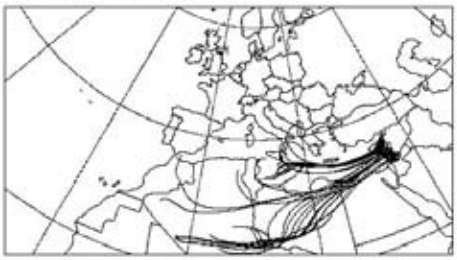

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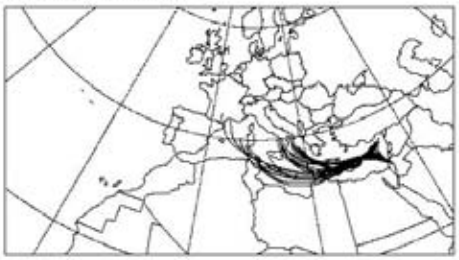

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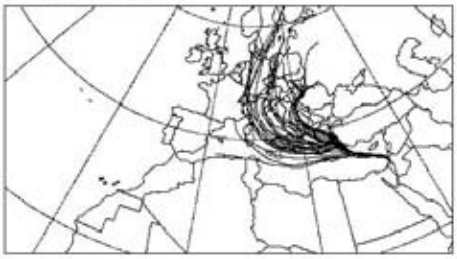

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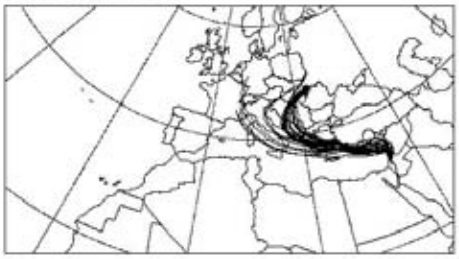

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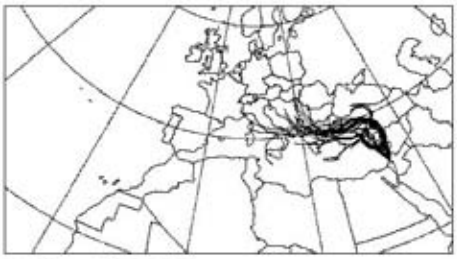

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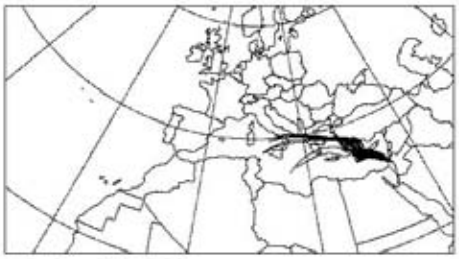
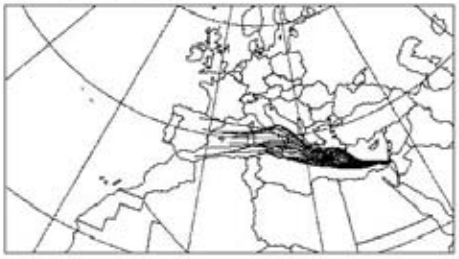
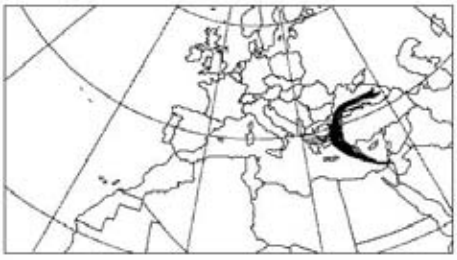


14 April 2003

15 April 2003



16 April 2003



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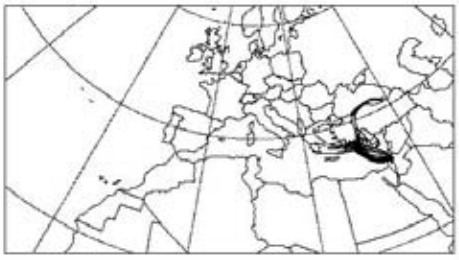

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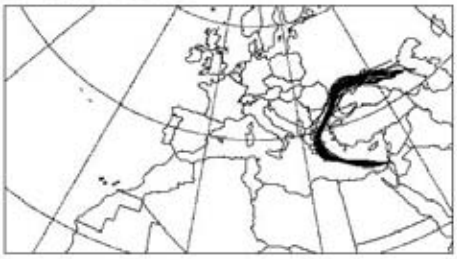

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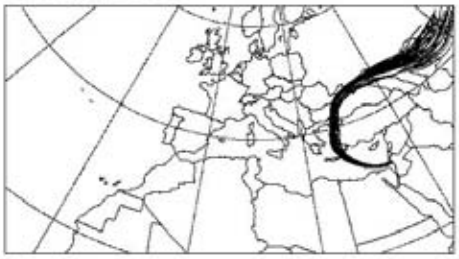

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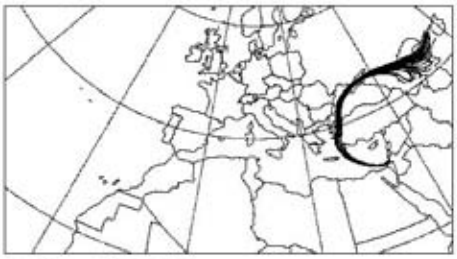

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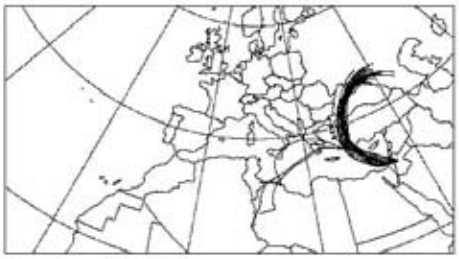

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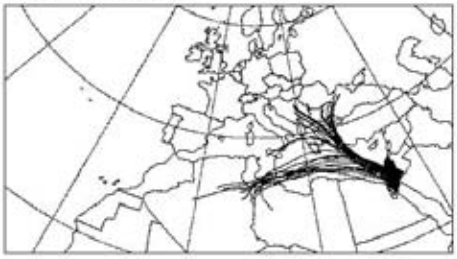

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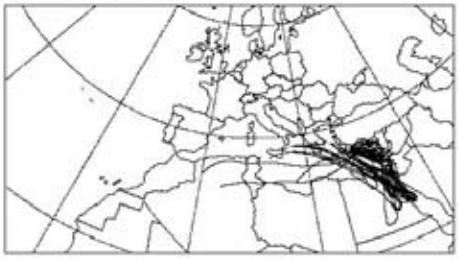

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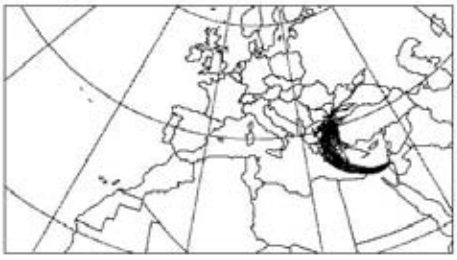
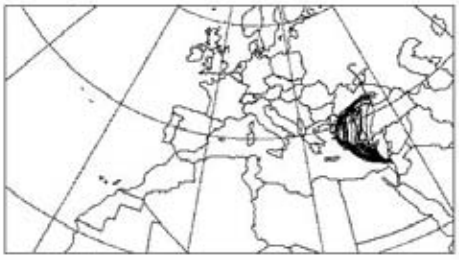
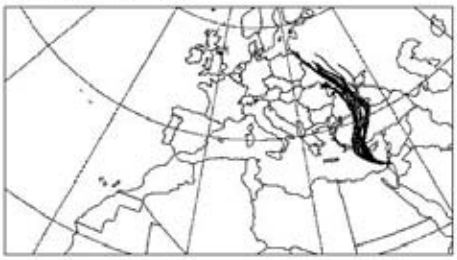


27 April 2003



28 April 2003



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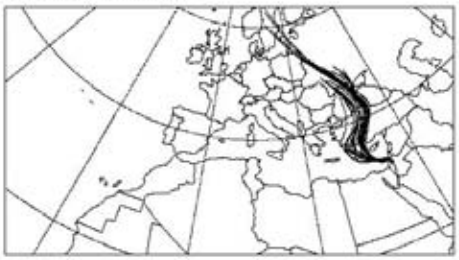

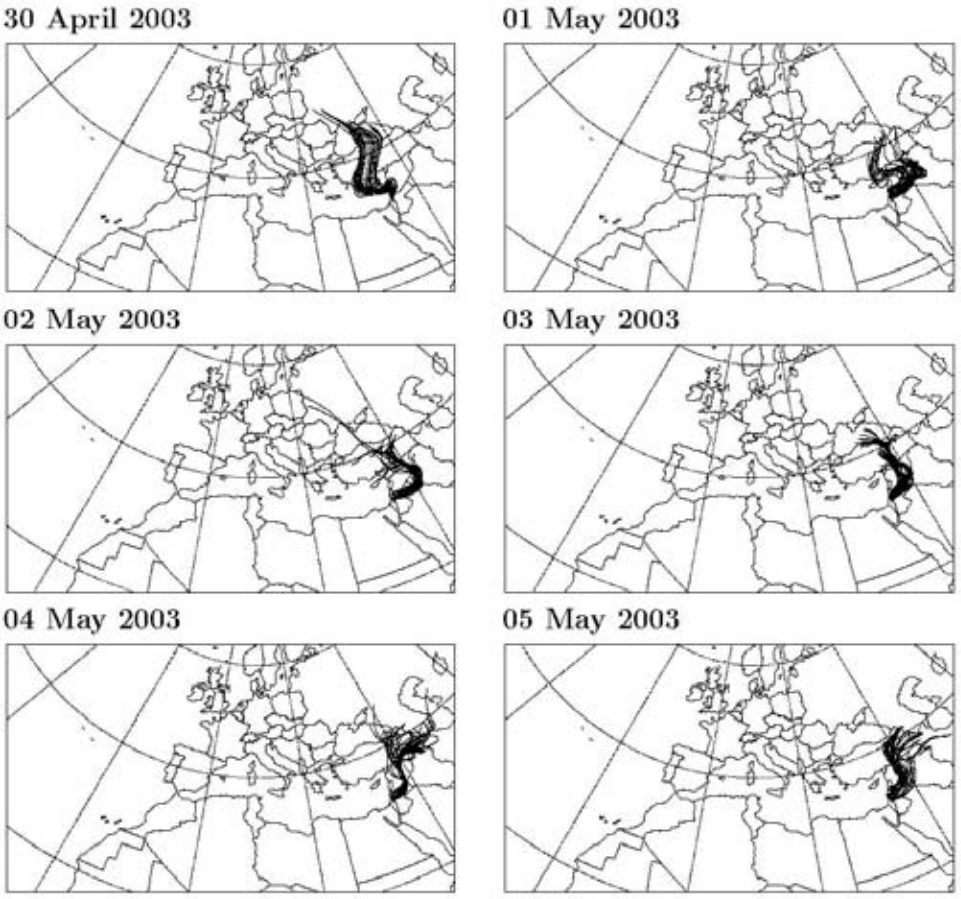

FIG. 9. Backtracking trajectory analysis from March to May 2003.

REFERENCES

[1] GAT, J.R., KARFUNKEL, U. NIR, A., Tritium content of rainwater from the eastern Mediterranean area, In: Tritium in the Physical and Biological Sciences, IAEA 1 (1962) 41–54.

[2] GAT, J.R., DANSGAARD, W., Stable isotope survey of freshwater occurrences in Israel and the Jordan Rift Valley, Journal of Hydrology 16 (1972) 177–211.

[3] GAT, J.R., CARMI, I., BAUMAN, N., The isotopic composition of precipitation at Bet-Dagan, Israel: the climatic record (1961-1990). Israel Meteorological Research Papers 5 (1994) 10–19.

[4] International Atomic Energy Agency, Statistical Treatment of Data on Environmental Isotopes in Precipitation, Technical Reports Series No. 331, IAEA, Vienna (1992).

[5] GAT, J.R., The isotopic composition of atmospheric waters in the Mediterranean Sea area and their interpretation in terms of air-sea interactions, In: Rapp. Comm. Int, Mer Medit. 19 (1969) 923-926.

[6] TZUR, Y., Isotope effects in the evaporation of water into air, Ph.D. thesis, The Weizmann Institute of Science, Rehovot (1971).

[7] RINDSBERGER, M., YAFFE, S., RAHAMIM, S., GAT, J.R. , Pattern of the isotopic composition of precipitation in time and space: data from the Israeli storm water collection program, Tellus 42B (1990) 263–271.

[8] WINDERBAUM, S.. MSc. Thesis, Dpt. of Meteorology, Hebrew Univ., Jerusalem (1992).

[9] LEVIN, M., GAT, J.R., ISSAR, A., Precipitation, flood and groundwaters of the Negev Highlands: an isotopic study of desert hydrology, In: Arid Zone hydrology; Investigations with Isotope Techniques, IAEA-AG-158 (1980) 3–23.

[10] LEGUI, C., RINDSBERG, M., ZANGWIL, M., ISSAR, A., GAT, J.R., The relation between the oxygen-18 and deuterium contents of rainwater in the Negev Highlands and air mass trajectories, Isotope Geosciences 1 (1983) 205–218.

[11] GAT, J.R., Variability (in time) of the isotopic composition of precipitation: consequences regarding the isotopic composition of hydrologic systems (Proceedings of a symposium on Use of Isotope Techniques in Water Resources Development), STI/PUB/757, IAEA, Vienna (1987) 551-563.

[12] GOODFRIEND, G.A., MAGARITZ, M., GAT, J.R., Stable isotope composition of land snail body water and its relation to environmental waters and shell carbonate, Geochim. Cosmochim. Acta 53 (1989) 3215–3223.

[13] AYALON, A., BAR-MATTHEWS, M., SASS, E., Rainfall-recharge relationships within a karstic terrain in the eastern Mediterranean semi-arid region, Israel. Journal of Hydrology 207 (1998)18-31.

[14] GAT, J.R., RINDSBERGER, M., The isotopic signature of precipitation originating in the Mediterranean sea area: a possible monitor of climate modification, Israel J. of Earth Sciences 34 (1985) 80–85.

[15] GAT, J.R., CARMI, I., Effect of climate changes on the precipitation pattern and isotopic composition of water in a climate transition zone; -case of the Eastern Mediterranean area, In: The Influence of Climate Change and Climate Variability on the Hydrologic regime and Water resources, IASH 168 (1987) 513–523.

[16] GAT, J.R., ADAR, E., ALBERT, P., Inter- and intra storm variability of the isotope composition of precipitation in southern Israel: -are local or large scale factors responsible? (Proceedings of an International Conference on the study of environmental change using Isotope Techniques), C&S Papers Series 13/P, IAEA, Vienna, (2000) CD-ROM.

[17] GAT, J.R., KLEIN, B., KUSHNIR, Y., ROETHER, W., WERNLI, H., YAM, R., SHEMESH, A., Isotope composition of air moisture over the Mediterranean Sea: an index of the air-sea interaction pattern. Tellus, 55B (2003) 953–965.

STABLE ISOTOPES ($\delta^{18}O$, $\delta^{2}H$) AND TRITIUM IN PRECIPITATION: RESULTS AND COMPARISON WITH GROUNDWATER PERCHED AQUIFERS IN CENTRAL ITALY

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Abstract. This report includes the isotopic results obtained on precipitation samples collected at nine monitoring stations in Italy. The work was carried within the framework of the current CRP on "Isotopic Composition of Precipitation in the Mediterranean Basin in relation to Air Circulation Patterns and Climate". Stable isotopes analyses were carried out for monthly and daily precipitation samples, while tritium analyses were performed for monthly samples only. The isotopic composition of precipitation is compared with that of groundwater in perched aquifers.

1. Introduction

We report here the isotopic results obtained on precipitation samples collected at nine Italian monitoring stations. These stations, six of which located in western-central Italy (Bono Research Unit), one in northern Italy (D'Amelio Research Unit), and two in Sardinia (Barrocu Research Unit), are part of a larger network originally planned for the whole country.

The location of Italian stations is shown in Fig. 1. For various reasons, at stations other than the nine reported here (indicated by numbered spots in the map), sampling and isotope analyses could be implemented only in part, and the results are not included in this report.

The collection of precipitation samples started in 1998 and was carried out for the Research Agreement awarded by IAEA within the framework of the current CRP "Isotopic Composition of Precipitation in the Mediterranean Basin in relation to Air Circulation Patterns and Climate". The project main investigator was first R. Gonfiantini and later P. Bono. Stable isotopes analyses were carried out on monthly and daily precipitation samples, while *tritium* analyses were performed on monthly samples only.

In detail, the Central Italy stations approximately lay along a transect first oriented South-North along the Tyrrhenian Sea coast and then West-East. From the sea to the Apennines (Simbruini mountains), at about 120 km from the coast (Fig. 2. Table 1).

FIG. 1. Location of the Italian sampling stations.

Table 1. Sampling station network

Stations	1 - Rome -DST	2 - Santa Scolastica	3 - Campo Staffi	4 - Ninfa	5 - Fogliano	6 - Zannone Island	7 - Trieste - Padriciano	8 - Capo Caccia	9 - Cagliari Elmas
Altitude	66	511	1750	35	5	119	365	200	1

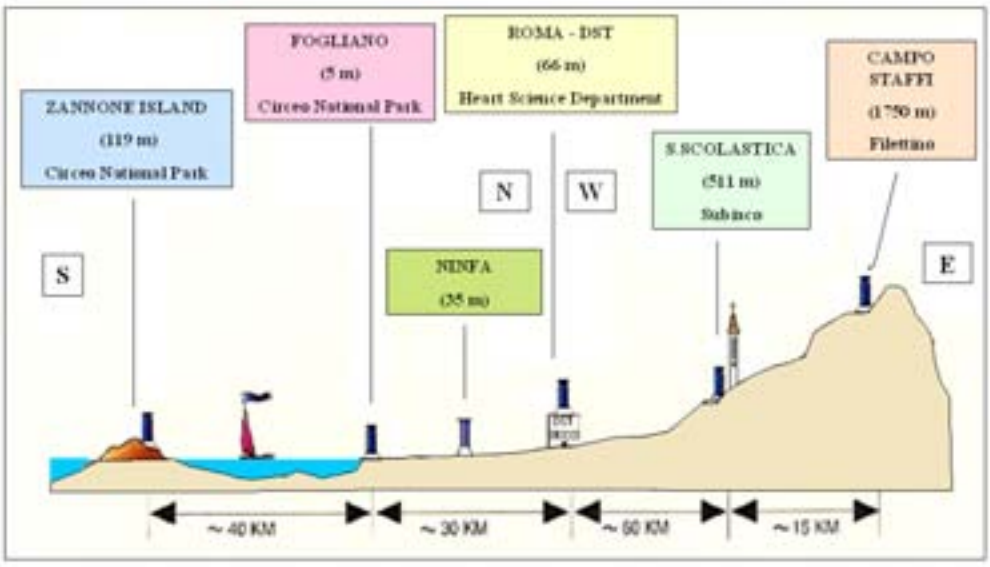

FIG.2. Transect of the monitoring stations from the Tyrrhenian Sea eastward (Central Italy).

The climatic parameters and the procedure of collection of precipitation are reported in Table 2.

Table 2. Precipitation sampling network and isotopic data available (D: daily; M : monthly)

Station and altitude	Sampling frequency	Sampling period	Number of stable isotope data ($\delta^{18}O$, $\delta^{2}H$)	Number of *tritium* data
ZANNONE ISLAND (119 m)	Monthly	From Sep. 1998 To Nov. 2002	23 $\delta^{18}O$ 20 $\delta^{2}H$	-
FOGLIANO (5 m)	Daily (D) Monthly (M)	From Sep. 1998 To Nov. 2002	15 $\delta^{18}O$, $\delta^{2}H$(D) 45 $\delta^{18}O$ (M) 30 $\delta^{2}H$ (M)	-
NINFA (35 m)	Monthly	From Jan. 2001 To Dic. 2001	12 $\delta^{18}O$ 12 $\delta^{2}H$	11
ROME - DST (66 m)	Daily (D) Monthly (M) Fraction (F)	From Dec. 1998 To Apr. 2003	97 $\delta^{18}O$, $\delta^{2}H$(D) 49 $\delta^{18}O$ (M) 22 $\delta^{2}H$ (M)	19
S. SCOLASTICA (511 m)	Daily (D) Monthly (M)	From Dec. 2000 To Apr. 2003	46 $\delta^{18}O$, $\delta^{2}H$(D) 25 $\delta^{18}O$ (M) 19 $\delta^{2}H$ (M)	-
CAMPOSTAFFI (1750 m)	Monthly	From Feb. 1999 To Apr. 2003	46 $\delta^{18}O$, $\delta^{2}H$(D) 25 $\delta^{18}O$ (M) 19 $\delta^{2}H$ (M)	11
TRIESTE (365 m)	Monthly	From Sep. 2001 To Dec. 2003	23 $\delta^{18}O$ 23 $\delta^{2}H$	-
CAGLIARI ELMAS (1 m)	Monthly	From Sep. 2001 To May. 2002	8 $\delta^{18}O$ 8 $\delta^{2}H$	-
CAPO CACCIA (200)	Monthly	From Oct. 2001 ToMay. 2002	8 $\delta^{18}O$ 8 $\delta^{2}H$	-

2. Results

2.1. Stable isotopes ($^{18}O/^{16}O$, $^{2}H/^{1}H$) — Monthly data

Stable isotopes of Ninfa, Cagliari-Elmas and Capo Caccia stations are not considered in the report because of their too short data set. However all the data are available in the IAEA monthly database.

$\delta^{18}O$ and $\delta^{2}H$ of monthly precipitation show a similar temporal trend in the three coastal stations of Zannone, Fogliano and Roma in western-central Italy (Fig. 3), which often includes also the month-to-month variations over-imposed on the general seasonal variations. Thus, the three stations are in principle interchangeable.

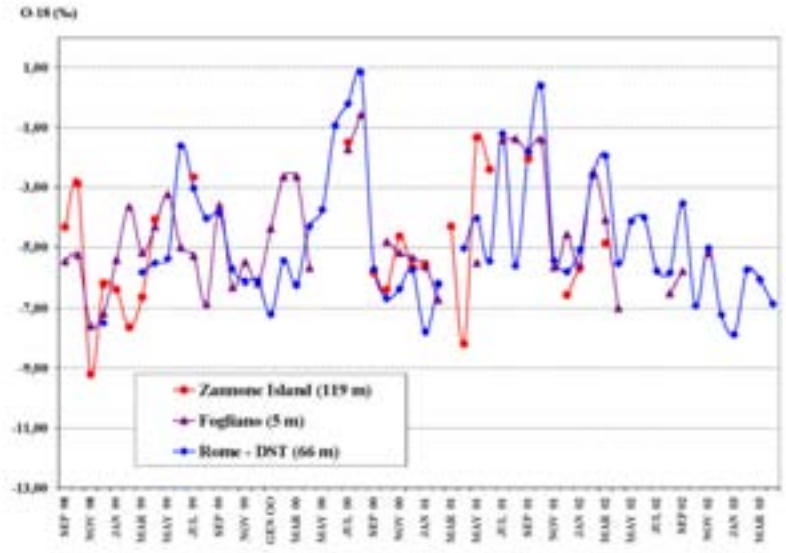

FIG. 3. Comparison of monthly isotopic values of Zannone Island, Fogliano and Rome-DST stations.

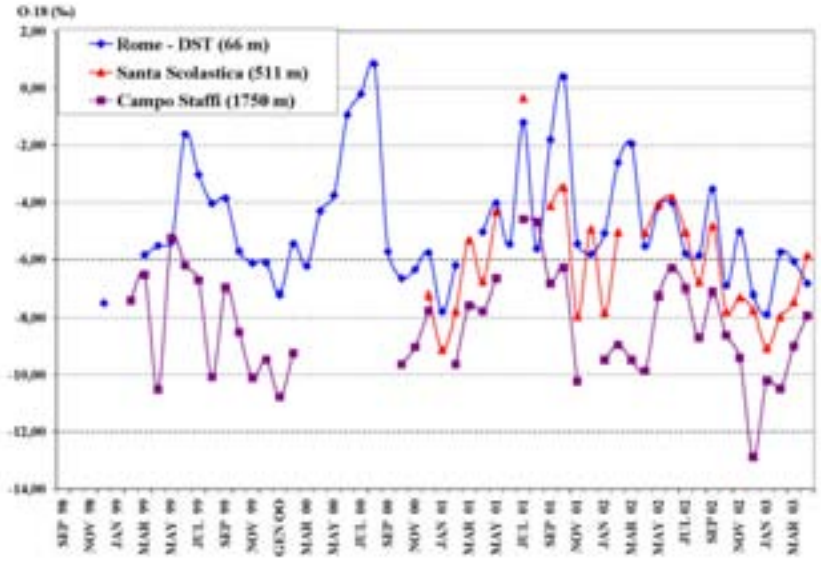

FIG. 4. Comparison of monthly isotopic values of Rome-DST, S. Scolastica, and Campo Staffi stations

On the contrary, a shift to more depleted values characterizes the inland stations located East of Rome-DST (66 m a.s.l.) namely Santa Scolastica (511 m a.s.l.) and Campo Staffi (1750 m a.s.l.) as a consequence of the altitude effect, together with a decrease of the evaporative process affecting the falling raindrops (Fig. 4). This last point is further illustrated by the relationship $\delta^{18}O - \delta^{2}H$ (Fig. 5), which shows an increasing slope of the Local Meteoric Line from Rome-DST to S.Scolastica and Campo Staffi.

The station of Trieste, on the Adriatic Sea in northern Italy, at higher latitude than the Central Italy stations, shows a slope and an intercept comparable to those of S. Scolastica.

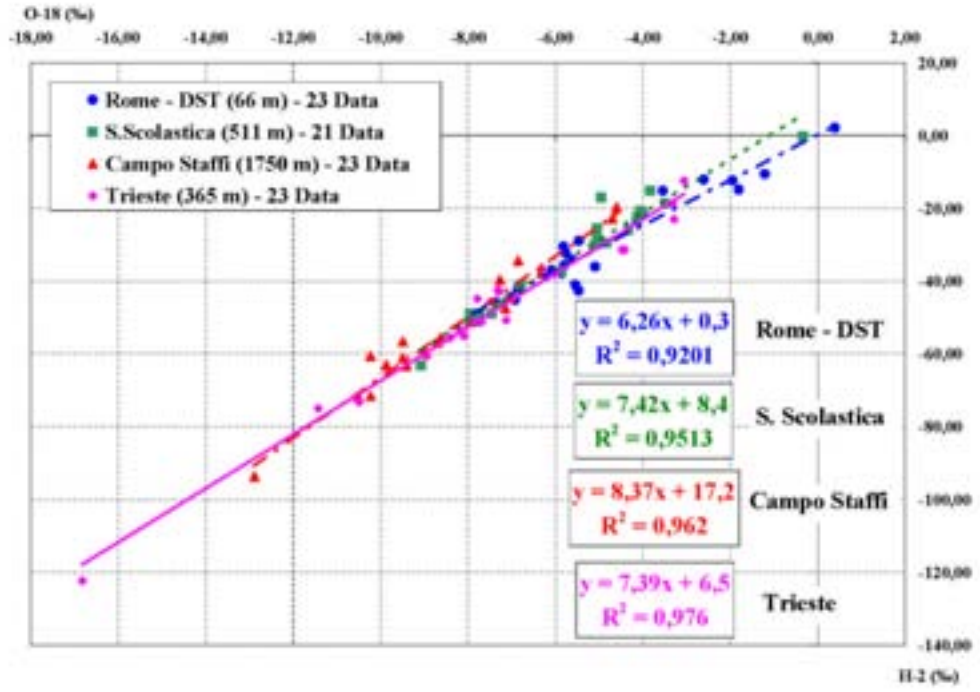

FIG. 5. Local Meteoric Water Lines based on isotopic monthly data of Rome-DST, S. Scolastica, Campo Staffi, and Trieste stations.

The mean weighted values (M.W.V.) for O-18 and H-2 of all the stations are given in Table 3.

Table 3. Mean weighted values of O-18 and H-2

LOCATION AND ALTITUDE	δ^{18} O ‰ (M.W.V.)	δ^{2} H ‰ (M.W.V.)	Number of data
ZANNONE IS. (119 m)	-5.35	-29.0	15
FOGLIANO (5 m)	-4.32	-22.7	26
NINFA (35 m)	-5.62	-30.2	12
ROME - DST (66 m)	-5.42	-33.0	23
S. SCOLASTICA (511 m)	-6.28	-38.2	21
CAMPOSTAFFI (1750 m)	-9.02	-58.8	21
TRIESTE (365 m)	-7.46	-45.3	23
CAGLIARI ELMAS (1 m)	-4.18	-19.8	8
CAPO CACCIA (200 m)	-5.56	-33.0	8

2.2. Stable isotopes ($^{18}O/^{16}O$, $^{2}H/^{1}H$) — Daily data

The $\delta^{18}O$ – $\delta^{2}H$ relationship (Fig.6) includes the δ-values of 139 selected precipitation samples collected mainly at Rome–DST (66 m) and Santa Scolastica (511 m). The mean *deuterium excess* value is d = 12‰, i.e. comparable to that reported for the Western Mediterranean region.

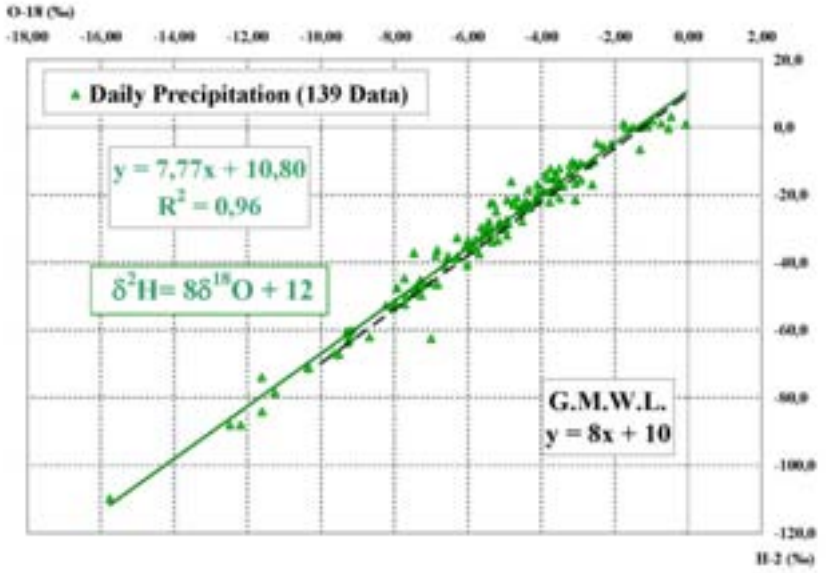

FIG. 6. Local Meteoric Water Line based on daily precipitation data.

The *deuterium excess* temporal variations for Rome-DST and S.Scolastica (Fig. 7 and 8) show higher values in winter. This is evident also from the extreme values:

in Rome-DST: maximum d = 23‰ on November 26, 2001, and minimum d = -2‰ on May 20, 2002;

in Santa Scolastica: maximum d = 22‰ on November 27, 2001, and minimum d = -7‰ on March 9, 2001.

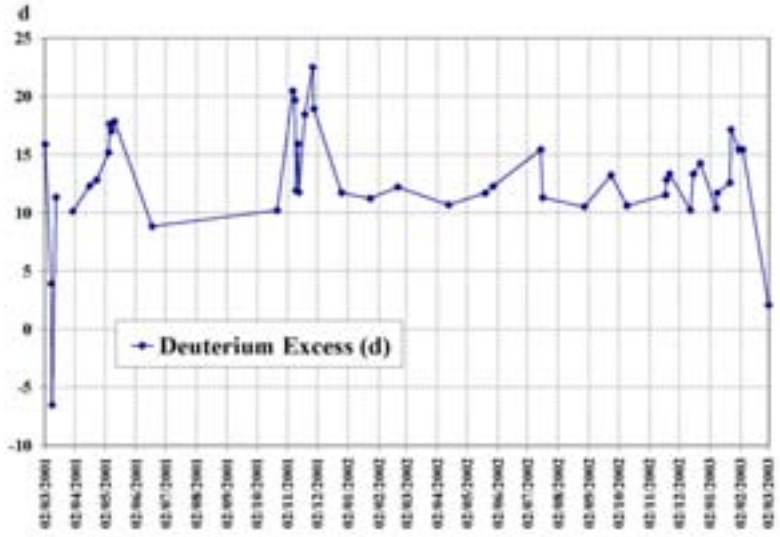

FIG. 8. Santa Scolastica Station (511 m a.s.l.): d-excess time series based on a selection of daily precipitation events from October 2000 to March 2003.

Based on "HYSPLIT TRAJECTORIES MODEL" from FNL Meteorological Dataset, the origin of different air masses was identified for the daily events of Rome-DST and Santa Scolastica stations. In general, there was not a significant difference among precipitations of different origin, though, broadly speaking, eastern events seem to be significantly different from those coming from West, South and (very few) from North (Fig. 9).

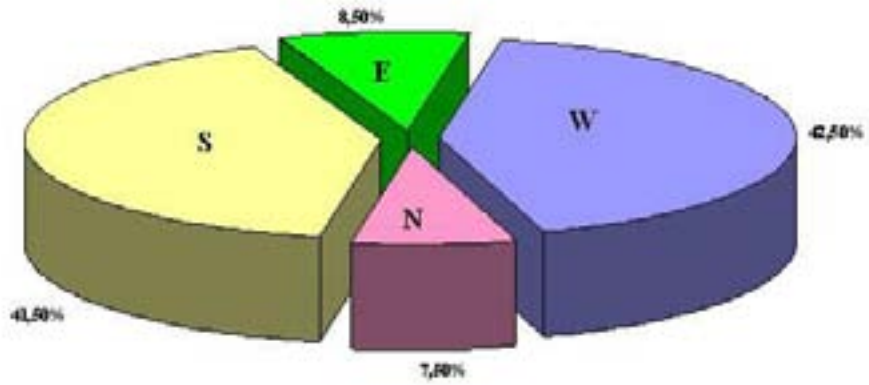

FIG. 9. Rome-DST Station: distribution of the precipitation daily events related to different provenance of the air masses.

Table 4. Rome-DST and Santa Scolastica "Daily Events": comparison of deuterium excess values related to West and South provenance of the air masses.

West Events

Santa Scolastica

Mean Weighted Value (d)	13
Mean Average (d)	13
Max (d)	20
Min (d)	9
St. Dev.	3
N° Events	24
Total Precipitation (mm)	410

DST - Rome

Mean Weighted Value (d)	12
Mean Average (d)	12
Max (d)	17
Min (d)	8
St. Dev.	2
N° Events	40
Total Precipitation (mm)	467

South Events

Santa Scolastica

Mean Weighted Value (d)	9
Mean Average (d)	13
Max (d)	22
Min (d)	-7
St. Dev.	7
N° Events	12
Total Precipitation (mm)	184

DST - Rome

Mean Weighted Value (d)	13
Mean Average (d)	11
Max (d)	18
Min (d)	7
St. Dev.	3
N° Events	37
Total Precipitation (mm)	516

2.3. Stable isotopes ($^{18}O/^{16}O$, $^{2}H/^{1}H$) – Altitude effect and comparison with groundwater

In order to compare the isotopic vertical gradient of precipitation (4 years of monthly data) with that of shallow groundwater (where the isotopic composition variations are greatly or totally damped) of the same area, 23 small springs fed by small perched aquifers at various altitude (from 5 m up to 1600 m a.s.l.) were repeatedly sampled in the period 2000-2003.

The $\delta^{18}O$ – *Altitude* relationship for precipitation and ground water is reported in Fig.10. From the mean weighted values of stations at different altitude (from 5 up to 1750 m a.s.l.), the O-18 vertical gradient is approximately of -0.19 ‰ per 100 m of elevation. This value is very close to that of perched springs of Mount Simbruini: -0.18 ‰ per 100 m. On the contrary the O-18 altitude gradient of perched springs of Mount Lepini is significantly different: -0.10 ‰ per 100 m of elevation.

M. Lepini and M. Simbruini are two parallel mountain ranges South of Rome, NW-SE oriented as the Tyrrhenian Sea shoreline. M. Lepini is closer to the sea (about 25 km) and exposed to prevailing winds from South and West.

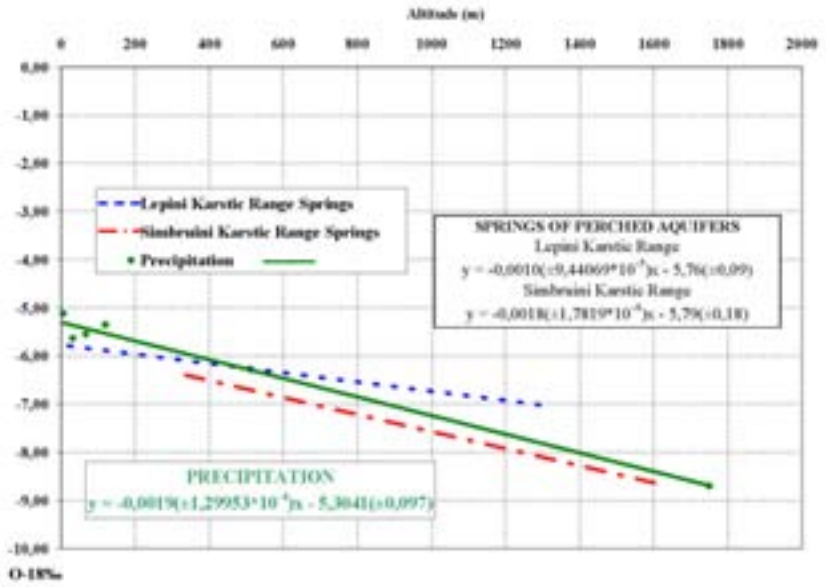

FIG. 10. O-18 vertical gradients related to precipitation and to springs of Mounts Lepini and Mounts Simbruini perched aquifers (Western Central Italy).

2.4. *Stable isotopes ($^{18}O/^{16}O$, $^{2}H/^{1}H$)* — Local MeteoricWater Line

Fig. 11 shows the various Local Meteoric Water Lines for western Central Italy (Latium Region) which can be obtained from monthly (n.116) and daily (n.139) precipitation and from perched groundwater.

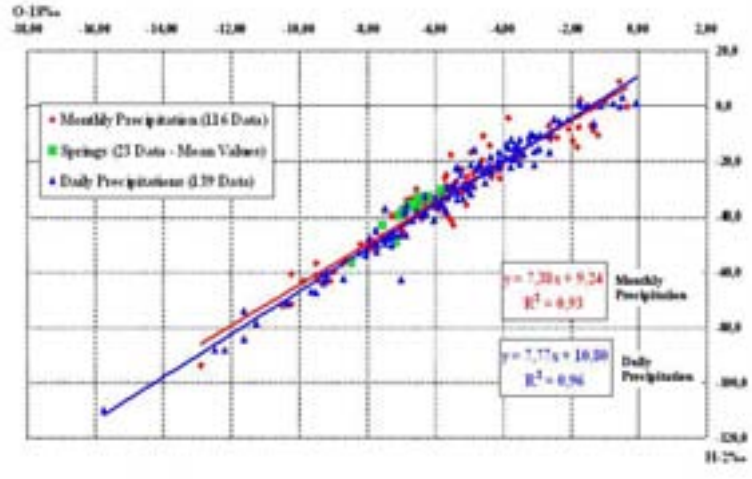

FIG. 11. Local Meteoric Water Lines related to precipitation and to perched springs of the Western Central Italy (Latium Region).

2.5. Tritium data

Tritium determinations were performed on monthly precipitation samples collected in three stations: Rome-DST (66 m a.s.l.), Ninfa (35 m a.s.l., 40 km SE of Rome) and Campo Staffi (1750 m a.s.l.).

A seasonal trend due to the "spring injection" is observed for all the sites. Higher *tritium* peaks are observed at Campo Staffi, the highest and more continental station (about 120 km from the coast).

The mean weighted values for the three stations are:

Ninfa (October 2000 – December 2001, 14 values): 4.5 T.U.

Rome-DST (January 2000 – December 2001, 19 values): 6.2 T.U.

Rome-DST (October 2000 – December 2001, 12 values): 5.4 T.U.

Campo Staffi (October 2000 – December 2001, 11 values): 6.1 T.U.

A particularly high and anomalous *Tritium* value — 15 T.U. — was observed in Roma in December 2001 (Fig. 12).

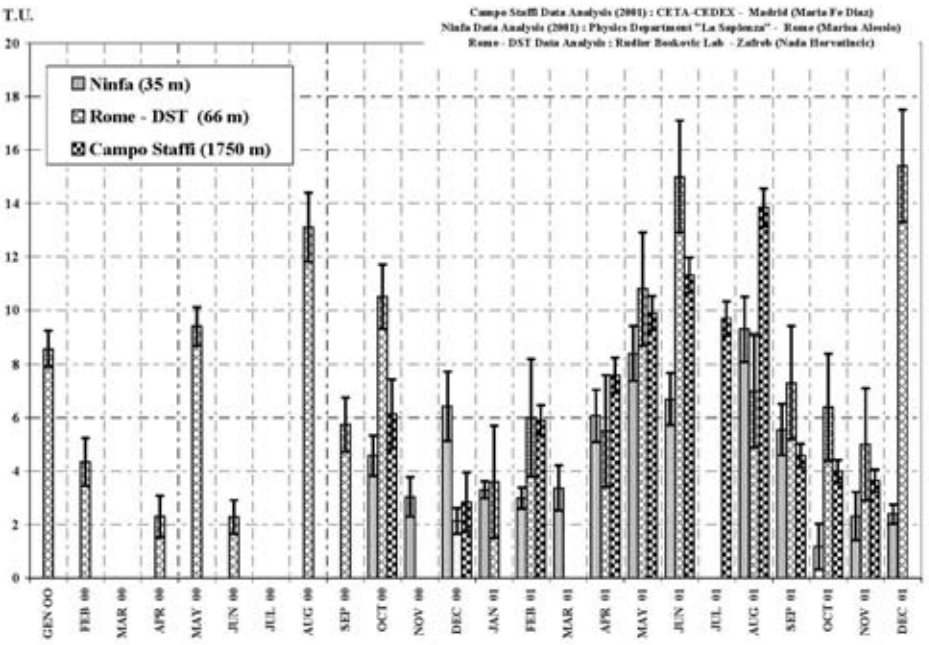

FIG. 12. Monthly Tritium activities referred to Rome-DST (66 m a.s.l.), Ninfa (35 m a.s.l.) and Campo Staffi (1750 m a.s.l.), from January 2000 to December 2001.

3. Achievements

Determination of altitude isotopic gradients (O-18) from precipitation and ground water data. Using springs issuing from small perched aquifers of M.Lepini and M. Simbruini, two different gradients were found, with that of M. Simbruini being greater. The deuterium excess also increases. M. Lepini and M. Simbruini are two parallel karstic mountain ranges which are NW-SE oriented and windward exposed with respect to the main origin (SW) of humid air masses. These effects are now being investigated in more detail.

Origin of daily rains. Daily rain events were subdivided in four classes according to their origin (northern, eastern, southern and western) on the basis of the "trajectories air masses maps". *Deuterium excess* values show a general homogeneity among the different classes.

Monthly rains. Monthly events collected in the five monitoring stations show for stable isotopes the well known dependence on altitude.

Tritium. Data highlight a general dilution due to seawater for stations located closer to the Thyrrenian Sea (Ninfa).

4. Future activities

For a better understanding of rainfall formation processes, a sequential sampling of precipitation is now being carried out in Rome-DST station.

Daily sampling of precipitation will continue at Fogliano, Rome-DST and Santra Scolastica, whereas monthly sampling of precipitation will be extended to all the stations including Ninfa, under the control of the Bono research Unit. These stations, at the eastern extreme of the Western Mediterranean Basin, seem well suited for studying the influence of long term air circulation patterns on the isotopic composition of precipitation.

Periodical sampling of perched and basal springs of different karstic ranges will also take place in order to monitor long-term isotopic variations, which may be related to the expected ongoing climatic variations.

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The collection of precipitation samples and the management of meteo and hydrological stations is aknowledged to the personnel of the National Park of Circeo (NPC) and to the Natural Reserve of Posta Fibreno (Regione Lazio).

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ISOTOPIC COMPOSITION OF PRECIPITATION AT THREE MOROCCAN STATIONS INFLUENCED BY OCEANIC AND MEDITERRANEAN AIR MASSES

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Abstract. Isotopic composition (oxygen-18 and deuterium) of daily and monthly rain events and water vapour was monitored during the period from 2000 to 2003 at three meteorological stations in Morocco. The main objective of these measurements is to characterize the isotopic content of precipitation and water vapour in relation with the air masses origins and meteorological conditions. Isotopic analyses reveal large variations in both $\delta^{18}O$ and $\delta^{2}H$. The observed variations are clearly related to different origins of the water vapour (Atlantic Ocean and Mediterranean Sea) as well as to different trajectories of precipitating air masses. Globally, the relations between $\delta^{18}O$ and local meteorological parameters were unreliable. According to the synoptic weather maps and the isotopic signature of almost all rain events sampled for isotope analyses in this study, three main origins of the precipitating air masses were defined in Morocco: *(a)* air masses coming from central Atlantic Ocean, *(b)* air masses coming from North Atlantic and travelling along the western part of the Mediterranean Sea and *(c)* air masses coming from the East Mediterranean Sea and travelling partly over the North Africa and along the western part of the Mediterranean Sea. The three trajectory/origin groups fit well the isotopic data in $\delta^{18}O$ / $\delta^{2}H$ plots. The evaporative isotopic enrichment of rain drops below the clouds is signalled in a few samples at the three stations.

