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Isotope geochemistry and the water cycle: a short review with special emphasis on Italy

La geochimica isotopica ed il ciclo delle acque: un breve sguardo retrospettivo con particolare riferimento all'Italia

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ABSTRACT - The growth of stable isotope hydrology started at the end of the second world war and reached its full development in the seventies. Its use for hydrological studies became more and more important through time and the IAEA in Vienna gave a vital impetus to the development of these studies. The basic principles of this relatively new branch of hydrology are briefly summarized, bypassing the physical and mathematical principles, to draw attention on the practical meaning and the possible interpretation of the isotopic data that may be obtained. The overall distribution of the isotopic values of precipitation in Italy is briefly reported as well as some anomalous results. These results, that sometimes seem to be in sharp contrast with the relationships that are generally accepted and normally found between the isotopic composition of precipitation and other variables, may be normally explained even though, in some case, they are not yet fully understood. First, the well known relationship between the isotopic composition of precipitation and the surface temperature is considered and some anomalies are reported. Then, the isotopic vertical gradient is considered and the results obtained from several pluviometers throughout Italy are reported. Some anomalous results obtained in northern Italy in the south Alpine area, not far from Trento, are also discussed and, at least partially, explained. However, the large number of variables affecting this value often prevent a correct interpretation of the measured values. A didactic example of the relationship existing between the isotopic composition and the amount of precipitation is also shown. Some examples of stable isotope studies applied to different hydrological problems are reported as well as a brief discussion on the existing relationship between the isotopic composition of groundwater and the isotopic composition of local precipitation.

KEY WORDS: Hydrogen isotopes, Italy, Oxygen isotopes, vertical isotopic gradients, water cycle.

RIASSUNTO - Sono ormai diversi decenni che la geochimica isotopica è entrata prepotentemente nel campo degli studi idrologici. Purtroppo, in Italia questa innovativa disciplina non ha incontrato il grande successo che, nel resto del mondo, ha caratterizzato la sua crescente utilizzazione. Vengono qui brevemente riassunti i principi di base di questa particolare branca dell'idrologia, trascurando gli aspetti più prettamente matematici e fisici, per mettere in evidenza il significato pratico e le possibili interpretazioni dei dati isotopici ottenuti studiando il ciclo delle acque. Si riporta una mappa con la distribuzione dei valori isotopici delle precipitazioni in Italia, essendo le precipitazioni il punto di riferimento per lo studio di qualsiasi acquifero, sia superficiale che profondo. La distribuzione generale dei valori è praticamente controllata dalla presenza della catena appenninica, almeno a livello della penisola, la pianura padana costituendo un corpo a sé sul quale il rilievo appenninico non ha in pratica alcuna influenza. La distribuzione dei valori isotopici sulla pianura padana è invece controllata, in buona parte, dai venti orientali che spingono verso ovest masse d'aria che trasportano vapore acqueo di origine adriatica. Non incontrando rilievi montuosi di qualche entità lungo il percorso da est a ovest, queste masse d'aria determinano precipitazioni relativamente poco negative che consentono di tracciare questo effetto fino quasi alla longitudine di Milano. Altra caratteristica apparentemente anomala è rappresentata dalla quasi costanza dei valori isotopici delle precipitazioni costiere dalla Sicilia alla Liguria, nonostante le sostanziali differenze climatiche latitudinali. Questo dato non è del tutto chiaro ma una possibile concausa può essere la relativa omogeneità latitudinale di temperatura superficiale del Tir-

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reno che può influire, in maniera sensibile, sulle precipitazioni strettamente litorali. La relazione positiva normalmente esistente tra composizione isotopica delle precipitazioni e temperatura al suolo viene esemplificata graficamente. Vengono anche discussi alcuni valori medi annui ponderati di composizione isotopica delle precipitazioni che sembrano contraddire tale correlazione. In particolare, si riportano i valori apparentemente anomali riscontrati nel corso del 2003 (anno con temperature estive eccezionalmente elevate). L'apparente anomalia viene spiegata tenendo conto dell'ammontare stagionale delle precipitazioni e dei relativi valori isotopici medi ponderati. Vengono riportati anche i valori dei gradienti isotopici verticali misurati in Italia da nord a sud e viene messa in evidenza la limitata ma sostanziale differenza tra la maggior parte di questi valori ed il valore medio, generalmente ottenuto nell'ambito del bacino mediterraneo. In particolare, si riportano valori anomali dei gradienti isotopici verticali riscontrati nell'area alpina in prossimità di Trento dati che, in buona parte, possono essere spiegati con l'effetto "ombra" determinato da rilievi montuosi di una certa entità. Si riporta anche un caso di particolare chiarezza ed evidenza che mette in relazione la composizione isotopica delle precipitazioni con periodi di piovosità particolarmente intensa. Vengono anche brevemente discussi alcuni esempi che dimostrano la diretta correlazione tra composizione isotopica di un acquifero e composizione isotopica delle precipitazioni nell'area di ricarica dell'acquifero stesso. Un ultimo aspetto di rilevante interesse è quello della rilevazione di infiltrazioni, in acquiferi di importanza particolare, di acque inquinate di origine superficiale (principalmente fiumi o altri corsi d'acqua). Le misure isotopiche permettono in genere di evidenziare chiaramente tali apporti: vengono riportati alcuni esempi pratici di particolare interesse. Inoltre, si discutono i risultati ottenuti da un dettagliato studio isotopico degli acquiferi del Carso triestino, risultati che hanno permesso di verificare l'inconsistenza delle ipotesi generalmente accettate sull'origine di queste acque e sul loro deflusso sotterraneo. E' stato anche possibile mettere in evidenza l'apporto, pressochè sistematico nel corso dei mesi di Maggio/Giugno di ogni anno, di acqua dal fiume Isonzo che in quel periodo riceve le acque di fusione della copertura di neve del suo bacino alpino.

PAROLE CHIAVE: Ciclo delle acque, gradienti isotopici verticali, isotopi dell'idrogeno, isotopi dell'ossigeno, Italia.