1. Introduction

Isotopic variations (^{18}O and ^{2}H) of precipitation are caused by isotope fractionation effects accompanying evaporation from Ocean and condensation during atmospheric transport of water vapour [1]. The magnitude of the deuterium excess is controlled by the source region of the evaporation process [2]. Therefore, the deuterium excess values observed in precipitation should reflect specific conditions in the vapour source regions.

The present study, based on measurements taken at three Moroccan meteorological stations, was undertaken with the main aim to characterize the isotopic content of precipitation and water vapour in relation with the air masses origins and meteorological conditions. One of the meteorological stations is located at Rabat, which is an Atlantic coastal city (Figure 1). The two others are continental sites, which are located respectively at an altitude of 500 meters (Beni-Mellal city) and 1500 meters (called Bab Bou Idir at Taza city). Daily/monthly rains and water vapour have been collecting during three years from 2000 to 2003 at the three stations.

FIG. 1. Administrative map of Morocco.

2. Climatological framework

Geographical situation of Morocco is characterized by three main features: mountainous ranges, wide extension in latitude and existence of two coasts which are Mediterranean Sea and Atlantic Ocean. Moroccan climate is influenced by each of these geographical features. The Atlas barrier influences the distribution of rainfalls which are more important in West than the ones in East. The wide scale in latitude (21° to 36° North) diversify the climate with a temperate to semiarid tendency in the North and arid and warm climate in the South. The Mediterranean and the Atlantic coasts play a regulating role of climate. Hence, a great spatial variability characterizes the rainfall pattern in Morocco.

The rainfall annual average ranges from 800 mm in the North-Western part of Morocco and some mountains of the high Atlas to fewer than 100 mm in the South and South-Eastern areas (Figure 3). The rain events are related to air masses which come from Atlantic Ocean and Mediterranean Sea and have an interaction with Saharan low that bring heat and humidity.

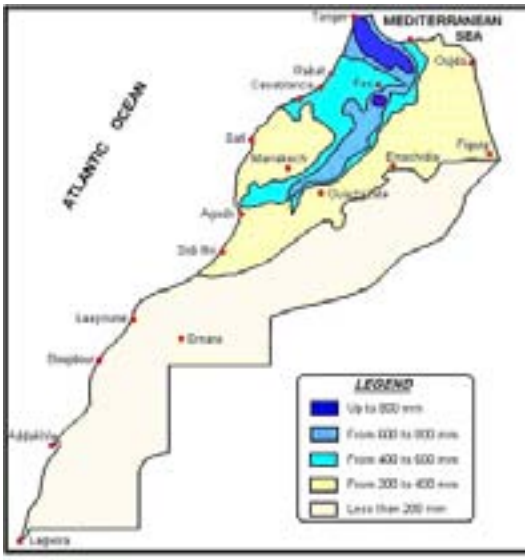


FIG. 2. Rainfall distribution map of Morocco.

3. Methodology of precipitation and water vapor sampling

Precipitation and water vapour sampling network is given in table 1. There are three meteorological stations which are located in Rabat, Beni Mellal and Taza cities (Figure 1). Daily samples have been collected for Rabat and Beni-Mellal and monthly samples have been collected for the three stations. Water vapour events have been collected in Rabat station. Daily rain samples were collected at each morning and a hermetic container where the rain events were accumulated has been used for the monthly rainfall sampling.

Table 1. Precipitation and water vapor sampling network of Morocco in this study

Location	Latitude	Longitude	Altitude (m.asl)	Frequency
Rabat	34°46' N	06°46' W	75.3	Daily/monthly rains and water vapor
Beni Mellal	32°22' N	06°24' W	468	Daily/monthly rains
Bab Bou Idir	34°13' N	04°00' W	1500	Monthly rains

In order to minimize the alteration of heavy isotopes by evaporation, we have followed in detail the IAEA sampling procedures. At the same time as sampling, the amount of each precipitation event has been also recorded. Precipitation event samples were collected during October to April period for each year from 2000 to 2003.

A water vapour sampling system was installed in Rabat station. For the pump, vacuum is 150 mbar maximum and the rate is 200 l/h maximum.

Oxygen-18 and deuterium measurements have been carried out in the isotopic analyses laboratory of DASTE – CNESTEN with a mass spectrometer delta plus equipped with an automatic equilibration system. The results were expressed in "δ" notation as per mille deviations from the internationally accepted standard V-SMOW (Vienna Standard Mean Ocean Water) using the followed equation:

$$\delta(‰) = \left(\frac{R_{sample}}{R_{VSMOW}} - 1 \right) \times 10^{-3}$$ where R denotes the $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratios.

The analytically accuracy is 0.15 ‰ for ^{18}O and 1 ‰ for ^{2}H.

4. Results and discussions

The results of isotopic analyses of precipitation and water vapour samples (daily and monthly events) collected mainly between November and April of each year from 2000 to 2003 at the three studied stations show wide variations in the isotopic individual data. Oxygen-18 values are ranging, respectively for daily event rains, monthly event rains and water vapour at the three stations, from -13.08‰ to +1‰ from -13.43‰ to -0.09‰ and from -17.03‰ to -0.38‰; deuterium from -103.05‰ to +14.7‰ from -87.57‰ to +10.01‰ and from -101‰ to +14.82‰ and deuterium excess from -11.66‰ to +34.5‰ from -4.02‰ to +33.6‰ and from -10.54‰ to +35.24‰ V-SMOW.

Rain isotopic composition results from the interaction between different meteorological parameters such as surface air temperature, rainfall amount, atmospheric humidity and global meteorological situations (origin and trajectory of air masses). Some meteorological parameters have a prominent influence according to the observation scale (daily or monthly).

4.1. Impact of local meteorological parameters

Oxygen-18/rainfall amount relationship informs about the amount effect that express the depletion in heavy isotopes for higher rainfall amount (R.A.) values. At the Atlantic station (Rabat), this correlation is globally not reliable (Figure 3). In fact, the enrichment in $\delta^{18}O$ recorded for the important rain events of 12-Oct. 2000 and 24-Nov. 2002, which the d-excess is respectively about 17 ‰ and 22.5 ‰, can be related to the intensive interaction between the precipitating air masses and the Eastern part of the Mediterranean Sea (Figure 4). The depletion in $\delta^{18}O$ registered for the lower rain events of 20-Dec. 00, 18-Dec. 01 and 04-Mar. 02 (< 5 mm) stems from the fact that these rain events dropped at an atmospheric profile with high values of the relative humidity (about 80% at these rainy periods).

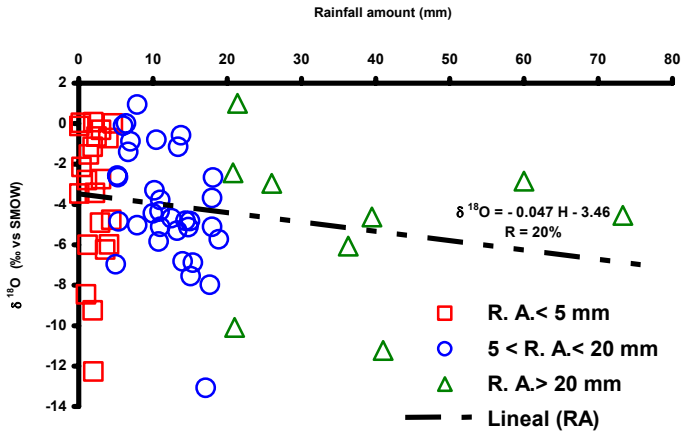


FIG.3a. $\delta^{18}O$ vs. rainfall amount at Rabat station (daily values 2000–2003).

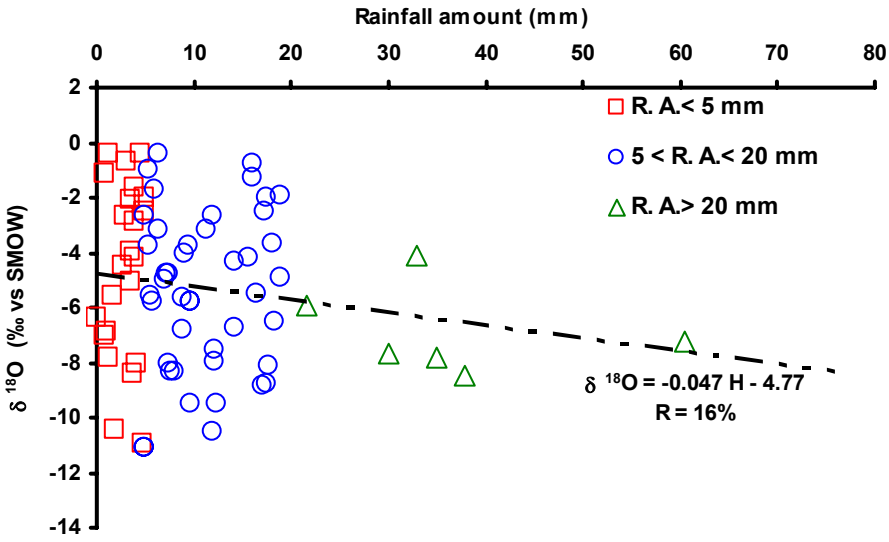


FIG. 3b: $\delta^{18}O$ vs. rainfall amount at Beni Mellal station (daily values collected between 2000 and 2003).

At the continental station (Beni Mellal), also the amount effect has not expressed in the $\delta^{18}O$/R.A. plot (Figure 3b).

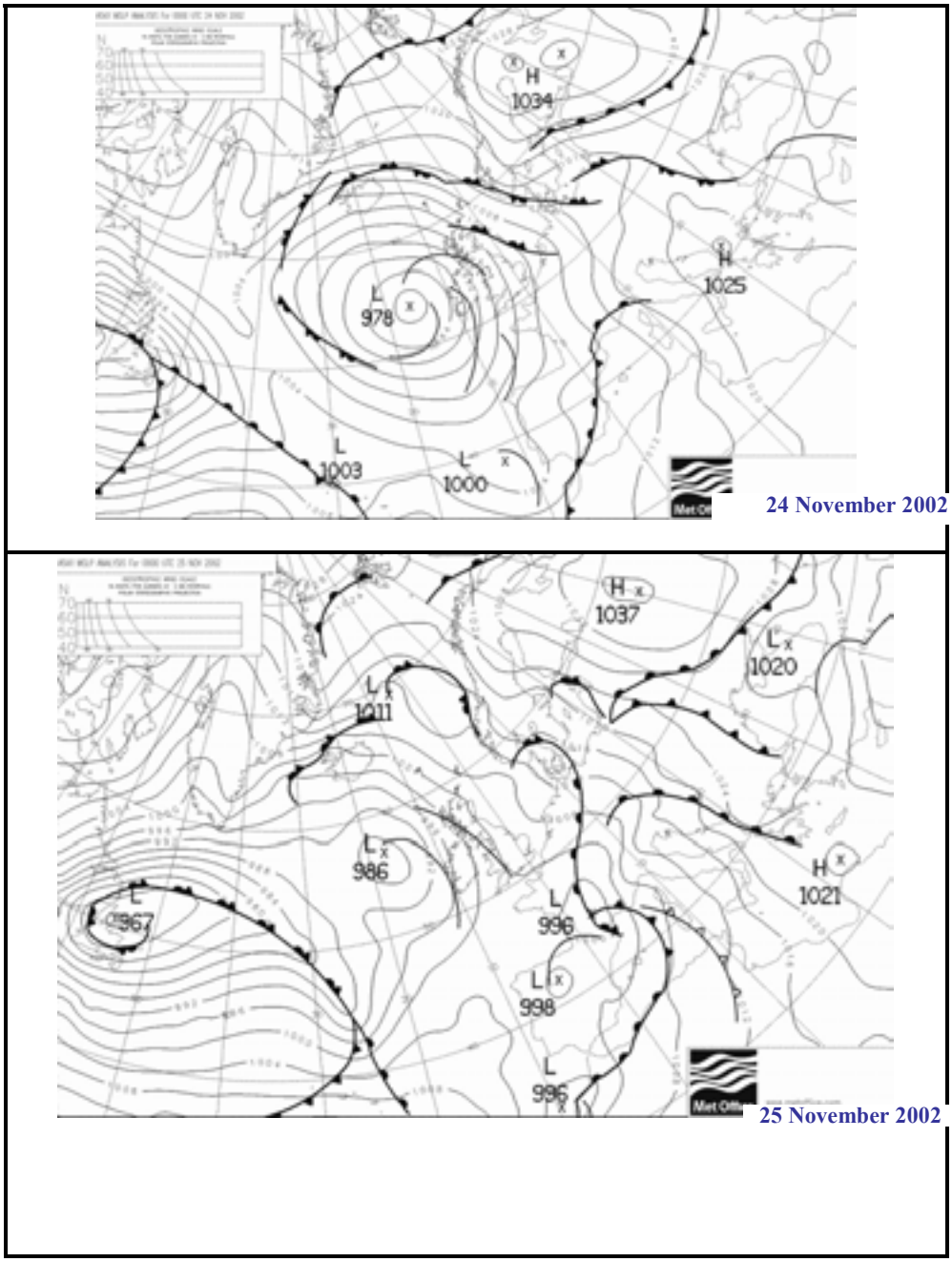


FIG. 4. Weather map showing the meteorological situation of 24 and 25 Nov. 2002.

$\delta^{18}O/T$ plot (Figure 5), shows unreliable relationship between the two parameters at Rabat and Beni Mellal stations (R < 10%). It should be related probably to the fact that the temperature parameter, at the local scale, was masked by others parameters such as relative humidity and/or meteorological situation like at the Atlantic station where the relative humidity show higher values.

The correlations between $\delta^{18}O$ of water vapour samples collected at Rabat station and both relative humidity and temperature have not a good correlation coefficient (Figure 6).

Globally, there are no significant relationships between heavy isotopes and local meteorological parameters at the two study stations. It stems from the fact that there are others parameters that more influenced the isotopic composition of precipitation such as the origin and trajectory of the precipitating air masses.

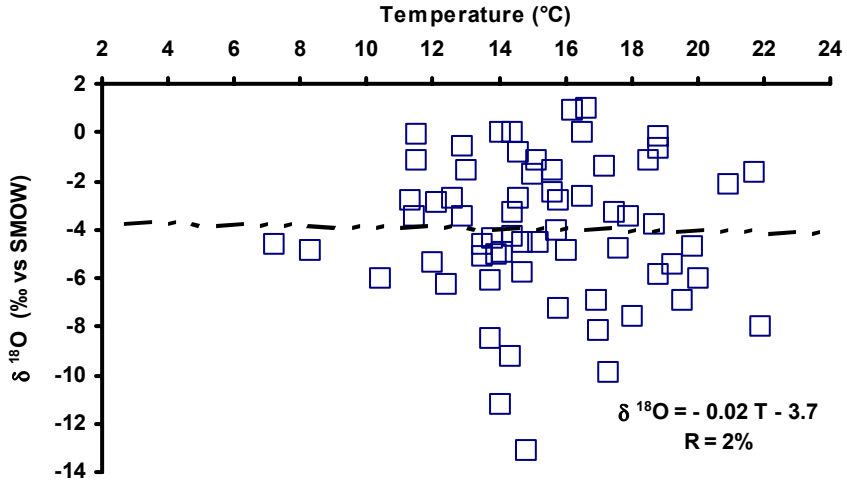


FIG. 5a: $\delta^{18}O$ vs. temperature at Rabat station (daily values collected between 2000 and 2003).

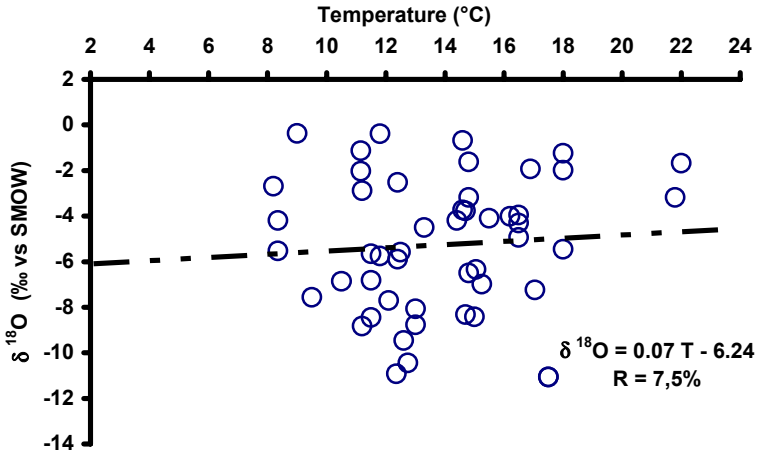


FIG. 5b: $\delta^{18}O$ vs temperature at Beni Mellal station (daily values collected between 2000 and 2003).

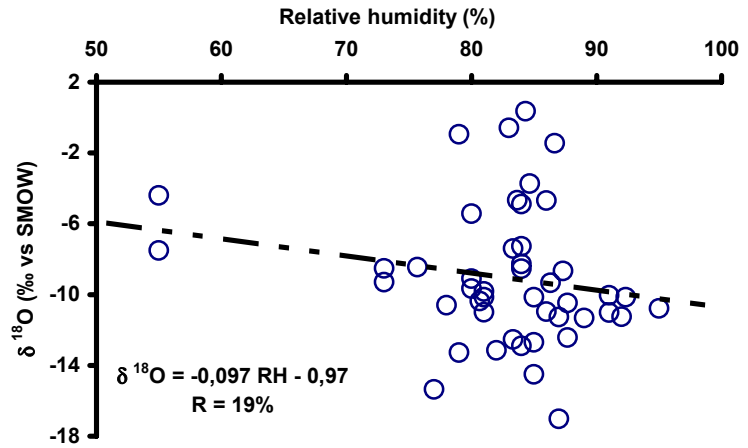


FIG. 6a: $\delta^{18}O$ of water vapour vs. atmospheric relative humidity at Rabat station.

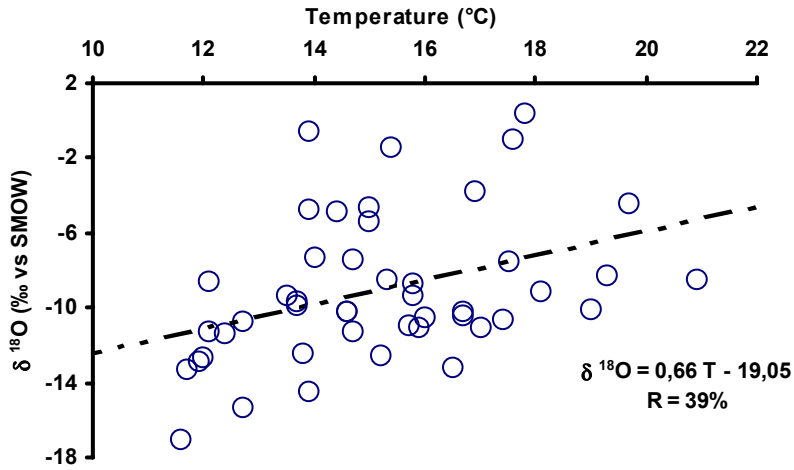


FIG. 6b: $\delta^{18}O$ of water vapour vs. surface air temperature at Rabat station.

4.2. Origin and trajectory of the precipitating air masses

According to synoptic weather maps of almost all rain events sampled for isotope analyses in this study, the majority of precipitation events were associated with three distinct meteorological situations as presented schematically in figure 7. The first one is characterized by a low pressure center moving from NW to SE. It results in a strong NW circulation bringing relatively cold and warm air masses from central Atlantic Ocean. This situation is characterized by the weather maps corresponding to 09 and 10 December 2002 (Figure 7a).

The second situation is associated with a low initially located over the British Islands and moving towards SE. The cold air masses coming from North Atlantic travelled along the western part of the Mediterranean Sea, which has an intense interaction with the air masses before reaching Morocco at its Mediterranean coasts. This situation is characterized by the weather maps corresponding to 14, 15 and 16 November 2002 (Figure 7b).

The third situation is associated with cold and warm air masses coming from the East Mediterranean Sea and travelled partly over the North Africa and along the western part of the Mediterranean Sea before reaching Morocco. The interaction of these air masses with the Mediterranean Sea is rather

intense, which explains the higher "deuterium excess" relative to that of the two others cases. This situation is characterized by the weather maps corresponding to 11 and 12 January 2003 (Figure 7c).

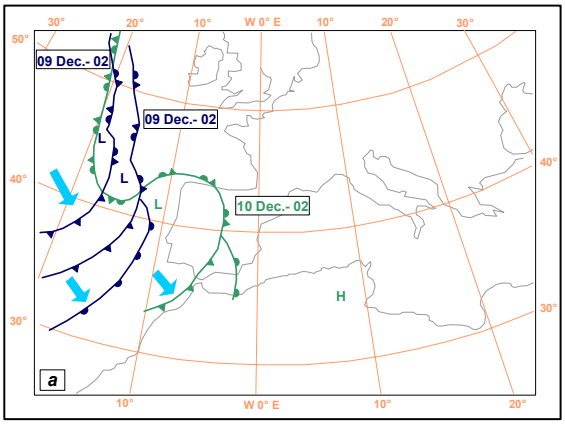


FIG. 7a: Schematic presentation of characteristic meteorological situation resulting in the Atlantic derived precipitation in Morocco.

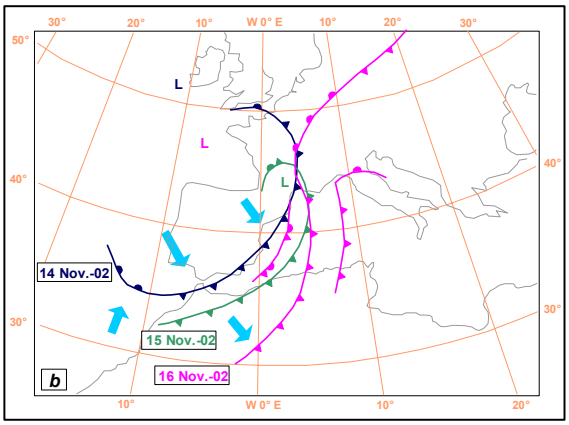


FIG. 7b: Schematic presentation of characteristic meteorological situation resulting in the Atlantic and West Mediterranean derived precipitation in Morocco.

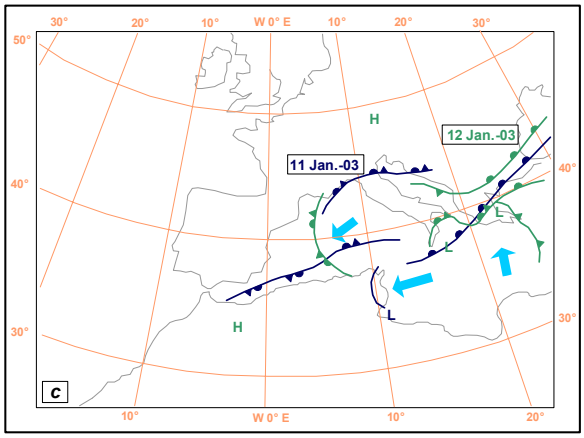


FIG. 7c: Schematic presentation of characteristic meteorological situation resulting in the East Mediterranean derived precipitation in Morocco.

4.3. Isotopic signature of rain events in relation with air masses origins

At Rabat station, a plot of $\delta^{18}O$ versus $\delta^{2}H$ is given in figure 8a. It is seen that almost all the points are located around Global and NIR meteoric water lines. The meteoric water line of these samples (LMWL) is $\delta^{2}H = 7.34\ \delta^{18}O + 10.19$ with a slope slightly less than 8 and d-excess about 10 ‰. However, the samples can be separated into three groups. Some points lie the Global meteoric water line namely $\delta^{2}H = 8\ \delta^{18}O + 10$ ‰ [3] which fits rather well the long-term mean values of coastal stations on a global scale [4]. This group is characterized by precipitations associated with air masses coming wholly from Atlantic Ocean (Figure 9). Others points lie over NIR line namely $\delta^{2}H = 8\ \delta^{18}O +$ 22‰ defined for the East Mediterranean Sea [5]. These samples are characterized by d-excess up to 20 ‰ and derived from precipitating air masses, which have intensive interaction with the East Mediterranean Sea; the meteorological situation of 24-Nov. 02 illustrates well this origin (Figure 4). Majority of the points lie in the region between the two meteoric water lines showing that the precipitating air masses were coming mainly from North Atlantic and travelled over the western part of the Mediterranean Sea, which more interacted with the cold air masses. The meteorological situations of 06, 10 December 2002 and 08 January 2003 illustrates well this type of origin (Figure 10). On the same plot, less than ten samples are located over the evaporation line, which the slope is close to 5.

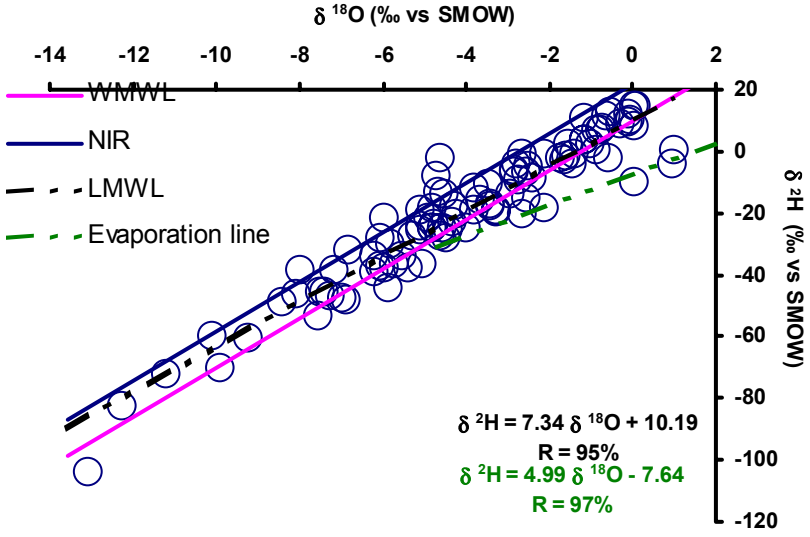


FIG. 8a: Isotopic composition of rain daily events from Rabat station.

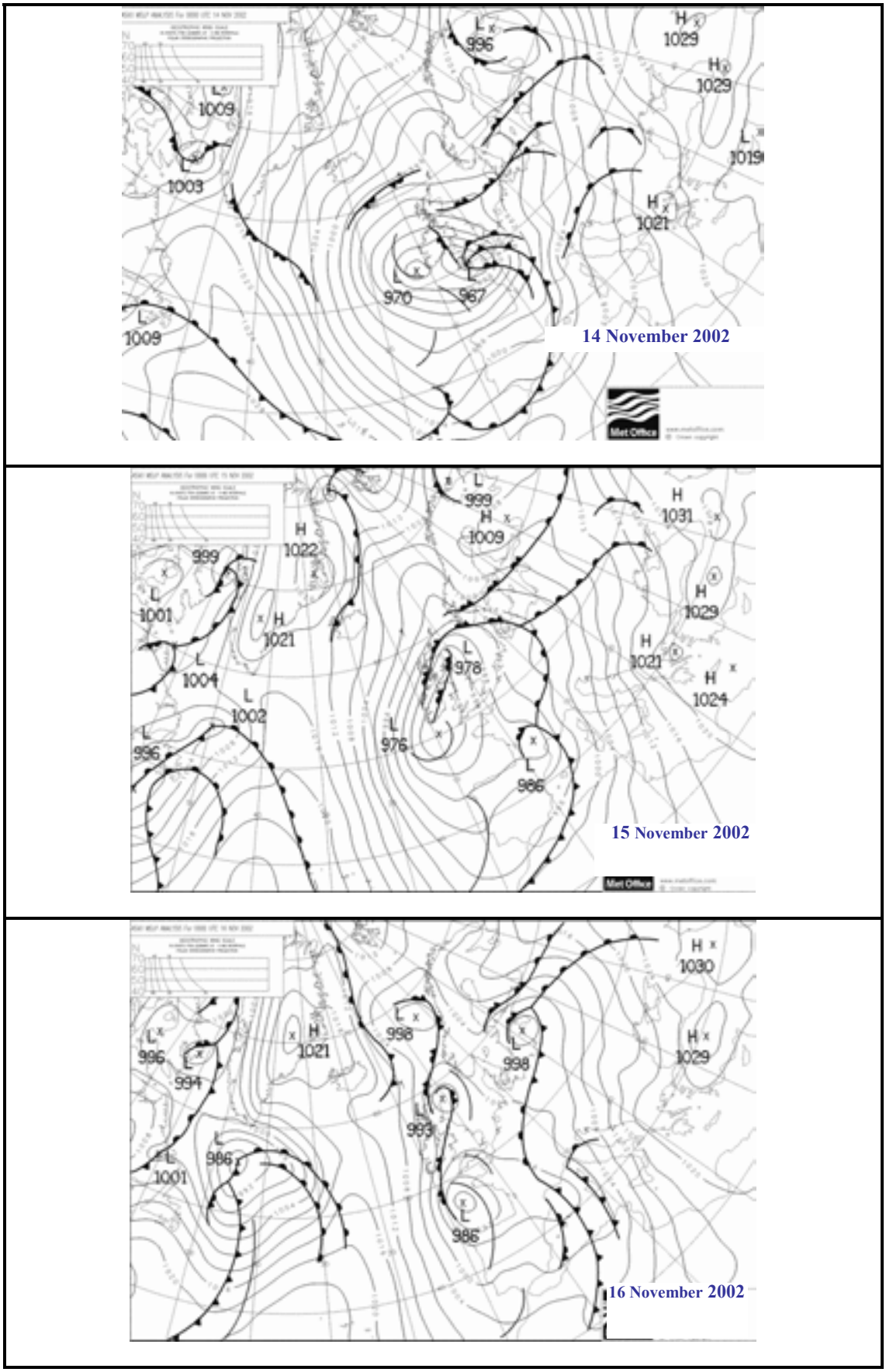


FIG. 9: Weather map showing the meteorological situation of 14, 15 and 16 November 2002.

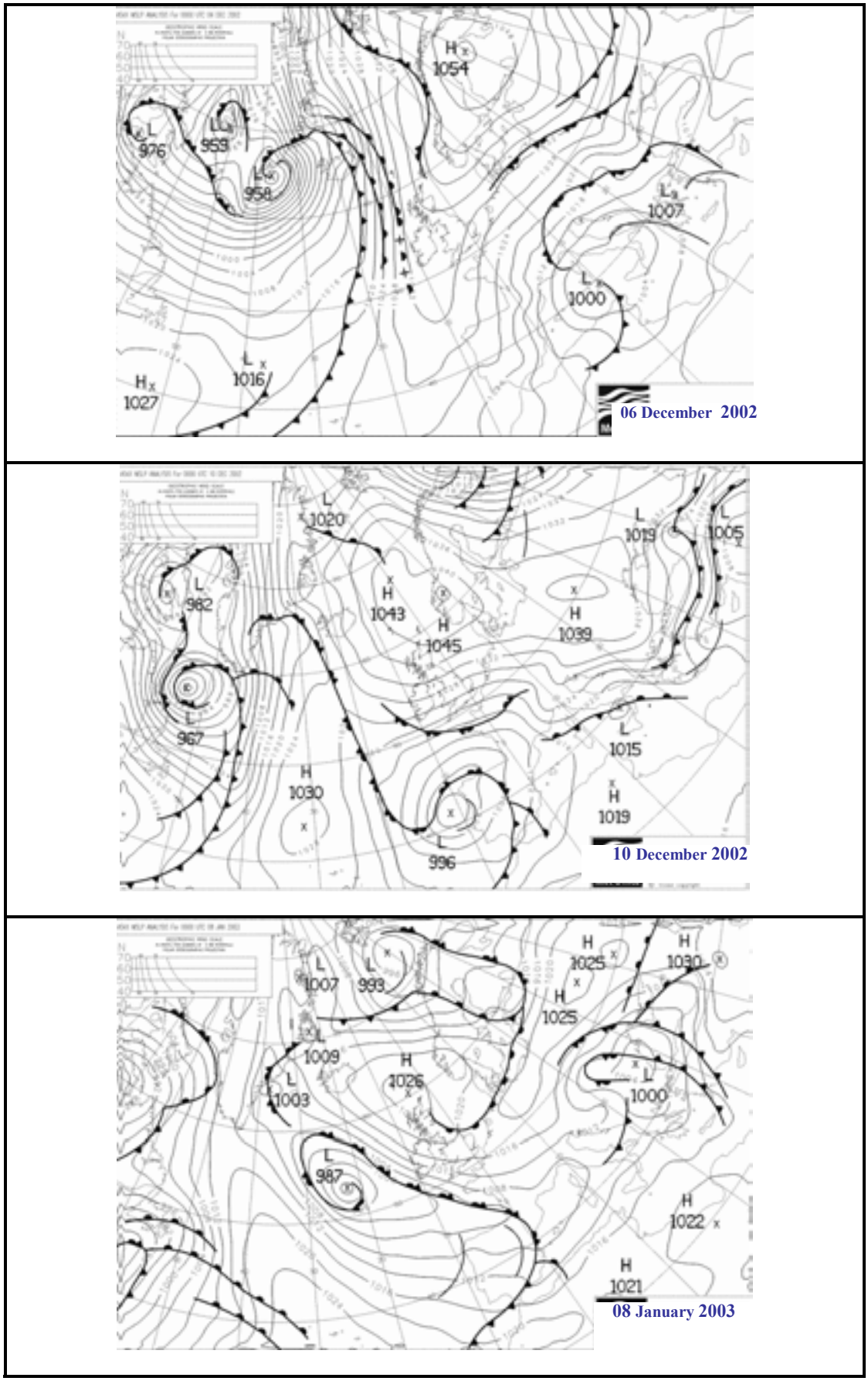


FIG. 11: Weather map showing the meteorological situation of 06, 10 December 2002 and 08 January 2003.

At Beni Mellal station, $\delta^{18}O$ / $\delta^{2}H$ relationship show globally the same distribution of the samples like at Rabat station (Figure 8b). However, the majority of points lie close or over NIR line. The evaporation phenomenal was observed only in two samples of 07 and 18 April 2002.

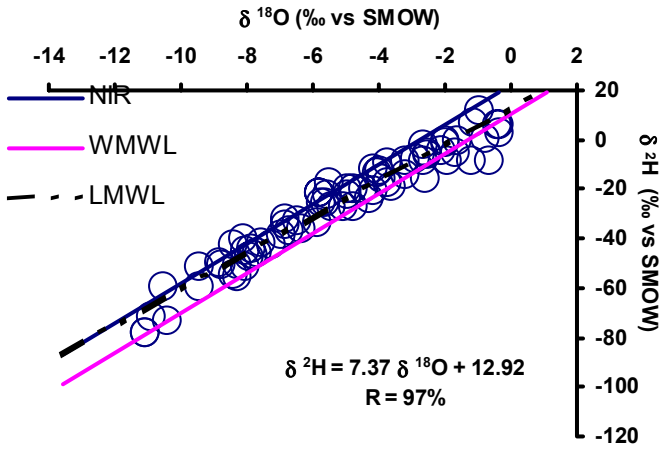


FIG. 8b: Isotopic composition of rain daily events from Beni Mellal station.

The same plot ($\delta^{18}O$ versus $\delta^{2}H$) is given for the water vapour collected at Rabat station (Figure 11). On this plot, some points which stable heavy isotopes are less than -9 ‰ in ^{18}O and less than -50 ‰ in ^{2}H, are located over NIR line. Others samples with stable heavy isotopes from -9 ‰ to -5 ‰ in ^{18}O and from -60 ‰ to -30 ‰ in ^{2}H are lying all in all over GMWL. Majority of samples with stable heavy isotopes from -11 ‰ to -8 ‰ in ^{18}O and from -75 ‰ to -45 ‰ in ^{2}H are located globally in the region between World and NIR Meteoric Water Lines. About five enriched samples in stable heavy isotopes (up to -4 ‰ in ^{18}O and up to -30 ‰ in ^{2}H) are located over the evaporation line. Water vapour with this isotopic composition is associated with air masses coming from Atlantic Ocean and had intensive interaction with the Mediterranean Sea during their travelling trajectory.

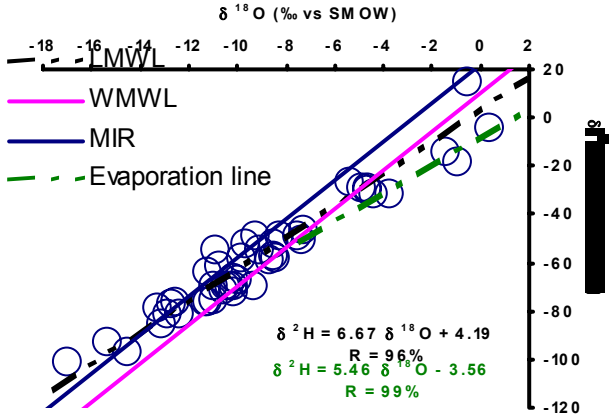


FIG. 11: Isotopic composition of water vapour from Rabat station.

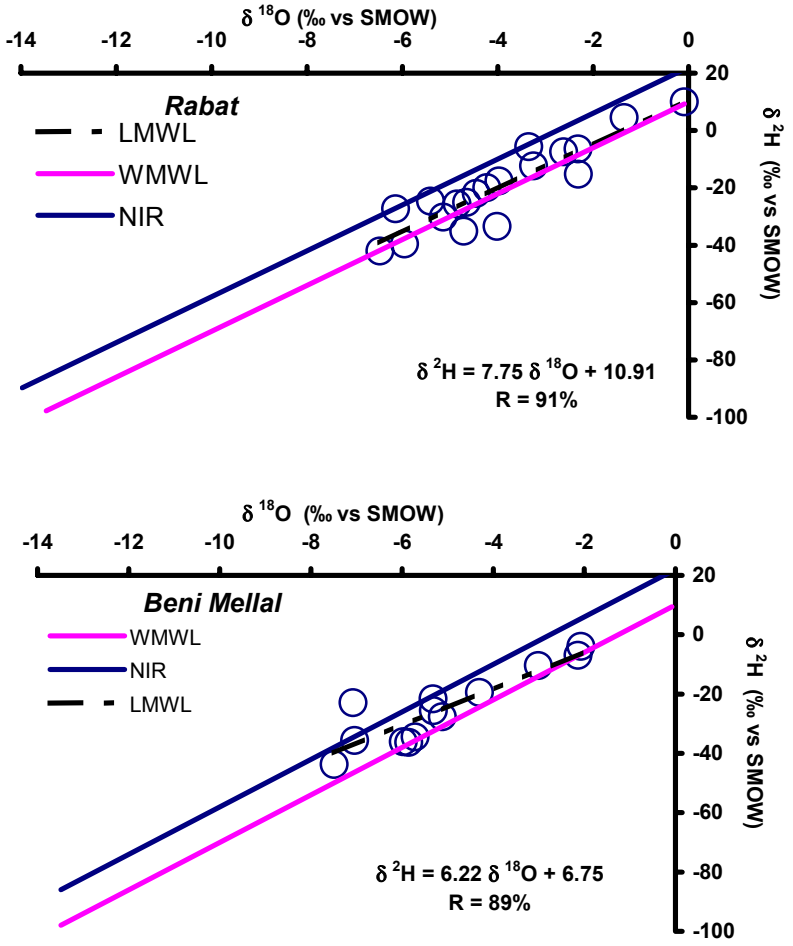
The monthly rains values obtained at the three stations are used in $\delta^{18}O$ *versus* $\delta^{2}H$ plots given in figure 12. It is seen that all points lie globally close to the MWL at Rabat station showing a large Atlantic Ocean influence on precipitating air masses. At Beni Mellal station, almost all points are located in the region between MWL and NIR line revealing the influence of the air masses coming

from Atlantic Ocean and interacted with the Mediterranean Sea. At Bab Bou Idir located into the continent, $\delta^{18}O$ *versus* $\delta^{2}H$ plot show that nearly all points lay close to the NIR line. This reveals that the air masses supplying precipitation in the region had an intensive interaction with the East Mediterranean Sea. Also, it is seen on these plots that some samples collected at Bab Bou Idir station are more depleted in the stable heavy isotopes than the ones collected at the others stations. The correlations between $\delta^{2}H$ and $\delta^{18}O$ for the monthly rains collected at Rabat, Beni Mellal and Bab Bou Idir stations are respectively:

$\delta^{2}H = 7.75\ \delta^{18}O + 10.91$ R = 0.91

$\delta^{2}H = 6.22\ \delta^{18}O + 6.75$ R = 0.89

$\delta^{2}H = 6.15\ \delta^{18}O + 5.48$ R = 0.94



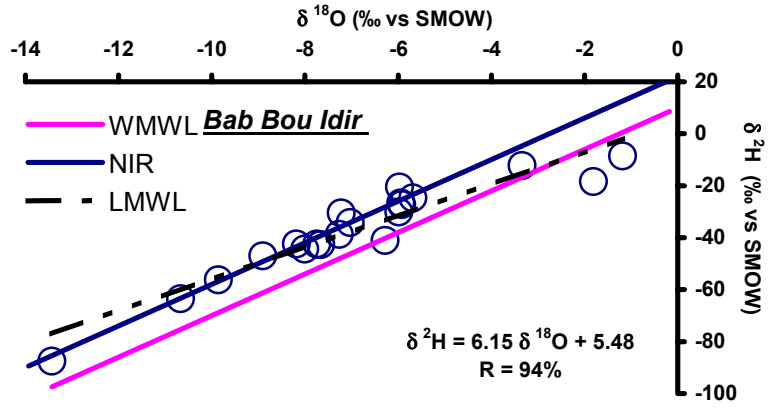


Figure 12: Isotopic composition of monthly rains from the three stations.

Weighted means for $\delta^{18}O$ and d-excess, weighted by the total amount of precipitation, have been calculated by the following formula of [6]:

$$M_w = \frac{\sum_{i=1}^{n} P_i \times C_i}{\sum_{i=1}^{n} P_i}$$

where Pi denotes the monthly precipitation and Ci denotes the respective value for isotopic content ($\delta^{18}O$ and d-excess).

The calculated values of weighted means for $\delta^{18}O$ and d-excess are used in correlation with altitude of the sampling stations in order to examine the continental climatic and altitude effects (Figure 13). Weighted means for $\delta^{18}O$ decrease with altitude (Figure 13a) while the monthly events recorded in all stations are characterized by a d-excess increasing with altitude (Figure 13b).

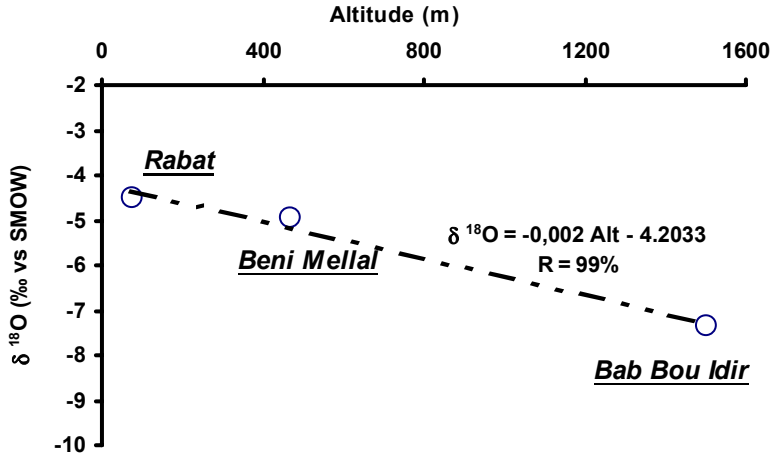


FIG. 13a: Mean weighted $\delta^{18}O$ versus altitude of sampling station.

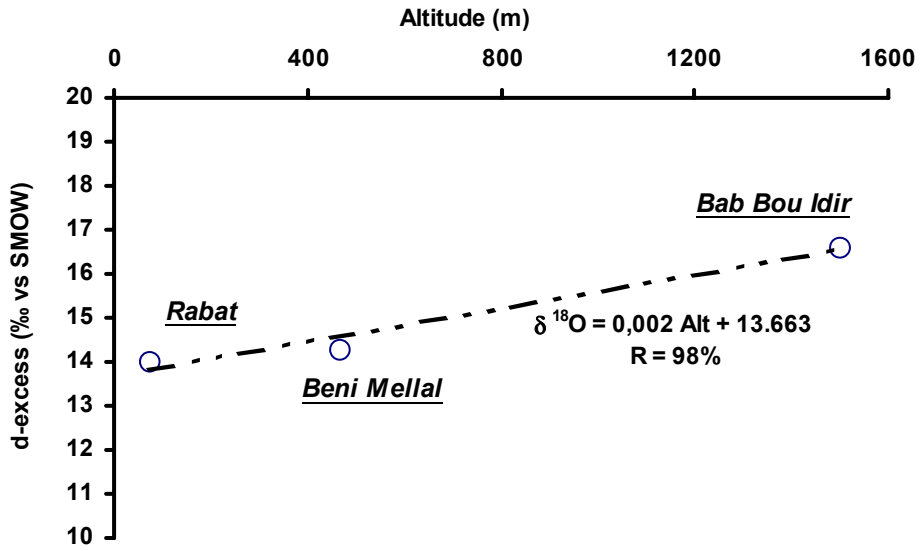


FIG. 13b: Mean weighted d-excess versus altitude of sampling station.

5. Conclusions

Isotopic composition (oxygen-18 and deuterium) of daily and monthly rain events was monitored during the period from November to April of each year from 2000 to 2003 at three meteorological stations in Morocco. Water vapour has been also collected at only Rabat station from January 2002 to April 2003. In parallel of the sampling, the amount of each precipitation event has been also recorded. Temperature and atmospheric humidity data were collected from National Meteorological Office of Morocco.

Isotopic analyses reveal large variations in both $\delta^{18}O$ and $\delta^{2}H$, as well as in the values of deuterium excess. The observed variations are clearly related to different origins of the water vapour (Atlantic Ocean and Mediterranean Sea) as well as to different trajectories of precipitating air masses.

Relations between stable heavy isotopes (^{18}O and ^{2}H) and between $\delta^{18}O$ and local meteorological parameters (air surface temperature, rain amount and relative humidity) were examined in order to search the prominent parameter, which allows to understand better the rain isotopic composition acquirement. The relations between $\delta^{18}O$ and local meteorological parameters were unreliable. Correlation coefficients were not exceeded 0.4 revealing that there are others parameters that more influenced the isotopic composition of precipitation like the origin and trajectory of the precipitating air masses.

$\delta^{18}O/\delta^{2}H$ plots show that the majority of samples collected at Rabat station (precipitation and water vapour) are associated with air masses coming from Atlantic Ocean. At Bab Bou Idir station, almost all samples are associated with air masses coming from the East Mediterranean Sea while the majority of samples collected at Beni Mellal station are located between WMWL and NIR line. These later samples are associated with air masses coming, for one thing, from Atlantic Ocean and reaching Morocco by its Atlantic coast and for another thing, from North Atlantic Ocean and crossing the western part of the Mediterranean Sea before reaching Morocco at its Mediterranean coast. The evaporative isotopic enrichment of raindrops below the clouds is signalled in a few samples at the three stations.

6. Future perspectives

The above conclusions must be confirmed by further investigations, which should take into account other precipitation events supplemented by meteorological information collected at others stations with a strategic situation. Hence, three meteorological stations may be proposed for this aim. The first one will be located at Tanger city, which is the meeting point of the Atlantic Ocean and the Mediterranean Sea. The second station will be situated at Nador, which is a Mediterranean coastal city. The third station will be located at Ouarzazate city near the Sahara area. For another thing, two supplemented meteorological stations can be proposed at Marrakech and Agadir cities in order to monitor wholly five stations located on transect line lying in NE-SW direction (Middle Atlas direction) from the Mediterranean Sea coast with Nador station to the Atlantic coast with Agadir station.

REFERENCES

[1] DANSGAARD, W., Stable isotopes in precipitation. Tellus 16 (1964) 567–584.
[2] MERLIVAT, L., JOUZEL, J., Global climatic interpretation of thr deuterium, oxygen-18 relationship for precipitation. J. Geophys. Res. 84 (1979) 5029–5033.
[3] CRAIG, H., Isotopic variations in meteoric waters, Science (1961) 133–1702.
[4] GAT, J.R., GONFIANTINI, R., Stable isotope hydrology, deuterium and oxygen-18 in the water cycle. Technical Report Serie No. 210, IAEA, Vienna (1981).
[5] GAT, J.R., CARMI, I., Evolution of the isotopic composition of atmospheric water. Journal of Geophysical Research 75 (1970) 3039.
[6] YURTSEVER, Y., GAT, J. R., Stable Isotope Hydrology. Deuterium and oxygen-18 in the water cycle. Technical Report Series No. 210, IAEA, Vienna, (1981) 103–139.

ISOTOPIC COMPOSITION OF RAIN AND WATER VAPOUR SAMPLES FROM LISBON REGION: CHARACTERIZATION OF MONTHLY AND DAILY EVENTS

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Abstract. The isotopic composition of precipitation is intimately linked with rain formation conditions, specifically with the temperature of formation, the origin of the air masses, the degree and mechanism of rainout. In this framework, the systematic study of the isotopic composition of monthly precipitation, rain events and atmospheric water vapour was initiated at ITN under the CRP — Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to air Circulation Patterns and Climate. The discussion of the results obtained in the Portuguese network was guided by distinct regularities and isotopic data approaches: correlation between the oxygen-18 and deuterium content in monthly precipitation with the geographic location of the stations, correlation between the isotopic content with the local surface air temperature distance to the Atlantic coast and altitude. The comparison between rain events and atmospheric water vapour will be discussed. The very depleted isotopic composition found in vapour and rain event samples are associated to the depressions over Atlantic (in front of the Portuguese coast — Mid North Atlantic) or over the British Islands, crossing Portugal mainland from W to E.

1. Introduction

In the following up of the IAEA/WMO Global Network for Isotopes in Precipitation, a systematic collection of data on isotope content of precipitation in Portugal was initiated in 1988 at the Instituto Tecnológico e Nuclear (ITN — Sacavém, Portugal). The main goal of this project is the determination of temporal and spatial variations of environmental isotopes (^{2}H, ^{18}O and ^{3}H) in precipitation, to obtain background information essential in hydrological and climatological investigations, with the main scope on water resources planning and development.

It is worth to mention, that the isotopic composition of precipitation is intimately linked with rain formation conditions, specifically with the temperature of formation, the origin of the air masses, the degree and mechanism of rainout. In this framework, the systematic study of the isotopic composition of precipitation water samples in Portugal was initiated with a monthly base, collecting samples in 10 meteorological stations, seven located in Continental Portugal, two in Azores and one in Madeira Island. After 1991, this continuous record of the national network was reduced to five stations (Porto, Penhas Douradas, Portalegre, Faro and Funchal (Madeira Island)). Since the early beginning of the project "Isotopes in Precipitation", the Portuguese isotopic database has been frequently used in many hydrogeological studies in national and international research programmes.

A station was set up in 2002 at ITN — *campus* for daily precipitation and a water vapour collection. In this work, the results obtained with the monthly database and daily events will be presented and discussed. The importance of this information to assess the orientation and/or variation of the air masses for climatic studies will be emphasised.

2. Methodology

The environmental isotopes ^{18}O, ^{2}H and ^{3}H determinations are being carried out at Instituto Tecnológico e Nuclear by Environmental Analytical Chemistry Group. The deuterium determinations of the daily precipitation events and water vapour samples from 2002-2003 were performed in the IAEA – Isotope Hydrology Section laboratories (Vienna Austria). In Portugal, the determinations of ^{18}O and ^{2}H were carried out using a mass spectrometer SIRA 10 VG-ISOGAS according to Epstein &

Mayeda [1] and Friedman [2] analytical methods used in the determinations of oxygen-18 and deuterium, respectively.

The tritium measurements are carried out in all monthly water samples, using an electrolytic enrichment followed by liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The detection limit of this equipment (liquid scintillation counting) is 0.5 TU. The associated error to the measurements varies with the tritium concentration in the samples, although usually is around 0.6 TU.

The results that are being discussed represent three different groups of samples:

- the first one corresponds to the monthly precipitation water samples from the Portuguese Network Isotopes in Precipitation (1988-2002);
- the second group stands for the daily precipitation at ITN *Campus* (Sacavém) for the period October 2002 – March 2003 (68 water samples);
- a third group representing 48 hours of continuous sampling of water vapour at ITN *Campus* from October 2002 to March 2003 (46 samples).

3. Results and discussion

3.1. Portuguese network isotopes in precipitation - Monthly data

From the climatic point of view Portugal is under a north circulation regime and the water vapour moisture is mostly representative of the Atlantic influence, being autumn and winter the seasons with the highest precipitation amount. Using the available isotopic record from continental Portugal, monthly database, of we try to visualize a spatial distribution of the results along Portugal mainland (Fig. 1). The geographic location, annual average temperature and mean amount of precipitation are presented in Table 1.

The discussion of the results obtained in the Portuguese network will be guide by distinct regularities and isotopic data approaches:

- Correlation between the oxygen-18 and deuterium content in monthly precipitation with the geographic location of the stations - latitude and longitude effect.
- Correlation between the oxygen-18 and deuterium content in monthly precipitation with the local surface air temperature - seasonal temperature effect.
- Correlation of the continuously depletion in deuterium and oxygen-18 in monthly precipitation averages with increasing altitude and distance from the Atlantic coast (altitude effect) associated with an increase of deuterium excess.

Table 1. Geographic location, climatic and isotopic features of the meteorological station from GNIP network

	Bragança	**VilaReal**	**Porto**	**P.Douradas**	**Portalegre**	**Beja**	**Faro**
Record	1988-91	1988-91	1988-04	1988-04	1988-04	1988-91	1988-01
Lat.	41.48 N	41.19 N	41.08 N	40.25 N	39.17 N	38.01 N	37.01 N
Long.	6.44 W	7.44 W	8.36 W	7.33 W	7.25 W	7.52 W	7.96 W
Alt. (m)	690	481	93	1380	597	246	9
Pr. (mm)	774	977	1042	1411	780	675	597
Tem (ºC)	13.0	14.0	15.2	9.7	15.7	16.9	17.6
$\delta^{18}O$ (‰)	-7.73	-6.40	-4.54	-7.20	-5.60	-5.84	-4.80
$\delta^{2}H$ (‰)	-50.0	-42.5	-26.9	-43.3	-33.2	-36.2	-24.4
d (‰)	11.8	8.7	9.4	14.3	11.6	10.6	14.0

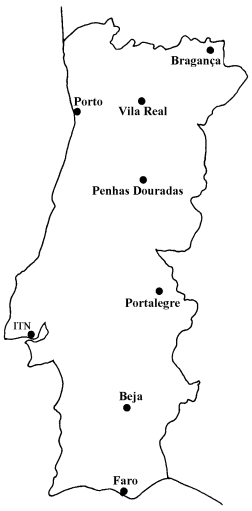

FIG. 1. Sampling of the "Portuguese Network of Isotopes in Precipitation".

Results of isotopic composition and meteorological data for the seven Portuguese stations part of the network isotopes in precipitation located in Portugal mainland were used to perform a basic statistic treatment. The regional meteoric water line (RMWL) for mainland Portugal was drawn up using the weighted monthly averages of deuterium and oxygen-18: $\delta^{2}H = (6.78 \pm 0.10)\ \delta^{18}O + (4.45 \pm 4.46)$, r=0.95 and n=405 (Fig.2).

A high positive correlation was obtained with this group of samples, although small differences have been observed among the isotopic composition. These differences are most probably related with the geographic location, altitude and local surface air temperature, in spite of the small dimensions of Portugal mainland (approximately 700 km *vs* 150 km).

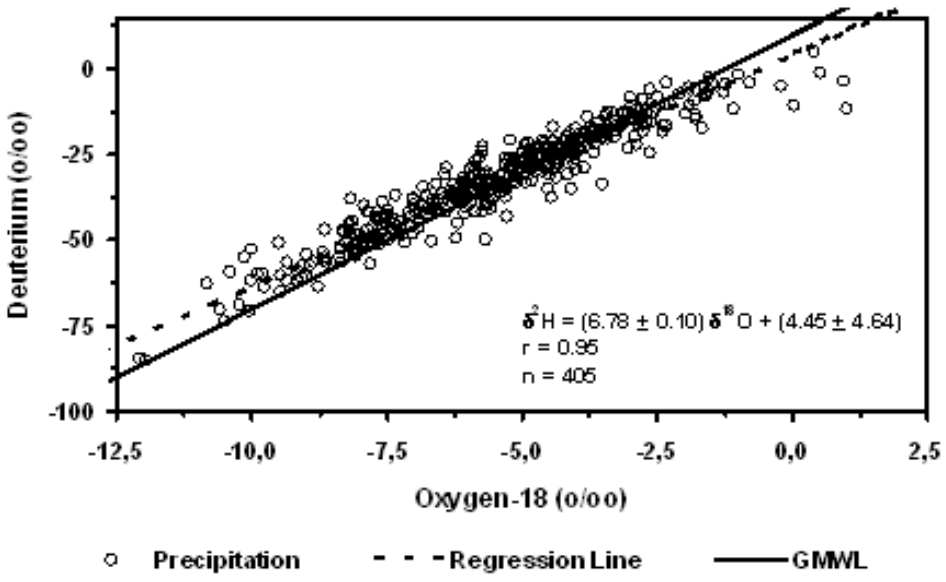

FIG. 2. Weighted $\delta^{18}O$ versus $\delta^{2}H$ in monthly precipitation collected in the Portuguese Network Isotopes in Precipitation.

In order to ascertain the spatial evolution of the air masses over Portugal mainland we have estimate the slope, intercept and correlation coefficient between ^{2}H and ^{18}O in monthly weighted means of precipitation samples for each of the seven meteorological stations:

Bragança:	$\delta^{2}H = (7.17 \pm 0.31)\ \delta^{18}O + (4.75 \pm 2.22)$	r = 0.97
Vila Real:	$\delta^{2}H = (6.25 \pm 0.40)\ \delta^{18}O + (2.71 \pm 2.36)$	r = 0.94
Porto:	$\delta^{2}H = (6.20 \pm 0.33)\ \delta^{18}O + (1.12 \pm 1.16)$	r = 0.93
Penhas Douradas:	$\delta^{2}H = (7.14 \pm 0.35)\ \delta^{18}O + (8.65 \pm 2.75)$	r = 0.95
Portalegre:	$\delta^{2}H = (6.38 \pm 0.36)\ \delta^{18}O + (3.24 \pm 2.28)$	r = 0.92
Beja:	$\delta^{2}H = (7.67 \pm 0.44)\ \delta^{18}O + (8.93 \pm 2.39)$	r = 0.96
Faro:	$\delta^{2}H = (6.44 \pm 0.24)\ \delta^{18}O + (3.41 \pm 1.13)$	r = 0.94

The intercept value varies from 1.12 to 8.93 in the seven stations, although the slope obtained in each station is close to the Global Meteoric Water Line.

The annual mean values of ^{18}O and ^{2}H content in precipitation are plotted in Figure 3, as a function of latitude of each station. Also in Figure 3 the same isotopic content are plotted as a function of longitude. A high positive correlation was obtained between the mean isotopic composition in monthly precipitation record and the geographic location of the stations. However, a latitudinal or longitudinal distribution of the deuterium excess for this group of stations derived also from the long-term annual means of $\delta^{2}H$ and $\delta^{18}O$ reveals a poor correlation, with large spread of d-values without any clear trend.

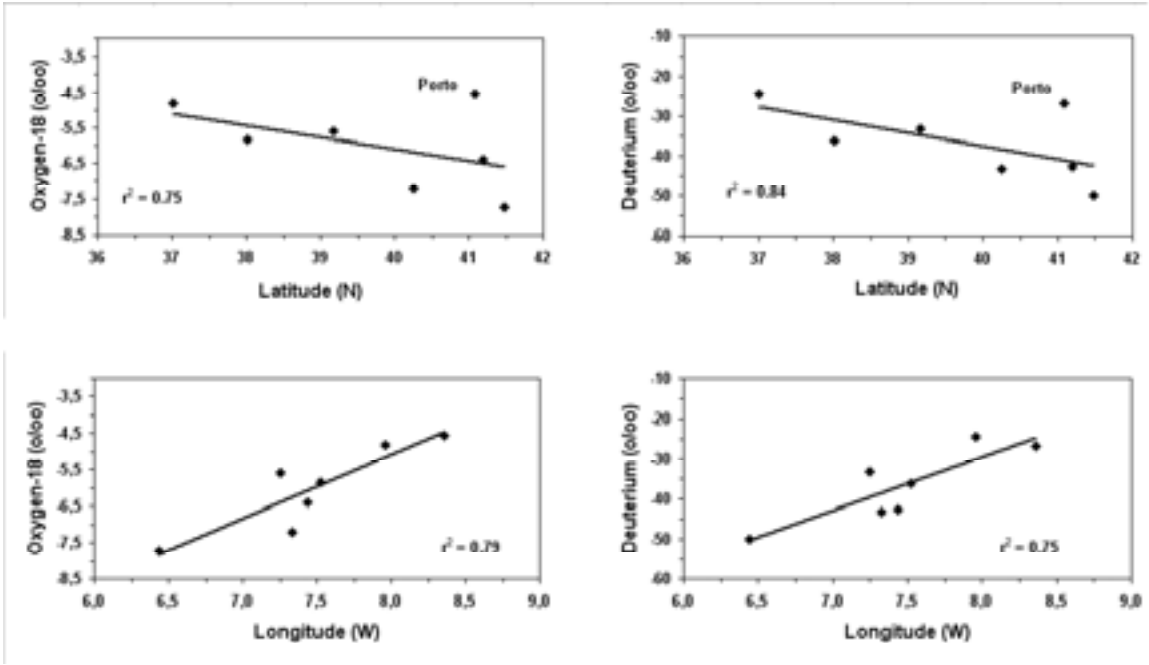

FIG. 3. Annual mean values of $\delta^{18}O$ and $\delta^{2}H$ content in precipitation vs. geographic (latitude and longitude) location of the meteorological stations.

In order investigate the origin of the water masses we have used the deuterium excess values along the year for these stations and plotted it in a diagram. A similar pattern of deuterium excess values can be observed (Fig. 4). The major global source of water vapour is the tropical ocean with about 65 % of the global evaporation flux over the oceans originates between 30ºS and 30ºN, and for stations with dominating winter precipitation an apparent increase of deuterium excess is observed [3]. The apparent seasonality of d-excess values is observed at this group of Portuguese stations, probably due to lower relatively humidity (normalized to the sea surface temperature) over the ocean during winter time.

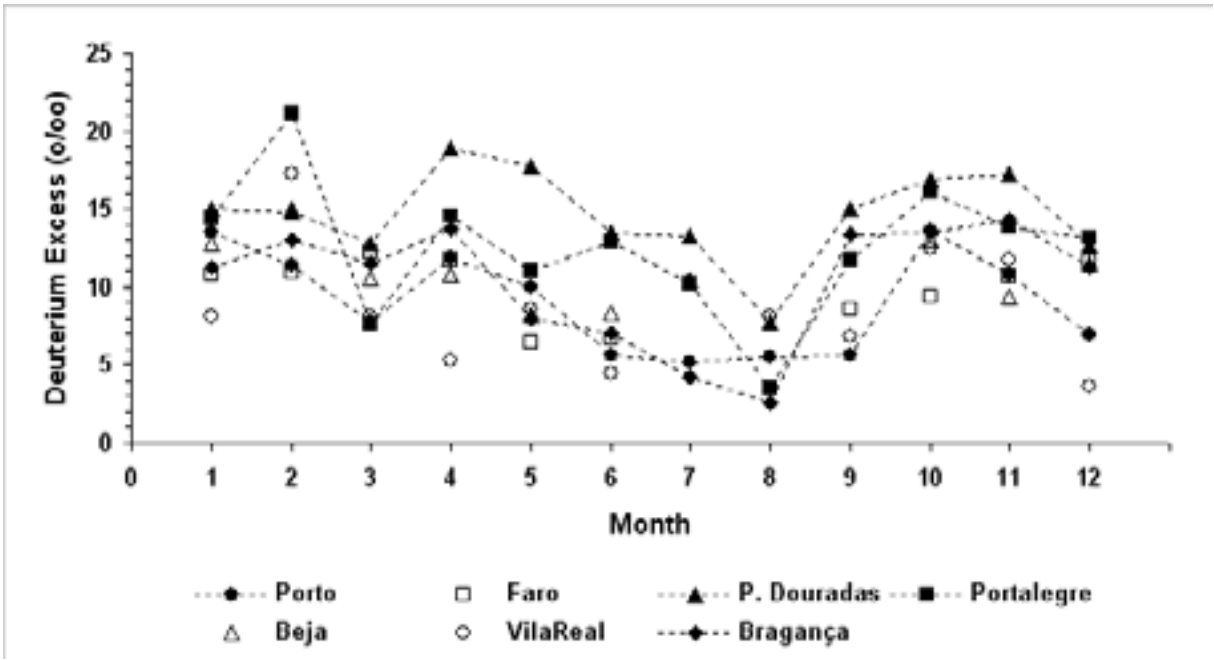

FIG. 4. Deuterium excess values along the year for network.

Additionally, an altitude effect is also found with the deuterium excess, the correlation coefficient is r^2= 0.75, higher altitudes present higher deuterium excess the coastal stations present the lowest values (Fig.5).

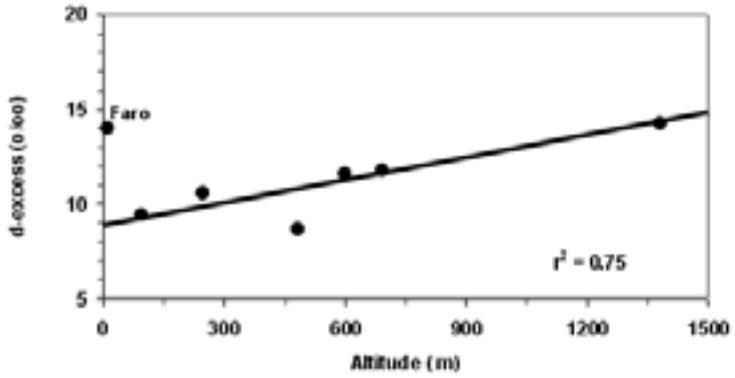

FIG. 5. Altitude effect in deuterium excess.

The relation between local surface air temperature and the isotopic composition of precipitation within the Portuguese network has provided important background information in different hydrogeological research studies carried out in Portugal. Among the most relevant studies are the palaeoclimatic signatures in Aveiro palaeowaters [5] and the identification of the recharge areas in the Monção geothermal systems [6] demonstrating the stable isotopes a potential importance as paleoclimatic indicators, in the reconstruction of past climatic changes and water management [3].

In Figure 6 is represented the relationship between the isotopic composition and the mean monthly temperature. The slope of this relationship is 0.21‰ per ºC for $\delta^{18}O$ and 1.21 per ºC for $\delta^{2}H$. The isotopic gradient - temperature effect - obtained show some deviation from those presented by Rozanski [3] namely 0.69 ‰ per ºC and 5.6 ‰ per ºC for oxygen-18 and deuterium respectively [8]. The authors point out that the $\Delta\delta^{18}O$-ΔTemperature relationship is non-linear, and in situations were assuming linear dependence the slope change from 0.66 ‰ per ºC to 0.17 ‰ per ºC, for surface air temperatures lower than –10ºC and higher than 10ºC respectively.

Also in Figure 6 is displayed the negative correlation between the amount of monthly precipitation and the isotopic composition of precipitation samples from the Portuguese network.

In general the distribution of ($\delta^{18}O$ and $\delta^{2}H$) mimics the topography of the continents; mountain chains are marked by more negative δ values. In the present study the hydrogen and oxygen heavy isotope content of the rain samples are directly correlated with the altitude of meteorological stations (Fig.7), by the following equations:

$$\delta^{18}O\ (‰) = -0.002\ \text{Altitude (m)} - 5.025 \qquad (r^2 = 0.61)$$

and

$$\delta^{2}H\ (‰) = -0.014\ \text{Altitude (m)} - 29.667 \qquad (r^2 = 0.49).$$

Consequently, the altitude effect for Portugal mainland is about -0.2 ‰ per 100 m for oxygen-18 and -1.4 ‰ per 100 m for deuterium. The lowering of temperature with increasing elevation in mountains regions usually leads to enhanced condensation and therefore to a progressive depletion in heavy isotopes of precipitation.

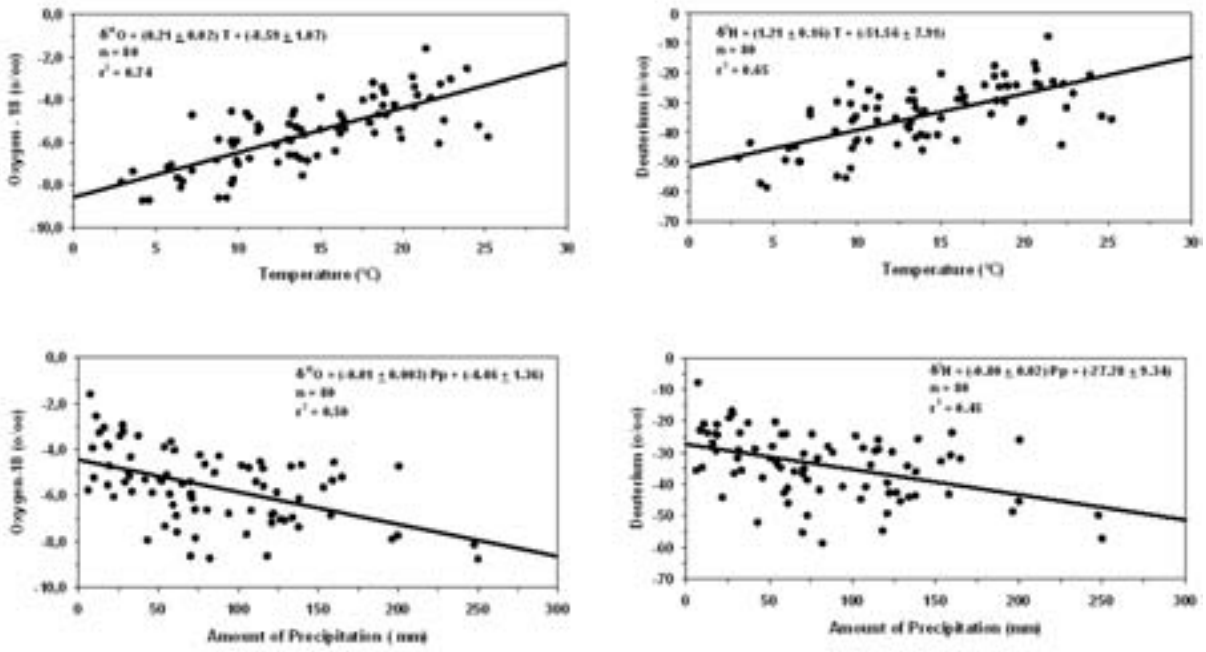

FIG. 6. Relationship between the isotopic composition and the mean monthly temperature and amount of precipitation.

This *"altitude effect"* has been used in numerous hydrological studies to identify the recharge areas and to investigate the origin and interconnection of water bodies. The isotopic gradient estimated is in agreement with the vertical isotope gradient found in literature, which varies between –0.15 ‰ and -0.50 ‰.100 m^{-1} for oxygen-18 and about –1 ‰ to –4 ‰.100 m^{-1} for deuterium [7].

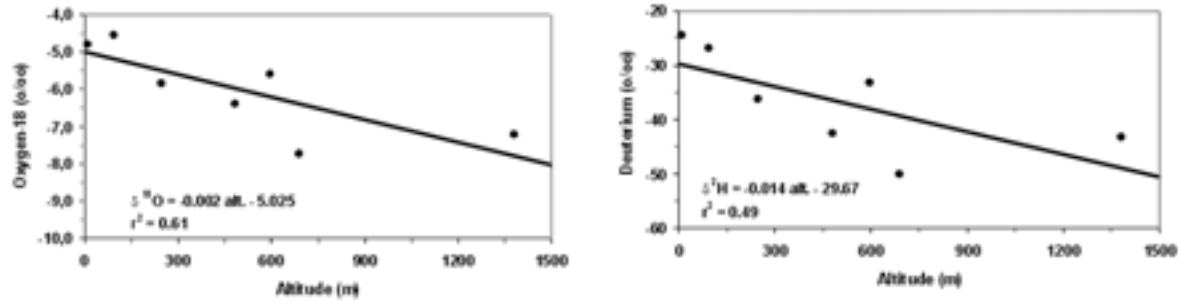

FIG. 7. Relationship between the mean isotopic composition and the sampling altitude.

3.2. Daily precipitation events – Lisbon Region

The systematic collection of individual rain events was carried out at ITN *Campus* between October 2002 and March 2003. Sixty eight precipitation samples were collected representing single rain events. In a first approach, a distribution pattern of the isotopic composition of the single events with the precipitation amount was established. It is important to mention that during this period, 2002-2003, an important increase of rain amount was recorded (Table 2). Simultaneously an increase in temperature was also verified in the last years, (and for the same period), when compared with a long-term monthly average values (Table 3).

Table 2. Precipitation record between the periods 2000 to 2003 compared with the long-term record

Month	**Long-term** 1961-1999	**2000 – 2001**		**2001 - 2002**		**2002 – 2003**	
September	26	18	(-31 %)	61	(+134 %)	81	(+211 %)
October	80	28	(-75 %)	151	(+89 %)	105	(+31 %)
November	114	170	(+49 %)	8	(-92 %)	193	(+69 %)
December	108	296	(+174 %)	42	(-61 %)	162	(+50 %)
January	110	192	(+74 %)	77	(-30 %)	134	(+22 %)
February	111	76	(-32 %)	16	(-86 %)	89	(-20 %)
March	69	154	(+123 %)	107	(+55 %)	76	(+10 %)
April	64	9	(-86 %)	43	(-33 %)	122	(+91 %)
May	39	52	(+33 %)	17	(-56 %)	2	(-96 %)
June	21	16	(-24 %)	7	(-67 %)	3	(-86 %)
July	5	2	(-60 %)	1	(-80 %)	2	(-60 %)
August	6	1	(-83 %)	0.2	(-97 %)	33	(+450 %)

Table 3. Temperature record between the periods 2000-2003 compared with the long-term record

Month	**Long-term** 1961-1999	**2000 - 2001**		**2001 - 2002**		**2002 – 2003**	
September	17.0	17.2	(+1.2 %)	17.4	(+2.3 %)	17.4	(+2.3 %)
October	14.6	14.7	(+0.7 %)	16.0	(+9.6 %)	16.2	(+10.9 %)
November	11.2	11.5	(+2.7 %)	10.4	(-7.1 %)	12.4	(+10.7 %)
December	8.9	11.6	(+30.3 %)	7.1	(-20.2 %)	11.2	(+25.8 %)
January	8.2	10.3	(+25.6 %)	9.5	(+15.8 %)	8.4	(+2.4 %)
February	9.0	10.1	(+12.2 %)	9.9	(+10.0 %)	9.1	(+1.1 %)
March	9.9	12.6	(+27.3 %)	11.3	(+14.1%)	11.6	(+17.1 %)
April	11.1	12.7	(+14.4 %)	11.7	(+5.4 %)	12.0	(+8.1 %)
May	13.0	14.0	(+7.7 %)	13.3	(+2.3 %)	15.1	(+16.1 %)
June	15.6	16.8	(+7.7 %)	15.7	(+0.6 %)	17.8	(+14.1 %)
July	17.4	17.7	(+1.7%)	17.6	(+1.1 %)	17.9	(+2.8 %)
August	17.7	18.4	(+3.9 %)	17.8	(+0.6 %)	20.8	(+17.5 %)

Figure 8 displays the lack of correlation between the isotopic composition and the rain amount. In both cases (oxygen-18 and deuterium) the correlation coefficient is close to 0.50.

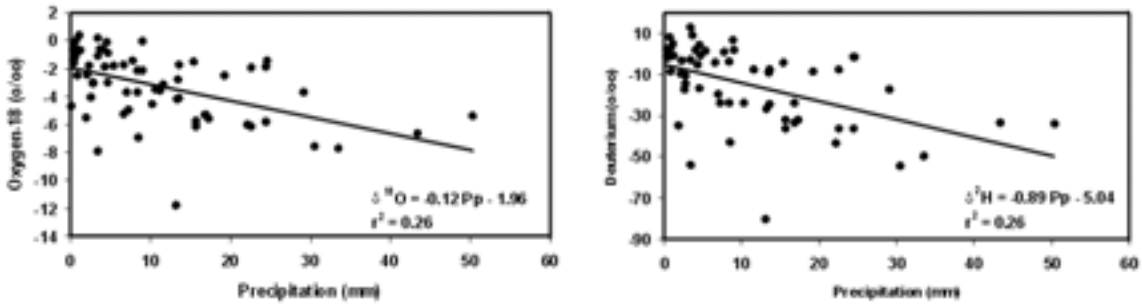

FIG. 8. Correlation between the isotopic composition and the rain events amount.

The isotopic composition of daily rain events varies between –11.85 ‰ up to 0.37 ‰ for oxygen-18 and from -80.4 ‰ up to 12.8 ‰ for deuterium. The most enriched rain event was associated to a small amount of precipitation, while, for the most depleted value measured in rain events it was not possible to identify any specific pattern associated to this content.

The relation $\delta^{18}O$ versus $\delta^{2}H$ was calculated by using the daily isotopic information of the rain events (Fig. 9):

$\delta^{2}H = 7.44\ \delta^{18}O + 8.66$ (n = 68, $r^2 = 0.96$)

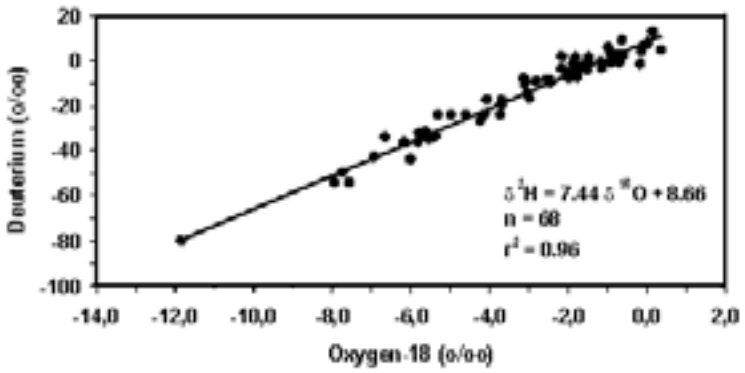

FIG. 9. $\delta^{18}O$ versus $\delta^{2}H$ in daily precipitation events.

Plotting the oxygen-18, deuterium and amount of rain as a function of the day of the event, an isotopic evolution cannot be observed between the beginning of October and end of March (Fig.10).

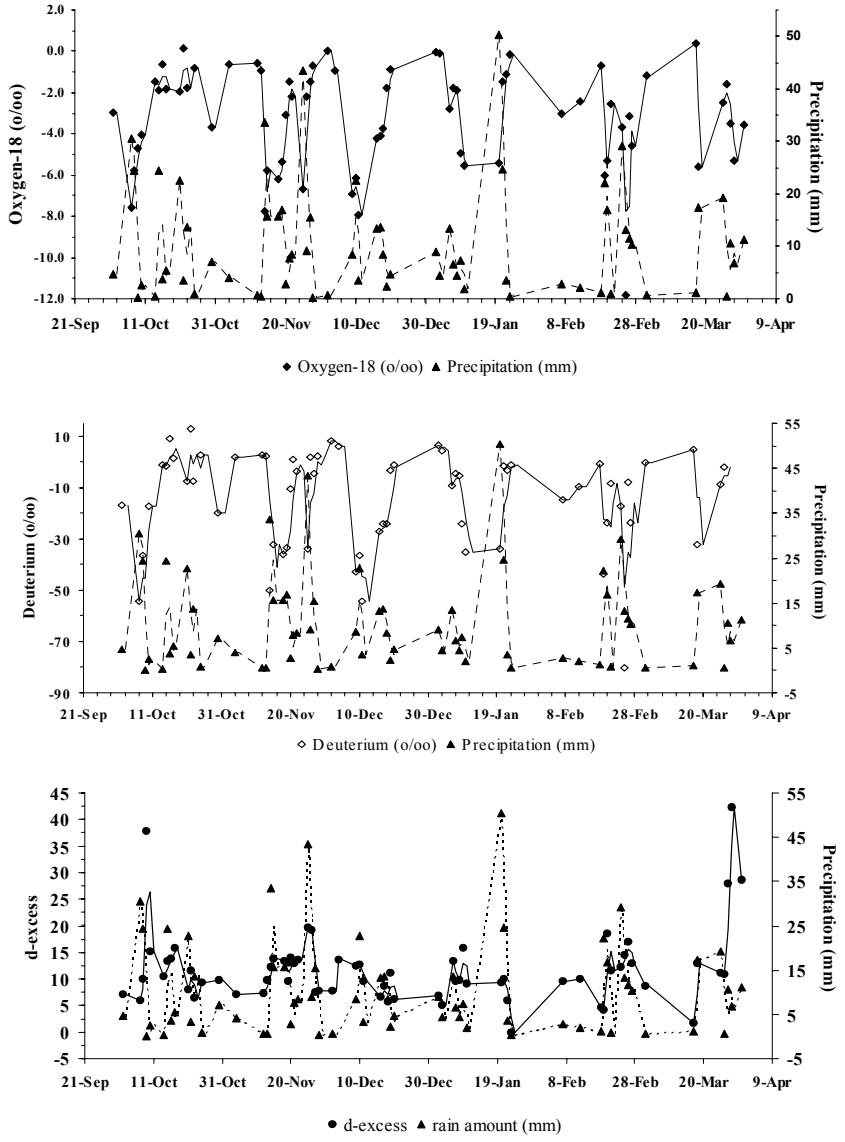

FIG. 10. Daily $\delta^{18}O$, $\delta^{2}H$, and d-excess composition of daily precipitation.

An overview of the data allowed identifying a progressive change in the isotopic composition of the water masses, without sharp variations for consecutive sampling days. Also, when the d-excess and amount of precipitation are plotted *versus* the sampling day, a similar pattern of the distribution of d-excess and rain amount can be found as a function of time (Fig 10). As mention before, no clear difference can be established in deuterium excess values during the sampling period, being the mean value about 10 ‰.

3.3. Atmospheric water vapour at Lisbon Region

The isotopic composition of water vapour was measured in forty six samples representing 48 hours of continuously sampling from the period October 2002 to end of March 2003. An overview of the isotopic composition reveals at a first approach, more depleted values when compared with the daily precipitation. The water vapour composition varies from –17.29 ‰ up to –11.33 ‰ in oxygen-18 and from –110.2 ‰ up to –71.5 ‰ in deuterium. The relation $\delta^{18}O$ *versus* $\delta^{2}H$ (Fig. 11) is the following:

$$\delta^{2}H = 5.66\ \delta^{18}O - 13.44 \qquad (n=46;\ r^{2} = 0.70)$$

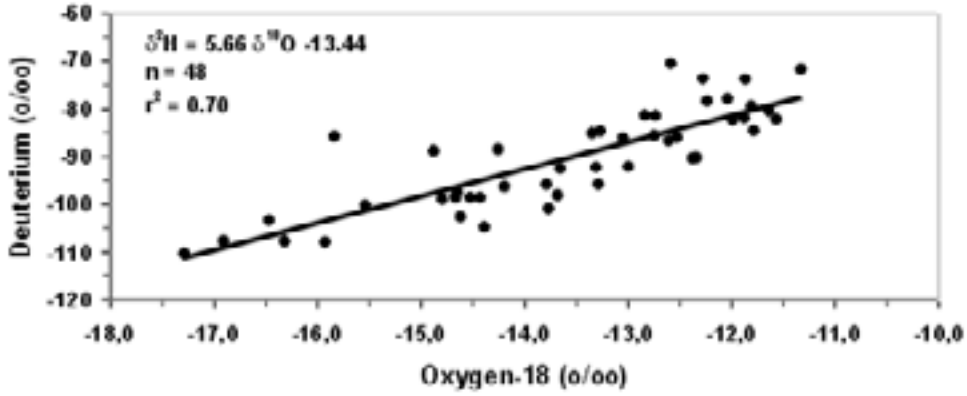

FIG. 11. $\delta^{18}O$ versus $\delta^{2}H$ in atmospheric water vapour.

The deuterium excess in these samples varies from 8.84 ‰ up to 40.92 ‰, with a mean d-excess of 18.39 ‰. The d-excess average decreases to 17.89 ‰, when the extreme d-excess value (40.92 ‰) is removed from the mean.

Plotting the oxygen-18, deuterium and d-excess versus time, an evolution in the isotopic composition of the water vapour (Fig. 12) from October - December 2002 (more enriched in heavy isotopes) to January- March 2003 (more depleted in heavy isotopes) can be observed. However, differences in temperature and amount of precipitation were also observed (Table 2 and Table 3) between these two periods of sampling, in Lisbon area.

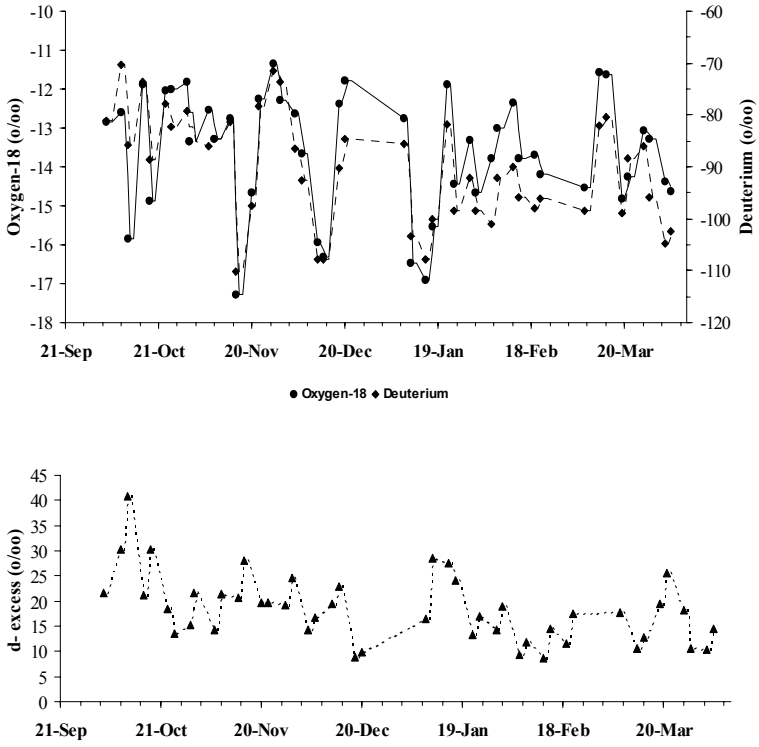

FIG. 12. Evolution in the isotopic composition of the water vapour during the sampling period.

The magnitude of the rainfall was higher for the first 3 months (October – December 2002) with a record of 460 mm in precipitation, nearly 154 % higher than the second period of sampling (January –

March 2003). Besides, during the first period temperatures were also higher. The observed trends in the isotopic composition of the water vapour and the temperature variations and relative humidity, indicate that the variation of the isotopic values from the first three months of sampling is higher than those determined for samples collected from January to March 2003.

October 2002 – December 2002

$\delta^{18}O_{mean}$ = -13.31 ± 1.67 (‰), n= 23 $\delta^{2}H_{mean}$ = -90.3 ± 11.1 (‰), n = 23

January 2003 – March 2003

$\delta^{18}O_{mean}$ = -13.86 ± 1.38 (‰), n= 23 $\delta^{2}H_{mean}$ = -94.7 ± 7.7 (‰), n = 23

3.4. Related stable isotopes variations (rain and vapour) with origin and trajectories of air masses

Comparing the isotopic composition of rain events with the water vapour samples depletion in heavy isotopes in the atmospheric water vapour calls the attention. However, these two groups of water samples exhibit similar distribution pattern along the sampling period (Fig. 13).

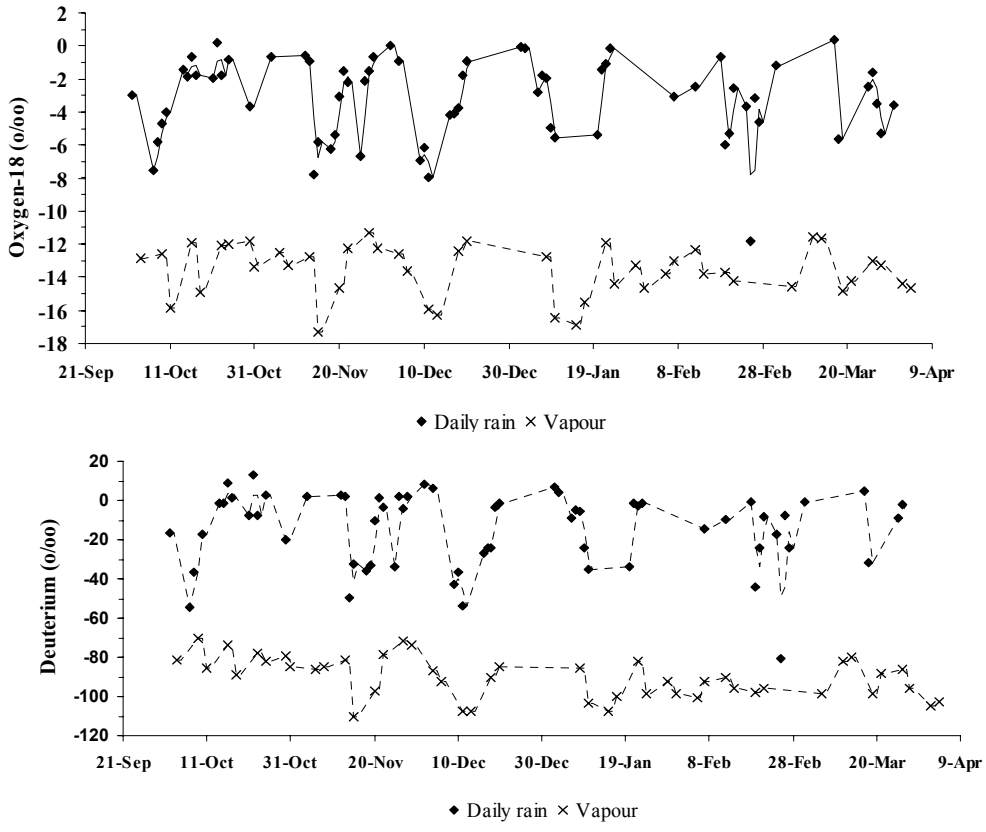

FIG. 13. Comparison of the isotopic composition of rain events with the water vapour samples from October 2002 – March 2003.