1. - INTRODUCTION

Nine different stable isotope water species occur in natural waters but only three of them are of importance for hydrological studies and are amenable to accurate analytical assay: $H_2{}^{16}O$, $H_2{}^{18}O$, and $HD^{16}O$. The first dedicated studies on the isotopic variations in natural waters were developed more than fifty years ago (EPSTEIN & MAYEDA,1953; CRAIG, 1961; DANSGAARD, 1954;1961;1964; CRAIG & GORDON,1965): besides the first sets of isotopic data, these studies suggested models for the evaporation, mixing, and precipitation processes. From that time a number of dedicated studies were developed on the use of stable isotope abundance in hydrological studies so that a few years later the need of summarizing the work carried out was already felt by the scientific community (FIDEL, 1976). More papers were published, particularly in the eighties, to fully understand the temporal and spatial distribution of the isotopic composition of precipitations and the relationship between ground waters and precipitations (e.g. GAT, 1980; SIEGENTHALER & OESCHGER,1980; ROZANSKI *et alii,* 1982; FÖRSTEL & HÜTZEN,1982; JOUSSAUME *et alii,* 1984; ROZANSKI, 1985; etc.). We must recall the deserving effort of the international organizations that designed the global IAEA/WMO precipitation network in order to provide worldwide basic data for hydrological applications as well as an averaged climatic characterization of precipitation, based on the study of monthly composite samples.
Nowadays, specific hydrological problems are studied by several national agencies by means of stable isotope surveys but, unfortunately, our country is again very late in this field taking into account the intensive isotopic study of precipitations and of surface and deep aquifers carried out by different countries all over the world.

2. - MAIN FEATURES OF THE ISOTOPE DATA

The prominent features of the isotope data that are of importance for hydrological studies can be summarized as follows taking into account that mean weighted monthly samples are generally used to study precipitations:

1) the isotopic composition of a water sample is reported in terms of delta units where delta (δ) is defined by:

$$\delta = [(R_{sample}-R_{standard})/R_{standard}] \times 1000$$

where R is the abundance ratio between the heavy and the light isotope: $R={}^{18}O/{}^{16}O$ or D/H;

2) the delta values of atmospheric precipitation from all the studied countries cluster along the so-called global meteoric water line (CRAIG, 1961) whose equation is:

$$\delta D = 8\,\delta^{18}O + 10 \qquad 1)$$

3) in the Mediterranean area precipitations often show a deuterium excess considerably larger than that given by equation 1): (this variable is defined by: $d_{excess} = \delta D - 8\delta^{18}O$);

4) a good correlation between the mean isotopic composition of precipitation and the mean surface temperature is generally found at various sites; the best results are obtained comparing yearly mean isotopic values with mean yearly temperature even though good correlations can be obtained also at the monthly level;

5) in the case of semi-arid and arid regions regional precipitation lines have a slope of less than 8 on the δD versus $\delta^{18}O$ diagram; this effect is explained with kinetic evaporation processes

affecting the rain drops during their fall;

6) heavy isotope species are depleted in precipitation relative to the ocean water source. This is the result of the isotopic fractionation taking place during evaporation from the sea-surface (preferential loss of isotopically light water molecules) and of the isotopic fractionation that takes place during the condensation of liquid water from vapour (preferential condensation of isotopically heavy water molecules). The former fractionation is generally kinetic while the latter fractionation is closely related to the temperature of condensation;

7) it follows that precipitations collected at different elevations in the same area show vertical isotopic gradients in the case of both oxygen and hydrogen: the average value of this gradient in Italy is of about -0.15 ‰/100 metres in the case of oxygen (LONGINELLI & SELMO, 2003), slightly higher than the mean value measured in the Mediterranean basin (about -0.20 ‰/100 m).

We can now consider in some detail these issues and briefly discuss some of the experimental results obtained in Italy so far.

Equation 1) was confirmed by YURTSEVER & GAT (1981) and by ROZANSKI *et alii* (1993) who considered all the isotopic results obtained from the IAEA/WMO network and calculated the following equation:

$$\delta D = (8.20 \pm 0.07)\delta^{18}O + (11.27 \pm 0.65) \qquad 2)$$

when weighted mean values were used. LONGINELLI & SELMO (2003) plotted all the weighted monthly $\delta^{18}O$ versus the δD values obtained from 80 stations all over Italy and calculated the following equation:

$$\delta D = 7.61\,\delta^{18}O + 9.21 \qquad 3)$$

not far from the global meteoric water line.

However, considering separately the mean monthly values obtained in northern Italy, in central Italy, and in southern Italy, three different equations were obtained, the differences being of importance when we study local hydrological problems. The three equations are the following:

Northern Italy $\delta D = 7.709\,\delta^{18}O + 9.403$ 4)

Central Italy $\delta D = 7.047\,\delta^{18}O + 5.608$ 5)

Southern Italy $\delta D = 6.970\,\delta^{18}O + 7.316$ 6)

The differences are even larger when we consider individual stations. The slopes of the equations obtained from individual stations range from 5.7 to 8.9 and the deuterium excess is also quite variable ranging from 9.2 to 19.1. These variations should be taken into account when studying relatively small areas where rather large variations may be found, related either to the morphology of the area or to its geographical position or to the main trajectory of atmospheric perturbations.

3. - OVERALL DISTRIBUTION OF THE ISOTOPIC VALUES IN ITALY

Rather large differences are found between the western and the eastern side of Italy, the Apennine ridge acting as a north-south barrier that separates this geographic area into two different sections. The section of Italy west of the Apennine barrier is mainly interested by westerly winds carrying water vapour from the Balearic basin and the Tyrrhenian basin. The Adriatic section is mainly interested by north-easterly winds from continental areas and/or by south-easterly winds carrying water vapour from the central and the eastern Mediterranean. The effect of this situation is clearly shown in figure 1 where the contour lines report the overall variability of the mean oxygen isotopic composition of precipitation in Italy, calculated for the period of this survey, variable for different stations from a couple of years to about ten years. The marked effect of the different conditions existing West and East of the Apennines and the importance of

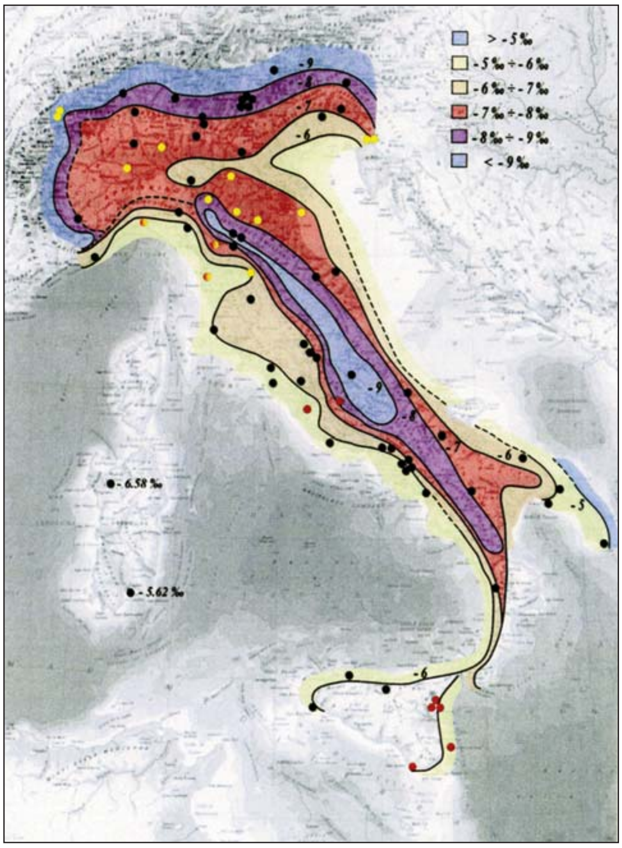

Fig. 1 – Contour lines reporting the overall variability of the mean oxygen isotopic composition of precipitation in Italy. Black and yellow dots are stations controlled by the authors; red dots are stations controlled by other colleagues (modified from figure 2 in LONGINELLI & SELMO, 2003).