The relation $\delta^{18}O$ *versus* $\delta^{2}H$ was calculated:

Rain events $\delta^{2}H = 7.44\ \delta^{18}O + 8.88$ $r^2 = 0.96$; n = 62

Vapour $\delta^{2}H = 5.66\ \delta^{18}O - 13.44$ $r^2 = 0.70$; n = 46

Plotting in a diagram the relation δ^2H *versus* $\delta^{18}O$ (Fig.14), two groups of samples we can observe, being the most depleted in heavy isotopes the atmospheric water vapour. An evaluation of the results using the weight mean isotopic composition reveals a difference of about 9 ‰ in oxygen-18 and around 65 ‰ in deuterium:

Rain events

$\delta^{18}O$ = -4.46 ‰; n = 63 δ^2H = -24.4 ‰; n= 63

d-excess = 10.82 ± 7.04 ‰ (mean value)

Water vapour

$\delta^{18}O$ = -13.35 ‰; n = 46 δ^2H = -89.0 ‰; n= 46

d-excess = 18.39 ± 6.79 ‰ (mean value)

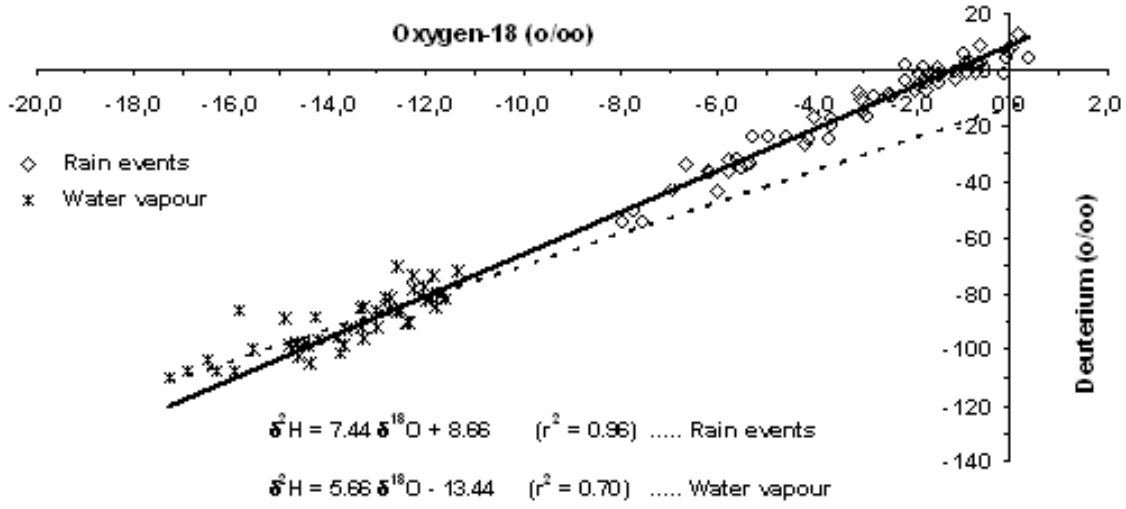

FIG. 14. $\delta^{18}O$ versus δ^2H in atmospheric water vapour and daily precipitation events.

The difference in the isotopic composition of the rain events and atmospheric water vapour is close to the equilibrium value in temperate and humid regions [9]. The correlation between the water vapour samples and precipitation events in most cases may not be clear, although a similar evolution can be observed, probably due to the different sampling period since the two sampling stations are in closely located.

In order to establish a relation between variations in the isotopic composition of the rain events and of the atmospheric water vapour with the origin and trajectories of air masses, we used the meteorological maps / information to draw back trajectories. The available data points out that the control of the air masses trajectories over Portugal has a dominant Atlantic origin. The most depleted isotopic values in vapour (Fig.15) and rain (Fig.16) is associated to the depressions over Atlantic (in front of the Portuguese coast – Mid North Atlantic) or over the British Islands, originating a series of fronts that cross the Iberian Peninsula (Portugal), from W to E. The associated fronts to the depression induce a progressive depletion both in rain and water vapour.

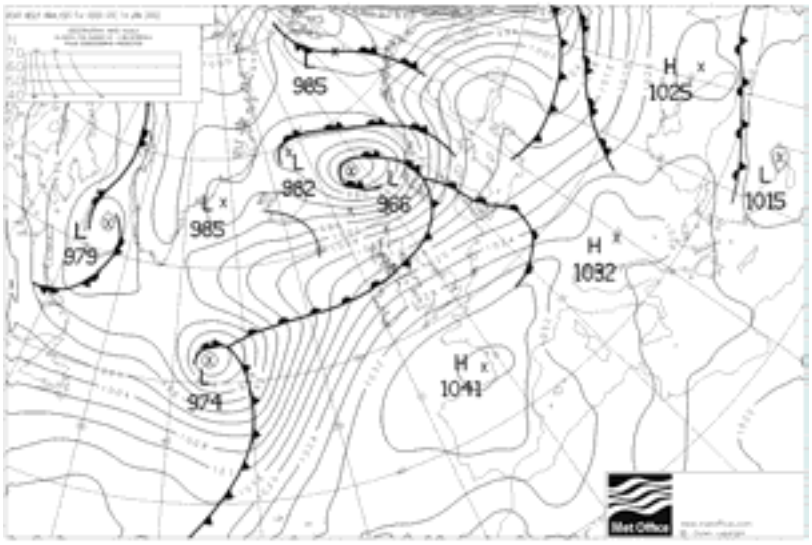

FIG. 15. Weather map corresponding to 14 January 2003 characterized by low depression in North Atlantic and over the British Islands.

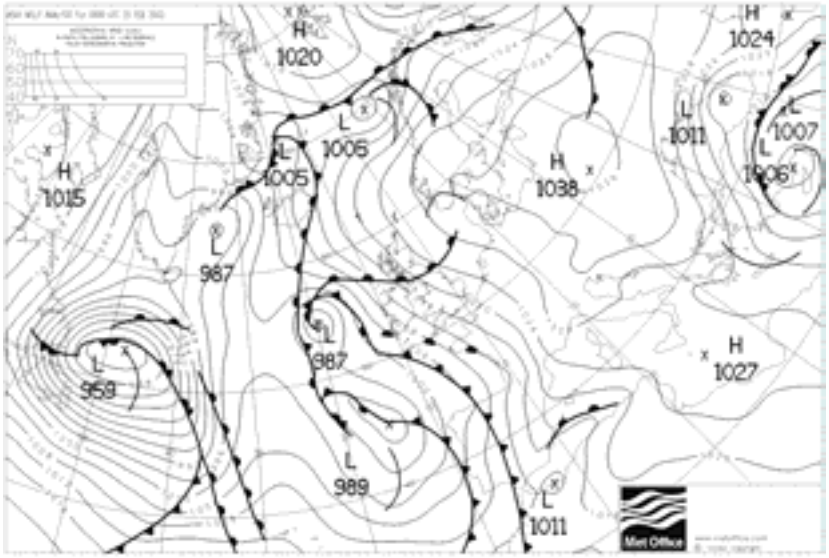

FIG. 16. Weather map corresponding from 25 of February 2003.

4. Conclusions

The data obtained have given a significant contribution to the improvement of the understanding of local and regional isotope hydrogeological features. Results of the project "Portuguese Network Isotopes in Precipitation" have provided important background information in research hydrological studies and they are available to the scientific community.

The correlation between the water vapour samples and precipitation events in most cases is not clear probably due to the different characteristics of the sampling periods, although a similar evolution can be observed.

The large depletion in the isotopic composition found in vapour and rain event samples are associated to the depressions over Atlantic (in front of the Portuguese coast – Mid North Atlantic) or over the British Islands, crossing Portugal mainland from W to E. The atmospheric weather depressions induce a progressive depletion both in rain and water vapour.

The results obtained under this CRP - Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to air Circulation Patterns and Climate allowed to follow air masses transport in some parts of the Mediterranean Basin. Besides, the obtained set of data is of significant importance to the establishment of the distribution patterns of precipitation providing background data to validation/calibration of climate models.

REFERENCES

[1] EPSTEIN, S., MAYEDA, T., Variations of ^{18}O content of waters from natural sources, Geochimica Cosmochimica Acta, 4 (1953) 213–224.

[2] FRIEDMAN, I., Deuterium content of natural waters and other substances, Geochimica et Cosmochimica Acta, 4 (1953) 89–103.

[3] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R., Isotopic patterns in modern global precipitation, American Geophysical Union, Geophysical Monograph 78, Climate Change in Continental Isotopic Records (1993) 1–36.

[4] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, R., Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate, Science, 258 (1992) 981–985.

[5] CARREIRA, P.M. et al., Application of environmental isotope methods in assessing groundwater dynamics of an intensively exploited coastal aquifer in Portugal (Proceedings of an International Conference on Isotopes in Water Resources Management), STI/PUB/970, vol. 2, IAEA, Vienna (1996) 45–58.

[6] CARREIRA, P.M. et al., Isotopic, geochemical and geophysical studies to improve Caldas de Monção thermomineral waters conceptual circulation model (NW-Portugal), Revista de Xeologia Galega e do Hercínico Peninsular, 29 (2004) 147–170.

[7] ARAGUÁS-ARAGUÁS, L., FROEHLICH, K., ROZANSKI, K., Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture, Hydrological Processes, 14 (2000) 1341–1355.

[8] GONFIANTINI, R., ROCHE, M.A., OLIVRY, J.-C, FONTES. J.-C., ZUPPI, G.M., The altitude effect on the isotopic composition of tropical rains, Chemical Geology, 181 (2001) 147–167.

[9] GAT, J. KLEIN, B., KUSHNIR, Y., ROETHER, W., WERNLI, H., YAM, R., SHEMESH, A., Isotope composition of air moisture over Mediterranean sea: an idex of Air –sea interaction pattern, Tellus 55B, (2003) 953–965.

ISOTOPIC COMPOSITION OF PRECIPITATION IN SLOVENIA

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Abstract. Three-years monitoring of isotopic composition ($\delta^{18}O$, $\delta^{2}H$ and ^{3}H) in precipitation in Slovenia was performed to obtain temporal and spatial variability and to trace changes of isotopic composition in W-E direction. Monthly as well as daily variations in isotopic composition were compared with climate-related parameters such as local air temperature and precipitation amount. Large variations in isotopic composition were observed especially during extremely dry year 2003. Relationships of $\delta^{2}H$ vs. $\delta^{18}O$ are close to the Global Meteoric Water Line with deviations related to the influence of different air masses and evaporation. Tritium activity distribution shows typical seasonal variations with winter concentrations approaching the natural pre-bomb level.

1. Introduction

Most European countries have established networks of stations where isotopic composition of precipitation is regularly determined on monthly basis. In Slovenia, the precipitation monitoring programme is performed in the framework of the regular activities of the Environmental Agency of the Republic of Slovenia as an institution directly established and financed by the Government – through the Ministry of Environment, Spatial Planning and Energy. However, monitoring of isotopic composition of precipitation is not included into the regular programme and was in the past performed only at one sampling station in Ljubljana by the Jožef Stefan Institute (JSI) in collaboration with the Ruđer Bošković Institute (RBI) from Zagreb, Croatia. The Jožef Stefan Institute has been participating in the regional monitoring of the isotopic composition of precipitation within the Global Network for Isotopes in Precipitation (GNIP) organized jointly by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) since 1976 when the first measurements of stable isotope composition of oxygen and hydrogen in precipitation from Zagreb were performed. Monitoring of isotopes in precipitation started in Ljubljana in 1981. Since then stable isotopic composition of oxygen and hydrogen in precipitation samples from Ljubljana and Zagreb have been determined at the Department of Environmental Sciences (JSI) and tritium activity has been measured at the Radiocarbon and Tritium Laboratory (RBI). Isotopic data ($\delta^{18}O$, $\delta^{2}H$ and ^{3}H) are recorded in the GNIP database [1] together with the relevant meteorological parameters (mean monthly temperature, monthly amount of precipitation, mean monthly vapour pressure).

The characteristic geographic diversity influences the climate in Slovenia considerably. There is a mixing of (1) continental climate that influences the major part of Slovenia, (2) Alpine climate that influences the northwestern part, and (3) Mediterranean climate that influences the southwestern part of the country. Therefore, a lack of isotope monitoring programme represents a common problem for isotope hydrologists and hydrogeologists who would need a reliable long-term record of isotopic data in precipitation in Slovenia. Within the IAEA Coordinated Research Project on "Isotopic Composition of Precipitation in the Mediterranean Region in Relation to Air Circulation Patterns and Climate" the existing network was extended in Mediterranean. In Slovenia the existing isotopes-in-precipitation monitoring programme was extended to Adriatic coast with two additional sampling sites (Portorož Airport and Kozina) in the southwestern part of the country in October 2000 where daily and monthly precipitation samples were collected.

The main objectives of our research were:

(1) to assess the monthly and daily variability of isotopic composition of precipitation in the Slovenian Mediterranean and continental region,
(2) to determine the variation of isotopic composition and deuterium excess in SW-NE direction in Slovenia and,
(3) to correlate these variations to the general meteorological parameters, such as temperature and amount of precipitation.

2. Sampling and analyses

2.1. Sampling of precipitation

In the framework of the IAEA Co-ordinated Research Project monthly sampling of precipitation in Slovenia was performed from October 2000 to December 2003 in Ljubljana (JSI), at Portorož Airport and in Kozina (Fig. 1, Annex 3). In addition daily sampling was performed during 1 Oct. to 31 Dec. 2000, 1 Oct. to 31 Dec. 2001 and 1 Oct. 2002 - 31 March 2003 at all three stations. Together 236 daily precipitation samples were collected (Table 1).

FIG.1. Location map of sampling sites Ljubljana, Portorož Airport, and Kozina.

2.2. Meteorological data

Monthly and daily meteorological data (air temperature and precipitation amount in Ljubljana and at Portorož Airport and only precipitation amount in Kozina) were obtained from the Environmental Agency of the Republic of Slovenia (Annex 3).

Table 1. Number of daily precipitation samples collected during selected periods

	Ljubljana	Portorož Airport	Kozina
1.10. - 31.12.2000	21	17	30
1.10. - 31.12.2001	14	9	16
1.10. - 31.12.2002	29	30	38
1.1. - 31.3.2003	8	11	13

2.3. Isotope analyses

Stable isotopic composition of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) in monthly and daily samples was measured on a mass spectrometer Varian MAT 250 at the Department of Environmental Sciences of the Jožef Stefan Institute. For $\delta^{18}O$ analysis water samples were equilibrated with CO_2 gas and for $\delta^{2}H$

determination water samples were reduced to H_2 after passing over hot chrome. Results are expressed in δ-notation, as per mil (‰) deviation of the isotope ratio from the international standard V-SMOW.

Tritium activity in monthly samples was determined at the Radiocarbon and Tritium Laboratory of the Ruđer Bošković Institute in Zagreb by the gas proportional counting technique. Results are expressed in Tritium Units (TU).

3. Results and discussion

3.1. Climatic characteristics

The mean annual air temperatures and annual precipitation amounts for the period 2000-2003 and 1961-90 normals for Ljubljana, Portorož Airport and Kozina are summarized in Table 2. Monthly distribution of air temperature and precipitation amount is shown in Fig. 2 and Fig. 3.

Table 2. Climatic and isotopic characteristics in Ljubljana, Portorož Airport and Kozina

Location	Year	Annual mean air temperature (°C)	Annual precipitation amount (mm)	Annual weighted mean $\delta^{18}O$ (‰)	Annual weighted mean $\delta^{2}H$ (‰)	Annual weighted mean *d*-excess (‰)	Annual weighted mean tritium activity (TU)
Ljubljana	2000	12.2	1363				
	2001	11.4	1328	-7.7	-52	9	9.7
	2002	11.8	1289	-7.7	-52	10	5.7
	2003	11.6	1091	-8.9	-60	12	
	1961-90	9.8	1394				
Portorož	2000	14.0	1103				
Airport	2001	14.0	979	-6.1	-41	8	9.5
	2002	14.0	1205	-6.1	-37	11	4.0
	2003	13.8	790	-6.7	-42	12	
	1961-90	12.5	1046				
Kozina	2000		1306				
	2001		1197	-7.5	-51	10	8.2
	2002		1540	-7.4	-47	12	3.2
	2003		898	-8.4	-53	15	
	1961-90		1511				

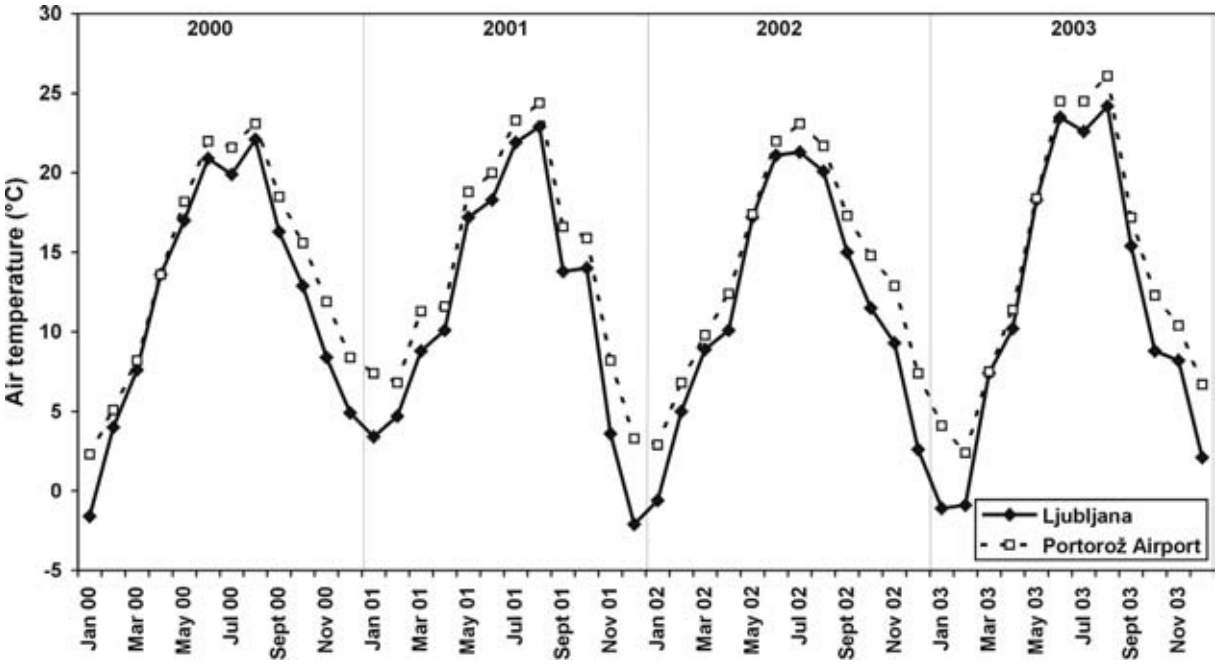

Fig. 2. Distribution of mean monthly air temperature.

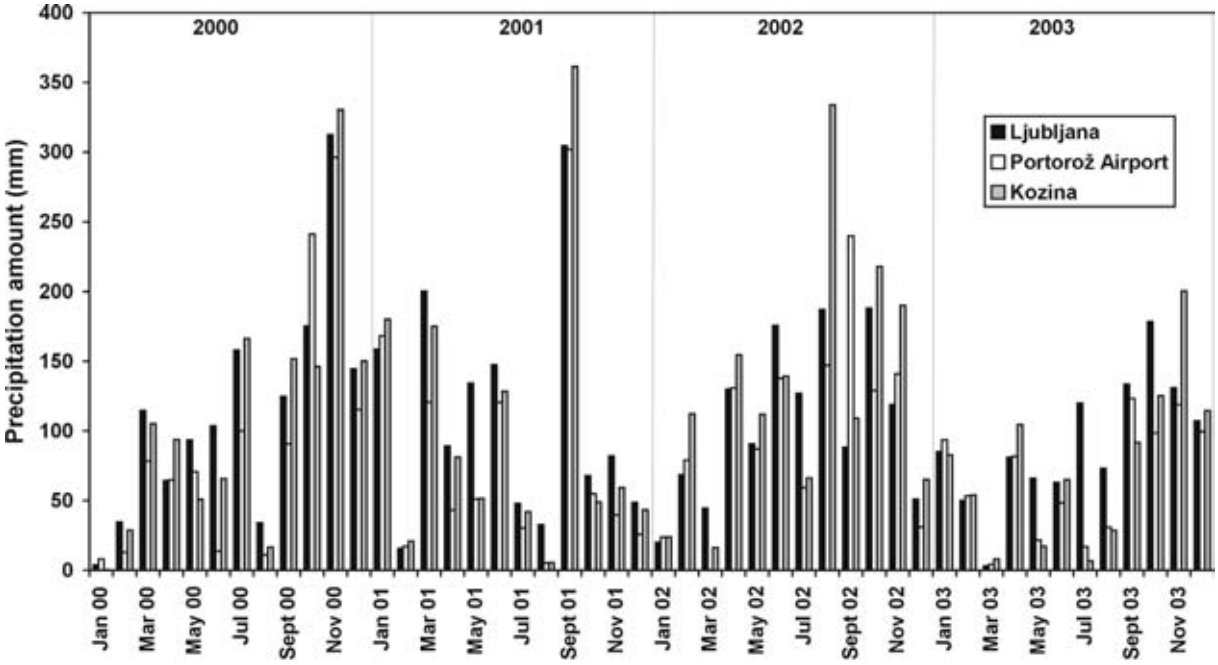

Fig.3. Distribution of monthly precipitation amount.

In 2000 the mean air temperature in Slovenia was 1 to 3°C above the 1961-90 normals [2] [3]. West part of the country got significantly more precipitation than on the average in the reference period [3], particularly in November 2000 when severe disasters (e.g. landslides, floods) occurred [4].

The mean annual air temperature in 2001 was above the 1961-90 normals and was statistically significant. Precipitation amount was mostly below the normals. Up to 7 m deep snow cover was observed in high mountains at the end of winter and the summer months were affected by drought [5].

The mean annual air temperature in 2002 was more than 1°C above the 1961-90 normals and was statistically significant. South and west parts of Slovenia got more precipitation than in the reference period, while north-eastern part of the country got significantly less precipitation than on the average [6].

The mean annual air temperature in 2003 was significantly above the normals and the anomaly was between 1 and 3°C. The year 2003 was among the warmest years in the last 50 years. The main characteristic of 2003 was also a drought and in major part of the country significant deficit of precipitation was observed [7].

3.2. Monthly variability of isotopic composition of precipitation

Isotopic composition in monthly precipitation collected in the period 2001-2003 varies considerably at all three locations. Isotopic composition of oxygen varies between –16.3 and –3.6 ‰ in Ljubljana, between –10.6 and –1.6 ‰ at Portorož Airport and between –13.8 and –2.2 ‰ in Kozina (Fig. 4). Isotopic composition of hydrogen varies between –127 and –22 ‰ in Ljubljana, between –80 and –8 ‰ at Portorož Airport and between –102 and –9 ‰ in Kozina.

The highest values of $\delta^{18}O$ and $\delta^{2}H$ are generally observed at the coastal station Portorož Airport and the lowest in Ljubljana (Table 2, Fig. 4). The continental station in Ljubljana shows larger seasonal variations (up to 12.7 ‰ in $\delta^{18}O$) than stations closer to the sea (i.e. 10 ‰ in Kozina and 9 ‰ at Portorož Airport) due to larger air temperature variations in Ljubljana. Variations in annual weighted mean isotopic composition of precipitation clearly show the influence of continental effect in southwest-northeast direction (Table 2). Obtained annual weighted mean isotopic composition at Portorož Airport and in Kozina is similar to isotopic composition of precipitation in Trieste and Basovizza in Italy [8].

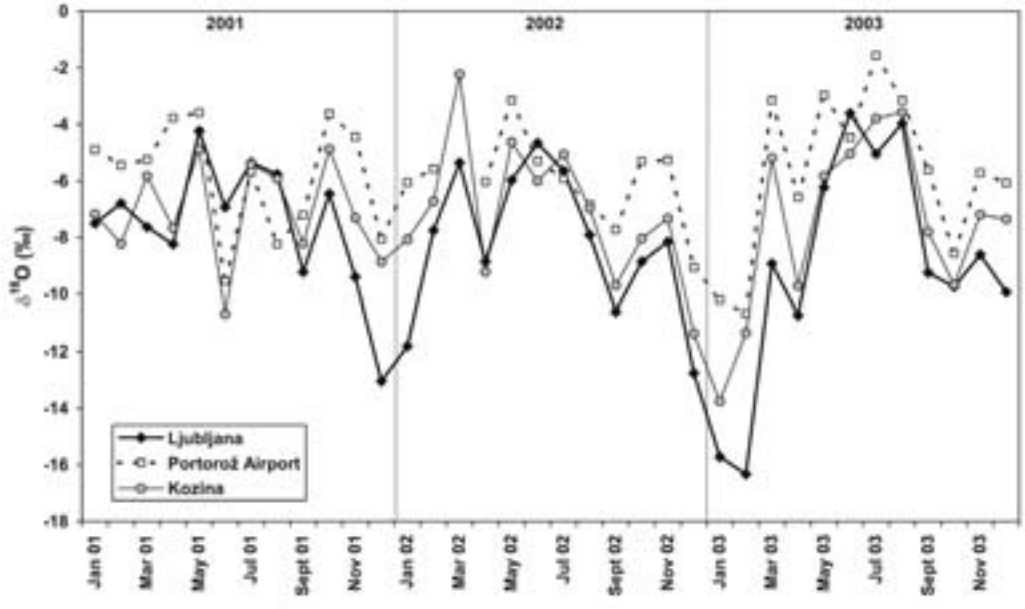

FIG. 4. Seasonal variations of the isotopic composition ($\delta^{18}O$) of precipitation.

The deuterium excess (*d*-excess) was calculated according to the equation proposed by Dansgaard [9]:

$$d = \delta^{2}H - 8 \times \delta^{18}O \qquad (1)$$

Monthly variations of *d*-excess are shown in Fig. 5. The observed pattern shows higher values in autumn-winter precipitation compared to lower spring-summer values that are characteristic for the Northern Hemisphere [10], however no clear seasonal distribution was observed. Obtained results can be explained by different distribution of precipitation amount during the sampling period (Fig. 3). Annual weighted mean *d*-excess values (Table 2) vary at all three locations around 10 ‰ that are typical for Atlantic air masses [11]. Values lower than 10 ‰ may be indicative of secondary evaporation processes (e.g. evaporation of falling raindrops in a warm and dry atmosphere) while values much higher than 10 ‰ can be attributed to precipitation from the Mediterranean Sea [11]. The highest values were observed in autumn and are probably related to the influence of Mediterranean air masses.

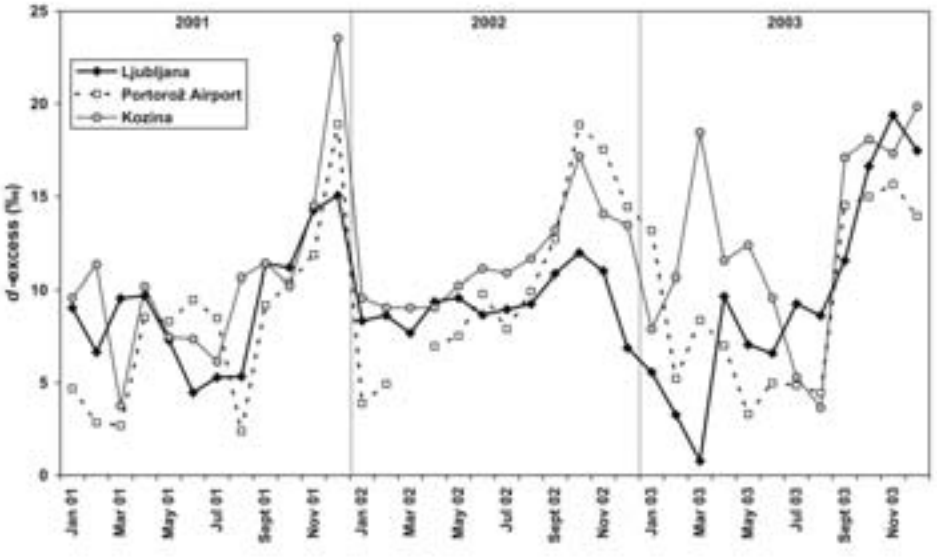

FIG. 5. Seasonal variations of the deuterium excess.

The relationship of δ^2H vs. δ^{18}O in monthly precipitation is shown in Fig. 6 where it can be seen that obtained data fit very well to the Craig's "Global Meteoric Water Line" (GMWL) [12]. We calculated the local meteoric water lines (LMWL) by using monthly data and the following correlations were obtained:

Ljubljana: $$\delta^2\mathrm{H} = 7.9\,\delta^{18}\mathrm{O} + 8.3 \quad (\mathrm{r} = 0.99) \tag{2}$$

Portorož Airport: $$\delta^2 H = 7.4\,\delta^{18}O + 5.6 \quad (r = 0.96) \tag{3}$$

Kozina: $$\delta^2 H = 7.5\,\delta^{18}O + 8.1 \quad (r = 0.97) \tag{4}$$

The deviations of monthly data from the GMWL can be explained by different source characteristics of moisture, evaporative enrichment in the falling droplets beneath the cloud base or high values of the d-excess associated with snow or hail [13].

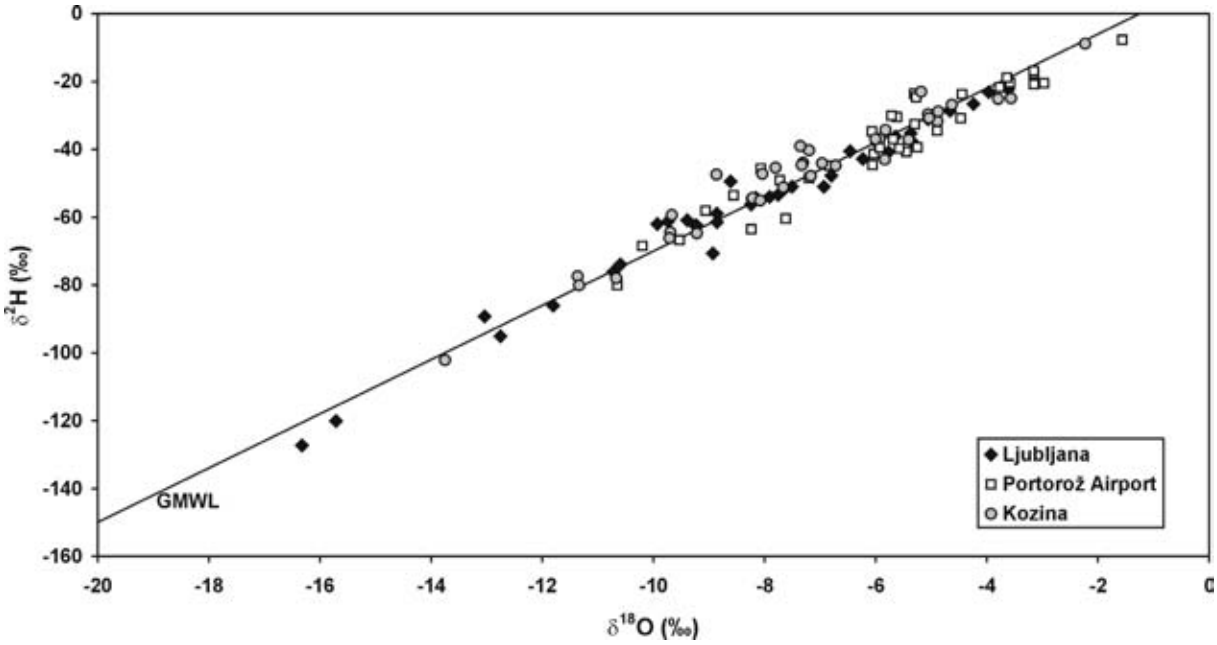

FIG. 6. The δ^2H vs. $\delta^{18}O$ relationship of monthly precipitation.

Monthly variations of tritium activities at all three stations are shown in Fig. 7. Annual weighted mean tritium activities are higher in Ljubljana than at Portorož Airport and in Kozina (Table 2). Observed seasonal variations with minimum in winter and maximum in summer, reaching up to 18 TU at Portorož Airport (Fig. 7), are typical for the Northern Hemisphere [14]. The minimal activities in winter approach the natural tritium level that was established before the thermonuclear bomb-tests in the second half of the 20th century. Long-term tritium records for Ljubljana and Zagreb show that in the past mean yearly tritium activities continuously decreased [15]. During the last decade tritium activity stayed almost constant with the mean value of 9.2 TU [16].

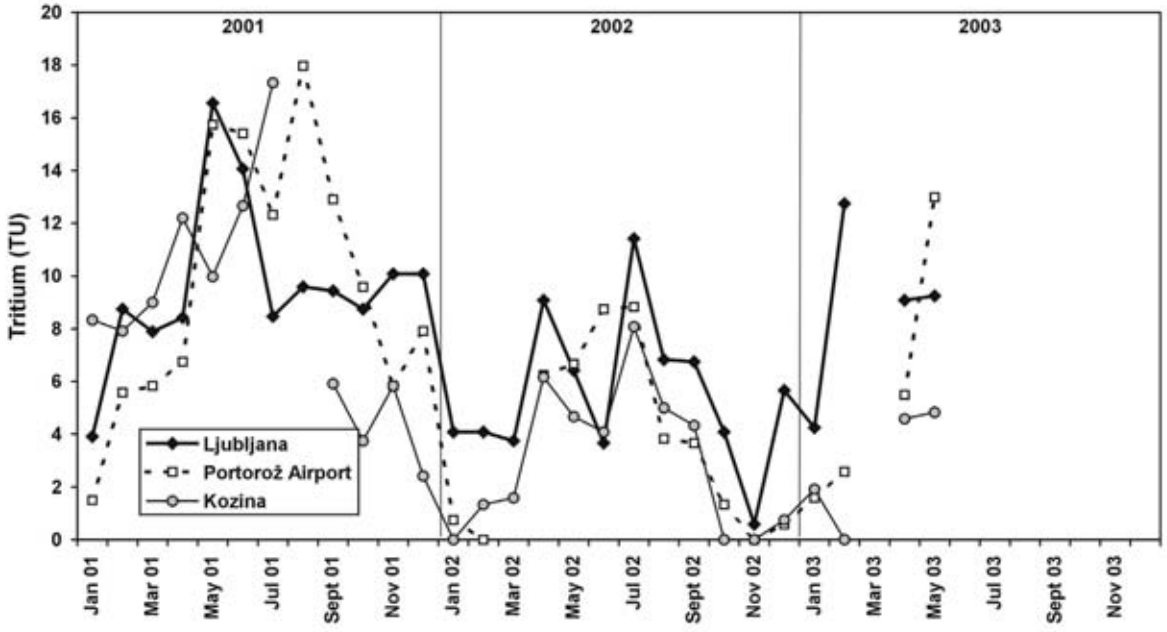

FIG.7. Seasonal variations of tritium activity.

The comparison of obtained $\delta^{18}O$ data in monthly precipitation in Ljubljana and at Portorož Airport with monthly mean air temperature is shown in Fig. 8. At both locations positive correlation between the stable isotope data and the air temperature (T) was observed:

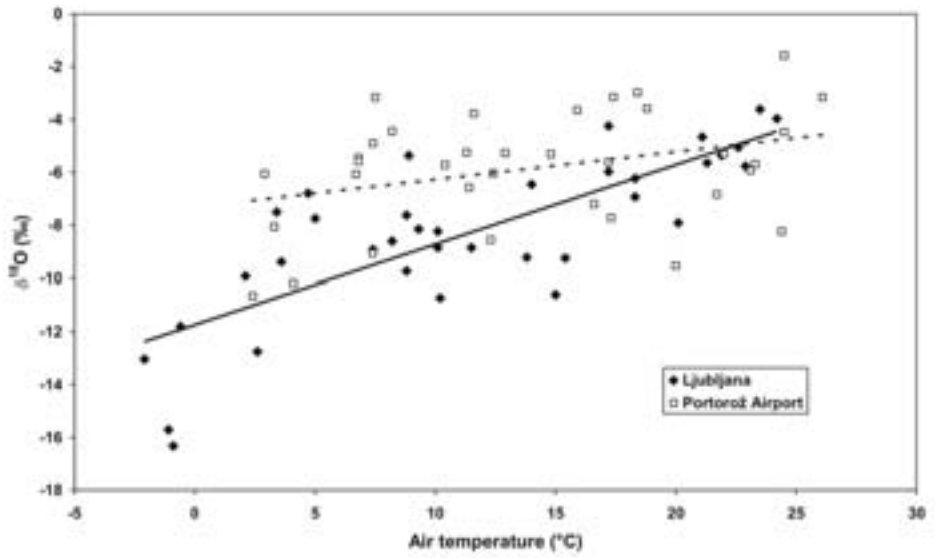

FIG. 8. The $\delta^{18}O$ of monthly precipitation vs. air temperature relationship.

Ljubljana: $$\delta^{18}\mathrm{O} = 0.3\,\mathrm{T} - 11.7 \quad (\mathrm{r} = 0.79) \tag{5}$$

Portorož Airport: $$\delta^{18}O = 0.1T - 7.3 \quad (r = 0.35) \tag{6}$$

The slope of the linear fit obtained for Ljubljana is similar to the long-term slopes for Ljubljana and Zagreb [15] and fits well with the value of 0.31‰ per °C characteristic for Northern Hemisphere [17]. At Portorož Airport the slope of the line is lower due to smaller temperature variations during the year and mean air temperature higher than 10°C [17].

The comparison of tritium activity in monthly precipitation in Ljubljana and at Portorož Airport with monthly mean air temperature is shown in Fig. 9. The following positive correlations between parameters were observed:

Ljubljana: $$^{3}H = 0.1T + 6.6 \quad (r = 0.24) \tag{7}$$

Portorož Airport: $$^{3}H = 0.3T + 0.9 \quad (r = 0.51) \tag{8}$$

The comparison of obtained $\delta^{18}O$ data in monthly precipitation at all three stations with precipitation amount is shown in Fig. 10 but no significant correlation was observed. The scattering of the data can be explained by rather variable distribution of monthly precipitation amounts with no clear seasonal maximum (Fig. 3).

Hydrological applications of the isotopic measurements strongly derive from the knowledge of the vertical isotope gradients (altitude effect) that are often used to calculate the mean elevation of the recharge area of the aquifers [8]. We determined the vertical $\delta^{18}O$ and *d*-excess gradients by using the isotope date obtained for Portorož Airport and Kozina. The calculated values range from –0.27‰ to –0.33‰ per 100 m for $\delta^{18}O$ and from 0.37‰ to 0.75‰ per 100 m for *d*-excess.

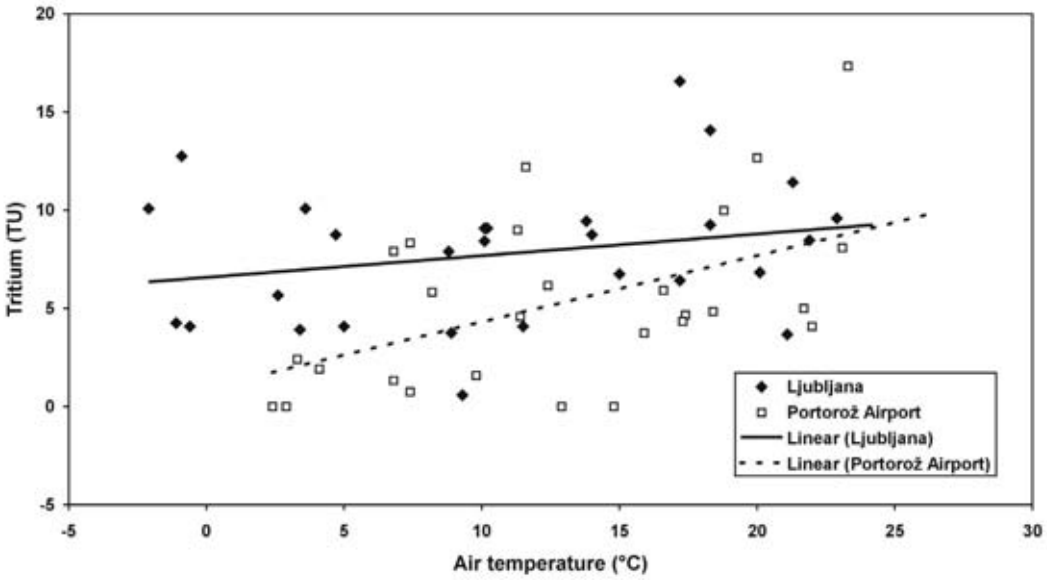

FIG. 9. The ^{3}H activity in monthly precipitation vs. air temperature relationship.

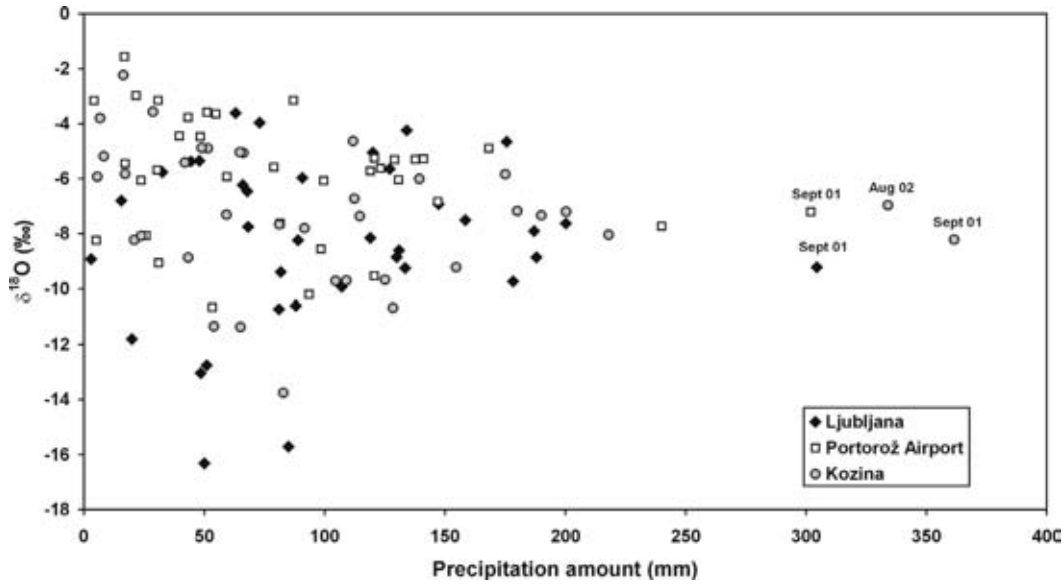

FIG.10. The $\delta^{18}O$ of monthly precipitation vs. precipitation amount.

3.3. Daily variability of isotopic composition

During the project three periods were selected for daily sampling of precipitation, 1 Oct. to 31 Dec. 2000, 1 Oct. to 31 Dec. 2001 and 1 Oct. 2002 to 31 March 2003. Data on climatic and isotopic

variations during selected periods are summarized in Table 3. To compare the same periods (October to December) the last sampling period was separated into two parts.

Table 3. Daily climatic and isotopic characteristics

Location	Sampling period	Minimum/ Maximum temperature (°C)	Mean air temperature (°C)	Precipitation amount (mm)	Minimum/ Maximum $\delta^{18}O$ (‰)	Minimum/ Maximum $\delta^{2}H$ (‰)	Minimum/ Maximum *d*-excess (‰)
Ljubljana	1.10.-31.12.00	-4.6/17.0	8.7	633	-17.6/-3.1	-135/-12	6/15
	1.10.-31.12.01	-10.0/19.6	5.2	200	-22.8/-4.2	-178/-19	4/17
	1.10.-31.12.02	-4.7/17.7	7.8	359	-22.6/-3.0	-161/-5	7/27
	1.1.-31.3.03	-10.8/12.9	1.8	140	-20.7/-6.0	-152/-46	0/18
Portorož	1.10.-31.12.00	-1.3/20.7	11.9	654	-9.9/-2.4	-68/-2	4/21
Airport	1.10.-31.12.01	-1.5/21.1	9.1	122	-7.0/-3.0	-36/-10	6/20
	1.10.-31.12.02	0.3/20.0	11.7	301	-9.7/-0.8	-73/6	4/27
	1.1.-31.3.03	-1.4/11.9	4.7	152	-14.9/3.6	-112/-17	3/16
Kozina	1.10.-31.12.00			627	-16.9/-2.2	-129/-4	-1/21
	1.10.-31.12.01			152	-11.0/-1.5	-79/+1	6/25
	1.10.-31.12.02			423	-17.5/-1.1	-134/+3	0/26
	1.1.-31.3.03			145	-16.6/-3.7	-126/-17	3/18

Selected periods had very different characteristics. The mean air temperature was during the period from October to December in 2000 and 2002 much higher than for the 1961-90 normals that are 5.0 and 8.8°C for Ljubljana and Portorož Airport, respectively [2],[5]. In 2001 the mean air temperature was only slightly higher than in the reference period. From January to March 2003 was the mean air temperature slightly lower than for the 1961-90 normals that are 1.9 and 4.9°C for Ljubljana and Portorož Airport, respectively [2],[5].

Cumulative precipitation amount from October to December 2000 was much higher than in the reference period (i.e. 351 mm in Ljubljana, 286 mm at Portorož Airport and 419 mm in Kozina). In 2001 significant deficit of precipitation was observed [5] while in 2002 precipitation amount was close to normals [6]. In the first three months of 2003 precipitation amount was significantly lower than in the reference period (i.e. 259 mm in Ljubljana, 209 mm at Portorož Airport and 322 mm in Kozina).

Similar as for monthly precipitation we observed changes in isotopic composition in the southwest-northeast direction, with more negative $\delta^{18}O$ and $\delta^{2}H$ values in Ljubljana than in Kozina and at Portorož Airport (Table 3, Fig. 11-14).