- Curve ipsometriche relative ai valori medi di composizione isotopica dell'ossigeno nelle precipitazioni sull'Italia. I punti neri e gialli si riferiscono a stazioni pluviometriche controllate dagli autori; i punti rossi si riferiscono a stazioni controllate da altri colleghi (modificata dalla figura 2 di LONGINELLI & SELMO*, 2003).*

this barrier from the hydrological point of view are shown by some peculiar distribution of the contour lines. The largest of these effects is the -6.0 and -7.0 ‰ contour lines entering deep inside the Po plane. This is the result of the inflow of water vapour from the Adriatic, carried by the north-easterly and easterly winds prevailing over the northern Adriatic.

If we compare the isotopic composition of precipitations at locations at the same latitude along the central section of the Adriatic and the Tyrrhenian coastal areas the former locations show mean isotopic values considerably lower (up to about 2 ‰) than those in the Tyrrhenian section. This is at least partially due to the "shadow" effect of the Apennines that strongly affects the distribution of the isotopic values along the whole Italian peninsula, with a marked elevation effect, particularly in the central section. The less negative isotopic values in the southeastermost section of Italy (Apulia) are probably the effect of the frequency in this area of the warm southeasterly wind. It is noteworthy that, despite the latitudinal extension of the Tyrrhenian coast no latitudinal isotopic gradient was observed despite some obvious temperature gradients between different sections of this coast. This peculiar behaviour may be, at least partially, related to differences between seasonal amounts of precipitation and to the homogeneous surface temperatures of the Tyrrhenian sea that may affect in some way the most littoral precipitations. A last remark should be made on the shadow effect of the Alps that is considerably smaller than expected.

4. - RELATIONSHIP BETWEEN ISOTOPIC VALUES AND SURFACE TEMPERATURE

Several studies were carried out to show the positive relationship existing between the isotopic composition of precipitation and the surface temperature. This relationship was first demonstrated by DANSGAARD (1964); YURTSEVER (1975) and YURTSEVER & GAT (1981) clearly showed the existence of a time variation in monthly $\delta^{18}O$ and temperature (°C) data from the Vienna IAEA station as well as from a group of 39 IAEA/WMO network stations with a minimum of six years of continuous monthly data. In the majority of the stations analyzed there is only a 12-month cycle in the $\delta^{18}O$-time series with lighter isotopic values (both oxygen and hydrogen) during winter and heavier isotopic values during summer. These isotopic variations are characteristic of most of the studied areas and their amplitude is directly related to the amplitude of the seasonal temperature gradients: a huge amplitude is normally found in polar areas and a very small one in tropical areas. However, it was demonstrated that the best coupling of these two variables usually occurs for annual mean values. Several stations among which Bamaho, Kinshasa, Reykjavik, Tokio, Midway Island and Hilo-Hawaii showed either shorter cycles superimposed on the 12-month cycle or no distinct variations in their $\delta^{18}O$-time series. These anomalous behaviours were related to local climatological conditions and/or to different effects super-imposed on each other (YURTSEVER & GAT, 1981).

In Italy, we generally observed quite normal $\delta^{18}O/t$ relationships as was the case e.g. with the Aosta pluviometer during 2002-2004 (fig. 2).

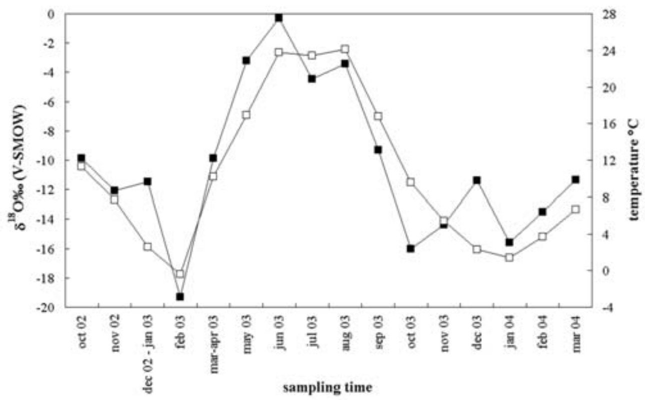

Fig. 2 – Mean monthly temperatures (°C, open squares) and $\delta^{18}O$ (full squares) of the mean monthly samples of precipitation at Aosta (north-western Italy) between October 2002 and March 2004.
– Temperature medie mensili (°C, quadrati bianchi) e $\delta^{18}O$ (quadrati neri) dei campioni medi mensili di precipitazioni ad Aosta tra l'Ottobre del 2002 ed il Marzo del 2004.

However, in a few cases anomalous results were obtained as was the case with the Basovizza pluviometer (north-eastern Italy, near the border with Slovenia, 397 m.a.s.l.) during 1998 (fig. 3). This is a very short period however, at Basovizza, the lack of a direct relationship between $\delta^{18}O$ and surface temperature is not exceptional: between November 1999 and October 2001 the overall range of $\delta^{18}O$ values was only 1.5 ‰, despite the normal seasonal temperature changes. During the same periods at the Trieste pluviometer, only a few kilometres away from Basovizza, the $\delta^{18}O/t$ relationship was normally respected. We have no plausible interpretation of the reported anomalous behaviour. However, we should point out that, during about a decade of isotopic measurements in Italy, very few anomalous behaviours were detected. In a general way, as demonstrated by MERLIVAT & JOUZEL (1979), there is a good relationship between the isotopic

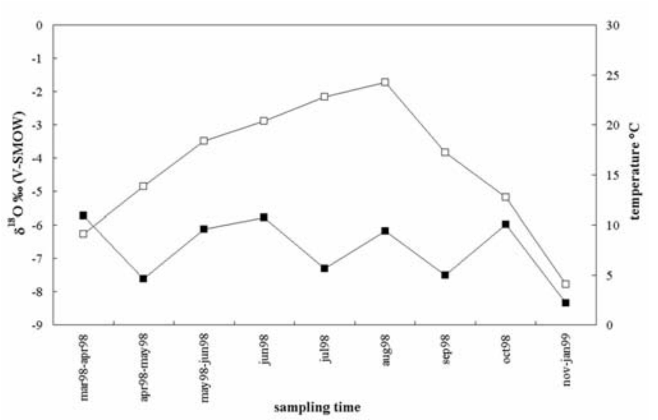

Fig. 3 - Mean monthly temperatures (°C, open squares) and $\delta^{18}O$ (full squares) of the mean monthly samples of precipitation at Basovizza (Trieste, north-eastern most Italy) between March 1998 and January 1999.
- *Temperature medie mensili (°C, quadrati bianchi) e $\delta^{18}O$ (quadrati neri) dei campioni medi mensili di precipitazioni a Basovizza (Trieste) tra il Marzo 1998 ed il Gennaio 1999.*

composition of precipitations (both oxygen and hydrogen) and climatic conditions.