Local meteoric water lines were calculated for each station during the individual sampling periods from daily data. The obtained slope values range from 6.1 to 8.7 while the *d*-excess values range from –2 to +19‰ (Table 4). The lowest *d*-excess was observed in Ljubljana (Table 4) during first three months in 2003 when precipitation events were rare and only 8 samples were collected (Table 1). Furthermore, February was much colder and dryer while March was warmer and dryer than in the reference period. Consequently, evaporation of falling snowflakes and raindrops probably affected the isotopic composition of precipitation. On the contrary, *d*-excess values were frequently higher than 10‰ at Portorož Airport and in Kozina during October to December (Fig. 15, Table 4) and can be attributed to the influence of Mediterranean air masses. In Ljubljana this influence was less distinctive.

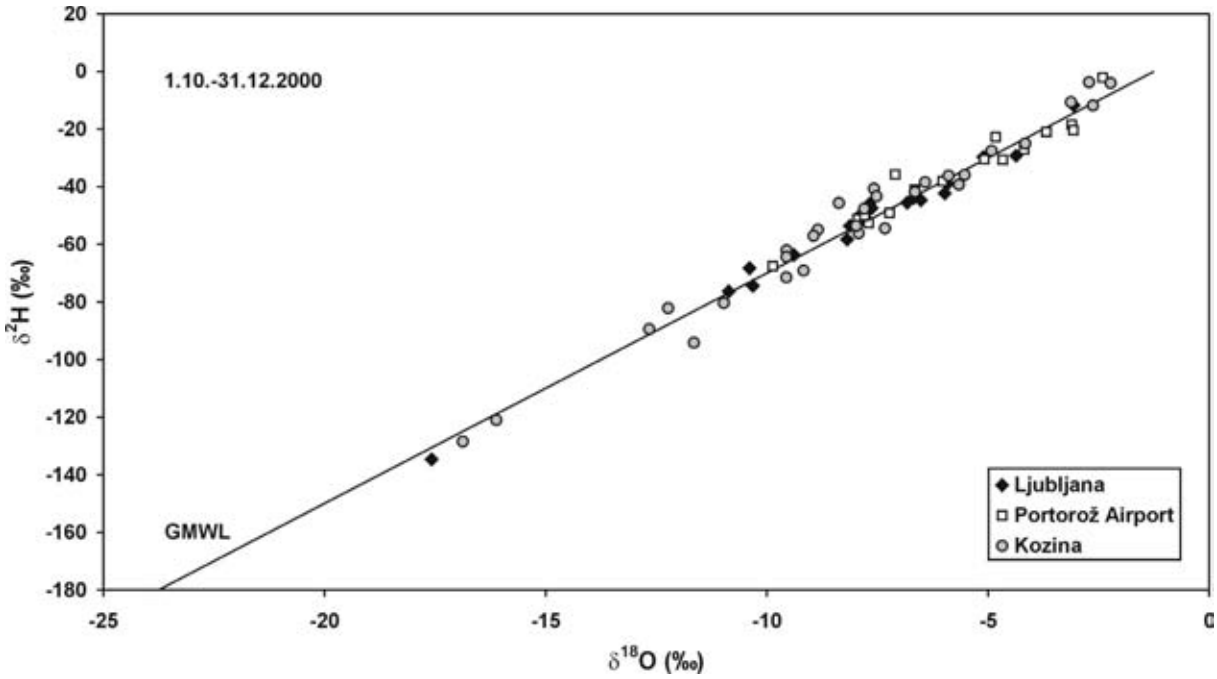

FIG.11. The δ^2H vs. $\delta^{18}O$ relationship of daily precipitation (1 Oct. to 31 Dec. 2000).

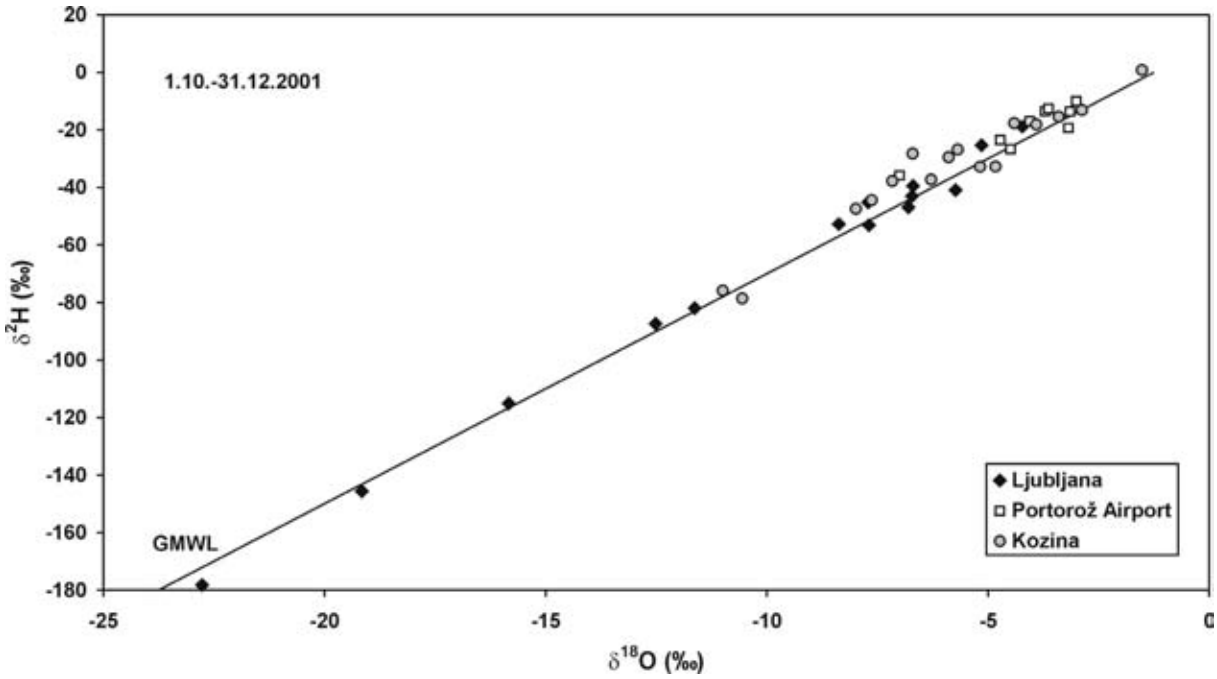

FIG. 12. The δ^2H vs. $\delta^{18}O$ relationship of daily precipitation (1 Oct. to 31 Dec. 2001).

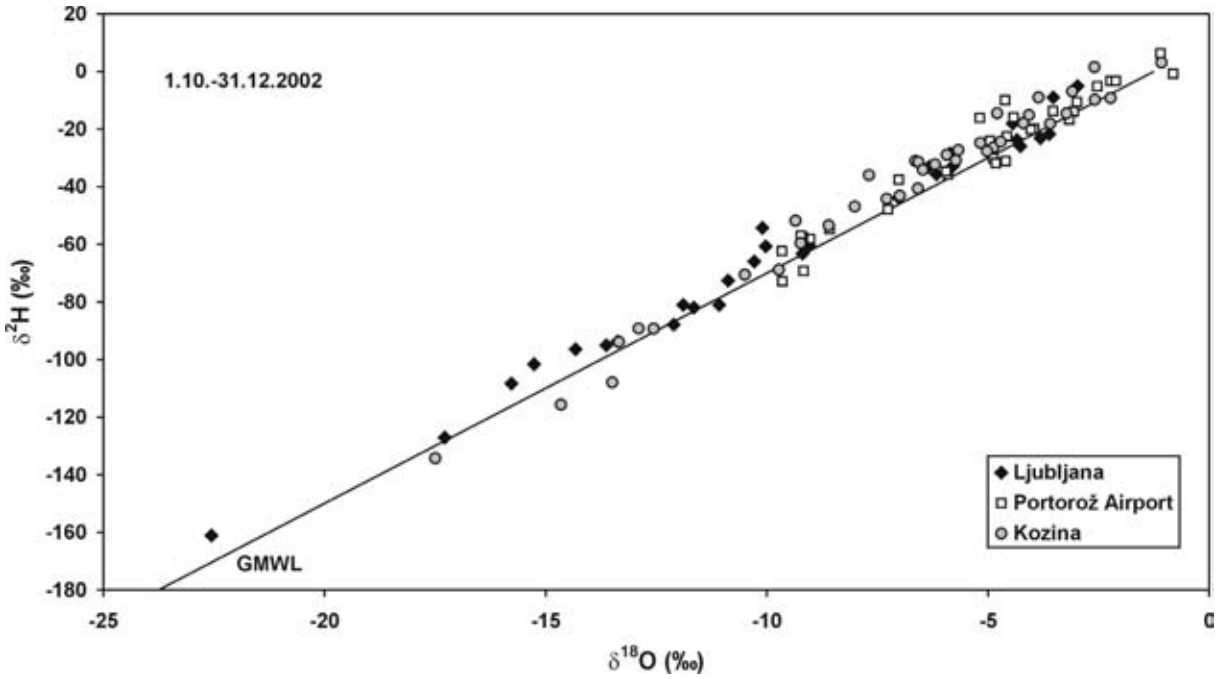

FIG. 13. The δ^2H vs. $\delta^{18}O$ relationship of daily precipitation (1 Oct. to 31 Dec. 2002).

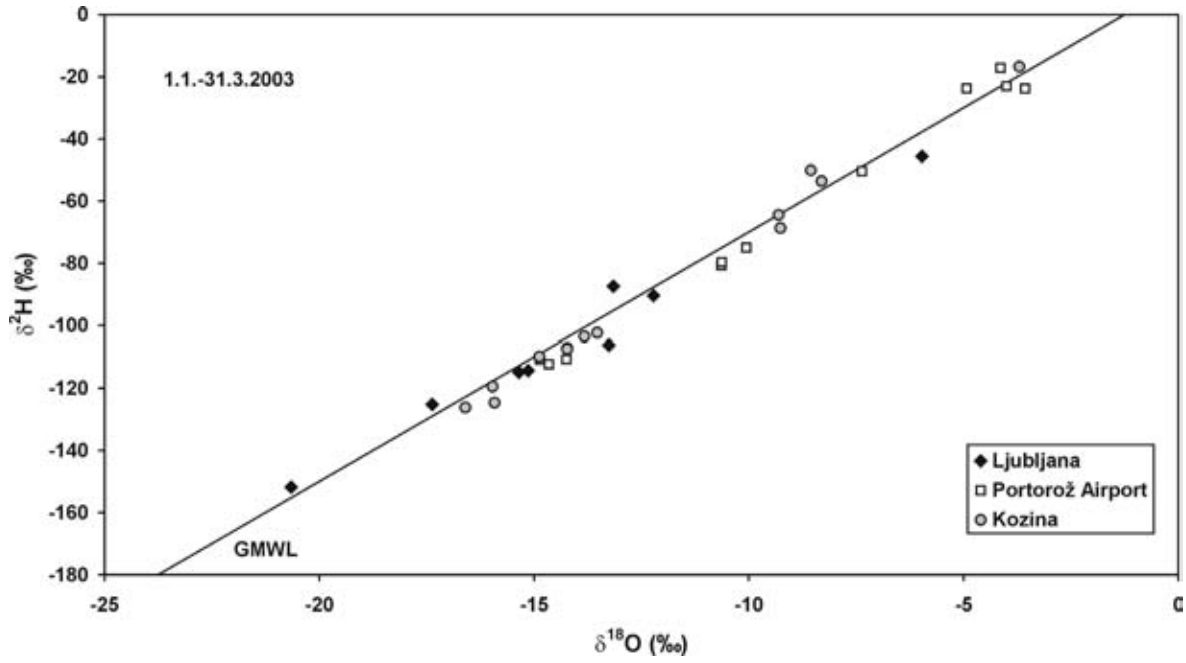

FIG.14. The δ^2H vs. $\delta^{18}O$ relationship of daily precipitation (1 Jan.to 31 March 2003).

The comparison of obtained $\delta^{18}O$ data in daily precipitation (October to December) in Ljubljana and at Portorož Airport with daily mean air temperature is shown in Fig. 16. At both locations positive correlation between stable isotope data and air temperature was observed:

Ljubljana: $\delta^{18}O = 0.5\,T - 12.9 \quad (r = 0.58)$ (9)

Portorož Airport: $\delta^{18}O = 0.2\,T - 8.3 \quad (r = 0.37)$ (10)

The slopes of the linear fit, 0.5‰ per °C for Ljubljana and 0.2‰ per °C for Portorož Airport, are higher than those obtained for three-years monthly $\delta^{18}O$ – air temperature relationship (Eq. 5 and 6, Fig. 8), and are typical for colder periods and regions [17].

The comparison of obtained $\delta^{18}O$ data in daily precipitation (October to December) at all three stations with precipitation amount is shown in Fig. 17 but no significant correlation was observed, as it was also the case for monthly precipitation (Fig. 10). The scattering of the data demonstrates that irregularly distributed daily precipitation amounts, individual weather patterns, storm tracks as well as different air mass mixing influence the isotopic composition of precipitation in Slovenia considerably.

Table 4. Local meteoric water lines for daily sampling periods

Location	Sampling period	Slope	*d*-excess (‰)
Ljubljana	1.10. - 31.12.00	8.1	11
	1.10. - 31.12.01	8.4	15
	1.10. - 31.12.02	7.8	13
	1.1. - 31.3.03	7.2	-2
Portorož	1.10. - 31.12.00	7.5	8
Airport	1.10. - 31.12.01	6.1	6
	1.10. - 31.12.02	8.1	14
	1.1. - 31.3.03	8.6	13
Kozina	1.10. - 31.12.00	8.4	14
	1.10. - 31.12.01	7.9	14
	1.10. - 31.12.02	8.6	19
	1.1. - 31.3.03	8.7	17

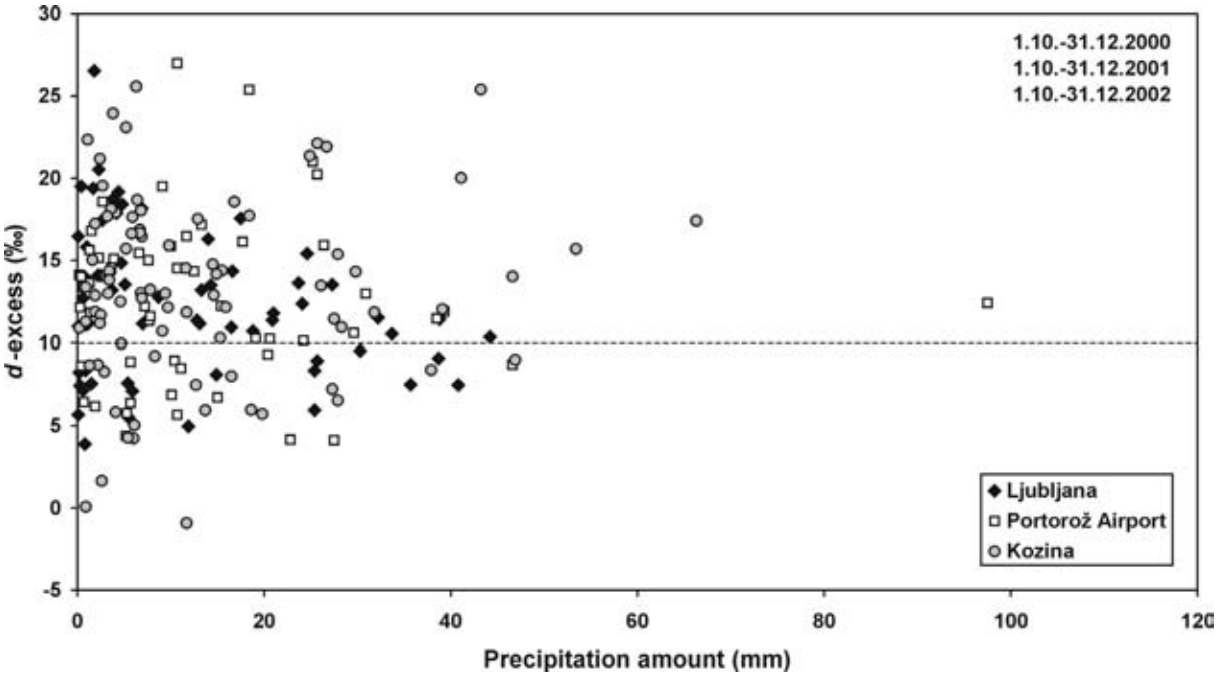

FIG. 15. Deuterium excess vs. daily precipitation amount.

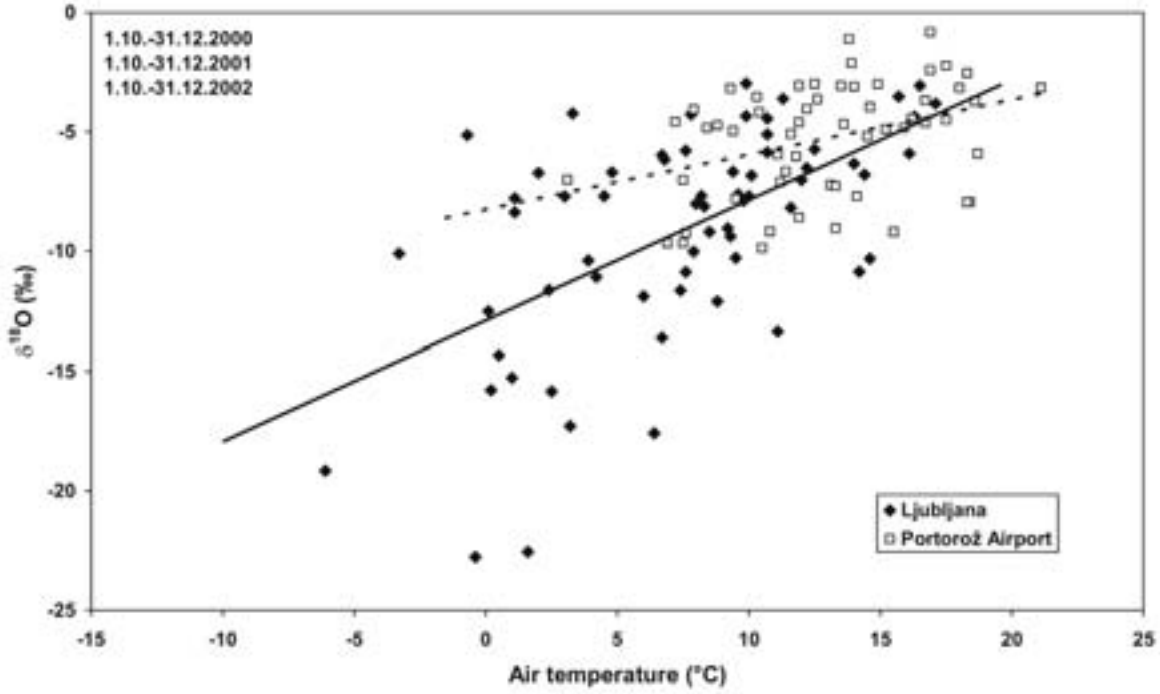

FIG. 16. $\delta^{18}O$ of daily precipitation vs. air temperature relationship.

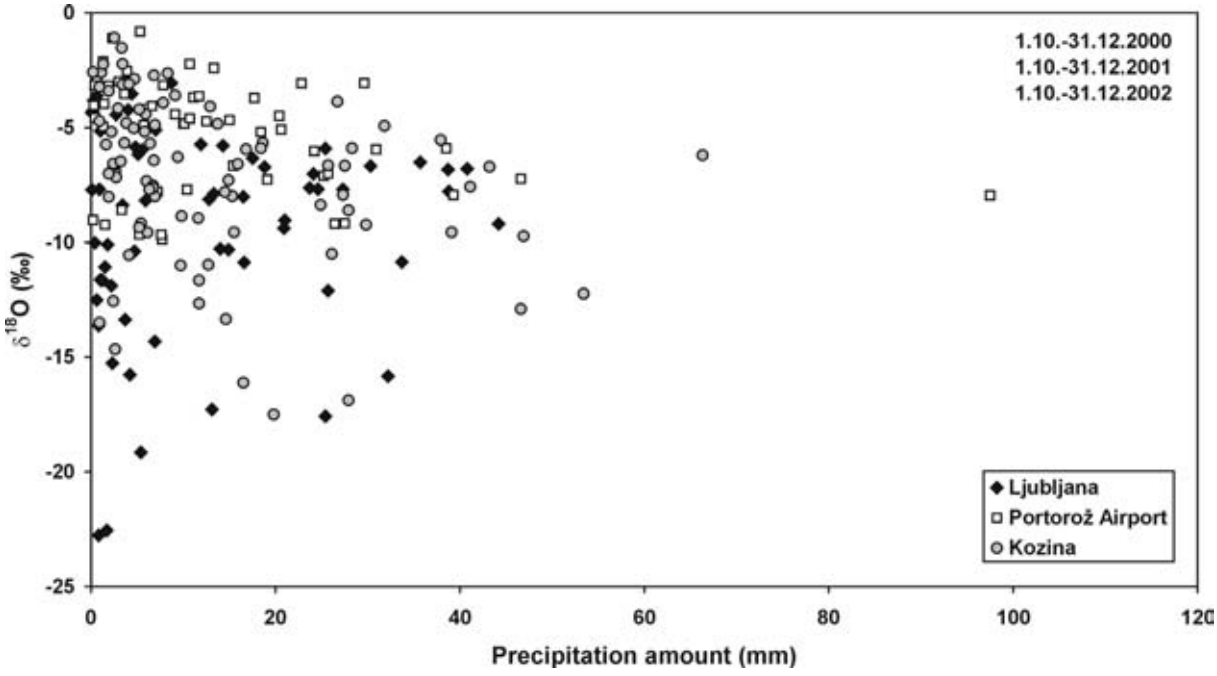

FIG.17. $\delta^{18}O$ of daily precipitation vs. precipitation amount.

4. Conclusions

Isotopic composition of oxygen, deuterium and tritium in precipitation was determined in monthly collected samples from three sampling stations in Slovenia from October 2000 to December 2003. In addition, stable isotopic composition was determined in daily collected precipitation samples during selected periods.

The set of obtained data allows the following conclusions:

(a) Distinct spatial and temporal variations were observed in monthly and daily precipitation in SW-NE direction with the highest $\delta^{18}O$ and $\delta^{2}H$ values at the coastal station Portorož Airport and the lowest in Ljubljana.
(b) Different deviations from the Global Meteoric Water Line were observed for each station and *d*-excess values vary around 10‰, however much higher values were observed in autumn.
(c) Positive correlations between stable isotopic composition and air temperature were observed for monthly and daily data with higher slopes in Ljubljana than at Portorož Airport.
(d) The relationship between stable isotopic composition and precipitation amount is quite poor for daily as well as for monthly data.
(e) The estimated vertical $\delta^{18}O$ gradient was the highest for extremely dry year 2003 (-0.33‰ per 100 m) and much lower during more rainy years 2001 and 2002.
(f) The lowest weighted mean tritium activities were observed at the coast and the highest in the central part of Slovenia. Observed tritium activity distribution is typical for the Northern Hemisphere.

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REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Isotope Hydrology Information System. The ISOHIS Database, http://isohis.iaea.org/.
[2] MINISTRSTVO ZA OKOLJE IN PROSTOR, HIDROMETEOROLOŠKI ZAVOD REPUBLIKE SLOVENIJE, Klimatografija Slovenije 1961–1990 (1995) (in Slovene).
[3] CEGNAR, T., Climate in Slovenia in 1999 and 2000 compared to the 1961–1990 reference period, UJMA 14-15: 14–25 (2000/2001) (in Slovene with English abstract).
[4] ŠIPEC, S., Natural and other disasters and incidences in Slovenia in 2000, UJMA 14-15: 29–31 (2000/2001) (in Slovene with English abstract).
[5] CEGNAR, T., Climate in the year 2001, UJMA 16: 12-23 (2002) (in Slovene with English abstract).
[6] CEGNAR, T., Climatic characteristics of the year 2002, Mesečni bilten 9, No. 12: 24-30 (2002) (in Slovene with English abstract).
[7] CEGNAR, T., Climatic characteristics of the year 2003, Mesečni bilten 10, No. 12: 23-32 (2003) (in Slovene with English abstract).
[8] LONGINELLI, A., SELMO, E., Isotopic composition of precipitation in Italy: a first overall map, Journal of Hydrology 270 (2003) 75–88.
[9] DANSGAARD, W., Stable isotopes in precipitation, Tellus 16 (1964) 436–468.
[10 ARAGUAS-ARAGUAS, L., FROELICH, K., ROZANSKI, K., Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture, Hydrological Processes 14 (2000) 1341–1355.
[11] CRUZ-SAN, J., ARAGUAS, L., ROZANSKI, K., BENAVENTE, J., CARDENAL, J., HIDALGO, M.C., GARCIA-LOPEZ, S., MARTINEZ-GARRIDO, J.C., MORAL, F., OLIAS, M., Sources of precipitation over South-Eastern Spain and groundwater recharge. An isotopic study, Tellus 44B (1992) 226–236.

[12] CRAIG, H., Isotope variations in meteoric waters, Science 133 (1961) 1702–1703.
[13] GAT, J.R., MOOK, W.G., MEIJER, H.A.J., Atmospheric water. In Environmental isotopes in the hydrological cycle, Principles and applications. Mook W.G. (Ed.), Technical Documents in Hydrology 39, Vol. II (2001).
[14] ROZANSKI, K., GONFIANTINI, G., ARAGUAS-ARAGUAS, L., Tritium in the global atmosphere: Distribution patterns and recent trends, Journal of Physical Geography 17: S523-536 (1991).
[15] KRAJCAR-BRONIĆ, I., HORVATINČIĆ, N., OBELIĆ, B., Two decades of environmental isotope records in Croatia: Reconstruction of the past and prediction of the future levels, Radiocarbon 40 (1998) 399–416.
[16] KRAJCAR-BRONIĆ, I., HORVATINČIĆ, N., BAREŠIĆ, J., OBELIĆ, B., VREČA, P., VIDIČ, S., Tritium and stable isotope variations in precipitation of Croatia and Slovenia, Berichte des Institutes fuer Erdwissenschaften Karl-Franzens-Universitaet Graz 8 (2004) 81–83, Isotope Workshop Volume.
[17] ROZANSKI, K., ARAGUAS-ARAGUAS, L., GONFIANTINI, G., Isotopic patterns in modern global precipitation, Geophysical Monograph 78 (1993) 1–36.

ISOTOPE COMPOSITION OF PRECIPITATION AND WATER VAPOUR IN THE IBERIAN PENINSULA
First results of the Spanish Network of Isotopes in Precipitation

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Abstract. The first set of isotope results ($\delta^{18}O$, δD and T) obtained by the Spanish Network of Isotopes in Precipitation (SNIP), obtained during the years 2000-2002 are presented and analysed in terms of the geographical and climatic factors controlling its seasonal and spatial distribution. SNIP maintains in operation 16 meteorological stations. The present evaluation of isotope data in precipitation focus on the governing atmospheric circulation processes in the vicinity of the Iberian Peninsula and the influence of Atlantic and Mediterranean marine air masses as well as the Central European or African continental air masses. Also in this paper are presented the first results of the stable isotope measurements carried out on single precipitation events and water vapour collected in a weather station located near the meteorological station of Madrid-Retiro. The long-term isotope values obtained in this programme show a reasonable agreement with the GMWL, with mean d-excess values for the different stations ranging from +7 to +14‰. These values are coherent with the prevailing westerly circulation, being the North and Tropical Atlantic the major sources of water vapour producing precipitation over the Iberian Peninsula. The most depleted isotope values in rain and snow were observed during the invasion of cold continental air masses from Russia and Northern Europe, but in all cases, associated to small amounts of precipitation. The most enriched isotope values in precipitation are measured in summer months when convective rains are formed. The most intense rain events in Portugal and western Spain are generally related to events involved humid air masses originated in the tropical Atlantic, especially during autumn and spring. The influence of the air masses generated over the Mediterranean is generally restricted to a short distance from the coastline, mainly in the form of extreme events (>100 mm in a few hours) during the months of September and October. The available measurements of these extreme events show $\delta^{18}O$ values in the range –4 to –6‰.

1. Introduction

The Spanish Network of Isotopes in Precipitation (SNIP) became operational in the year 2000, incorporating 15 meteorological stations to the long-term station of Madrid-Retiro, which has been maintained in operation by CEDEX (Centro de Estudios y Experimentación de Obras Públicas, Ministry of Public Works) since 1970 (with some interruptions). This monitoring programme is jointly operated by the Meteorological Survey of Spain (INM) and CEDEX. The precipitation collection programme on monthly basis in the new stations was initiated in February 2000. The names, geographical coordinates and the mean weighted isotope values obtained so far in the stations belonging to SNIP, and other stations situated in the Iberian Peninsula (IBP), are presented in Table 1. The approximate location of most of the station listed in Table 1 is shown in Figure 1. This paper represents the first evaluation of the data gathered after two years of operation.

As a complementary activity to this programme, aimed to the characterisation of the stable isotope composition of precipitation over the IBP, a research project dealing with the collection and isotope measurement of single precipitation events and water vapour has been conducted by CEDEX between the years 2000 and 2003, during the rainy periods (October to March).

In the year 2000, following the mentioned initiative of the IAEA to launch a Co-ordinated Research Project (CRP) on the subject on the isotopic content of precipitation and water vapour in the Mediterranean area, CEDEX also installed a device for collection of water vapour. At the same time, the systematic collection of single rain events was initiated in a station located at a short distance from the meteorological station of Madrid-Retiro.

FIG. 1. Meteorological stations in the Iberian Peninsula and surrounding areas included in the GNIP database, providing isotope data in precipitation. Points in grey colour represent stations belonging to SNIP and operative in 2004.

Besides the data provided by SNIP, additional isotope results discussed in this paper have been obtained from nearby stations included in the GNIP database. The meteorological and isotope data analysed includes a number of the Portuguese stations located in the IBP, station in islands, such as Ponta Delgada (Azores Islands), Gibraltar (operated by the IAEA), and the short record available for the station of Barcelona [1].

As indicated, some of the activities carried out in connection with this project have been co-ordinated with the CRP organized by the Isotope Hydrology Section of the IAEA, after fixing the sampling periods (October to March) and frequency of water vapour sampling (generally 48-hour intervals). Sampling of single precipitation events and water vapour was conducted by staff of the Isotope Hydrology Laboratory of CETA-CEDEX. Precipitation sampling at this station has been arranged, for routine operation, on event-basis as well as composite monthly samples. Water vapour sampling was conducted for two consecutive autumn-winter seasons, i.e. 2001-2002 and 2002-2003. The meteorological data discussed in this paper, and included in the database submitted to GNIP, has been supplied by the INM (Spanish Meteorological Institute).

2. Main climatic features of the Iberian Peninsula

The Iberian Peninsula is located in SW Europe, between 36º and 43º latitude N, and therefore under the dominant influence of air masses originated in the North and Tropical Atlantic, due to the prevalence of the westerly circulation at hemispheric scale. The dominant air masses affecting the IBP and the period of maximum influence are shown in Table 1 [2][3]. Due to the relatively high elevation (Figure 2) of the Iberian Plateau (about 900 m.a.s.l. in the Northern half and about 700 m.a.s.l. in the Southern half), a substantial part of the IBP is characterized by a continental climate, with hot and dry summers and cold and, to some extent, humid winter-spring seasons. The total amount of precipitation estimated for the different hydrographic basins of the IBP ranges from 1480 mm/a in the Northern parts of the IBP, to about 600 mm/a over the Meseta, and 380-500 mm/a in the basins located in the Southern half of Spain and Portugal [2].

The Iberian Peninsula represents therefore a climatic transition zone from the humid western and northern coastal areas (reaching up to 2000 mm/a in some mountainous stations in the NW), to the arid zones in the south-eastern coastal areas on the Mediterranean side (less than 300 mm/a) [2]. Late autumn and winter are the seasons of highest precipitation in Western Spain and Portugal, when the depressions and air masses originated in the North Atlantic are more active. Strong low pressure centres develop over the North Atlantic, generating a series of cold fronts, crossing the IBP from NW to SE, originating weather patterns characterized by several days of regular precipitation. The heaviest rains (higher intensity) are produced from humid air masses formed over the tropical Atlantic Ocean, generally in spring, affecting Portugal and the Western section of Spain.

During the winter period, if the depressions over the North Atlantic remain at high latitudes, the high pressure centre over the Azores Islands controls the weather patterns over the IBP, blocking the arrival of cold fronts, leading to dry, stable and cold weather over Spain and Portugal. Less often, severe cold episodes, related to the entrance of cold continental air from Russia and northern Europe, reach the IBP. Generally, these cold episodes are linked to very small amounts of precipitation.

Table 1. Main air masses affecting the climatic features of the Iberian Peninsula

Type	**Origin**	**Code**	**Period**
Marine cool	Arctic	mA	Winter+April
Marine cool	Greenland	mP	Winter
Continental cool	Russia, Siberia	cP	February, Dec+Jan
Marine warm	Subtropical Atlantic	mT(s)	Summer, rest of the year
Marine warm	Tropical Atlantic	mT	Autumn, winter
Continental warm	North Africa	cT	Summer
Mediterranean	Western Mediterranean	-	Summer, autumn

The influence of the Western Mediterranean air masses in precipitation are generally limited to short distances from the coast line, due to the rapid increase in elevation towards the Iberian Meseta and the dominance of the westerly circulation. However, in early autumn, extreme heavy events (very often above 100 mm in a few hours) are produced in the coastal areas of the Mediterranean due to the rapid cooling of humid air masses generated over the Mediterranean Sea and moving eastward, where this mass interacts with cold air for high altitudes situated over the continent.

Convective rains can also produce heavy storms, especially during the summer period, but generally, these storms represent less than 10-15% of annual precipitation. The number of days of precipitation per year ranges from more than 160 days in the NW, to less than 20 days in the SE of the IBP. Recurrent dry spells, extending from 2 to 5 years, are recorded in the climatic registry. The alternation of humid and dry period has been linked to the North Atlantic Oscillation index (NAO), whose records the difference in pressure between one station location in the tropical Atlantic and other in the North Atlantic. Positive phases correspond to humid conditions over the IBP and Western Europe.

Table 2. Summary of the long-term isotope and meteorological data for the stations of the Iberian Peninsula and surrounding areas included in the GNIP database. Data from Ponta Delgada (Azores Islands) and Tenerife (Canary Islands) are included as representative of the first condensate of water vapour generated over the north and tropical Atlantic Ocean. Stable isotope data are weighted by the amount of precipitation.

Station name	Longitude	Latitude	Altitude (m.a.s.l.)	Mean annual precipitation (mm)	Mean air temperature (ºC)	$\delta^{18}O_w$ (‰)	δD_w (‰)	d_w (‰)	Tritium T.U . (2000-2002)
Atlantic influence									
La Coruña	08 25 10 W	43 22 02 N	57	1008	14.4	-6.06	-39.9	8.6	2.8
Santander	03 47 59 W	43 29 30 N	52	1268	14.2	-6.07	-36.7	11.8	3.6
Porto	08 36 00 W	41 08 00 N	95	1150	14.4	-4.61	-27.4	10.4	---
Vila real	07 44 00 W	41 19 00 N	479	1019	13.6	-6.65	-43.5	9.1	---
Portalegre	07 25 00 W	39 17 00 N	597	836	15.9	-5.89	-33.8	12.7	---
Beja	07 52 00 W	38 01 00 N	272	550	16.2	-5.73	-35.1	10.7	---
Faro	07 55 00 W	37 01 00 N	36	453	17.8	-4.72	-25.9	11.5	---
Sevilla (Morón)	05 36 57 W	37 09 30 N	88	551	17.3	-4.68	-24.6	12.9	3.6
Gibraltar	05 35 00 W	36 15 00 N	5	720	15.5	-4.69	-25.1	12.0	---
Ponta Delgada	25 40 00 W	37 45 00 N	35	959	17.4	-4.10	-20.7	11.7	
Tenerife (Can.)	16 14 56 W	28 27 18 N	36	116	21.3	-2.00	-2.0	14.0	2.3
Continental influence									
Leon	05 39 07 W	42 35 10 N	913	556	10.9	-9.29	-67.4	6.9	4.6
Bragança	06 44 00 W	41 48 00 N	690	972	11.6	-7.75	-50.2	11.6	---
Valladolid	04 46 27 W	41 38 40 N	735	435	12.3	-7.77	-52.5	9.6	4.8
Madrid-Retiro	03 40 41 W	40 24 40 N	667	436	14.6	-6.04	-39.9	8.4	4.7
Penhas Dourad.	07 33 00 W	40 25 00 N	1383	1916	8.9	-7.61	-47.1	14.1	---
Cáceres	06 20 22 W	39 28 20 N	405	523	16.1	-6.49	-45.1	6.8	3.3
Ciudad Real	03 56 11 W	38 59 22 N	627	396	14.7	-7.56	-49.9	10.6	4.2
Zaragoza	01 00 29 W	41 39 43 N	247	318	15.0	-6.01	-40.3	7.7	5.1
Mediterranean influence									
Gerona	02 45 37 E	41 54 05 N	129	724	14.3	-5.33	-35.6	7.0	5.8
Barcelona	02 11 00 E	41 48 00 N	65	601	16.5	-5.41	-30.6	11.9	---
Tortosa	00 29 29 E	40 49 14 N	48	524	17.3	-4.86	-29.7	9.2	5.1
Valencia	00 22 52 W	39 28 48 N	13	454	17.8	-5.02	-31.9	8.2	7.0
Murcia S Javier	01 10 10 W	38 00 10 N	62	301	17.8	-6.05	-38.4	10.1	6.2
Almería	02 23 17 W	36 50 35 N	21	196	18.7	-4.31	-22.2	12.3	4.3
Palma Mallorca	02 37 35 E	39 33 18 N	3	427	17.9	-5.60	-35.4	9.4	5.3

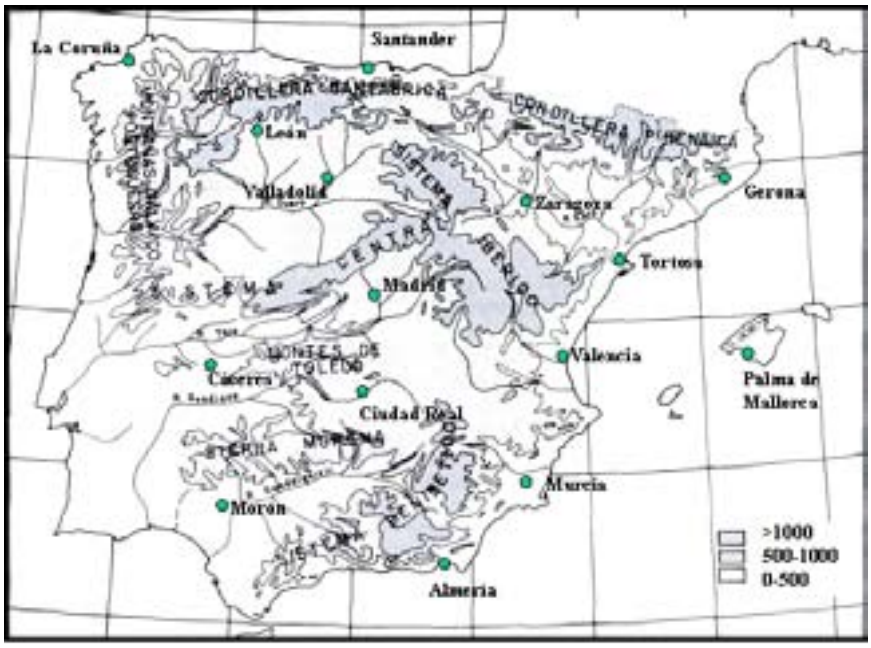

FIG. 2. Main topographic features (mountainous ranges and major hydrographic basins) of the IBP. The map also shows the elevation ranges (m.a.s.l.) and the meteorological stations included in SNIP. A large fraction of the area of the Iberian Peninsula is above 500 m.a.s.l.

The prevalence of the westerly circulation over the IBP is clearly shown by the available aerological data, which computes the net water vapour flux crossing the borders of the Mediterranean Sea [4]. The estimated net annual flux entering the Western Mediterranean Sea through the eastern coast of Spain in the order of 5,9 kg/cm·s. The analysis of weather patterns originating precipitation over the IBP also shows the importance of the low-pressure centres and the associated fronts crossing Spain and Portugal from West to East [2] (see below).

Weather patterns generating precipitation over the Iberian Peninsula

The analysis of synoptic weather maps in the vicinity of the IBP has revealed the existence of characteristic weather patterns, responsible for both, the stable conditions in winter and summer, as well as the situations generating precipitation [2]. Among the situations generating precipitation, seven weather patterns have been identified as the most relevant to account for the total annual precipitation measured over the IBP:

(a) Development of a large depression centre over the North Atlantic (west of Ireland and the UK), with steady displacement of the centre (and the associated cold fronts) to the west. This situation is the dominant feature producing intense and continuous rains in the Atlantic and Northern basins of the IBP, although rain is extended to the whole IBP.

(b) Development of depressions exclusively affecting the northern half of Spain. The displacement to the south of the fronts is controlled by the magnitude of the High Pressure Centre over the Azores Islands, limiting the effects of the depressions and the associated fronts. Precipitation is restricted to the Atlantic and Northern basins.

(c) Depressions developed in the tropical Atlantic, moving at low latitudes. Rain starts in the Gulf of Cadiz and extends to the Mediterranean area. Good weather in Northern Spain and Portugal coincides with intense precipitation in the southern part of the Iberian Peninsula. This weather pattern is more common in autumn and spring.

(d) Precipitation over the Atlantic regions produced by depressions centres located far away from the Iberian Peninsula, usually the North Atlantic, above latitude 65ºN. Usually, this situation induces cold weather (producing snow) and windy conditions in Northern Spain.

(e) Depressions located on the western Mediterranean area close to southern France. Special situation inducing the entrance of cold air from the European continent or the Atlantic Ocean. Heavy rains are produced in the northern part of the Mediterranean coast of Spain.

(f) Humid air from the SW Mediterranean (Alboran Sea) generates precipitation in coastal areas. The influence to the west is limited by the high-pressure centres over the Atlantic and the IBP. Precipitation is restricted to the Mediterranean area.

(g) Depressions over the Western Mediterranean area in autumn, where the rapid cooling on the continent and the relative warm surface of the Mediterranean Sea create conditions for heavy floods. Rain is restricted to a short distance from the Mediterranean coast. High intensity rains (up to 100-200 mm/day) are frequent in September and October.

3. First results of the Spanish network for isotopes in precipitation (SNIP)

The operation of the SNIP programme was organized according to the protocols issued by the IAEA, i.e. monthly collection of precipitation samples and compilation of the isotope ($\delta^{18}O$, δD and T) and relevant meteorological data in a dedicated database maintained at CEDEX. All meteorological and isotope results compiled during the duration of this project by the INM are being submitted to the IAEA for inclusion into the GNIP database.

Isotope measurements were conducted at the CEDEX laboratory on a double-inlet IRMS, following the usual procedures for deuterium and oxygen-18 analysis, and referring the results to the VSMOW-SLAP scale. Typical uncertainty is ± 0.1 ‰ for $\delta^{18}O$ and ± 1.0 ‰ for δD. Tritium measurements are carried out on composite annual samples (except Madrid-Retiro station), by liquid scintillation counting after electrolytic enrichment. Typical uncertainty for present-day levels in precipitation in the IBP is ± 0.3-0.4 T.U.

The available monthly isotope data for the new 15 stations only covers the years 2000 and 2001. However, for this analysis, additional data provided the Portuguese stations and previous studies conducted in Spain and Portugal [3], have been used to validate the results obtained.

3.1. Spatial variability of stable isotope contents in the Iberian Peninsula

As indicated, the first systematic compilation of isotope data with the aim of studying the spatial distribution of oxygen-18 and deuterium in precipitation over the IBP was carried out in 1994 [3]. The analysis was based on the isotope measurements of a large number of shallow groundwater samples collected from springs and shallow groundwater in Spain, and a short record of monthly data from several Portuguese and Spanish meteorological stations. The summary map including the long-term means of $\delta^{18}O$ for all available stations, using as reference map, the initial distribution map based on the $\delta^{18}O$ contents of springs and shallow groundwater, is presented in Fig. 3.

The $\delta^{18}O$ distribution map shown in Fig. 3 illustrates the influence of the relative high elevation of the Meseta, as shown in Fig. 2. Long-term weighted $\delta^{18}O$ values in the Meseta range from –6.5 to -10 ‰, while in the coastal sites, the values are 3 to 5‰ more enriched. Long-term mean values in the Atlantic coast range form –4.7 ‰ in the southern half of Portugal and Spain (Porto, Faro, Gibraltar, Sevilla-Morón), to values around -6.0 ‰ in La Coruña and Santander. Less negative isotope values are found in the stations located on the Mediterranean coastline (Gerona, Barcelona, Tortosa, Valencia, Murcia and Almería), with mean values ranging from –4.3 to –6.0 ‰. This difference in the coastal stations is probably a consequence of the influence of air masses originated in the Mediterranean Sea and the higher mean annual temperature of the cited stations.

As expected, the $\delta^{18}O$ values obtained for Ponta Delgada (Azores islands) and Tenerife (Canary islands) are even more enriched (Table 1), since they represent the first condensate of water vapour generated over the North Atlantic and the Tropical Atlantic, respectively. In all other cases, the precipitation samples represent more evolved air masses from the areas where the vapour is generated.

As mentioned, the stations located inland, generally at elevations above 500 m.a.s.l., present a progressive depletion as distance to the coast and elevation increase, reaching a value of -9.3 ‰ for the station of León (elevation of 913 m.a.s.l.). In the mountainous regions, (Sistema Central, Cordillera Cantabrica, Pyrenees, Betic Ranges), even more depleted $\delta^{18}O$ values (-10 to -13 ‰) are generally found in springs and shallow groundwater systems [3][5][6].

It is worth noting that, despite the general agreement between the map elaborated by Plata Bedmar [3] and the present study, several discrepancies became apparent. The largest difference is found in the Madrid basin, where groundwater shows values ranging from –8 to –10 ‰, while precipitation shows a mean weighted mean close to -6.5 ‰. Most likely, this difference is probably because for the elaboration of the map, the $\delta^{18}O$ value of deep groundwater was used. The $\delta^{18}O$ of paleowaters in the Madrid aquifer is the result of the marked isotope shift between Pleistocene groundwater and present-day precipitation [7]. The discrepancy on the isotope composition in the Northern half of the Meseta is less pronounced [3]. Similarly, more depleted values than those found by SNIP are found in springs and groundwater on the Mediterranean coast. In this case, the preferential recharge of winter rains may explain this systematic difference for several stations. Another explanation, at least for certain coastal aquifers, may be related to the recharge derived from flash floods produced from heavy rains in early autumn.

The observed $\delta^{18}O$ gradient from coastal stations on the Atlantic coast to those in the Meseta (well above the typical value of 2‰ per 1000 km) is therefore increased by the altitude of the sampling stations. The altitude gradient of the $\delta^{18}O$ content of precipitation has been determined in several areas in Spain e.g. [5][6], showing the typical values found for other European countries (-0.2 to -0,25‰ per 100 m). This influence is clearly observed when plotting the mean annual temperature (or amount of precipitation) vs. the weighted mean $\delta^{18}O$, since continental stations clearly depart from the general tendency. For this reason, the regressions obtained are poorly correlated for amount of precipitation (r^2= 0.2), while the correlation coefficient between temperature and $\delta^{18}O$ is better (r^2= 0.7 to 0.8).

3.2. Spatial variability of tritium contents in the Iberian Peninsula (2000-2002)

The tritium monitoring programme in the 15 new meteorological stations was initiated in 2000. The data obtained in the period 2000-2002 has provided complementary information to the monthly sampling conducted at the Madrid-Retiro station, for defining the spatial variability of tritium over the IBP, and to use this tool for hydrogeological studies. The tritium content in Madrid-Retiro still is measured on monthly basis to account for seasonal variations [8].

Tritium in seawater is regularly monitored by CEDEX in a series of harbour stations located at variable distance from the Spanish coast. The analysis of the recent tritium data shows systematic higher values in the stations located in the Mediterranean Sea. The mean tritium content for the period 2000-2002 for the seven Spanish stations located on the Bay of Biscay and the Atlantic Ocean was 1.4±0.2 T.U. For the remaining six stations on the Mediterranean Sea, the computed value was 2.3±0.2 T.U. No clear differences were found between the coastal stations located on the northern sector and those on the southern area.

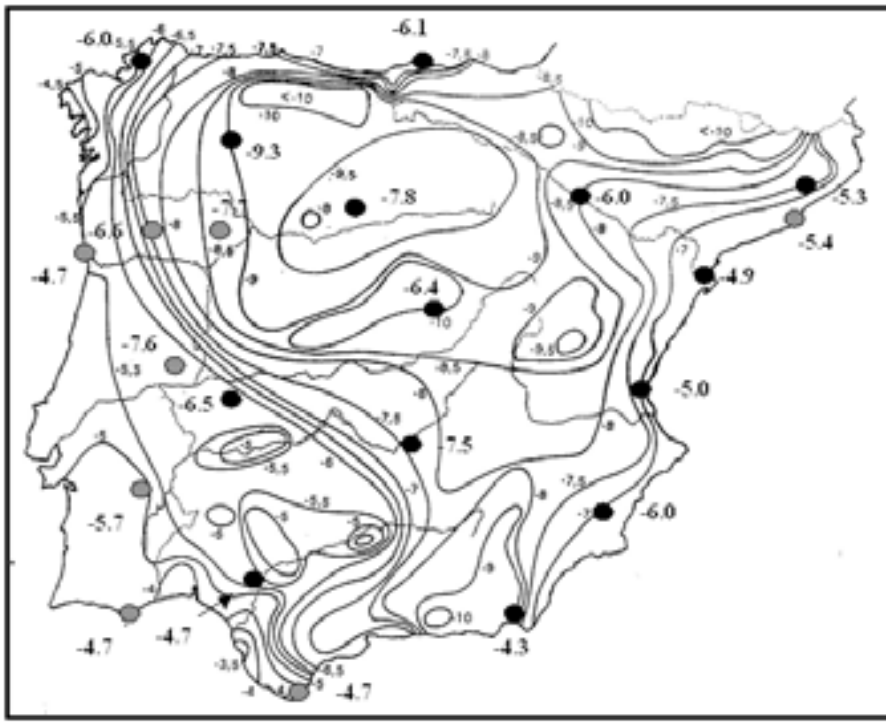

FIG. 3. Long-term weighted $\delta^{18}O$ in precipitation in the SNIP stations (black dots) and other stations located in the Iberian Peninsula (grey dots). The values are plotted in a previous isotope distribution map, based on isotope measurements of springs and shallow groundwater in Spain [3].

The lowest tritium contents in precipitation have been reported by the coastal stations subject to a dominant influence of Atlantic air masses (Tenerife and La Coruña), with values below 3 T.U. for the period 2000-2002, Table 2 and Fig. 4). Slightly higher values are found in stations located inland, but under the same influence (Cáceres, Sevilla, Santander, with values ranging from 3.0 to 4.0 T.U.). The values show a clear increasing trend towards the Mediterranean, with annual means between 5.0 and 7.0 T.U. on the coastal sites. This "continental" tritium gradient is similar to the trend found on continental Europe from Ireland and France to Belgium, Netherlands and Germany. This trend reflects the contribution of land sources and the lack of dilution effect produced in areas close to the sea.

The seasonal variation in the tritium content in precipitation is monitored at the Madrid-Retiro station (see Table 3, below). A clear maximum is observed in spring, due to the tropospheric injection, reaching values close to 9 T.U. in May-June. This pattern with the spring maximum was observed for the period of maximum tritium in precipitation (1962-1967), as well after the return to pre-bomb levels after 1990s [8].

FIG. 4. Mean weighted tritium contents in the SNIP stations for the period 2000-2002. Higher tritium values are found in the coastal stations located on the Mediterranean Sea. Mean tritium contents measured on 13 stations collecting surface seawater in the Western Mediterranean and North Atlantic on the Spanish coast, are also presented.

3.3. Stable isotope content of precipitation in Madrid-Retiro station

3.3.1. Seasonal variation of $\delta^{18}O$ in continental stations

The distance to the coast of Madrid (about 400 km to the Atlantic coast in Portugal) and the elevation (667 m.a.s.l.) are responsible of the continental character of the climate of Madrid and its relatively depleted $\delta^{18}O$ contents. The mean annual amount of precipitation is less than 450 mm/a while the mean annual temperature is close to 14.6 ºC (Table 3). The distribution of precipitation in Madrid shows two maxima, one in late autumn-winter (October-December) and a second maximum in April-June. In both cases, the long-term monthly means are above 50 mm. The summer period (July-August) corresponds to the lowest precipitation of the year, generally in form of sporadic storms.

The marked annual cycle in temperature (6 ºC in January to 25 ºC in July) is reflected in a parallel evolution in the $\delta^{18}O$ contents in precipitation, with mean values close to –8.8 ‰ in winter months, to contents close to –1‰ in summer months, (Fig. 5). The good apparent positive correlation of $\delta^{18}O$ and mean monthly temperature is shown in Fig 6., providing a good correlation coefficient (0.90) and a typical slope for this relationship (0.37 ‰ per ºC) [9][10][11]. For the Madrid station, the oxygen isotope content of precipitation may be a good proxy of mean annual temperature.

Fig. 7 shows the seasonality of the amount of precipitation and the long-term monthly $\delta^{18}O$ contents in precipitation for the Madrid station. Clearly there is again and apparent negative correlation, with more positive $\delta^{18}O$ values in summer, when the amount of precipitation is the lowest, and the opposite situation in winter and spring. This is reflected in Fig. 8, where these two parameters are compared. Discarding the winter months (January, February and March), a relative good negative correlation is obtained (0.88), with a slope close to 0.13 ‰ per mm of rain.

Table 3. Long-term average monthly climatic and isotope values for the Madrid-Retiro station

Month	Amount of precipitation (mm)	Mean air temperature (ºC)	$\delta^{18}O$ (‰)	δD (‰)	d (‰)	Tritium* T.U.
January	37	6.1	-8.82	-59.4	11.2	4.1
February	35	7.9	-7.54	-55.2	5.2	4.1
March	26	10.7	-8.08	-52.3	12.3	5.1
April	47	12.3	-5.31	-39.1	3.3	6.9
May	52	16.1	-4.98	-33.3	6.5	9.2
June	25	21.0	-3.45	-28.0	-0.4	5.5
July	15	24.8	-2.05	-18.2	-1.8	3.4
August	10	24.4	-1.30			3.4
September	28	20.5	-3.25	-25.8	0.2	4.3
October	49	14.6	-7.54	-52.1	8.2	4.1
November	56	9.7	-8.10	-50.7	14.1	3.7
December	56	7.0	-7.85	-53.8	9.0	3.6
Year	**436**	**14.6**	**-6.43**	**-44.1**	**7.1**	**4.70**

* Mean values for the period 2000-2003.

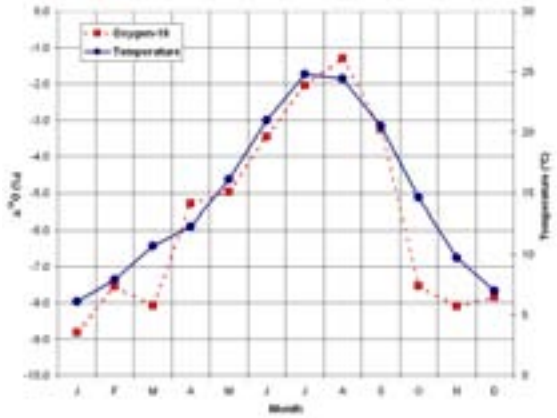

FIG. 5. Seasonal trends of the mean monthly air temperature and $\delta^{18}O$ in the continental station of Madrid-Retiro (667 m.a.s.l.).

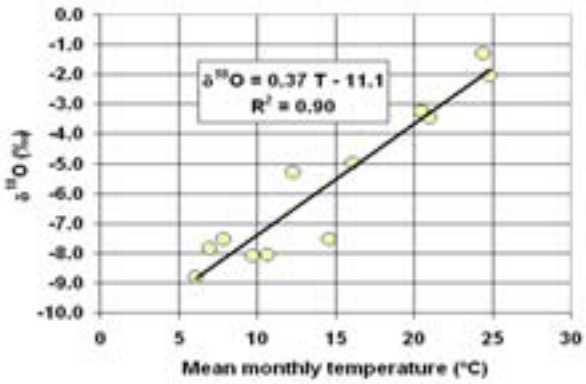

FIG. 6. Relationship between the long-term mean monthly air temperature and monthly $\delta^{18}O$ in the continental station of Madrid-Retiro (667 m.a.s.l.).

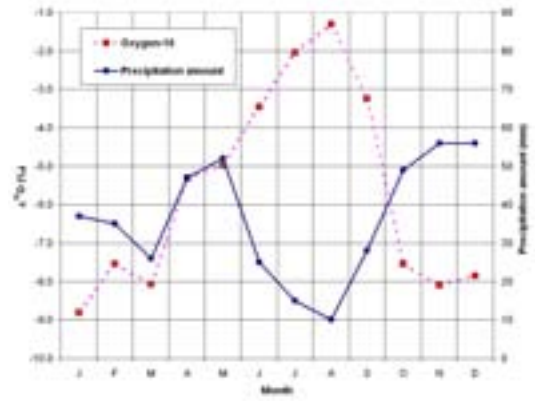

FIG. 7. Seasonal trends of the mean monthly amount of precipitation and $\delta^{18}O$ in the continental station of Madrid-Retiro.

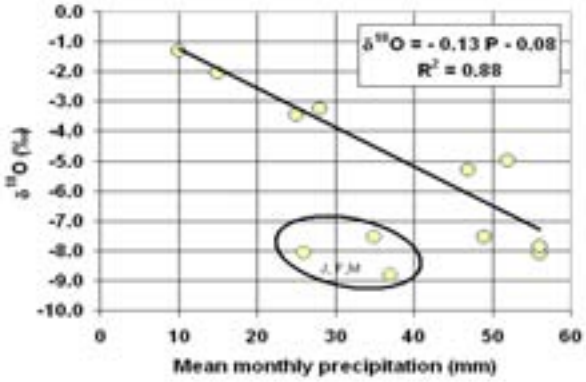

FIG. 8. Relationship between the long-term mean monthly amount of precipitation and monthly $\delta^{18}O$ in the continental station of Madrid-Retiro (667 m.a.s.l.).

3.3.2. Single events: March 2001–October 2002

Single precipitation events and water vapour samples representing 48-h intervals were collected during the seasons 2001-2002 and 2002-2003, following the procedure indicated by the IAEA. The common sampling period for the participants in the CRP was fixed from October to March, i.e. the rainy season for most of the Mediterranean stations.

The δD-$\delta^{18}O$ relationship of both single rain events and water vapour samples collected during the period October 2001 - March 2003 is presented in Figure 9. The isotope contents of rain samples cluster along a line very similar to the GMWL, ($\delta D = 8.0\ \delta^{18}O + 7.8$; $r^2 = 0.96$). It is worth indicating that the equation obtained using the long-term monthly means (1970-2000) shows a much lower slope ($\delta D = 6.45\ \delta^{18}O + 3.2$; $r^2 = 0.91$). This difference is probably reflecting the evaporation effects associated to the sampling protocol traditionally used for the monthly sampling at the meteorological station. This effect should be more relevant for stations located in arid and semiarid regions, where low d-excess precipitation is often found.

On the other hand, the isotope contents of water vapour samples shown in Fig. 9, also present a slope lower than 8 and the intercept even negative ($\delta D = 6.25\ \delta^{18}O - 16.7$; $r^2 = 0.88$). In this case, the slope is the result of the high d-excess values found in the most depleted samples. These results are similar to those found in other station in Central Europe and Israel [12][13][14]. Generally, the episodes in which water vapour presents more depleted isotope contents are not associated to important rain events in terms of the amount of precipitation.

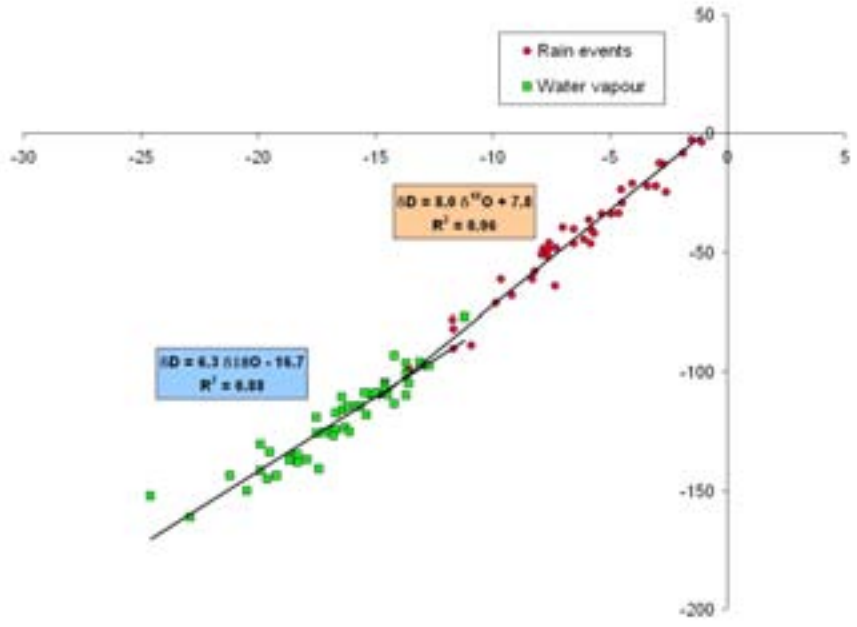

FIG. 9. δD-$\delta^{18}O$ relationship for precipitation (single events) and water vapour (48-h intervals) collected at the Madrid-Retiro station from October 2001 to March 2003.

The isotope contents of the rain events monitored at the Madrid-Retiro station between October 2001 and March 2003 are listed in Table 4 and Table 5. Table 4 contains the monthly means obtained in two consecutive rainy seasons, and compared to the long-term means, as well as the relevant meteorological data. Table 5 contains the list of events producing more than 5 mm of rain and the weighted $\delta^{18}O$ content of the rain sample and the corresponding isotope value measured in the water vapour at the time of the event.

The $\delta^{18}O$ and δD contents of the rain samples for the period October to March shows a wide range (-1 to –15 ‰ for $\delta^{18}O$), reflecting the different air masses and weather situations generating rain over

Madrid. Rainy events above 30 mm generally present $\delta^{18}O$ values lower than -8 ‰, but in some cases above 40 mm, the $\delta^{18}O$ contents may show enriched values in the order of -6 ‰ (Table 5). The most depleted rains (~ -15 ‰) are always associated to small amounts of precipitation in wintertime, when the influence of continental air masses from Central or Northern Europe are more frequent.

3.4. Stable isotope contents of water vapour in Madrid-Retiro station

The isotope contents of the water vapour collected during the seasons 2001–2002 and 2002–2003 are summarized in Tables 4 and Table 5, and shown in Figs. 9 and 10. The main features of the δD vs. $\delta^{18}O$ relationship presented in Fig. 9 have been discussed above. Fig. 10 shows the time variation of the $\delta^{18}O$ values of both single precipitation and water vapour samples for the two complete sampling seasons at the Madrid-Retiro station. The mean $\delta^{18}O$, δD and d-excess values of the water vapour samples collected in Madrid (expressed as deviations in ‰) are summarized in Table 4 in form of monthly means.

As shown in Table 4, the interannual variability in the amount of precipitation is important, as well as the respective isotope abundances. The $\delta^{18}O_w$ of the 2001-2002 season was relatively depleted (--8.7 ‰), when compared to the 2002–2003 season (-6.9 ‰). This difference is probably related to the different meteorological conditions for both periods. The 2001-2002 season corresponds to a dry and cold phase (~ 200 mm and 7.9 ºC), while the next season was relatively wet and warm (~365 mm and 8.9 ºC).

Table 5 shows that the difference between the $\delta^{18}O$ contents water vapour and rain ($\delta^{18}O_v - \delta^{18}O_p$) ranges between 6 to 10 ‰, as expected from the fractionation factors between the liquid and vapour phases in the cloud and the ground temperatures [9].

As shown in Fig. 9, the water vapour samples are characterized by a higher d-excess than the corresponding precipitation events (mean +15.1 ‰, ranging from +2 to +32 ‰ for vapour vs. +8.9 ‰, ranging from –5 ‰ to +20 ‰ for rain).

The relationship between the daily temperature and the $\delta^{18}O$ of the rain events and the water vapour samples obtained for the Madrid station is presented in Fig. 11. In both cases, a similar slope is obtained (0.32 ‰ per ºC for the rain samples and 0.37 ‰ per ºC for water vapour samples). The last value is identical to the seasonal value obtained for the same station (Fig. 6), and to the values reported in the literature [10][11].

4. Analysis of the isotope contents of precipitation events in relation to typical weather patterns

As previously shown, during the two rainy seasons included in the period March 2001 to October 2003, more than 30 rain events were recorded, sampled and analysed for stable isotope contents at the Isotope Hydrology Laboratory of CEDEX. The isotope contents of the major events were presented in Table 5.

Table 4. Long-term mean climatic and isotope content of precipitation for the rainy period in Madrid-Retiro station, compared to values measured during the periods 2000-2001 and 2001-2002, including mean monthly $\delta^{18}O$ of water vapour

Month	Temperature (ºC)			Amount of precipitation (mm)			$\delta^{18}O$ (‰) precipitation – single events			$\delta^{18}O$ (‰) water vapour	
	Long term mean	2001-2002	2002-2003	Long term mean	2001-2002	2002-2003	Long term mean	2001-2002	2002-2003	2001-2002	2002-2003
October	14.6	15.9	14.9	45	59	58	-7.54	-5.62	-5.25	-13.4	-14.2
November	9.8	7.3	9.9	64	12	91	-8.10	-14.74	-7.53	-17.1	-16.8
December	6.8	2.8	8.3	51	19	63	-7.85	-8.19	-7.06	-17.7	-17.6
January	6.1	6.4	5.7	46	48	51	-7.54	-10.73	-6.45	-15.9	-17.4
February	7.6	7.9	6.2	44	9	58	-8.08	-4.74	-7.93	-14.5	-19.0
March	10.2	6.8	8.2	33	51	43	-5.31	-9.81	-6.59	-15.9	-16.5
Oct-March	9.2	7.9	8.9	283	197	363	-7.98	-8.69	-6.89	-15.8	-16.9

Table 5. $\delta^{18}O$ of rain and water vapour during rainy events (above 5 mm) in the Madrid-Retiro station for the period October 2001 to March 2003

Date 2001-2002	Amount of prec. (mm)	$\delta^{18}O_p$ (‰)	$\delta^{18}O_v$ (‰)	Date 2002-2003	Amount of prec. (mm)	$\delta^{18}O_p$ (‰)	$\delta^{18}O_v$ (‰)
27/09/2001 - 28/09/2001	7.1	-10.23		30/09/2002 - 01/09/2002	14.5	-4.46	-13.70
06/10/2001	5.0	-2.64	-15.14	08/10/2002 - 10/10/2002	26.0	-8.70	-14.90
11/10/2001 - 12/10/2201	9.0	-5.29	-13.96	20/10/2002 - 22/10/2002	15.2	2.44	-11.20
16/10/2001 - 20/10/2001	42.3	-6.13	-12.60	30/10/2002 - 01/11/2002	8.2	-1.53	-14.60
03/11/2001	5.1	-15.41		12/11/2002 - 16/11/2002	34.0	-8.52	-19.60
15/11/2001 - 17/11/2001	6.1	-15.53	-20.44	19/11/2002 - 24/11/2002	38.2	-8.74	-14.70
23/12/2001	5.7	-8.07		28/11/2002 - 01/12/2002	15.8	-5.20	-15.00
30/12/2001 - 04/01/2002	46.0	-11.09		09/12/2002 - 10/12/2002	21.0	-10.52	-19.90
21/01/2002 - 23/01/2002	8.3	-6.45	-16.85	12/12/2002 - 13/12/2002	7.1	5.77	-17.00
05/02/2002	5.0	-5.21	-14.23	16/12/2002 - 19/12/2002	18.0	-6.41	-16.80
03/03/2002	9.0	-10.26	-18.35	24/12/2002 - 27/12/2002	10.4	-5.90	
13/03/2002 - 16/03/2002	41.0	-9.97	-17.62	05/01/2003 - 09/01/2003	30.4	-6.76	-17.50
05/04/2002 - 07/04/2002	18.4	-6.87		18/01/2003 - 22/01/2003	13.7	-5.96	-13.70
10/04/2002 - 12/04/2002	17.0	-10.99		12/02/2003	8.0	-3.05	-18.60
04/05/2002 - 12/05/2002	45.7	-5.87		18/02/2003 - 20/02/2003	18.3	-7.74	-22.52
				22/02/2003 - 26/02/2003	31.2	-9.34	-17.07
				26/03/2003 - 31/03/2003	41.4	-6.79	-14.50

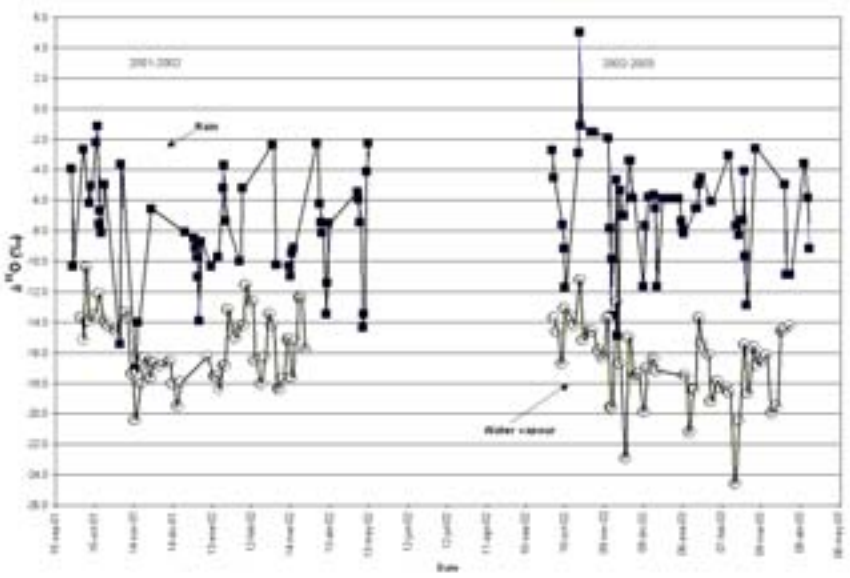

FIG. 10. Evolution of the oxygen-18 contents of precipitation (single events) and water vapour (48-h intervals, twice weekly) collected at the Madrid-Retiro station from October 2001 to March 2002.

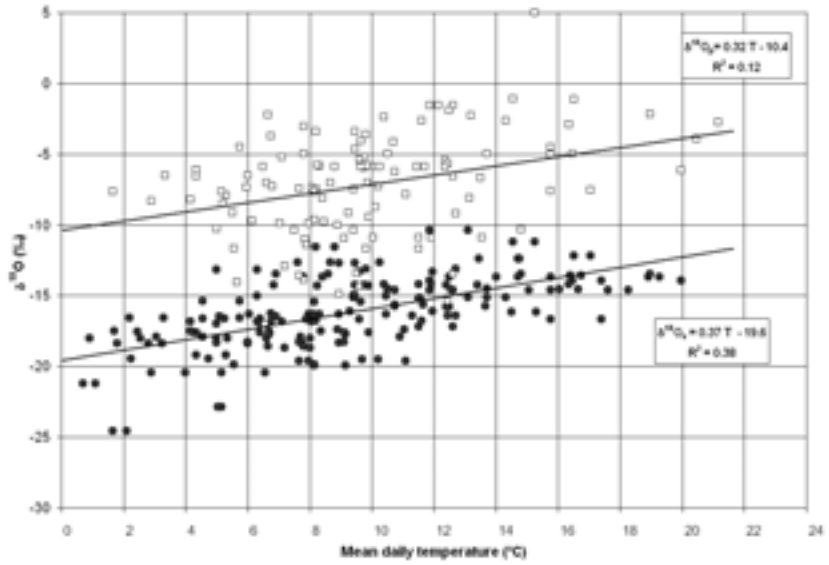

FIG. 11. $\delta^{18}O$ contents of precipitation and water vapour vs. mean daily temperature for the precipitation events collected in the Madrid station from October 2001 to March 2003.The $^{18}O/T$ slope found in water vapour samples is identical to the value shown in Fig. 6.

In this section, four events representing common situation producing large amounts of precipitation or unusual isotopic values are described. The analysis is based on the available synoptic weather maps at surface and different altitudes, daily produced by the INM. Previous studies of this nature in the Mediterranean area were conducted in the Eastern area [12][13][15] or in southern France [16].

4.1. Event of 19–20 September 2000 (in Valencia, Mediterranean coast)

As previously indicated one of the climatic features of the Mediterranean coast in Southern France and Spain is the development of intense precipitation events at the beginning of autumn season. The well-known situation develops when cold air from the upper atmospheric levels interacts with humid air generated over the still warm Mediterranean Sea. Generally, the easterly wind facilitates the displacement of the humid air mass towards the continent. The mountainous character of numerous

areas coastal areas in the Western Mediterranean area leads to the orographic uplift of this humid air mass and the rapid condensation close to the first mountainous areas, resulting in intense and damaging rains in the form of flash floods.

One of these events was sampled in the coast of Valencia in the year 2000. The amount of precipitation measured at the different meteorological stations affected by such event on 19-20 September 2001, ranged from 110 to 180 mm. The event produced a value of –4.45‰ for $\delta^{18}O$, while the sample representing the monthly composite sample for the station of Valencia was -3.91‰.

The precipitation in this case was not associated to a large atmospheric disturbance of regional scale. Both the surface synoptic weather map and 850-hPa map, indicate the absence of fronts, and the nearest low-pressure centre was situated in Central Europe. These events may have a great importance as the main mechanisms of recharge in coastal areas of the Western Mediterranean.

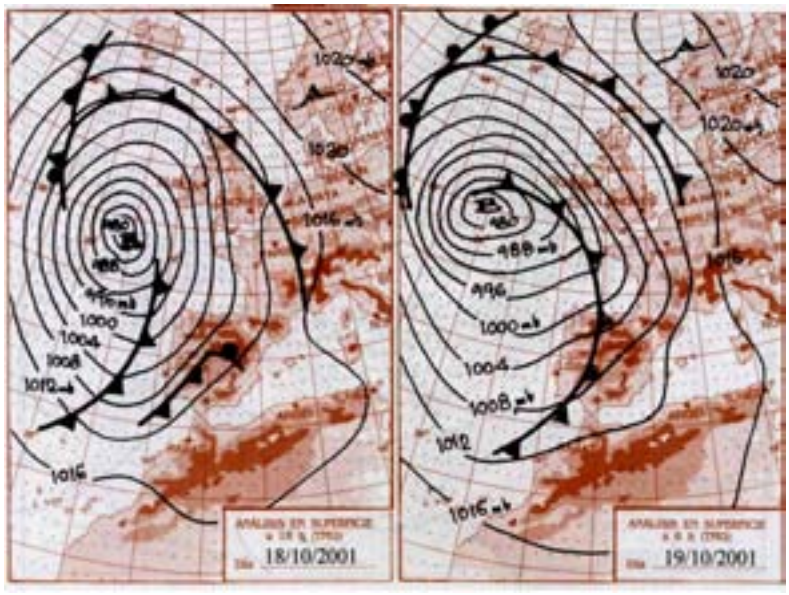

FIG. 12. Synoptic weather map (surface situation at 18 h and 06 h) corresponding to the rain event (40 mm in Madrid) of 17 to 20 October 2001, showing the development of a deep low centre and the associated cold front crossing the Iberian Peninsula.

4.2. Event of 16–20 October 2001 in Madrid

This example is a typical meteorological situation in autumn, producing about 40 mm in an event extending over three days in Central Spain. The development of a deep low-pressure centre offshore of Ireland results in a series of cold fronts crossing the IBP from West to East. This situation forces the continuous entrance of humid air from the North Atlantic, due to presence of cold air in altitude associated to the low-pressure centre. The surface weather map corresponding to the days 17 and 18 October 2001 is presented in Figure 12.

The $\delta^{18}O$ value for this event was –6.13 ‰ (Table 5.) and the d-excess unusually higher considering the dominant westerly circulation during this period (+17‰). This situation can be considered as the typical weather situation for the Meseta for autumn, presenting a value slightly enriched for the typical isotope value for precipitation in October.

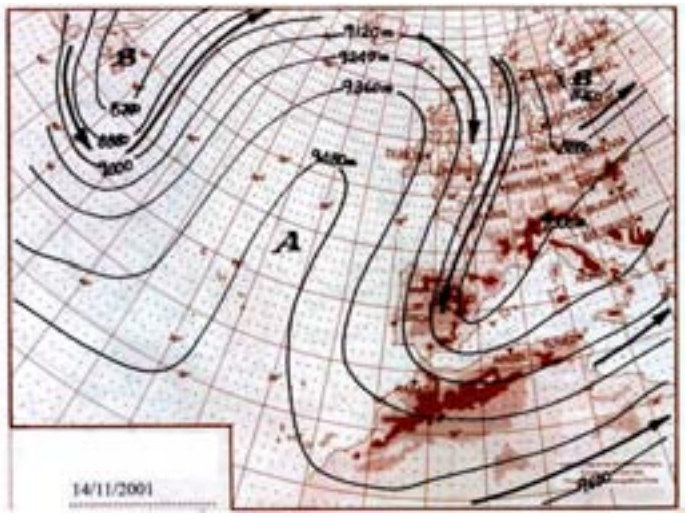

FIG. 13. Synoptic weather map (surface situation at 12h, 14 November 2001) corresponding to the rain event (4 mm in Madrid) from 14 to 15 November 2001, showing the entrance of a cold air mass from northern Europe.

4.3. Event of 15-17 November 2001 in Madrid

This rain event was selected due to the unusually depleted isotope value measured (-15.5 ‰ in $\delta^{18}O$ and –112 ‰ in δD). As explained before, the weather situation responsible for such situation allows the direct entrance of cold air from Northern Europe (Fig. 13), resulting in cold and humid conditions. Under these circumstances, the expected amount of precipitation is very small (4 mm). The $\delta^{18}O$ value of the water vapour collected during this period was –20.4 ‰ (Table 5.).

4.4.Event of 31 December 2001 to 5 January 2002 in Madrid

This event also constitutes a typical example of a weather situation producing persistent rainy conditions in Central Spain. In this case, the entrance of humid air from the Tropical Atlantic (mT) enters the IBP from the SW. The main feature of these air masses from the Tropical Atlantic is the high humidity content, due to the higher mean temperature of this air mass (Fig. 14). The presence of cold air over the continental area of Spain results in intense precipitation sustained for several days.

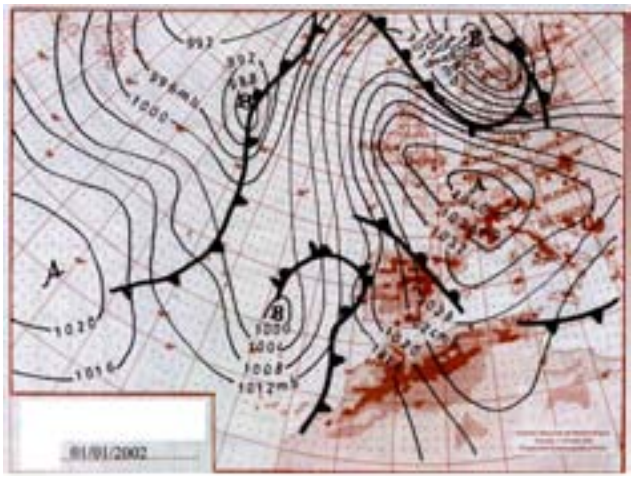

FIG. 14. Synoptic weather map (surface situation at 12h of 01 January 2002) corresponding to the rain event (46 mm in Madrid) from 31 December 2001 to 5 January 2002, showing the entrance of a humid air mass from the tropical Atlantic in the Iberian Peninsula.

5. Concluding remarks

The initial results produced by SNIP have provided, for the first time, a good spatial coverage to assess the spatial distribution of isotope contents in precipitation over Spain and surrounding areas. The analysis of the weather patterns resulting in large precipitation events over Spain and Portugal has shown the importance played by the air masses originated in the North and Tropical Atlantic as major sources of water vapour. At the latitude of the IBP, the dominant westerly circulation and the relative mean altitude of the Meseta are the major factors controlling the isotope values over the IBP [17]. The importance of Atlantic air masses as major sources of precipitation in the IBP is also reflected by the mean d-excess values observed in rain samples over the whole IBP, with mean weighted values ranging from +7 to +14 ‰. Most of the stations in central Spain show a continental character, presenting rather depleted $\delta^{18}O$ values (-7 to -10‰). This feature explains the good correlation found between the mean isotope contents and air temperature, but not with the amount of precipitation. The coefficient relating the isotope and temperature variations for the Madrid-Retiro station, using both the long-term monthly isotope contents in precipitation and available water vapour data measured on daily basis, is almost identical, 0.37 ‰ per ºC. The influence of air masses incorporating water vapour originated over the Mediterranean Sea is restricted to a narrow band parallel to the Eastern coast of Spain. The frequency of weather situations permitting the entrance of water vapour generated (or isotopically modified) over the Mediterranean is very small. Only in early autumn, low-pressure centres over the Mediterranean allow the existence of the easterly circulation at mid-latitudes. This situation results in intense precipitation events in coastal areas. However, these events may produce relative enriched isotope contents despite its intensity.

Tritium data monitored in 16 meteorological stations has shown that the declining trend in concentrations observed in the 1990s for the Madrid station was maintained until the year 2000. Only the last few years have shown a relative constant tritium contents, confirming that the natural production of tritium in the atmosphere was lower than anticipated (about 4 T.U. for continental stations of the IBP and 2-3 T.U for coastal stations under the Atlantic Ocean influence).

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REFERENCES

[1] IAEA/WMO (2004): Global Network of Isotopes in Precipitation. The GNIP database [on-line]. Accessible at http://isohis.iaea.org [Cited: 04 May 2004]

[2] FONT TULLOT, I., Climatología de España y Portugal. 1st ed. Vol. I. Instituto Nacional de Meteorología, Madrid (1983).

[3] PLATA BEDMAR, A., Composición isotópica de las precipitaciones y aguas subterráneas de la Península Ibérica. M-39, CEDEX, Madrid (1994).

[4] PEIXOTO, J. P., DE ALMEIDA, M., ROSEN, R. D., SALSTEIN, D.A., Atmospheric moisture transport and the water balance of the Mediterranean Sea. Water Resour. Res. **18(1)** (1982) 83–90.

[5] CRUZ-SANJULIAN, J., ARAGUÁS ARAGUÁS, L., ROZANSKI, K., BENAVENTE, J., CARDENAL, J., HIDALGO, M.C., GARCÍA-LÓPEZ, S., MARTÍNEZ-GARRIDO, J.C., MORAL, F., OLIAS, M., Sources of precipitation over south-eastern Spain and groundwater recharge. An isotopic study. Tellus 44B (1992) 226–236.

[6] ANDREO, B., LIÑÁN, C., CARRASCO, F., JIMÉNEZ DE CISNEROS, C., CABALLERO, F., MUDRY, J., Influence of rainfall quantity on the isotopic composition (^{18}O and ^{2}H) of water in mountainous areas. Application for groundwater research in the Yunquera-Nieves karst aquifers (S Spain). Appl. Geochem. 19 (2004) 561–574.

[7] LÓPEZ-VERA, F., LERMAN, J.C., MULLER, A.B., The Madrid Basin aquifer: preliminary isotopic reconnaissance. J. Hydrol. 54 (1981) 151–166.

[8] ROZANSKI, K., GONFIANTINI, R., ARAGUÁS ARAGUÁS, L., Tritium in the global atmosphere: distribution patterns and recent trends. Journal of Physics 17 (1991) S523-S539.
[9] ARAGUÁS ARAGUÁS, L., FROEHLICH, K., ROZANSKI, K., Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. Hydrological Processes 14 (2000) 1341–1355.
[10] ROZANSKI, K., ARAGUÁS ARAGUÁS, L., GONFIANTINI, R., Isotopic patterns in modern global precipitation. Chap. 1. In: Climate change in Continental Isotopic Records. Vol. 78. (Eds: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S.), Geophysical Monograph, American Geophysical Union, Washington, (1993) 1–36.
[11] ROZANSKI, K., ARAGUÁS ARAGUÁS, L., GONFIANTINI, R., Relation between long-term trends of oxygen-18 isotope composition of precipitation and climate. Science 258 (1992) 981–985.
[12] RINDSBERGER, M., MAGARITZ, M., CARMI, I., GILAD, D., The relation between air mass trajectories and the water isotope composition of rain in the Mediterranean Sea area. Geophysical Research Letters 10(1) (1983) 43–46.
[13] RINDSBERGER, M., JAFFE, S., RAHAMIM, S., GAT, J.R., Patterns of the isotopic composition of precipitation in time and space: data from the Israeli storm water collection program. Tellus 42(B) (1990) 263–271.
[14] JACOB, H., SONNTAG, C., An 8-year record of the seasonal variation of ^{2}H and ^{18}O in atmospheric water vapour and precipitation at Heidelberg, Germany. Tellus 43(B) (1991) 291–300.
[15] GAT, J.R.; KLEIN, B.; KUSHNIR, Y.; ROETHER, W.; WERNLI, H.; YAM, R.; SHEMESH, A., Isotope composition of air moisture over the Mediterranean Sea: an index of the air-sea interaction pattern. Tellus 55B (2003) 953–965.
[16] CELLE-JEANTON, H., GONFIANTINI, R., TRAVI, Y., SOL, B., Oxygen-18 variations of rainwater during precipitation: application of the Rayleigh model to selected rainfall in Southern France. Journal of Hydrology 289 (2004) 165–177.
[17] ROZANSKI, K., SONNTAG, C., MÜNNICH, K.O., Factors controlling stable isotope composition of European precipitation. Tellus 34 (1982) 142–150.

THE TEMPORAL AND SEASONAL VARIATION OF H-2 AND O-18 IN ATMOSPHERIC WATER VAPOUR AND PRECIPITATION FROM ANKARA, TURKEY IN RELATION TO AIR MASS TRAJECTORIES AT MEDITERRANEAN BASIN

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Abstract. This study discusses the factors controlling the variation of δ^2H, $\delta^{18}O$ in daily composite samples of water vapor and precipitation together with relevant meteorological parameters for the years January 2001 to March 2003 in Ankara. Within the scope of a coordinated research project supported by IAEA, continuous time series of isotopic data for atmospheric water vapor and precipitation at Ankara are available which range from January 2001 to February 2003. This two years record makes it possible to determine and better define the seasonal variations of the isotopic composition in water vapor and precipitation. Daily basis measurements of isotopic composition of precipitation were conducted at Ankara. The observed spatial and temporal variations of the stable isotope content ($\delta^{18}O$ and δ^2H) of atmospheric water vapor and precipitation are related with the parameters of water vapor transport in the atmosphere. The results suggest that observed spatial and temporal variations of the stable isotope content of atmospheric water vapor and precipitation are strongly related with the water vapor transport in the atmosphere. The stable isotope content of water vapor is correlated with the stable isotope composition of daily precipitation. A theoretical isotopic composition of water vapor was calculated by using the daily means of δ^2H and $\delta^{18}O$ composition of precipitation that would be in equilibrium with the precipitation. The calculated data shows that there are large deviations between calculated isotopic composition of equilibrium water vapor and measured water vapor. Daily wet precipitations were collected at one station in Ankara from January 2001 to December 2002. Major ions were analyzed in a wet only precipitation study for 24 months. The main source of wet deposited soluble ions were correlated with the geographic sectors obtained from the air mass trajectories.

1. Introduction

1.1. Purpose

This paper discusses the factors controlling the variation of δ^2H, $\delta^{18}O$ in daily composite samples of water vapor and precipitation together with relevant meteorological parameters for the years January 2001 to February 2003 in Ankara, Turkey (Fig.1). Many natural processes cause spatial and temporal variations in the isotopic composition (δ^2H, $\delta^{18}O$) of precipitation such as isotope fractionation together with evaporation from the ocean and condensation during atmospheric transport of water vapor [1], [2]. It has been demonstrated in numerous studies that isotopic composition of local precipitation is controlled by evaporation of surface ocean water, and the progressive raining out of the vapour masses as they move towards regions with lower temperatures, i.e. higher latitudes and altitudes [3], [4], [5], [6]. The value of deuterium excess "$d=\delta^2H-8\ \delta^{18}O$" is believed to relate to the relative humidity over the evaporating surface and wind speed under which evaporation takes place at the source area for atmospheric moisture [4]. The subsequent rainout from air mass that is the source of water vapor is invariant with regards to d-value. However, re-evaporation of falling rain droplets under dry conditions may decrease the value of the deuterium excess in the residual rainwater. The causes of spatial and temporal variations of δ^2H or $\delta^{18}O$ in precipitation and water vapor are isotopic fractionation associated with evaporation and condensation process during the global water vapor circulation. In this processes water molecule species (H^2HO and $H_2{}^{18}O$) remain in the liquid phase or transferred into the liquid phase. During the process of water vapor adiabatic cooling, precipitating air masses are progressively being depleted in ^2H and ^{18}O. This shows the correlation between δ^2H and $\delta^{18}O$ content of precipitation and local temperature variations. To understand the isotopic variation processes in precipitation, it is necessary to determine the isotopic composition of recent precipitation related to the climatic condition of today. The large-scale synoptic weather patterns and degree of

rainout of the moisture in the air masses have dominative effect for a few days time scale [7]. Water vapor sampling program in Germany and precipitation sampling program in Israel gave similar results [8], [9]. Within the scope of a coordinated research project supported by IAEA, continuous time series of isotopic data for atmospheric water vapor and precipitation at Ankara are available from January 2001 to February 2003. This two-years record makes it possible to determine and better define the seasonal variations of the isotopic composition in water vapor and precipitation. The statistical interpretation of these data was showed the way by four questions: First one is to determine relation between isotopic composition of precipitation, water vapor and comparison of calculated and measured isotopic composition of water vapour. The second is relation between seasonal variation of isotopic composition of water vapor, precipitation and changes in local ground level temperature. The third one is the classification of air masses flow patterns and isotopic results. The last one is to determine the relation between the isotopic composition of water vapor and daily precipitation and various synoptic parameters.