A very interesting feature which could be erroneously interpreted as an anomaly to the $\delta^{18}O/t$ relationship was observed between 2002 and 2004 when exceptionally high temperatures were experienced, particularly during summer 2003. During this period Italy, as well as almost all Europe, recorded summer temperatures among the most elevated of the last 200 years. Accordingly, one could expect a shift of the mean isotopic values of precipitation towards less negative results. On the contrary, weighted mean yearly values resulted considerably more negative than "normal" values almost all over Italy. As examples of the results obtained we report the mean monthly values measured at two stations in northern Italy, Milano and Parma (tab. 1) (LONGINELLI *et alii*, 2006). At Milano the mean yearly temperature of 2003 was higher than the 2002 and the 2004 temperatures by about one degree centigrade, the highest temperature anomaly taking place between May and September 2003. During these five months the amount of precipitation was only 213 mm, about 25% of the amount during the same period in 2002; however, the amount of precipitation between January and April was also considerably lower than normal. As a result, the weighted yearly mean $\delta^{18}O$ value of 2003 was heavily affected by the amount of precipitation during the last three months of the year and by their negative isotopic values. Consequently, despite the increase in the isotopic summer values, the 2003 weighted mean isotopic values resulted considerably more negative than those of the previous year. If we now consider the 2004 isotopic values they look even more anomalous since the yearly mean temperature was quite normal while the yearly weighted mean $\delta^{18}O$ values were more negative than the 2003 values. This is clearly due to the small amount of summer precipitation (identical to that of the previous year), to the large amount of precipitation during the first four months, with very negative isotopic values, and to the very negative isotopic values of the precipitation during the last three months of 2004. In this case the weighted mean isotopic values would misrepresent the climatic situation suggesting drastically decreasing mean yearly temperatures.

The results obtained at Parma (tab. 1) are only slightly different from those obtained at Milano. Also at Parma the 2003 summer precipitations were extremely reduced and their $\delta^{18}O$ substantially shifted towards less negative values. However, the very negative isotopic composition of winter, spring and fall precipitations caused a marked decrease of the weighted mean yearly values. A large amount of precipitations during

Tab. 1 - Mean t values, amount of precipitation and weighted mean isotopic values.
- *Valori medi di t, quantità di precipitazioni e valori isotopici medi ponderati.*

Period	mean y.t°C	mean t°C	mm rain	mean $\delta^{18}O$	mean δD	w.$\delta^{18}O$	w.δD
Milano							
01/04/'02		9.0	430	-7.13	-48.9		
05/09/'02	14.9	22.0	815	-6.88	-46.7	-6.99	-46.9
10/12/'02		10.8	460	-7.05	-45.6		
01/04/'03		8.8	112	-8.94	-61.6		
05/09/'03	15.9	25.5	213	-5.22	-33.1	-8.36	-54.2
10/12/'03		9.5	430	-9.76	-62.8		
01/04/'04		8.3	424	-10.28	-72.2		
05/09/'04	14.8	22.5	218	-5.68	-39.3	-9.23	-64.2
10/12/'04		10.5	250	-10.53	-72.3		
Parma							
01/04/'02		6.9	225	-7.19	-45.0		
05/09/'02	14.4	21.2	372	-6.27	-41.8	-7.79	-51.8
10/12/'02		9.4	382	-9.63	-65.5		
01/04/'03		5.8	198	-13.09	-96.6		
05/09/'03	14.9	23.5	120	-4.50	-26.8	-10.18	-69.4
10/12/'03		7.9	317	-10.51	-68.6		
01/04/'04		6.5	432	-11.47	-80.4		
05/09/'04	14.1	21.5	310	-5.83	-36.4	-9.61	-64.7
10/12/'04		10.0	336	-10.70	-70.5		

The isotopic values are reported in ‰ versus VSMOW

2004 and quite negative isotopic values of winter, spring and fall precipitations determined a negative weighted yearly mean value while the mean yearly temperature of 2004 was only slightly lower than normal. In this case, the yearly mean isotopic values alone could lead to a distorted interpretation of the climatic conditions.

5. - AMOUNT EFFECT AND EVAPORATION EFFECT

Another peculiar feature that could be erroneously considered an anomaly in the $\delta^{18}O$/t relationship while it is related to different causes, is the so-called "amount effect". This effect on the isotopic composition of precipitation (isotopic results lighter than those expected for the recorded temperature in the case of very heavy rain) was recognized long ago by DANSGAARD (1964). The mechanism of this effect is not yet fully understood, however it has been at least partially explained considering that during a precipitation the isotopic composition of water vapour in the lower air layers is continuously modified by exchange processes with rain water drops. Consequently, it is brought isotopically closer to the following rain, the duration and the amount of rain affecting, as an additional parameter, the isotopic composition of precipitation. Not many quantitative examples of such an effect were reported in the Mediterranean area. We have a really didactic example observed in 1997 while studying the isotopic composition of precipitation at some stations in the southern pre-Alps for applied hydrological purposes. During June, July and August 1997 at the station of Boario Terme (about 50 km North of Brescia) anomalous $\delta^{18}O$ mean monthly values were measured, between two and four per mil more negative than expected (fig. 4). It must be pointed out that during these three summer months the amount of rain was 785 mm, (296, 352, and 137 mm respectively) about three times higher than the mean value of precipitation during the same period.

Normally, rain represents the cloud base composition only in the case of humid climates. In the case of arid or semi-arid areas when the air below the cloud is relatively dry, rain drops partially evaporate during their fall. The effect of this non-equilibrium fractionation is a final increase of the heavy-isotope content of the drops reaching the ground level and a decrease of the value of the deuterium excess. In Italy this effect can be sometimes observed during summer, particularly in southern Italy, but normally it does not seriously affect the weighted mean isotopic values that are used for hydrological applications, also because of the relatively small amount of summer precipitation. However, evaporation and isotope exchange between rain drops and water vapour are probably at least partially responsible for values lower than 8 of the coefficient in equation 1) as is the case with equations 5) and 6) for central and southern Italy.

6. - VERTICAL ISOTOPIC GRADIENTS

Hydrological applications of stable isotope measurements are strictly related to an accurate knowledge of the vertical isotopic gradients that are generally used to calculate the mean elevation of the recharge area of aquifers. Air masses, raising at progressively higher elevations, expand adiabatically: subsequent fractional condensations of water vapour take place at decreasing temperatures from a water vapour that is progressively depleted in heavy molecules. This composite effect causes isotopically lighter precipitations with increasing elevations and is generally referred to as "vertical isotopic gradient". In Italy we measured this variable at 26 different stations all over the country (fig. 5 and tab. 2) (LONGINELLI & SELMO, 2003) and found that, on average, the mean value of this variable is close to -0.15 ‰/100 metres, slightly higher than the -0.2 ‰ /100 metres generally considered a reliable mean value, frequently found in the Mediterranean area. Normal or quasi-normal values had been repeatedly found in this area, e.g. in Sicily by HAUSER *et alii* (1980), at the island of Vulcano, along the Tyrrhenian coast of Sicily by CAPASSO *et alii* (1990), and along the eastern side

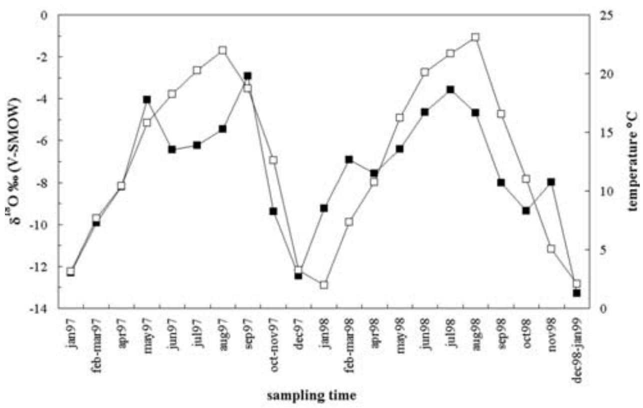

Fig. 4 – Isotopic amount effect at the pluviometric station of Boario (northern Italy, southern pre-Alps) during June, July and August, 1997. Open squares are temperatures and full squares are $\delta^{18}O$ (from LONGINELLI & SELMO, 2003).

- Effetto isotopico della quantità di precipitazioni alla stazione pluviometrica di Boario durante i mesi di Giugno, Luglio ed Agosto 1997. I quadrati bianchi si riferiscono alla temperatura ed i quadrati neri ai valori di $\delta^{18}O$ *(da* LONGINELLI & SELMO*, 2003).*

Fig. 5 – Location and number of pluviometres at which the vertical isotopic gradients were measured (from LONGINELLI & SELMO, 2003).
- Posizione e numero di pluviometri utilizzati per la misura dei gradienti isotopici verticali (da LONGINELLI & SELMO*, 2003).*

of the Apennines by CONVERSINI & TAZIOLI (1993); slightly lower gradients were calculated by MUSSI *et alii* (1998) for the Apennines and the Apuane Alps. Several anomalous values were found, particularly in Northern Italy, in the Alpine area around Trento where five stations at different elevations were monitored for about two years (BORSATO *et alii*, 2000). The results obtained (tab. 3) show that, at the yearly level, large negative and positive anomalies are found either between stations at very close elevations (e.g. Rifugio Graffer and Paganella) or between stations with moderate differences in elevations (e.g. Campo C. Magno and Andalo) or between stations with large differences in elevation (e.g. Paganella and Trento). The problem of the variability of the vertical isotopic gradient, particularly in Alpine areas, was already discussed; STICHLER *et alii* (1997) suggested a variability between -0.1 ‰/100 m and -0.3 ‰/100 m, mainly related to the position of the mountains with respect to the direction of the prevailing wind, i.e. with the prevailing trajectory of the rain-clouds front. In the case of the Trento area the calculated vertical gradients (tab. 3) largely exceed the values suggested by STICHLER *et alii* (1997) ranging from -

Tab. 2 - *Vertical isotopic gradients measured in Italy. Pluviometers Gallo, Vairano and Valle Agricola are reported in figure 5 as Vairano pluviometers.*
- Gradienti isotopici verticali misurati in Italia. I pluviometri Gallo, Vairano e Valle Agricola sono riportati in figura 5 come pluviometri di Vairano.

Collecting station	Elevation m.a.s.l.	$\delta^{18}O$ (VSMOW)	Collecting station	Elevation m.a.s.l.	$\delta^{18}O$ (VSMOW)	$\Delta\delta^{18}O$/100m (‰)
Basovizza	400	-7.36	Trieste	10	-6.60	-0.19
Passo Presolana	1290	-8.75	Darfo-Boario	208	-7.66	-0.10
Passo Presolana	1290	-8.75	Sarnico	197	-7.70	-0.10
Graniga	1100	-9.04	Pallanza	208	-7.40	-0.18
Fanano 1	1280	-8.50	Fanano 3	660	-7.57	-0.15
Fanano 1	1280	-8.50	Fanano 2	935	-8.46	-0.01
Monte T. Maggiore	1000	-7.29	San Gemini	350	-6.39	-0.14
Roccamonfina	620	-6.64	Riardo	110	-6.03	-0.12
Roccamonfina	620	-6.64	Campagnola	350	-6.33	-0.11
Campagnola	350	-6.33	Riardo	110	-6.03	-0.13
Gallo	825	-6.85	Vairano 2	135	-5.96	-0.14
Gallo	825	-6.85	Valle Agricola	680	-7.13	0.19
Valle Agricola	680	-7.13	Vairano 1	155	-5.72	-0.27
Etna 3	950	-8.23	Etna 2	570	-7.18	-0.28
Etna 3	950	-8.23	Etna 1	2	-5.49	-0.29
Etna 2	570	-7.18	Etna 1	2	-5.49	-0.30

Tab. 3 - *Vertical isotopic gradients (Δδ¹⁸O/100m): Trento area.*
- Gradienti isotopici verticali ($\Delta\delta^{18}O$/100m): area di Trento.