Daily wet precipitations were collected at one station in Ankara from January 2001 to December 2002. Major ions SO_4^{-2}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, and K^+ were analyzed in a wet only precipitation study for 24 months. The pH exhibited large variation from 4.59 to 8.66 pH unit. Although the pH values of individual precipitations varied excessively within these ranges, the annual mean pH values for 2001 and 2002 years are 6.22 and 6.39 respectively. The volume weighted mean concentration of anthropogenic ions SO_4^{-2}, NO_3^-, NH_4^+ were 25.93, 45.52 and 10.92 μeq/l, respectively. Chloride and all cation concentrations were similar in this study and that carried out in 1993-1998 indicating similar resources, namely aerosol and crustal material. Calcium ions were the dominant neutralization ions. The annual wet only deposition rates were calculated for the major species and were found to be comparable to those reported in the past studies. Concentrations of crustal ions are higher in summer season due to very low seawater contribution and enhanced re-suspension of soil particles from dry surface soil. The wet deposition of soluble ions was characterized by two dominant factors; the geographical distribution of precursor production through natural and anthropogenic activities, and the meteorological conditions. The main source of anthropogenic elements were found to be fossil fuel. High SO_4^{-2}, NO_3^- anthropogenic ions concentrations were observed in continental polar and maritime polar originated precipitations. Wet deposition fluxes of measured parameters are episodic. The main source of wet deposited soluble ions were correlated with the geographic sectors obtained from the air mass trajectories. Both isotopic studies and Br^-/Cl^- ratios have been used to identify the salinity origin. The use of both chemical tracers (Cl^-, Br^-) and isotopes (^{18}O, ^2H) has shown that precipitation constituents the essential origin of precipitated air mass. Chemical composition of wet precipitation in Mediterranean basin are well established through studies performed since 1980s. The city of Ankara is the capital city in Turkey. The heavy sulfur based air pollution was environmental problem until few years ago. Research indicated that the pollution was due to the use of low quality fossil fuels for space heating [12], [13], [14], [15]. Most of the air pollution research was concentrated on the emissions from coal and oil combustion with little importance on other pollution sources, such as motor vehicles.

The analysis of trace species in atmospheric particles and precipitation is very important because certain species are emitted from particular sources and they can be used as tracers for these sources [16]. Turkey has quite temperate climatic conditions, the diverse nature of the landscape, and the existence in particular of the mountains that run parallel to the coasts, results in significant differences in climatic conditions from one region to the other. While the coastal areas enjoy milder climates, the inland Anatolian plateau experiences extremes of hot summers and cold winters with limited rainfall. Mediterranean sea, which is the biggest in-land sea in the world owing to this place, is a secondary cyclogenesis area for the air masses. Turkey is a Mediterranean country therefore this sea affects all of the air masses directly or indirectly. In other words, air masses affecting Mediterranean Sea, affects Turkey at the same time.

The seasonality of mean rain fall in Turkey: The winter rainfall maximum is most characteristic over the western and southern parts of Turkey, whereas autumn and spring rainfall maximums are dominant over the Black Sea Region and continental interior regions, respectively. Contribution of the winter rainfall to the annual total is greater that 40% over the Mediterranean and Continental Mediterranean rainfall regions with about 64% country-wide and less than 20% over the Northeastern Anatolia with

about 12%. Spring rainfall contributes more than 30% of the annual rainfall total almost all over the continental interiors. In summer, maximum rainfall is concentrated over the Northeast Anatolia with 40%. The summer rainfall contributes only less than 5% of the annual rainfall total throughout the Continental Mediterranean region, with about 0.5% county-wide, and most of the Mediterranean region. The contribution of the autumn rainfall increases from below 15% of the annual total, along the Turkey-Syria border to above 30%, along the Black Sea Coast [17]. Turkey's water resources depend mostly on rain water for surface and groundwater recharges, therefore rainwater quality is an important factor. This paper presents 2 years study of precipitation composition carried out on daily basis in Central Turkey. In this study daily precipitation samples collected for stable isotope (δ^2H and $\delta^{18}O$) and mayor ion analyses from this region and the possible sources contributing to observed chemical composition have been discussed.

1.2. Study area

The lands of Turkey are located at a point where the three continents making up the old world, Asia, Africa and Europe are closest to each other, and straddle the point where Europe and Asia meet. Geographically, the country is located in the northern half of the hemisphere at a point that is about halfway between the equator and the north pole, at a latitude of 36^{o}N to 42^{o}N and a longitude of 26^{o}E to 45^{o}E. Turkey is roughly rectangular in shape and is 1660 km long and 550 km wide.

Water vapor and daily precipitation samples were collected at Ankara Nuclear Research and Training Center (ANRTC) in Ankara which is located in the center of Turkey, Latitude: 39^{o}94'N and Longitude: 32^{o}83'E (Fig. 2). Ankara's inner continental location is 400 km from Mediterranean Sea coast, 500 km from Aegean Sea coast and 200 km from Black sea coast.

Turkey is in the middle-belt, in other words; it is placed between Equator and North Pole, therefore; it is affected all of the major air masses. There are seven geological regions in Turkey. The climatic conditions of these regions are slightly differing from each other because of geography and air masses. There are also two coastal mountains, which are parallel to the Mediterranean Sea and Black Sea. In the north, the eastern Black Sea mountain chain runs parallel to the Black Sea; in the south, the Toros Mountains sweep down almost to the narrow, fertile coastal plain along the sea cost. Between these two mountains there is large Anatolian plateau lies on the center of Turkey.

1.3. Climate and precipitation sources

Although Turkey is situated in a geographical location where climatic conditions are quite temperate, the diverse nature of the landscape, and the existence in particular of the mountains that run parallel to the coasts, results in significant differences in climatic conditions from one region to the other. While the coastal areas enjoy milder climates, the inland Anatolian plateau experiences extremes of hot summers and cold winters with limited rainfall. Mediterranean Sea, which is the biggest in-land sea in the world owing to this place, is a secondary cyclogenesis area for the air masses. Turkey is a Mediterranean country therefore this sea affects all of the air masses directly or indirectly. The seasonality of mean rain fall in Turkey: The winter rainfall maximum is most characteristic over the western and southern parts of Turkey, whereas autumn and spring rainfall maximums are dominant over the Black Sea Region and continental interior regions, respectively.

FIG. 1. Localisation map.

Contribution of the winter rainfall to the annual total is greater that 40% over the Mediterranean and Continental Mediterranean rainfall regions with about 64% country-wide and less than 20% over the North-eastern Anatolia with about 12%. Spring rainfall contributes more than 30% of the annual rainfall total almost all over the continental interiors. In summer, maximum rainfall is concentrated over the Northeast Anatolia with 40%. The summer rainfall contributes only less than 5% of the annual rainfall total throughout the Continental Mediterranean region, with about 0.5% county-wide, and most of the Mediterranean region. The contribution of the autumn rainfall increases from below 15% of the annual total, along the Turkey-Syria border to above 30%, along the Black Sea Coast.

1.4. Air masses affecting Turkey

Turkey is mainly affected by two different kinds of air masses either generated in Mediterranean Sea or passes over Mediterranean, depending upon seasons. In general air masses, which pass over Mediterranean, have some changes both thermal and dynamical. These air masses are polar (P) and tropical (T). Sometimes maritime arctic (Ma) reaches and settled over Turkey. But Ma losses their main characteristic because of it is affected from land; it gets heat and decreases the amount of humidity which is consisted [17]. Out of above air masses, Turkey is affected from polar air masses in winter and tropical air masses in the summer. As a result of these air masses the temperature differences between winters and summers are too extreme.

Continental Polar (cP) air mass: In winter, the origin of this air mass is Russia. Especially in winter, when anticyclone settled on North Russia and Finland, it affects main parts of Europe. In summer continental polar moves to north parts of the north hemisphere and decreases the affect over Turkey. In other words, Mediterranean and Turkey are affected by maritime tropical and continental tropical air masses.

Maritime Polar (mP) air mass: When Azores anticyclone doesn't affect to Europe then maritime polar air mass flows to Mediterranean Sea and generates small-scale cyclone systems. It cools over the land, gets stable but if it passes over the seas than it gains humidity, changes its position from stable to unstable. Generally over Turkey it has a characteristic of instability and causes rain showers. In summer, it is stable over seas but it becomes unstable over the land therefore a little convectional rain showers can be seen.

Continental Tropical (cT) air mass: In winter, main source area is North Africa and Sahara Deserts. In its source, weather is too hot, dry and stable. It moves to the north and meets maritime tropical, gains humidity become unstable. Sometimes, it is a reason for frontal system, cyclones, cyclonic storms and rain showers. In summer all pressure belts move to the north, continental tropical has a big area in the south. North Africa, Anatolia, Asia and southern Balkanian become a main source of Continental Tropical. The source region is dry, hot and so unstable. In summer Turkey is mostly affected by this air mass.

Maritime Tropical (mT) air mass: In winter, source region is North Atlantic Ocean and the tropical areas, which are between 30 – 40^{O} altitudes. Under the effect of Azores anticyclone it has own characteristics. This air mass effects Europe and Turkey completely. It is a supporter for cyclogenesis over Atlantic Ocean. In summer maritime tropical has a larger area than winter, and puts relations with continental tropical. Polar fronts go to the north. For Turkey, it doesn't bring rainfall but causes for cool with northerly winds.

2. Methodology

2.1. Precipitation collection

Daily precipitation samples were collected every morning at ANRTC by using a standard pluviometer. After sample collection, the volume of daily composite precipitation samples were measured and transferred into 30 ml glass bottles with tight cap, and then rain collector was dried with a clean dry cloth before returning it to its collecting position. Collected daily precipitation samples were kept in a cool, dark place. $\delta^{18}O$ and $\delta^{2}H$ analyses of the collected precipitation samples were analyzed by isotope laboratory of UAEA. Forty daily precipitation samples were collected for major ion analysis using an Anderson precipitation sampler between October 2001 and September 2002 at Beşevler-Ankara. Chemical analysis of these samples was performed by State Mineral Research Institute, Hydrogeology Department of Avignon and Hacettepe Universities. After September 2002, the daily precipitation data of EMEP network were used. Ankara station of this network is located at Çubuk, which is a rural area approximately 50 km to the city center of Ankara (Fig.2). Seventy-one samples have been collected at Çubuk station until January 2003 and analyzed by Ministry of Health Laboratories at Ankara.

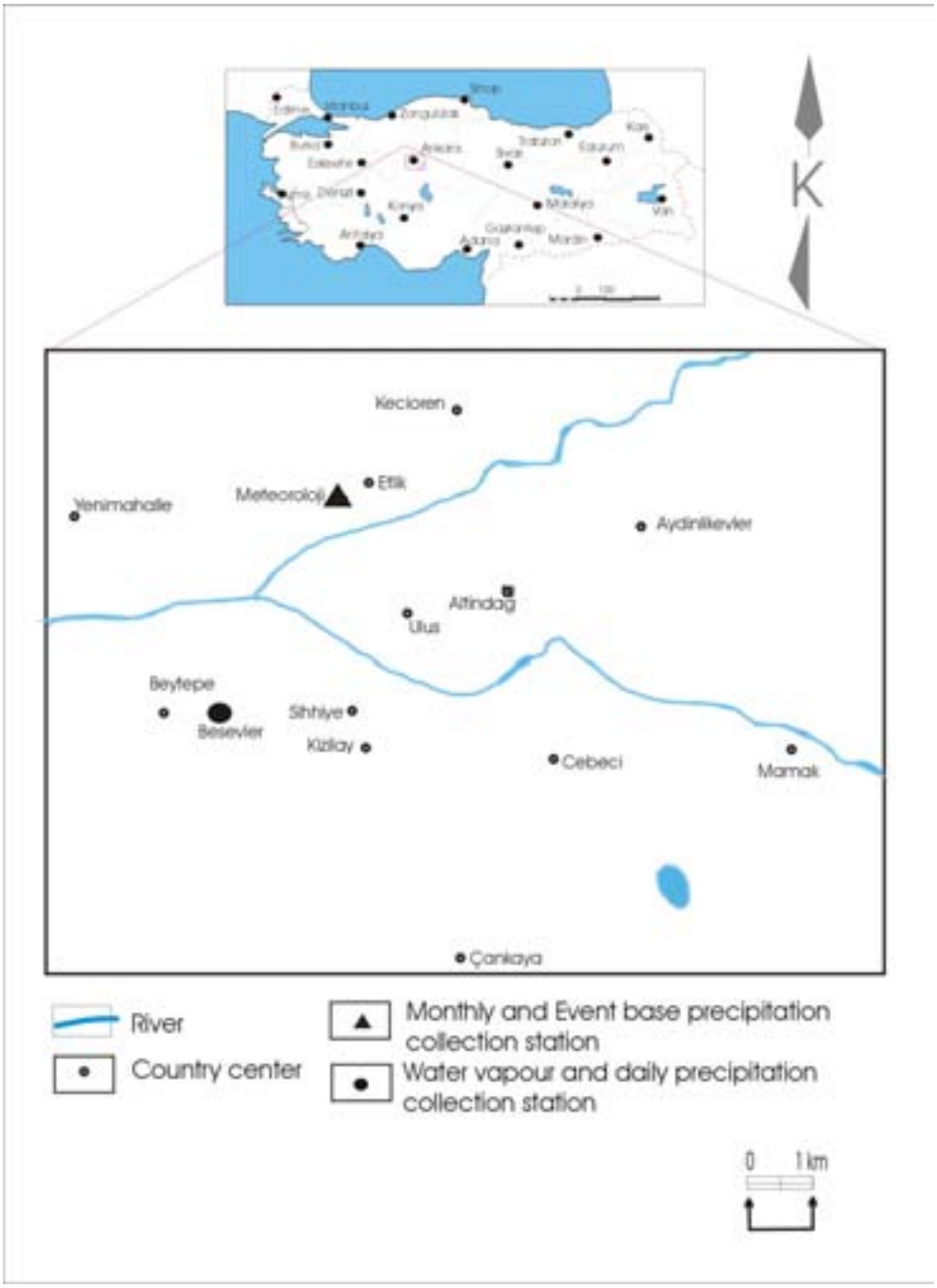

FIG. 2. Map showing the precipitation and water vapour sampling site at Ankara.

2.2. Atmospheric water vapor collection

Atmospheric water vapor is collected at the grounds of ANRTC at Ankara in an altitude 5 m and with the aid of the apparatus shown in Annex 2. Atmospheric water vapor samples were collected during 48 hours period starting on each Monday morning by applying above procedure. Accumulated water vapor sample in the sampler was transferred into a 10 ml glass bottle and closed with a good cap tightly. Similar sampling procedure was repeated for Wednesday afternoon to Friday afternoon period. As a result, two atmospheric water vapor samples were collected per week. 225 water vapor samples were collected between January 2001 and February 2003. Stable isotope analyses were performed at the Isotope Laboratory of the IAEA. Stable isotope analyses are reported in δ units expressed as per mill (‰) deviations with respect to the international standard (VSMOW). The analytical error is ± 0,2 ‰ for ^{18}O, ± 2 ‰ for ^{2}H.

3. Stable isotopic composition of precipitation in Turkey

Composite monthly samples of precipitation were collected over different periods of time ranging from one month to 38 years at 26 stations throughout Turkey. These samples were collected and measured for their oxygen and hydrogen isotopic composition to obtain information about one of the input parameter precipitation for hydrological, hydro geological and meteorological studies in this area (Table 1). A map of the stable isotopic composition of precipitation in Turkey has been drawn (Fig. 3).

Table 1**.** Evaluation mean oxygen and hydrogen values, deuterium excess (d) and sampling period for 26 sampling stations all over Turkey

Sampling Station	Location	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰	d	Sampling period
Ankara	Lat:39,95N;Long:32,88E;Alt:902m	-8.6	-57.2	11.9	1/63 – 12/2001
Antalya	Lat:36,88N;Long:30,70E;Alt:49m	-5.4	-27.2	16.2	1/63 – 12/2001
Adana	Lat:36,98N;Long:35,30E;Alt:73m	-5,2	-24,0	18.1	1/66-12/2000
Adıyaman	Lat:37,45N;Long:38,17E;Alt:672m	-8.5	-55.0	13.1	3/91-3/96
Diyarbakır	Lat:37,20N;Long:40,92E;Alt:686m	-9.9	-59.1	20.1	12/66 – 01/68
Şanlıurfa	Lat:37,35N;Long:38,57E	-5.2	-24.4	17.1	01/81-05/82 (*)
Kozağaç(Aydın)	Lat:37,03N;Long29,39E;Alt:610m	-6.5	-37.9	14.3	01/87-11/93
Milas (Aydın)	Lat:37,03N;Long29,39E;Alt:610m	-6.4	-37.5	13.9	01/87-11/93
Muğla	Lat:38,13N;Long:28,22E;Alt:641m	-4.9	-25.8	13.1	04/91-93/11
Acıpayam(Denizli)	Lat:37,25N;Long:29,20E;Alt:941m	-7.8	-49.8	12.5	09/94-11/94(*)
Yeşiloba(Denizli)	Lat:37,47N;Long:29,05E	-7.8	-50.5	12.2	09/94-11/94(*)
Hozan(Denizli)	Lat:37,46N;Long:29,16E	-7.6	-50.0	11.4	12/86-07/87(*)
Marmaris(Muğla)	Lat:36,51N;Long:28,16E;Alt:16m	-5.4	-28.9	14.7	10-11/94(*)
Dalaman(Muğla)	Lat:36,42N;Long:28,47E;Alt:9m	-5.2	-26.4	15.2	09-11/94(*)
Köyceğiz(Muğla)	Lat:36,58N;Long:28,41E;Alt:24m	-6.6	-38.3	14.9	09-11/94 (*)
Bodrum(Muğla)	Lat:37,02N;Long:27,26E;Alt:26m	-3.9	-20.7	10.8	10/94(*)
İzmir	Lat:38,26N;Long:27,10E	-6.5	-	-6.5	11/83-04/86
Dalbahçe(Erzurum)	Lat:39,31N;Long:41,49E;Alt:1695m	-9.5	-63.6	12.5	04/90-04/92
Şenyurt(Erzurum)	Lat:39,38N;Long:41,01E;Alt:2160m	-9.2	-58.0	16.2	03/90-01/93
Van	Lat:38,27N;Long:43,19E;Alt:1661m	-11.1	-67.0	21.9	12/95-05/98
Erdemli(Mersin)	Lat:36,36N;Long:34,22E;Alt:10m	-6.2	-34.5	15.1	02/91-02/93(*)
Güzeloluk(Mersin)	Lat:36,54N;Long:34,07E;Alt:1400m	-7.5	-44.4	16.0	05/90-02/93
Koçbeyli(Isparta)	Lat:36,88N;Long:30,70E;Alt:49m	-9.0	-59.5	12.9	10/89-04/93
Sinop	Lat:42,03N;Long:35,17E;Alt:32m	-11.4	-68.1	23.4	12/66-01/68(*)
Edremit(Bursa)	Lat:39,36N;Long:27,01E	-5.54	-33.7	10.5	04/79-09/80
Ayaklıköyü(Bursa)	Lat:40,11N;Long:29,04E	-7.3	-47.7	10.7	05/79-09/90

(*) Yearly measurements incomplete

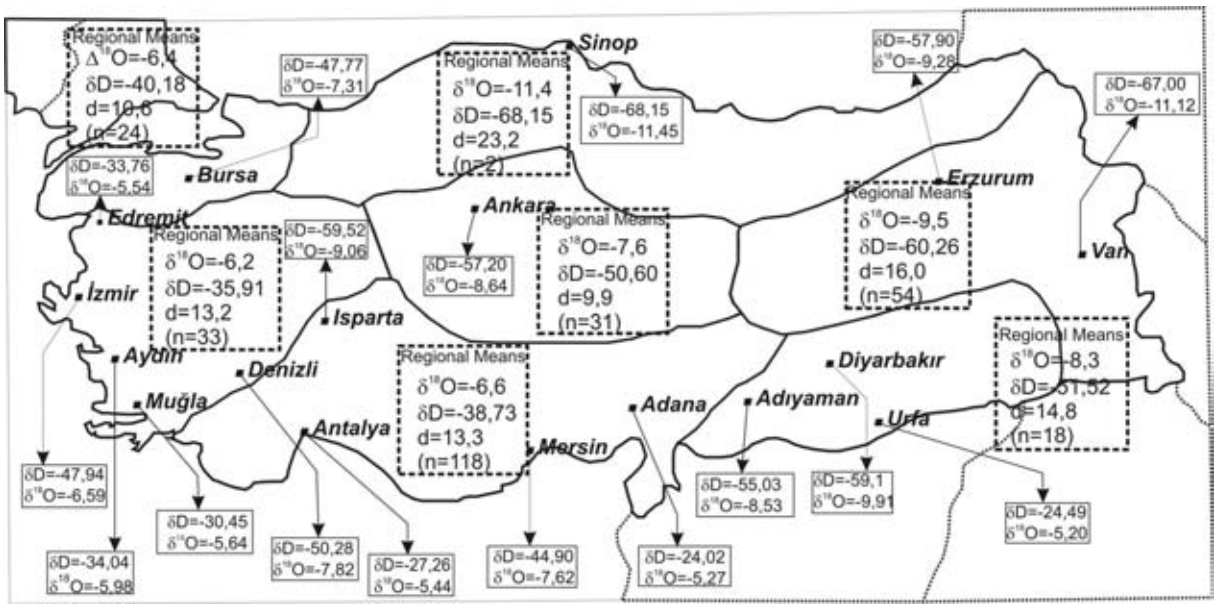

FIG. 3. Location of the stations at which mean monthly samples of precipitation for isotope measurements.

The relationship between $\delta^{18}O$ and $\delta^{2}H$ in precipitation is controlled by condensation processes related to Rayleigh distillation. $\delta^{18}O$ and $\delta^{2}H$ values of precipitation generally plot along the Global Meteoric Water Line (MWL), defined by Craig (1961) as;

$$\delta^{2}H = 8\,\delta^{18}O + 10$$

This equation was more recently confirmed by Rozanski et al. (1993) who obtained the following equations by considering all updated isotopic results.

$$\delta^{2}H = (8.17\pm0.06)\,\delta^{18}O + (10.35\pm0.65)$$

This equation is not applicable to precipitation in Mediterranean basin. In the case of our stations, the slope values ranged from 5.40 to 7.79 thus confirm a deviation from the rule of the precipitations on the Mediterranean basin. The low slope for precipitation data from Turkey is affected by secondary evaporation during precipitation. This effect on slope is greatest for light precipitation. In order to exclude this effect from our calculations we excluded the monthly data for precipitation less than 20mm. The deuterium excess is also varying from +10.4 to +21.9 ‰. However, plotting all the available monthly $\delta^{18}O$ and $\delta^{2}H$ values, the following equation can be calculated.

$$\delta^{2}H = 7.74\,\delta^{18}O + 13.10$$

This equation is very near to the global meteoric water line despite the variability at each single station. However if we separate the mean monthly samples according to the seven geological regions of Turkey, seven local meteoric water line equations reported in Fig. 4 can be calculated. The values from Central Anatolia region of Turkey are close to the average global behavior while those from Mediterranean region, Aegean region and South east Anatolia region are affected by the influence of the Mediterranean Sea; Black sea region is affected by Black Sea, Marmara region is affected by the Marmara Sea. East Anatolia region especially Van is affected by the influence of the Van Lake which is biggest and deepest soda lake in Turkey. Both slope and deuterium excess departing from the values of the global meteoric line.

Based on the δ – temperature relationship observed by Dansgaard, it is expected that precipitation at higher attitudes tends to have more negative $\delta^{18}O$. The latitude effect is about –2 ‰/degree of latitude for coastally and continental stations in Europe [1], [18].

The isotopic and meteorological data of these stations updated and analyzed statistically. The values of daily and monthly precipitation and corresponding $\delta^{18}O$ and $\delta^{2}H$ and deuterium excess (d) values are presented in table 2.

Table 2. The coefficients of meteoric water lines and weighted, arithmetic mean values from stations in Turkey. The water line equation is $\delta 2H=A\ \delta^{18}O+B$

Station	Slope A	Intercept B	Weighted mean $\delta^{18}O$ ‰	Arithmetic mean $\delta^{18}O$ ‰	Weighted mean $\delta^{2}H$ ‰	Arithmetic mean $\delta^{2}H$ ‰
Ankara[1]	7.79	8.46	-8.3	-8,4	-56.3	-58,7
Ankara[2]	7.75	9.36	-8.2	-7.5	-54.3	-51.7
Antalya[2]	7.30	12.89	-5.8	-5.4	-29.3	-27.4
Adana[2]	6.53	6.87	-5.6	-5.0	-28.2	-25.7

[1:] Daily precipitation (January 2001- February 2003), [2:] Monthly precipitation (1963-2001)

For Ankara station $\delta^{18}O$ values ranged from -5.48 to -9.92 ‰ and $\delta^{2}H$ values ranged from -31.4 to -69.1 ‰. These ranges are typical of mid continental stations [19]. For Antalya and Adana stations $\delta^{18}O$ values ranged from -4.26 to -7.88 ‰ and -3.57 to -7.67 ‰ and $\delta^{2}H$ values ranged from -16.4 to -46.8 ‰ and -17.3 to -35.4 ‰ respectively. These ranges are typical marine and costal stations [19].

The Ankara meteoric water line plots slightly below the global meteoric water line (i.e. lower d-excess). Such deviations results from different climatic conditions such as temperature, evaporation, seasonality of precipitation and moisture source [20].

Some studies suggest that the isotopic composition of precipitation may be more related to air mass trajectories than to temperature relationships alone [21], [22], [23]. However temperature seems to be controlling factor in Ankara. A reasonably good correlation can be seen between daily $\delta^{18}O$ and $\delta^{2}H$ values and daily temperature. We obtained better correlation with monthly data than daily data.

The regression equations relating the daily Ankara oxygen and deuterium values to daily temperature are;

$$\delta^{18}O_{Daily} = 0.49T(^{o}C) - 13.62 \ (r^{2}=0.48)$$

$$\delta^{2}H_{Daily} = 3.68T(^{o}C) - 96.91 \ (r^{2}=0.44)$$

A much stronger correlation exists between monthly mean $\delta^{18}O$ and $\delta^{2}H$ values and monthly mean temperature. The regression equations for Ankara station are;

$$\delta^{18}O_{Monthly} = 0.35T(^{o}C) - 11.56 \ (r^{2}=0.63)$$

$$\delta^{2}H_{Monthly} = 2.52T(^{o}C) - 79.5 \ (r^{2}=0.60)$$

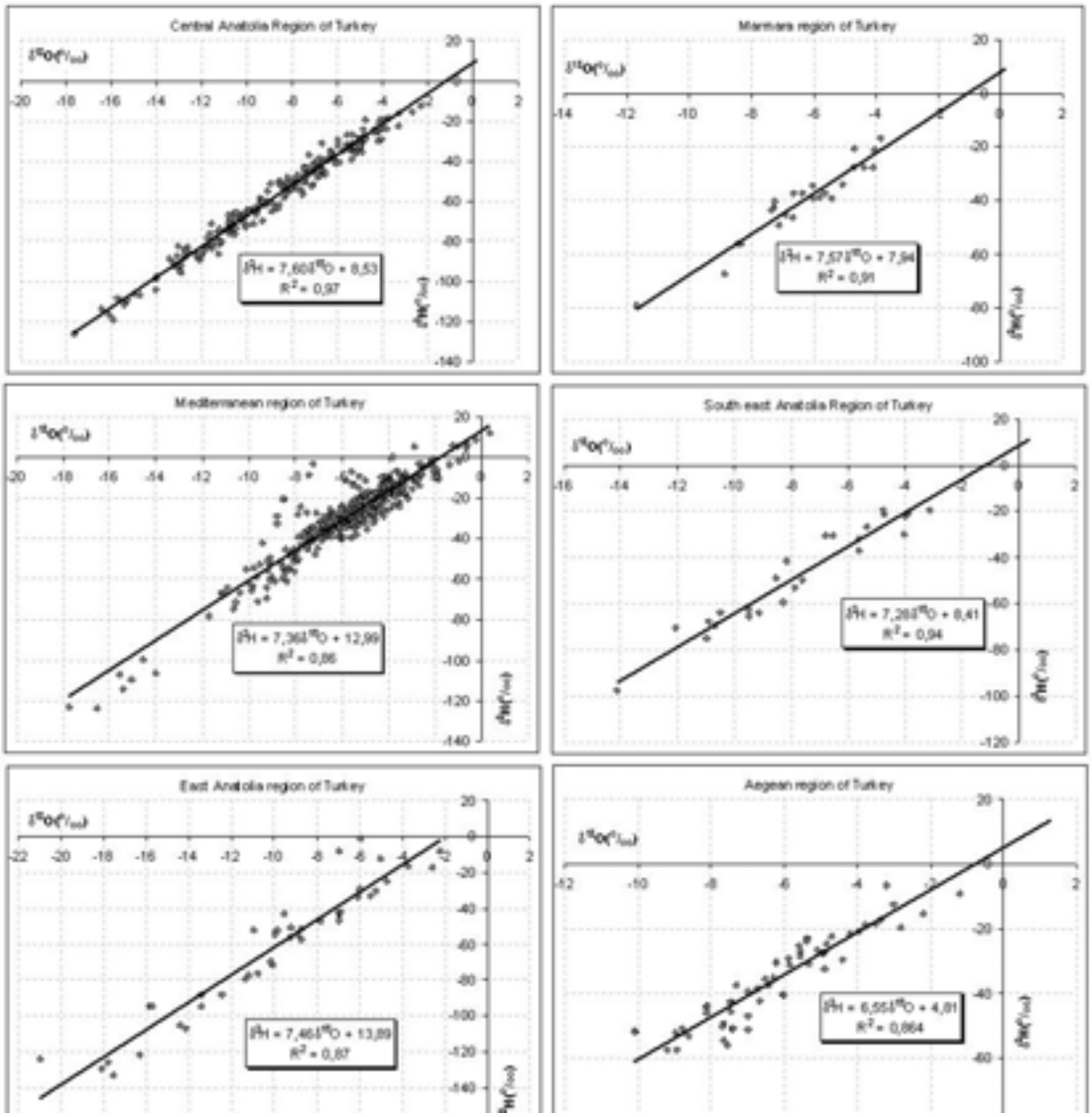

FIG. 4. $\delta^{18}O$ and $\delta^{2}H$ relationship of mean monthly samples collected in six regions of Turkey.

Daily $\delta^{18}O$ and $\delta^{2}H$ values for January 2001-March 2003 shows the seasonal effect on precipitation relating from increasing precipitation events and amounts and higher temperature over the summer months (June-August) (Fig. 6). Winter precipitation (December-February) has more depleted signature while summer precipitation is enriched relative to the yearly $\delta^{18}O$ and $\delta^{2}H$ averages -8.4 and -58.7 ‰ respectively.

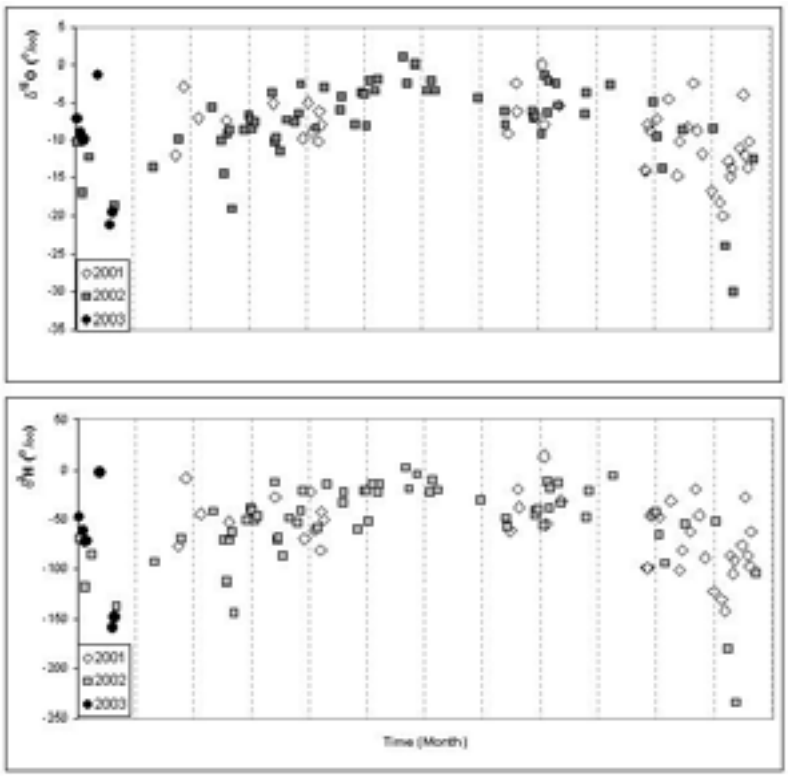

FIG. 5. The seasonal changes of the daily $\delta^{18}O$ and $\delta^{2}H$ composition of precipitation for years 2001-2003 at Ankara.

4. The relation between the $\delta^{18}O$ and $\delta^{2}H$ contents of daily precipitation in Ankara and air mass trajectories based on synoptic chargers and back trajectory method

The majority of daily precipitation sampled for isotope analyses were associated with five distinct meteorological events (air mass) which are Maritime polar (mP), Continental polar (cP), Maritime tropical (mT), Continental tropical (cT) and Mediterranean engendered air mass with descending order. In addition to these Asiatic monsoon depression type air mass is the another important meteorological event. In this study three different levels were used at 1000, 1500 and 2000m (corresponding at ~ 900, ~ 850 and ~ 800 hPa, respectively). Trajectories were classified into the following five sectors and Mediterranean endangered air mass as shown in Figure 3.5 according to the air masses over Mediterranean basin. Our classification of flow patterns is i) The location of the air mass three days preceding the rainy day ii) the direction of approach to the central Turkey iii) the region in which the air mass entered the Mediterranean basin. In this paper we present data from a detailed daily precipitation collection program at a 26 stations in Mediterranean basin, their isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) and synoptic analysis of the air mass trajectories and 500 hPa synoptic maps associated these daily precipitations are argued. Six distinct types of air mass path ways have been identified [25, 26]. Each pathways is associated with a different isotopic composition, reflecting both the origin of the moisture and the subsequent interaction pattern with the waters of the Mediterranean Sea [24]. Daily precipitations were classified according to air mass flow patterns and isotopic values. Trajectories were classified into the following six sectors as shown in Fig. 6 according to the spatial distribution of stable isotopic composition ($\delta^{18}O$, $\delta^{2}H$) of daily precipitation and geographical features in Mediterranean basin.

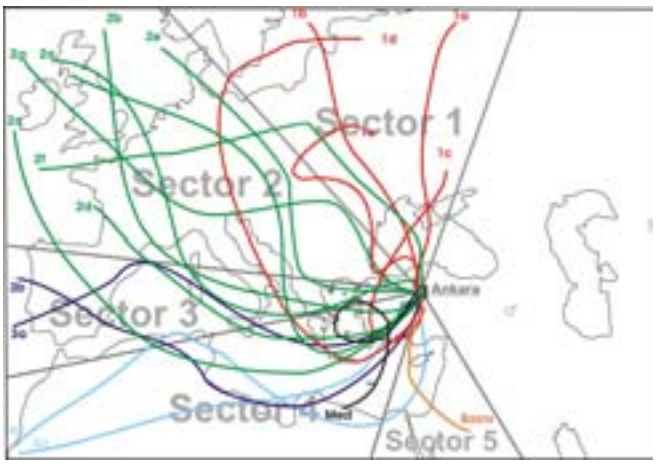

FIG. 6. Classification of back-trajectories.

Sector 1: Continental Polar air mass Transported from the north and north east part of Europe. In this sector we have defined five sub air masses flow patterns. The trajectory type of this sector originates from continental arctic or polar air masses.

Sector 2: Maritime Polar air mass Transported from the central part of Europe. In this sector we have defined six sub air masses flow patterns. The trajectory type of this sector originates from maritime polar or arctic air masses.

Sector 3: Maritime Tropical air mass Transported from the South west Europe. In this sector we have defined two sub air masses flow patterns. The trajectory type of this sector originates from either polar or tropical air masses.

Sector 4: Continental Tropical air mass Transported from the northern part of Africa Continent. In this sector we have defined two sub air masses flow patterns. The trajectory type of this sector originates from tropical air masses.

Sector 5: Air mass transported from Eastern part of Africa Continent. Westward and northwestward extensions of the thermal originated Asiatic monsoon depression, which in Turkish is referred to as the Basra low-pressure, also has some importance for Turkey from May-October. In summer months when fresh cool air stream invades the Eastern Mediterranean, a weak frontal depression may develop with the northwest extension of the Asiatic monsoon low to Turkey.

Sector 6: Air mass transported from the Eastern part of the Mediterranean Sea. These air masses interact with the Mediterranean Sea for a relatively long time before reaching the Turkey Coast from south.

The isotopic composition of daily precipitation is determined by regional scale processes, i.e., by water vapor transport patterns into the continents, and by the average “rainout history” of the air masses precipitating at a given place which accompany the atmospheric part of the hydrological cycle [4][5][6]. The “deuterium excess” is indicative to the intensity of air-sea interaction [19]. Hence, the higher “deuterium excess” values which are observed in 1c sub-group of Sector 1, 2d sub-group of Sector 2 and Sector 6 are a result of intense air-sea interaction in the eastern part of the Mediterranean Sea. The lower “deuterium excess” observed in 1b sub-group of Sector 1; 2a sub-group when the air masses enter the Mediterranean Sea from over Italy or West of Italy, 2b, 2e and 2f sub-group of Sector 2 and 3a sub-group of Sector 3 may be attributed to the longer over sea path and thus loser to equilibrium processes during air sea interaction, mostly with the western part of Mediterranean and Black Sea.

The daily precipitation which are most depleted in the heavy stable isotopes are associated with cold polar air masses. The trajectories of which approaching the concerned region from the north observed

in 1a, 1d and 1e sub-group of Sector 1. The average $\delta^{18}O$ and $\delta^{2}H$ composition of these sub-groups are typical of mid continental stations globally [19]. The average "deuterium excess" values for 2a, 2c and 2g sub-groups of Sector 2 are 12,13 ‰ 11,93 and 10,33 respectively. These values are very near to global value of d = 10 ‰. The air mass trajectories within this sector originating from North Atlantic Ocean and cross the Europe Continent. Although source regions are different, the average deuterium excess values of 4a,b and 3b sub-groups are in the same order of magnitude as global value. The Asiatic monsoon depression is less common air mass type in Turkey but in summer months when fresh cool air stream invades the Eastern Mediterranean from the south east carrying moisture originating from the Indian Ocean, a weak frontal depression may develop. The isotopic composition of precipitation caused by this type of air masses can be grouped in Sector 5, which shows same stable isotope composition as maritime precipitation. According to the available meteorological observations trajectories were classified into the six sectors. For each sector an average oxygen-18, deuterium and percentage frequencies were calculated by using computed trajectories. The calculated percentage frequencies are given in brackets.

For Sector 1: $\delta^{18}O_{average}$= -8.14 ‰, $\delta^{2}H_{average}$= -56.77 ‰, n=27 (25% in 2001, 26.2% in 2002)
For Sector 2: $\delta^{18}O_{average}$= -9.14 ‰, $\delta^{2}H_{average}$= -63.13 ‰, n=51 (55% in 2001, 36.9% in 2002)
For Sector 3: $\delta^{18}O_{average}$= -7.27 ‰, $\delta^{2}H_{average}$= -51.68 ‰, n=14 (5% in 2001, 16.9% in 2002)
For Sector 4: $\delta^{18}O_{average}$= -8.12 ‰, $\delta^{2}H_{average}$= -53.52 ‰, n=12 (10% in 2001, 12.3% in 2002)
For Sector 5: $\delta^{18}O_{average}$= -4.58 ‰, $\delta^{2}H_{average}$= -33.38 ‰, n=5 (0% in 2001, 7.7% in 2002)
For Sector 6: $\delta^{18}O_{average}$= -13.92 ‰, $\delta^{2}H_{average}$= -96.87 ‰, n=3 (5% in 2001, 36.9% in 2002)

In Sector 1, before precipitation even (three days preceding the rainy day) oxyen-18 compositions of water vapors were depleted. This depletion ranged from 7 to 15 ‰ depends on the flow patterns of air mass trajectories. In Sector 2, before precipitation event (three days preceding the rainy day), when the air masses traveled along south coasts of Europe continent, oxyen-18 compositions of water vapors were depleted. This depletion ranged from 4 to 13 ‰ depends on the flow patterns of air mass trajectories. When the air masses traveled along north coasts of Africa Continent, oxyen-18 compositions of water vapors were enriched (ranged from 3 to 14 ‰) depends on the flow patterns of air mass trajectories. In Sector 3, before precipitation even (three days preceding the rainy day) oxyen-18 compositions of water vapors were depleted. This depletion ranged from 4 to 6 ‰ depends on the flow patterns of air mass trajectories. In Sector 4, before precipitation even (three days preceding the rainy day) oxyen-18 compositions of water vapors were enriched (ranged from 2 to 4 ‰) depends on the flow patterns of air mass trajectories. In Sector 5 and Sector 6, before precipitation even (three days preceding the rainy day) oxyen-18 compositions of water vapors were depleted. These depletions are about 10 ‰ and 4 ‰ respectively, depends on the flow patterns of air mass trajectories. The same depletion or enrichment was also observed in deuterium and oxygen-18 composition of water vapor depends on the flow patterns of air mass trajectories.

5. Two year record of seasonal variation of $\delta^{2}H$ in atmospheric water vapor in Ankara

The monthly means isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) of water vapor and precipitation are presented for January 2001 to February 2003 at Ankara together with the amount of precipitation and the monthly mean temperature in Annex 3.

Comparision between daily precipitation and atmospheric water vapor:

$\delta^{2}H$/ $\delta^{18}O$ correlations of water vapor and precipitation have been calculated in Heielberg, Cracow and Paris by Schoch-Fischer et al. and in Heidelberg by Jacob H. And Sonntag C. [7, 27]. $\delta^{2}H$/ $\delta^{18}O$ correlations of water vapor and precipitation were calculated for Ankara station by using two years data.

$$\delta^{2}H_{precip} = 7.59\ \delta^{18}O_{precip} + 5.87 \quad (r^{2}=0.985)$$

$$\delta^{2}H_{vap} = 6.64\ \delta^{18}O_{vap} - 7.37 \quad (r^{2}=0.986)$$

These lines closer to the meteoric water line $\delta^2H=8*\ \delta^{18}O+10$ [3]. The calculated mean value of deuterium excess $d= \delta^2H - 8*\ \delta^{18}O$ calculated for precipitation and water vapor are $d_{precip}= 9.2$ ‰. and $d_{vap}= 18.1$ ‰ respectively. The significantly lower d-values were obtained for precipitation than for water vapor. This may be caused by partial evaporation of rain drops beneath the cloud level [27]. The higher value of water vapor may be explained by admixture of water vapor evaporated from nude soil (upper part of unsaturated zone of soil). The following relationships were obtained between isotopic composition of monthly (daily) precipitation and water vapor.

$$\delta^2H_{vap} = 0.63\ \delta^2H_{precip} - 97.12\ (r^2=0.73),\ \delta^{18}O_{vap} = 0.74\ \delta^{18}O_{precip} - 12.80\ (r^2=0.74)$$

Rain is close to equilibrium with the moisture in surface air this was indeed confirmed on land by the simultaneous surface air moisture and precipitation collection [27, 5]. Because of low correlation coefficients these relations are not suitable to apply for individual months. Using the daily means of δ^2H and $\delta^{18}O$ composition of precipitation, we calculated a theoretical isotopic composition of water vapor that would be in equilibrium with the precipitation. The equilibrium fraction factors used in this calculations were calculated by inserting daily means of air temperature in to the following equations given by Majoube [28].

$$10^3 \ln {}^{18}O_{W-V} = 1.137\left(10^6/T^2\right) - 0.4156\left(10^3/T\right) - 2.0667$$

$$10^3 \ln {}^{2}H_{W-V} = 24.844\left(10^6/T^2\right) - 76.248\left(10^3/T\right) + 52.612$$

If there was a complete equilibrium between the water vapor and the precipitation, then the calculated values should be rather close to the measured daily mean isotopic composition of water vapor. The calculated relationships for the two years data are;

$$\delta^2H_{eqvap} = 1.27\ \delta^2H_{vap} + 28.84\ (r^2=0.73),\ \delta^{18}O_{eqvap} = 1.19\ \delta^{18}O_{vap} + 3.62\ (r^2= 0.70)$$

It is expected that the correlation of the deuterium content of measured water vapor with equilibrium water vapor gets along with oxygen-18 correlation. However the data shows that there are large deviations between calculated isotopic composition of equilibrium water vapor and measured water vapor. As can be seen from the Fig. 7, there are rather large deviations of the calculated δ_{eqvap} from measured δ_{vap} for individual days of 2001, 2002 and 2003 years. Although there is a good correlation between isotopic composition of water vapor and precipitation on some days the isotopic composition of water vapor cannot be derived from isotopic composition of the precipitation. It seems possible to determine the isotopic composition of water vapor from the isotopic composition of precipitation for winter months.