Collecting stations and elevation	Period	$\Delta\delta^{18}O$/100m
		(‰)
Paganella (2125m) - Trento (312m)	10/1997- 09/1999	-0.05
Campo C. Magno (1685m) - Andalo (1005m)	10/1997- 09/1999	-0.21
Paganella (2125m) - Campo C. Magno (1685m)	10/1997- 09/1999	0.30
Rifugio Graffer (2263m) - Paganella (2125m)	10/1997- 09/1999	-1.46
Paganella (2125m) - Andalo (1005m)	10/1997- 09/1999	-0.009

1.46 ‰/100 m to +0.30 ‰/100 m. This anomalous behaviour can be at least partially explained. The eastern face of the Paganella mountain is mainly exposed to southern winds blowing along the river Adige valley. This elevated wall causes a marked "shadow effect", particularly in the direction of the town of Andalo, only a few kilometres north-west of the Paganella mountain. The other two stations (Rifugio Graffer and Campo Carlo Magno) are located north-west of the Paganella and are exposed to a prevailing wind direction from the western quadrant. Before reaching these two stations rain-clouds are forced to climb over high mountains where repeated fractional condensations affect the pristine isotopic values of the atmospheric moisture.

We know that, in the case of vertical gradients, several different variables, besides the dynamic of air masses, may interfere and modify these values, such as atmospheric pressure, atmospheric humidity, etc. However, it is of interest to point out that the measured anomalies are not found only at the yearly level but also at the monthly and even at the daily level, as shown by the results reported in table 4. The results reported on the left side of the table [gradients between Paganella (2125 m.a.s.l.) and Andalo (1005 m.a.s.l.)] clearly show that during winter and spring of 1998 the mean monthly values reversed the vertical effect showing more negative isotopic values at the lower station. The results reported on the right side of the table show the anomalies that were found (in this case, far away from the Mediterranean) between high mountain stations in the Tianshan Mountains, Xinjiang Autonomous region, westernmost China (GU WEIZU & LONGINELLI, 1993). The reported vertical gradients refer to the isotopic values of daily samples of precipitation collected at the reported stations. In this case, a huge range of values was

Tab. 4 - *Anomalies in the vertical isotopic gradient (δ¹⁸O vs. VSMOW).*
- Valori anomali di gradienti isotopici verticali ($\delta^{18}O$ vs. VSMOW).

Samples	Paganella* 2125 masl	Andalo* 1005 masl	Samples	Tianshan Mts.** stations (m.a.s.l.)	$\Delta\delta^{18}O$/100m (‰)
Oct. 1997	-11.43	-10.20	06/15/1989	A 3693 - B 3539	-0.66
Nov. 1997	-12.27	-11.38	06/19/1989	A 3693 - C 2650	-0.37
Dec. 1997	-15.10	-15.01	06/30/1989	C 2650 - F 2336	**1.02**
Jan. 1998	-10.13	-11.00	06/30/1989	B 3539 - C 2650	-0.64
Feb. 1998	-11.74	-12.39	07/13/1989	C 2650 - F 2336	**0.11**
Mar. 1998	-3.31	-6.99	07/30/1989	B 3539 - F 2336	-0.24
Apr. 1998	-4.69	-10.19	08/12/1989	K 3805 - B 3539	-0.93
May. 1998	-8.90	-10.03	08/12/1989	B 3539 - C 2650	**0.32**
June.1998	-6.87	-5.96	08/20/1989	A 3693 - B 3539	-3.59
July. 1998	-6.86	-5.47	08/24/1989	K 3805 - A 3693	**1.87**
weighted mean values (2 years)	**-9.36**	**-9.26**			

* Italian Alps, Trento area

** Xinjiang Autonomous region, Western China obtained, from -3.59 ‰/100 metres to +1.87 ‰/100 metres. Strangely enough, inverse isotopic gradients were found for the same precipitation event when snow was collected at higher stations and rain at lower stations. Some of these vertical gradients clearly show that small differences in elevation often yield anomalous results.

7. - RELATIONSHIP BETWEEN PRECIPITATION AND GROUNDWATER

The European Community recommended long ago the use of stable isotope studies to support the hydrological research and several european countries produced a commendable effort in this direction. Detailed maps of the isotopic composition of precipitation and of the main surface and deep aquifers were produced, German and Israel agencies being particularly active in this field. In Italy nothing has been done at the nation level and only a few agencies have produced relatively large sets of data, among which the Emilia-Romagna region is one of the most active in this field. Several commercial enterprises performed detailed isotope studies on relatively small areas, particularly to define the catchment basin of aquifers exploited for mineral water sale. However, we are still far away from a nationwide systematic survey that would be particularly welcome in a country whose hydrological systems are deeply related to geological and geomorphological conditions.

The study of the origin of groundwaters has been a very successful area of application of natural stable isotope variations. This is mainly due to the conservative nature of the stable isotope composition of water in an aquifer: the original isotopic composition of a groundwater is normally preserved over extremely long periods and, consequently, the isotopic composition of meteoric groundwater is often found to match reasonably the mean isotopic composition of precipitation over the recharge area. Consequently, shallow and locally derived groundwaters are often used to characterize the isotopic content of meteoric waters when, for some reason, the drawn-out process of precipitation sampling is avoided. This was the case with a study carried out by MUSSI *et alii* (1998) in northern Tuscany (Alpi Apuane-Garfagnana area) that enabled a useful reconstruction of the local distribution of the isotopic composition of rainfall starting from the measurement of surface and spring waters and using a limited number of samples per single station.

Under arid conditions an evaporative heavy isotope enrichment of groundwater may easily take place, in parallel with a decrease in the value of the deuterium excess. Changes in the isotopic composition of groundwater may also result from mixing of groundwaters from different points of origin, mixing with fossil water bodies, and interactions and isotope exchange between water and the rock matrix. Particularly large interactions take place in deep aquifers at rather elevated temperatures. This process is specific of geothermal areas. It should be pointed out that in the first half of the twentieth century, the origin of steam in geothermal areas, and particularly at Larderello, was related to the emission of magmatic (and/or "juvenile") water from a deep granite intrusion. The measurement of the isotopic composition of steam from Larderello (CRAIG, 1963) clearly demonstrated the meteoric origin of the steam whose oxygen isotopic composition was deeply modified by high temperature exchange processes with limestones (systematically ^{18}O enriched when compared with meteoric water) while the hydrogen isotopic composition preserved its meteoric signature, mainly because of the lack of hydrogen rich materials in the geological sequence involved. Similar results were also obtained from other geothermal areas like the Geysers, Lassen Park and Steamboat Springs in the USA (CRAIG, 1963).

The meteoric origin of waters whose chemical composition was drastically modified by water-rock mass transfer can be demonstrated by the preservation of the rain water isotopic signature also when no thermal anomaly affected the hydrological system. This was the case with a survey of spring waters from the Genova province ranging from neutral $Mg\text{-}HCO_3$ waters to some high-pH, Ca-OH waters found in association with serpentinites (BRUNI *et alii*, 2002).

In the case of alluvial deposits like the Po plain, the recharge of aquifers by infiltration from rivers is of great importance. BORTOLAMI *et alii* (1973) studied in some detail the origin of groundwaters in the plain of Venice by means of stable isotope measurements. This investigation clearly showed that phreatic aquifers in the middle and upper part of the plain underwent marked infiltration from the Brenta and Piave rivers. The oxygen isotopic composition of these aquifers was quite negative (around -10 ‰) and very close to that of the rivers, far away from the isotopic composition of local precipitation whose average value was close to -7 ‰.

A completely different situation was found in the case of the Karst area where the dissolution processes of limestone formations and the resulting morphological features deeply affect the hydrological processes. In the classical Karst area of Trieste, a sort of metropolitan tale (often accepted also by local hydrologists) says that the water discharged in the Gulf of Trieste at the mouth of the Timavo river comes from the so called "upper Timavo river" which disappears underground in the S. Canziano caves, about 35 km south-east of the "Timavo mouth" near Monfalcone. From the S. Canziano cave a sort of sealed pipe would carry the water to the river mouth, crossing directly the Karst area. Results of tracing experiments (ERIKSSON *et alii*, 1963) already proved that the contribution of the "Upper Timavo water" to the outflow was only of a few units per cent. To confirm these results, a long and detailed study of the isotopic composition of waters from several springs and rivers in the Karst area was carried out from 1985 to 1988 (LONGINELLI, 1988; FLORA *et alii*, 1990). A marked seasonal isotopic inversion with heavier isotopic values in winter becoming progressively lighter through spring and summer is apparent (fig. 6). The isotopic disturbances at the end of 1986 should be probably related to marked disturbances in the meteorological trend with very heavy rain in October.

The dramatic seasonal inversion may be explained as follows. The isotopic composition of the outflow of the Timavo river in winter is identical to the mean isotopic composition of precipitation on the coastal Karst section; it follows that, during winter, this outflow comes from a reservoir which is basically fed by local atmospheric precipitation. The isotopic evolution from the winter to the summer values (normally followed by a decrease in the outflow) is the effect of a variable mixing of water of this reservoir with an isotopically lighter water that may come only from the internal (slovenian) section of the Karst area with mean elevations of about 900/1000 metres a.s.l. Coastal rain water should prevail during winter (high hydraulic pressure) while internal water should prevail during summer when the hydraulic pressure of the local system is reduced by output and reduced precipitation. A third minor component may come from the Isonzo river, essentially according to the hydraulic pressure gradients between different aquifers. This contribution is suggested by the minor negative variations recorded in May/June by the Timavo water when the Isonzo river reaches its highest flow and its most negative isotopic values related to the snow melting in its alpine basin. The old hypothesis of a direct connection between the "Upper Timavo" and the "Timavo mouth" is clearly contradicted by the isotopic results obtained.

Acknowledgements

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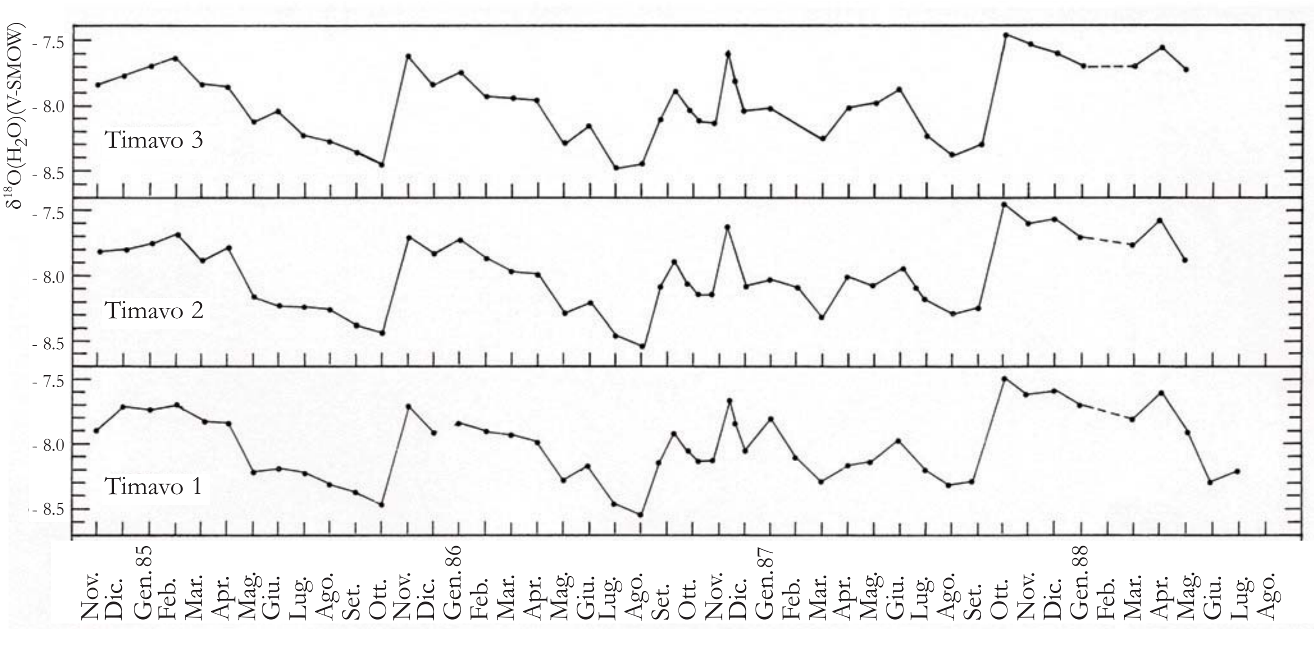

Fig. 6 - *Oxygen isotopic composition of monthly water samples from the three main Timavo mouths.*
- Valori della composizione isotopica dell'ossigeno di campioni mensili di acqua prelevati da quelle che vengono considerate le tre bocche principali del Timavo.

REFERENCES

BORSATO A., FRISIA S., CORRADINI F., LONGINELLI A., ARTIOLI G.F. *et alii* (2000) - *Acquiferi carsici in Trentino: caratteristiche fisico-chimiche, vulnerabilità e inquinamento.* Rapporto Interno Provincia Autonoma di Trento, Dipartimento dell'Ambiente, 280 pp.

BORTOLAMI G., FONTES J.CH. & PANICHI C. (1973) - *Isotopes du milieu et circulations dans les aquifères du sous-sol Vénétien.* Earth Planet. Sc. Letters, **19**: 154-160.

BRUNI J., CANEPA M., CHIODINI G., CIONI R., CIPOLLI F., LONGINELLI A., MARINI L., OTTONELLO G. & VETUSCHI ZUCCOLINI M. (2002) - *Irreversible water-rock mass transfer accompanying the generation of the neutral, Mg-HCO$_3$ and high-pH, Ca-OH spring waters of the Genova province, Italy.* Applied Geochem., **17**: 455-474.