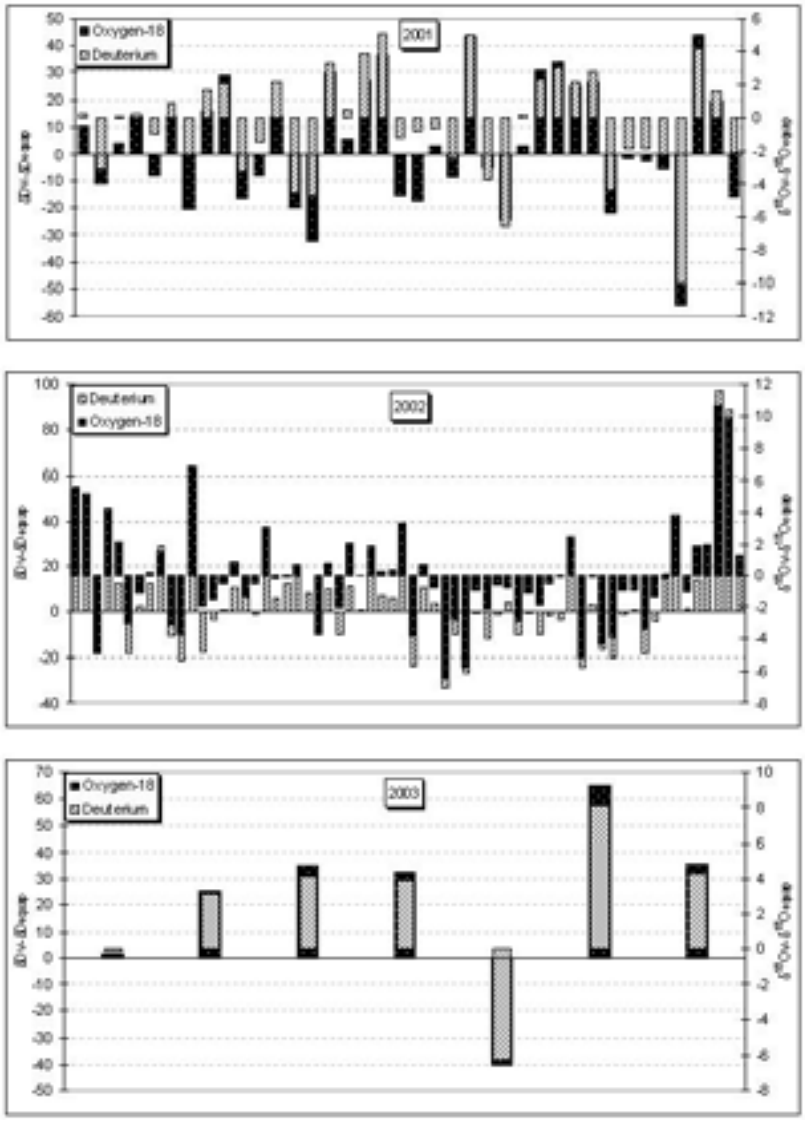

FIG. 7. The differences between the measured daily δ^2H and $\delta^{18}O$.

The isotopic composition of water vapor or precipitation is controlled by the temperature but observed relation between temperature and isotopic composition shows much scatter and is not linear, except in the far north. The variations of isotopic composition are cased by isotopic fractionation depending on condensation and evaporation processes. $\delta^{18}O$ and $\delta^{2}H$ composition of atmospheric water vapor and precipitation vary with evaporation and condensation process during global water vapor circulation. Because of adiabatic cooling $\delta^{18}O$ and $\delta^{2}H$ composition of precipitation depleted. Temporal variation of $\delta^{18}O$ and $\delta^{2}H$ in water vapor and precipitation based on continuous time series of the isotopic composition of atmospheric water vapor rather than precipitation. Fig. 8 shows daily values of a two year records at Ankara, demonstrating seasonal variations.

The $\delta^{2}H$ vs. $\delta^{18}O$ relations for precipitation and water vapor data recorded at Ankara are examined in seasonal basis (Fig. 9). In all seasons the data points lie close to the world meteoric water line, although systematic deviations from this relation can be observed.

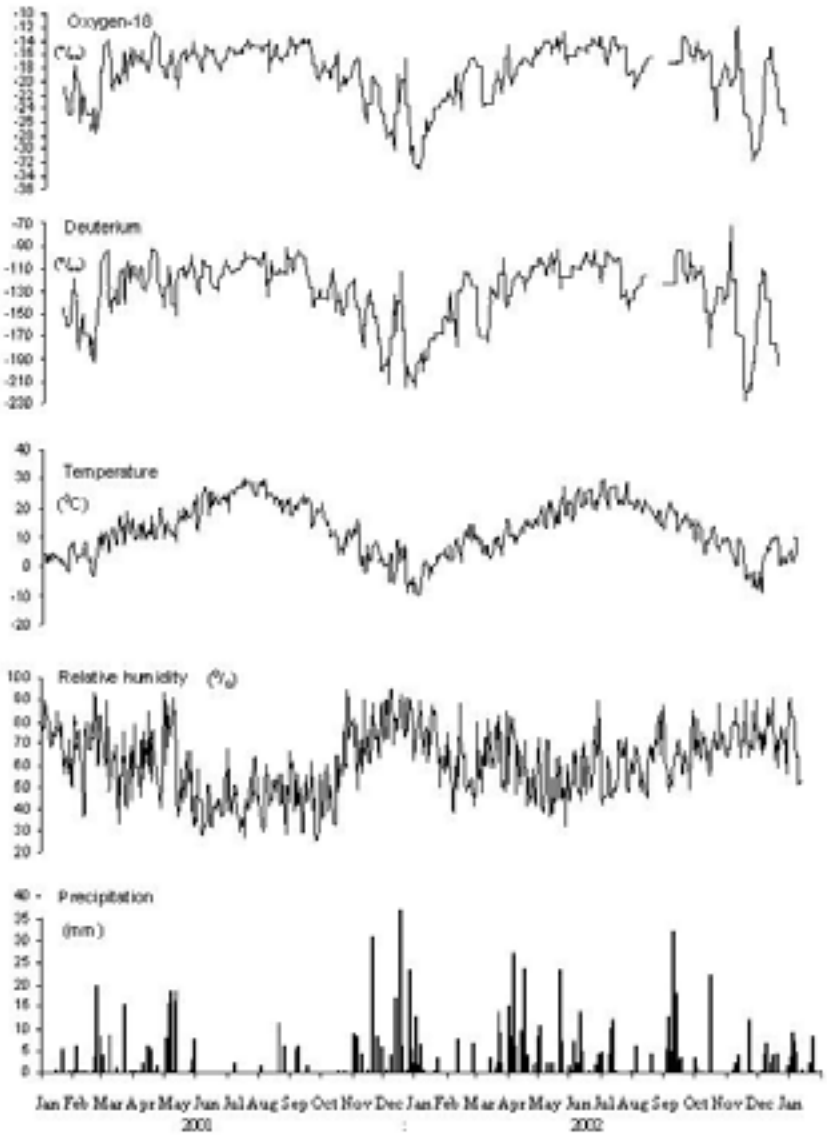

FIG. 8. Two years record of daily time series of deuterium, oxygen-18 content in atmospheric water vapour and hydrometeorological parameters from the Ankara station (2001 and 2002).

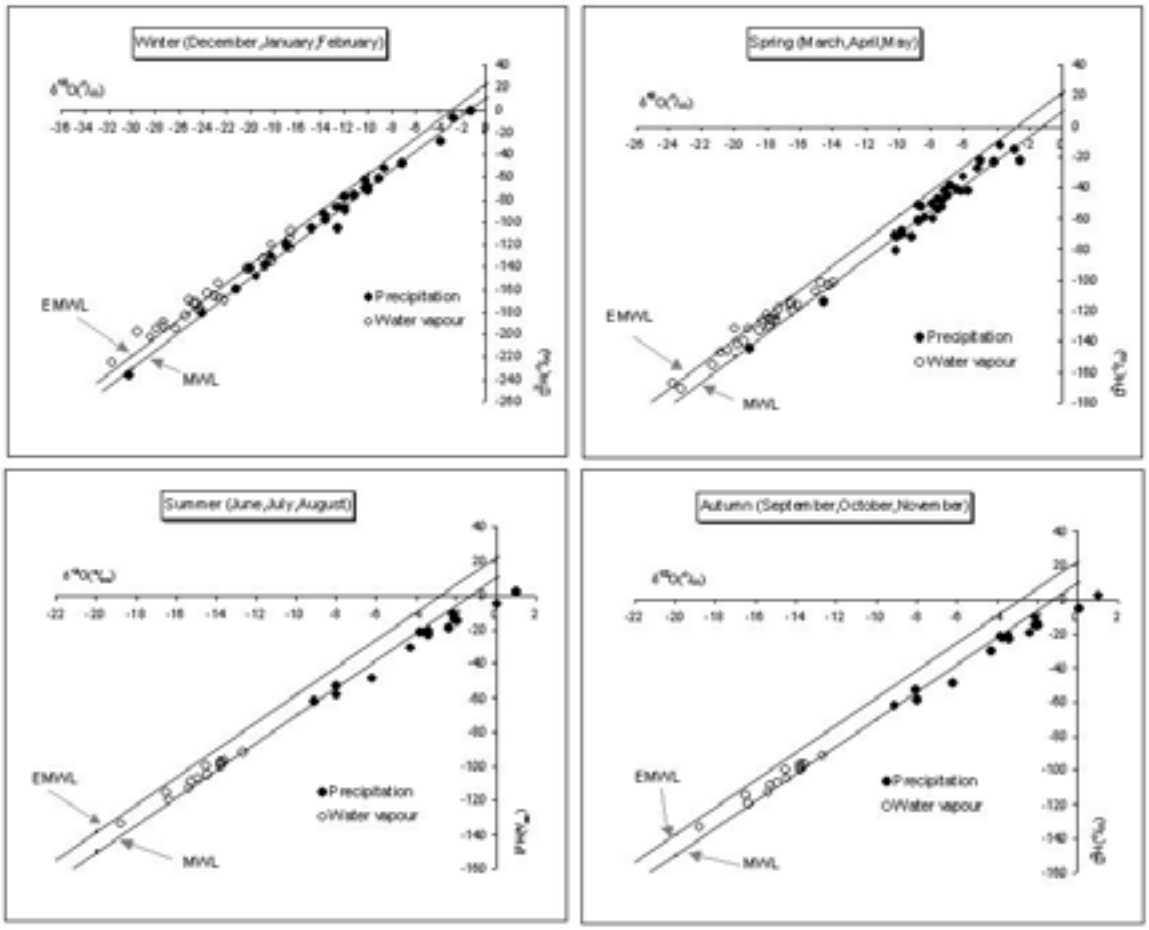

FIG. 9. δ^2H vs. $\delta^{18}O$ relationship for atmospheric water vapour and daily precipitation samples collected at Ankara (2001 and 2002).

The water vapor and precipitation data show a slight shift towards more depleted values due to the kind of air masses and temperature during winter months. The deuterium excess values of water vapor show a slight shift towards higher values. The possible explanation of this shift could be admixture of evaporated soil moisture to the sampled vapor [7]. The precipitation data show a shift towards to water vapor data in winter season. However opposite shift was observed in spring, autumn and summer season with ascending order. The reason of this shift could be explained by air temperature variations, source region and transport mechanism of water vapor. The variations of the stable isotope content in atmospheric water vapor in relation with air masses circulation patterns on short term is shown in figure 10. At 22.10.2002 the low pressure center moved from central Atlantic Ocean to the west part of Mediterranean basin. It was called as a maritime air mass.

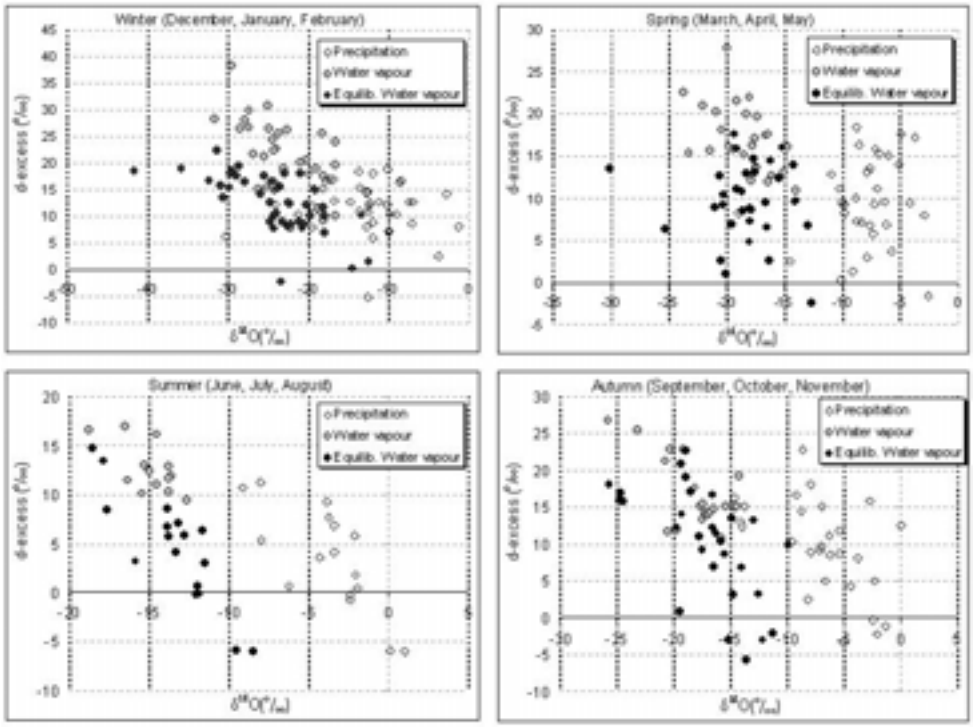

FIG. 10. $\delta^{18}O$ vs. d-excess relationship for measured atmospheric water vapour, calculated equilibrium water vapour and daily precipitation samples collected at Ankara (Jan. 2001- Mar. 2003).

The deuterium content of the local water vapor decreased rapidly by about 30 ‰ at Madrid. During the next two days Ankara and Vienna effected by the maritime polar air masses The deuterium values of water vapor depleted about 40 ‰ in Vienna and Ankara. Around 13 November 2002 a low pressure area situated above North Atlantic changed the circulation patterns over western, Central and Eastern Europe and Mediterranean basin. During this circulation deuterium content of water vapor depleted about 50 ‰ in Madrid and 60 ‰ in Ankara. At the end of November 2002 west and central part of Europe (Madrid, Vienna) effected by maritime polar air masses, whereas east part of Mediterranean basin (Ankara and Rabat) effected by continental polar air masses. The depletion in deuterium content of water vapor is about 60 ‰ and 80 ‰ at Madrid and Ankara respectively. At the beginning of the January 2003 maritime polar air masses affected all Europe and east part of Mediterranean Sea. The deuterium content of the local atmospheric water vapor decreased rapidly. This rapid decrease can be explained by snowfall area. In equilibrium conditions deuterium excess values of water vapor lower than the d-excess values of precipitation. In this study d-excess values of measured atmospheric water vapor is obtained higher than the d-excess values of precipitation. The causes of these higher values are probably re-evaporation of rain drops during rain event and evapotranspiration (Fig.11).

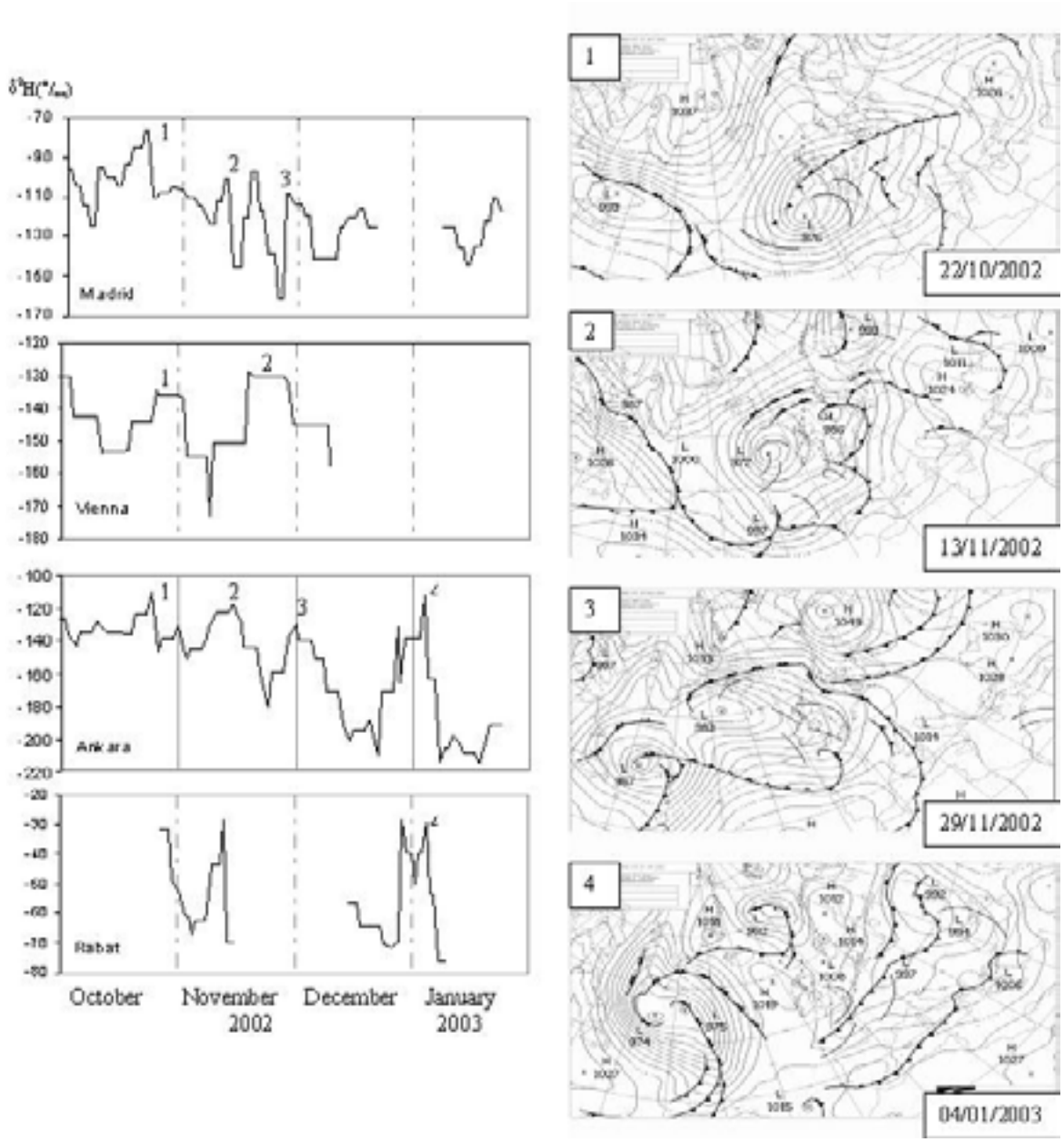

FIG. 11. Daily variation of deuterium content of atmospheric water vapour at Madrid, Vienna, Ankara and Rabat during the last three months of 2002 and first month of 2003.

6. Ion concentration and stable isotopes (^{18}O, ^{2}H) of wet – only precipitation at Ankara (Central Turkey)

111 samples comprising above 90% of all daily precipitation in the study period were completely analyzed for major ions. 100% of all daily precipitation were analyzed for stable isotopes. Data quality of major ions was checked from the ratio of Σcations/ Σanions. The average of this ratio was 1.60 and 1.90 for 2001 and 2002 respectively. The reason for this high value was the contribution of alkaline precipitation. These alkaline precipitations contained not measured high HCO_3^- concentrations. HCO_3^- can be calculated from the carbon dioxide concentration in the atmosphere (350 ppm), the Henry's law constant and dissociation constant of $CO_2.H_2O$. If the calculated HCO_3^- is accounted for the Σcations/ Σanions ratio decreased to 1.30 and 1.60. The effect of CO_2 of the atmosphere is more important in precipitation from the sector 4 (North Africa) due to their higher pH. After the correction due to atmospheric carbon dioxide the Σcations/ Σanions ratio in this sector remains relatively high at 1.40. The volume-weighted average concentrations of major ions and average stable isotopes and pH for

Ankara precipitation is presented in Table 4. pH exhibited large deviation. The lowest pH of 4.59 was measured on September 2002 and highest of 8.66 on March 2002 (Fig. 12). About 18% and 15% of precipitation showed a pH of less than 5.6 in 2001 and 2002 respectively. On the other hand, about 12% and 18% of the precipitation had pH above 7.0, suggesting strong inputs of alkaline species to precipitation. The pH distribution was drawn due to the origin of air masses (Fig. 13). As shown in this figure maximum pH values observed in sector 4. In this sector continental tropical air mass transported from the northern part of Africa Continent. Fig. 15 presents the volume weighted mean concentrations of major ions for each trajectory sector. It should be noted that SO_4^{2-} concentrations for sector 1, 2 and 3 were high. Concentrations of most ions had the tendency with minima for sector 6. The high SO_4^{2-} concentration for sectors 1, 2 and 3 caused by the transport of acid air mass originated in Siberia and Europe. High values of the sulfur isotopic ratio in atmospheric fallout during winter.

Many studies have pointed out the role of meteorological factors in determining the chemical feature of precipitation [12][13][14][15][16]. To evaluate this hypothesis we classified all bulk daily precipitation observations into the six meteorological classes based on meteorological synoptic charts and back-trajectory analysis. For each classes we calculated volume weighted mean concentrations Table 4., Fig. 12, 13 and 14 present the distribution of pH and Fig. 14 present the total ionic content for the six meteorological classes.

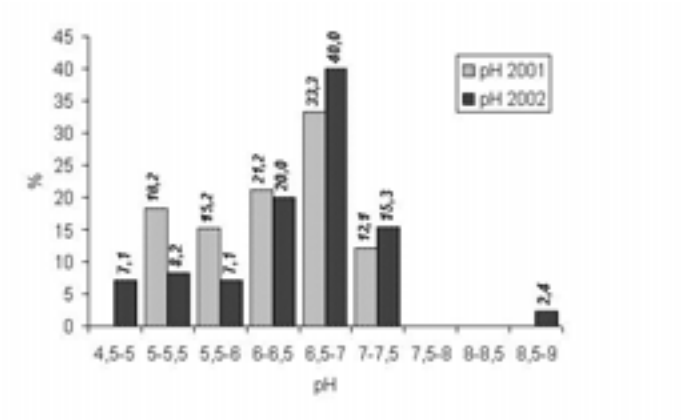

FIG. 12. Distribution of daily precipitation pHs in Ankara, Turkey.

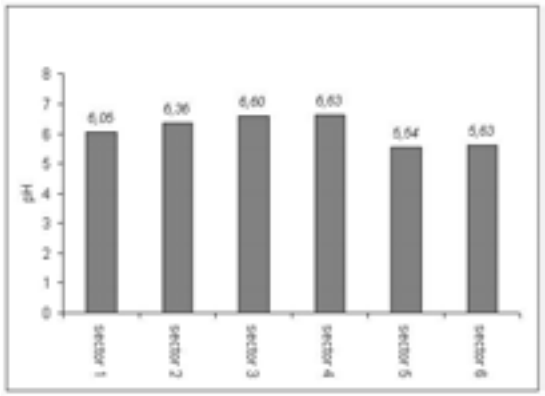

FIG. 13. Distribution of the pH values of daily precipitation due to sectors.

All of the measured ions show short term (episodic) and long term (seasonal) variations. Episodes in the concentrations of anthropogenic elements are due to episodic transport from high emission areas. Most of the trajectories that correspond to episodic high SO_4 concentrations come from NW and W sectors. Source regions for SO_4^{2-}, NO_3^- were investigated with trajectory statistics. Belarus, Germany, Czechoslovakia, Hungary, Ukraine and Balkan countries are found to be the source regions affecting SO_4^{2-} concentrations at Ankara. Wet deposition fluxes of most of the ions are high in winter and low summer, closely resembling the variation in precipitation amount. In general the Cl^- content in

precipitation over the continents; the highest concentrations are found near the coast as the result of a rapid washout of the largest sea salt particles, and the Cl^- concentration decreases exponentially inland to a background concentration and contributes to Br^-/Cl^- ratios. Bromide and chloride concentration of daily precipitation is plotted as Cl^- vs Br^-/Cl^- in Fig. 15. As shown in this figure there is an enrichment of Br concentration in precipitation with lower salinities, when compared to the marine ratio.

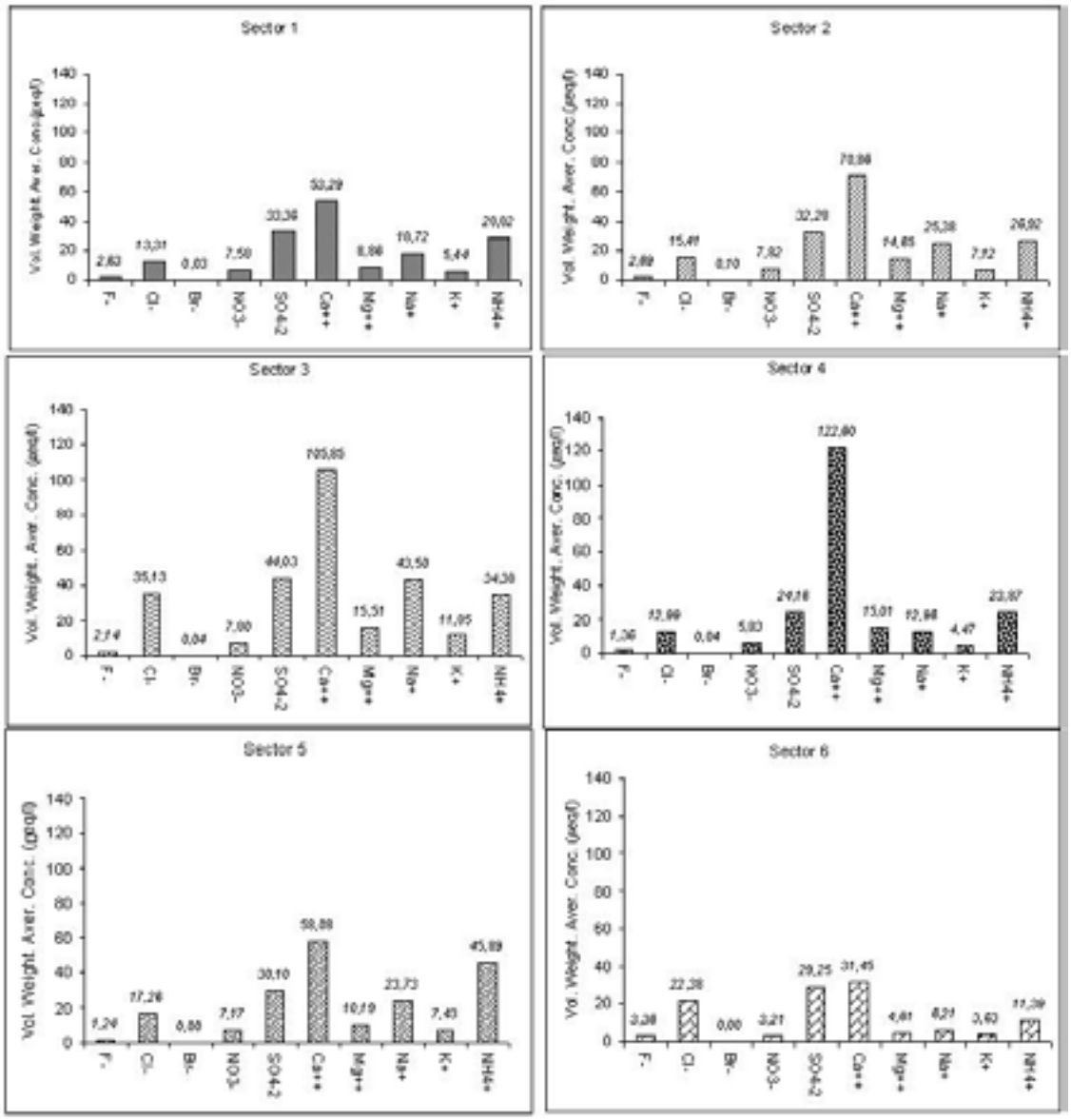

FIG. 14. Volume weighted average concentrations (μeq/l) in each sector obtained from air mass back trajectories.

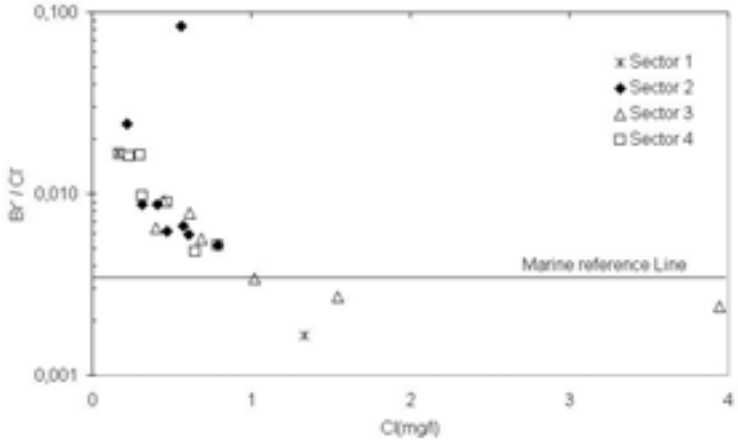

FIG. 15. Relationship between Br^-/Cl^- ratio and chloride for 2001 and 2002 daily precipitation from Ankara associated with the air mass origin.

7. Conclusions

The data set of stable isotope values obtained from mean monthly samples of precipitation collected at 26 stations throughout the country allows the following results to be drawn: Water vapor from Mediterranean Sea, Aegean Sea and Black Sea is responsible for the relatively heavy isotopic values in Mediterranean, Aegean, Black Sea and Central Anatolia regions. The relationship between mean monthly temperatures and mean monthly isotopic composition of precipitation is better than the relationship obtained with daily values. The strong seasonal variation in the isotopic abundance of precipitation will allow us to ascertain which water vapor source region (Atlantic Ocean, Mediterranean Sea, Aegean Sea and Black Sea) plays dominant role in winter or summer precipitation. A final consideration that can be drawn from the above conclusions is that Turkey acts like a transition area between wet and arid regions not only from the geographical and morphological point of view but also as regards meteorology, precipitations, water vapor and their isotopic composition. The western part of Turkey (Aegean Region), South part of Turkey (Mediterranean Region) dominated by westerly winds supplies Aegean Sea and Mediterranean Sea water vapor that characterizes the precipitations along the west and south coasts of Turkey respectively. North part (Black Sea), North-west part (Marmara Region) of Turkey dominated by northerly and north-westerly winds supplies Black Sea and Atlantic Ocean water vapor that characterizes the precipitations along the north and north-west costs of Turkey respectively. Central part of Turkey (Central Anatolia Region) dominated time to time by all winds supplies as indicated above depends on seasonal variations. The isotopic attributes of precipitation colleted in Turkey at Ankara are similar to the findings from other mid-continental regions.

The data compiled by this research will be used in ongoing investigations whose preliminary results have been reported in the literature. These studies (various national or international research projects) examine groundwater and surface water problems in Turkey. Daily basis measurements of isotopic composition of precipitation were conducted at Ankara. The observed spatial and temporal variations of the stable isotope content ($\delta^{18}O$ and $\delta^{2}H$) of atmospheric water vapor and precipitation are related with the parameters of water vapor transport in the atmosphere. The stable isotope content of the vapor or precipitation collected at a given place is controlled by the conditions prevailing at the vapor source regions and by the whole rainout history of the precipitating air masses. The results presented in this paper that the stable isotope content of the vapor or precipitation controlled by the conditions prevailing at the vapor source regions and by the whole rainout history of the precipitating air masses. The results suggest that observed spatial and temporal variations of the stable isotope content of atmospheric water vapor and precipitation are strongly related with the water vapor transport in the atmosphere. The stable isotope content of water vapor is correlated with the stable isotope composition of daily precipitation. A theoretical isotopic composition of water vapor was calculated

by using the daily means of δ^2H and $\delta^{18}O$ composition of precipitation that would be in equilibrium with the precipitation. The calculated data shows that there are large deviations between calculated isotopic composition of equilibrium water vapor and measured water vapor.

The stable isotope contents of precipitation and water vapor showed a shift along meteoric water line depends on seasons and temperature variations. Continental polar air masses caused more depletion in deuterium content of atmospheric water vapor than maritime polar air masses. During the maritime air masses passage over Europe, enrichment could be observed in deuterium content of atmospheric water vapor. The data obtained in this study could serve as a tool in hydro meteorological studies as well as being a source of data for validation atmospheric general circulation models incorporating isotope water tracers [10], [11] and a contribution to GNIP (Global Network of Isotopes in Precipitation). The conclusions are summarized as follows; i) the total non sea salt ion concentrations in Ankara precipitation, suggesting that the composition of precipitation is controlled not only by the emissions but also by the regional environment ii) the concentrations of non sea salt SO_4^{2-} and NO_3^- are as high as those in typical acid rain regions, Balkans and Central Europe. However, most of them exists in neutralized forms of base cations Ca^{2+} and Mg^{2+} iii) the concentrations peaked in winter and bottomed out in summer for all ions, which were mainly defined by precipitation patterns. The chemical composition of the precipitation in Ankara was due to a marine aerosol under the influence of an alkalinity, namely calcite dust transported from North Africa, with local calcareous soils having a minor effect. Under meteorological conditions, shown by air mass trajectory analysis, the Saharan influence may be strong and then alkaline precipitation would occur.

ACKNOWLEDGMENTS

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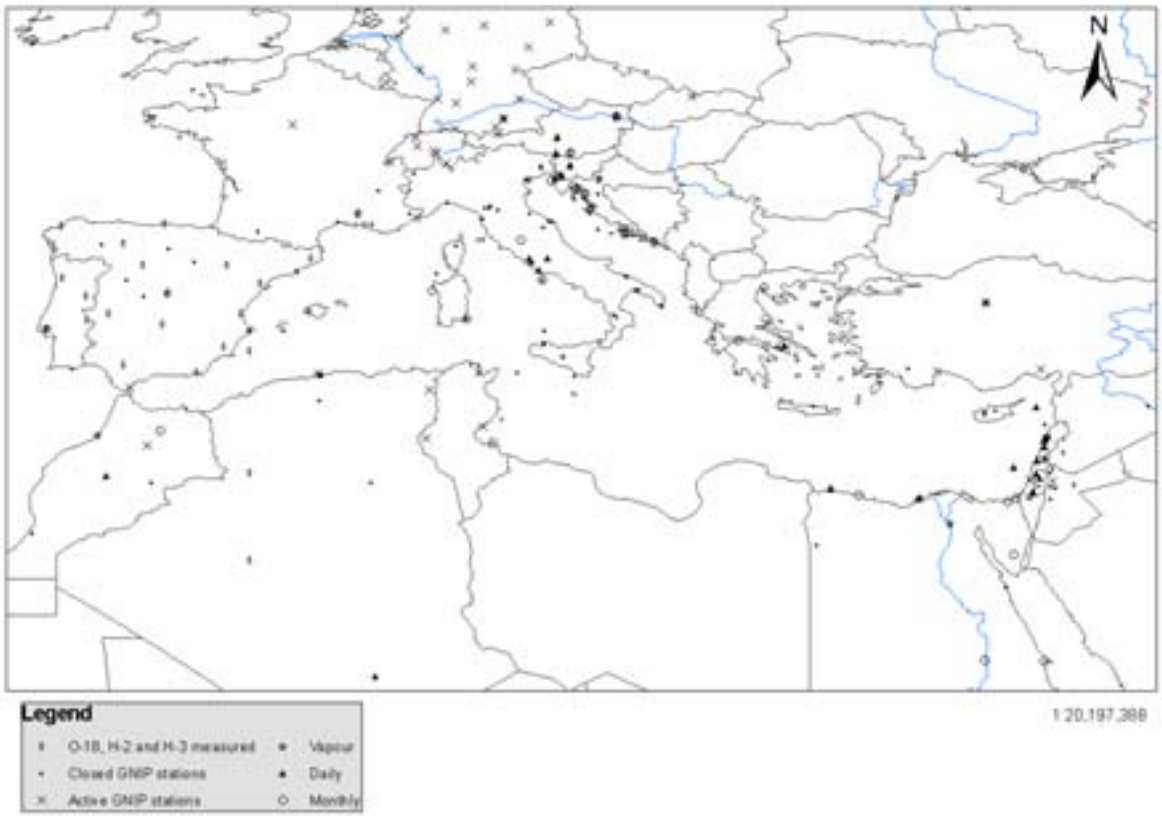
REFERENCES

[1] DANSGAARD, W., Stable isotopes in precipitation. Tellus 16 (1964) 567–584.
[2] CRAIG, H., GORDON L.L., Deuterium and Oxygen 18 variations in the ocean and the marine atmosphere. Stable isotope in oceanographic studies and paleotemperatures spoleto, (1965) 9–130.
[3] CRAIG, H., Isotopic variations in meteoric water. Science, 133 (1961) 1702–1703.
[4] MERLIVAT, L., JOUZEL, J., Global climatic interpretation of the deuterium-oxygen 18 relationship for precipitation. Journal of Geophysical Research 84 (1979) 5029–5033.
[5] ROZANSKI, K., SONNTAG, CH., MUNNICH, K.O., Factors controlling stable isotope composition of modern European precipitation. Tellus 34 (1982) 142–150.
[6] FISHER, D. A., A zonally-averaged stable-isotope model coupled to a regional variable-elevation stable isotope model. Annals of Glaciology 14 (1990) 65–71.
[7] SCHOCH-FISCHER, H., ROZANSKI, K., JACOB, H., SONNTAG, C., JOUZEL, J., ÖSTLUND, G., GEYH, M.A., Hydrometeorological factors controlling the time variation of D, 18 O and 3 H in atmospheric water vapor and precipitation in the northern west wind belt (Proceedings of an International Conference on Isotope Hydrology), STI/PUB/650, IAEA, Vienna (1984) 3–30.
[8] J. HELMUT, S.CHRISTIAN, "An 8-year record of the seasonal variation of 2H and 18O in atmospheric water vapor and precipitation at Heidelberg, Germany", Tellus, 43B (1990) 291–300.
[9] RINDSBERGER, M., JAFFE, M., RAHAMIM, S., GAT, J.R., Patterns of the isotopic composition of precipitation in time and space: data from the Israeli storm water collection program. Tellus 42B (1990) 263–271.

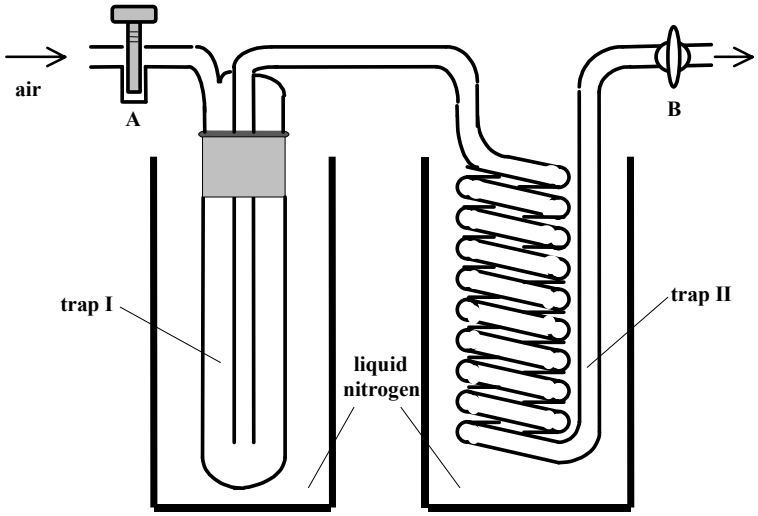
[10] JOUZEL J., KOSTER R., SUOZZO, R., RUSSELL, G., WHITE, J., BROECKER, W., Simulations of HDO and $H_2{}^{18}O$ atmospheric cycles using the GISS general circulation model: Sensitivity experiments for present-day conditions. Journal of Geophysical Research 96 (1991) 7495–7507.
[11] HOFFMANN, G., HEIMANN H., Water tracers in the ECHAM general circulation model. (Proceedings of an International Symposium on Applications of Isotope Techniques in Studying Past and Current Environmental Changes in the Hydrosphere and the Atmosphere), STI/PUB/908, IAEA, Vienna (1993) 3–14.
[12] ULUG, E.S., Local effect of mobile sources in the METU campus. In proceedings of the 1st national air pollution and control symposium. Istanbul (1993) 126-136 (in Turkish).
[13] GUNDOĞDU, M.N., Atmospheric lead pollution: global and local. Çevre Bilimleri 1 (1994) 37–45 (in Turkish).
[14] YATIN, M., TUNCEL, S., ARAS, N.K., OLMEZ, I., AYGUN, S., TUNCEL, G., Atmospheric trace elements in Ankara, Turkey: 1. factors affecting chemical composition of fine particles, Atmospheric Environment 13-18 (2000) 1305.
[15] TUNCER, B., BAYAR, B., YEŞILYURT C., TUNCEL G., Ionic composition of precipitation at the central Anatolia (Turkey), Atmospheric environment 35 (2001) 5989-6002.
[16] RAHN, K.A., LOWENTHAL, D.H., Pollution aerosol in the Northeast: Northeastern-Midwestern contributions. Science 228 (1985) 275-284.
[17] DENIZ A., KARACA M., Analysis of cyclone tracks over Turkey, J. İstanbul Tech. Univ. (1995) 1-2 (in Turkish).
[18] YURTSEVER Y., Worldwide Survey of Stable Isotopes in Precipitation, IAEA internal report (1995).
[19] GAT J. R., GONFIANTINI R., Stable Isotope Hydrology, Deuterium and Oxygen-18 in the water Cycle, Technical Reports Series No. 210, IAEA, Vienna (1981) 339.
[20] CLARK D. I., FRITZ P., Environmental Isotopes in Hydrogeology, Lewis Publishers, New York (1997).
[21] FRITZ, P., DRIMMIE, R.J., FRAPE, S.K., OSHEA, K., The isotopic composition of precipitation and groundwater in Canada (Proceedings of an International Symposium on the Use of Isotope Techniques in Water Resources Development), STI/PUB/757, IAEA, Vienna (1987).
[22] LAWRENCE J. R., WHITE J.W.C., The Elusive Climate Signal in the Isotopic Composition of Precipitation, Geochem. Soc. Spec. Publ. 3 (1991) 169–185.
[23] ROZANSKI, K., ARAGUAS L., GONFIANTINI, R., Isotopic patterns in modern global precipitation. Geophys. Monogr. Am. Geophys. Union 78 (1993) 1-36.
[24] GAT, J.R., CARMI, I., Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. J. Geographys. Res. 75 (1970) 3039-3048.
[25] ÇÖLERI M., Sinoptik meteoroloji III-IV, Devlet Meteoroloji İşleri Genel Müdürlüğü yayınları (1982) 1–11.(in Turkish).
[26] TÜRKEŞ M., Air mass types in Turkey. PhD thesis, Ankara Üniversitesi Sosyal Bilimler Enstitüsü Coğrafya Aba Bilim dalı, (1985) (in Turkish).
[27] JACOB, H., SONNTAG, C., An 8-year record of the seasonal variation of 2H and 18O in atmospheric water vapor and precipitation at Heidelberg, Germany, Tellus 43B (1991) 291–300.
[28] MAJOUBE M., Fractionnement en oxygen-18 et en deuterium entre l'eau et sa vapeur. J., Chim. Phys. 68 (1971) 1423–1436.

ANNEX 1
Sampling Network



ANNEX 2

Atmospheric water vapour sampling device



Stopcock B is opened and traps I and II are evacuated, then the traps are immersed in liquid nitrogen and regulating valve A is opened. The air flow-rate is measured using a flow meter at the outlet of the pump. Using valve A to adjust the air flow to a desired rate. The sampling process is allowed to continue until a necessary amount of water for δ^2H and $\delta^{18}O$ analysis is collected in the liquid nitrogen traps. After the sampling, valve A is closed and the traps are evacuated. Stopcock B is closed. The liquid nitrogen is removed from trap II and the CO_2 and water in trap II are transferred to trap I. The liquid nitrogen is removed from trap I to raise the temperature to about -70°C. Stopcock B is opened and the CO_2 in the cold trap is pumped out. The water collected in trap I is retained for δ^2H and $\delta^{18}O$ analysis.

The collected water amount depends on pumping rate, sampling time, and absolute humidity of the air. The latter is a function of the relative humidity and temperature. The following table gives values of ***pumping rate × sampling time*** for different air humidities and temperatures for collecting ~ 4g of sample water. For the determination of δ^2H and $\delta^{18}O$ in atmospheric water vapour it is required that a given mass of vapour should be condensed completely, since any loss of vapour (breakthrough) will cause an isotopic fractionation of the condensed mass. With this in mind, for a given value of *pumping rate × sampling time*, the pumping rate should be chosen as small as possible, depending on the realizable sampling time.

Rel. hum.	Pumping rate (L/min) × sampling time (hour)									
(%)	-20°C	-15°C	-10°C	-5°C	0°C	5°C	10°C	15°C	20°C	25°C
5	1560	996	644	425	285	203	147	108	80	60
10	780	498	322	212	143	102	74	54	40	30
20	390	249	161	106	71	51	37	27	20	15
30	260	166	107	71	48	34	25	18	13	10
40	195	124	80	53	36	25	18	14	10	8
50	156	100	64	42	29	20	15	11	8	6
60	130	83	54	35	24	17	12	9	7	5
70	111	71	46	30	20	15	11	8	6	4

For the pump, vacuum should be inf. to 200 mbar and flow 1-5 L/min in order to integrate 2 days of atmospheric water. With 50% of humidity, to have 6g of water (minimum require) we need to pump 1 m^3 of air.

ANNEX 3

Monthly and daily precipitation and water vapour data
obtained from 2001 to 2004 around the Mediterranean basin

Electronic file in Excel format.
File available for viewing on the attached CD

1 – Monthly data per country. The various spreadsheets contains the composite total rainfall for each month from January 2001 to December 2003 - Annual mean of air temperature, total yearly precipitation and weighted annual averages of ^{3}H, ^{18}O and ^{2}H are also given.

2 – Daily data per station. The spreadsheet contains precipitation and water vapour data. Precipitation is sampled at the end of the day. The water vapour is continuously performed during 48 hours starting Monday morning and Wednesday afternoon. The isotopic values are reported in the file on the first day of the sampling.

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