CAPASSO G., DONGARRÀ G., FAVARA R., HAUSER S. & VALENZA M. (1990) - *Composizione isotopica delle piogge, dell'acqua dei pozzi e del vapore fumarolico dell'isola di Vulcano.* CNR, Pubblicaz. Istituto Geochim. dei Fluidi, Palermo, pp. 38-52.

CONVERSINI P. & TAZIOLI G.S. (1993) - *Indagini idrogeologiche nella media e alta valle del fiume Menotre, Umbria orientale.* Atti Ticin. Sci. Terra, **36**: 153-164.

CRAIG H. (1961) - *Isotopic variations in meteoric waters.* Science, **133**: 1702-1703.

CRAIG H. (1963) - *The isotopic geochemistry of water and carbon in geothermal areas.* In: E. TONGIORGI (Ed.): «*Nuclear geology in geothermal areas*». CNR, Pisa, 17-53.

CRAIG H. & GORDON L.I. (1965) - *Deuterium and oxygen-18 variations in the ocean and the marine atmosphere.* In: E. TONGIORGI (Ed.): «*Stable isotopes in oceanographic studies and paleotemperatures*». CNR, Pisa, pp. 9-130.

DANSGAARD W. (1954) - *The ^{18}O abundance in fresh water.* Geochim. Cosmochim. Acta, **6**: 241-252.

DANSGAARD W. (1961) - *The isotopic composition of natural waters.* Medd. om Grönland, **165** (2): 1-120.

DANSGAARD W. (1964) - *Stable isotopes in precipitation.* Tellus, **16**: 436-468.

EPSTEIN S. & MAYEDA T. (1953) - *Variation of ^{18}O content of waters from natural sources.* Geochim. Cosmochim. Acta, **4**: 213-224.

ERIKSSON E., MOSETTI F., HODOŠČEK K. & OSTANEK L. (1963) - *Some new results on the karstic hydrology with the employ of tritiated water as a tracer.* Boll. Geof. Teor. Appl., **5**: 18-32.

FIDEL R. (1976) - *Bibliography of hydrogen and oxygen stable isotope hydrology*, The Hebrew University of Jerusalem.

FLORA O., GALLI G., NEGRINI L. & LONGINELLI A. (1990) - *Studio geochimico-isotopico di alcune sorgenti carsiche: un nuovo modello idrologico.* Atti e Mem. Commiss. Grotte "E. BOEGAN" , **29**: 83-102.

FÖRSTEL H. & HÜTZEN H. (1982) - *^{18}O/^{16}O ratios of groundwater at the Federal Republic of Germany.* In: H.L. SCHMIDT, H. FÖRSTEL. & K. HEINZINGER (Eds.): *Stable isotopes, Analytical Chemistry Symposium Series*, **11**: 173-178, Elsevier, Amsterdam.

GAT J.R. (1980) - *The isotopes of hydrogen and oxygen in precipitation.* In: P. FRITZ & J.CH. FONTES (Eds.): *Handbook of environmental isotope geochemistry*, **1**, *The terrestrial environment*, pp. 21-47, Elsevier Publ. Co., Amsterdam.

GU WEIZU & LONGINELLI A. (1993) - *A case study on the hydrological significance of stable isotope data on alpine catchments with snow cover and glaciers, Xinjiang, China.* In: W. LAURIER (Ed.): *Proceedings of the ISSGH Katmandu Conference.* IAHS Publication, **218**: 371-383.

HAUSER S., DONGARRÀ G., FAVARA R. & LONGINELLI A. (1980) - *Composizione isotopica delle piogge in Sicilia. Riferimenti di base per studi idrogeologici e relazioni con altre aree mediterranee.* Rend. Soc. Ital. Mineral. Petrol., **36**: 671-680.

JOUSSAUME S., SADOURNY R. & JOUZEL J. (1984) - *A general circulation model of water isotope cycles in the atmosphere.* Nature, **311**: 24-29.

LONGINELLI A. (1988) - *Stable isotope hydrology of the classical Karst area, Trieste, Italy.* In: F. BARBERI, F. INNOCENTI, M. LEONE & F.P. SASSI (Eds.): Special volume in memory of M. Carapezza, Rend. Soc. Ital. Mineral. Petrol., **43**: 1175-1183.

LONGINELLI A., ANGLESIO E., FLORA O., IACUMIN P. & SELMO E. (2006) - *Isotopic composition of precipitation in Northern Italy: reverse effect of anomalous climatic events.* J. of Hydrol., **329**: 471-476.

LONGINELLI A. & SELMO E. (2003) - *Isotopic composition of precipitation in Italy: a first overall map.* J. of Hydrol., **270**: 75-88.

MERLIVAT L. & JOUZEL J. (1979) - *Global climatic interpretation of the deuterium-oxygen-18 relationship for precipitation.* J. Geoph. Res., **84**: C, 5029-5033.

MUSSI M., LEONE G. & NARDI I. (1998) - *Isotopic geochemistry of natural waters from the Alpi Apuane-Garfagnana area, Northern Tuscany, Italy.* Mineral. Petrogr. Acta, **41**: 163-178.

ROZANSKI K. (1985) - *Deuterium and Oxygen-18 in European groundwaters - links to atmospheric circulation in the past.* Chem. Geol., **52**: 349-363.

ROZANSKI K., ARAGUÀS-ARAGUÀS L. & GONFIANTINI R. (1993) - *Isotopic patterns in modern global precipitation.* AGU, Geophys. Monogr., **78**: 1-36.

ROZANSKI K., SONTAG C. & MÜNNICH K.O. (1982) - *Factors controlling stable isotope composition of European precipitation.* Tellus, **34**: 142-150.

SIEGENTHALER U. & OESCHGER H. (1980) - *Correlation of ^{18}O in precipitation with temperature and altitude.* Nature, **285**: 314-316.

STICHLER W., TRIMBORN P., MALOSZEWSKI P., RANK D., PAPESCH W. & REICHERT B. (1997) - *Isotopic investigations.* Acta Carsologica, **26** (1): 213-259.

YURTSEVER Y. (1975) - *Worldwide survey of stable isotopes in precipitation.* Internal report IAEA, Vienna.

YURTSEVER Y. & GAT J. (1981) - *Atmospheric waters.* In: J.R. GAT & R. GONFIANTINI (Eds.): *Stable isotope Hydrology: Deuterium and Oxygen-18 in the water cycle*, IAEA, Techn. Rep. Ser., **210**: 103-142. IAEA, Vienna, Austria.