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Isotopic composition and secondary evaporation effects on precipitation from the urban centre of Bologna, Italy

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Abstract. — Forty-nine monthly precipitations were collected in the densely urbanized centre of the city of Bologna during the four years from March 1996 to March 2000. These samples were measured for their hydrogen and oxygen isotope composition, and the results were compared with literature data on monthly precipitations collected in Bologna in a suburban, green-belt, open-air site between August 1997 and August 2001. The δ^2H-$\delta^{18}O$ meteoric lines in the two sites differ significantly in slope and intercept, both parameters being lower in the urban site by 12% and 9‰ delta-units, respectively. The amount weighted mean deuterium excess ("d") is also lower by 2‰ than the suburban value. These findings all support that the isotopic composition of the samples studied are appreciably influenced by secondary evaporation during falling through the atmosphere.

Riassunto. — Sono stati raccolti 49 campioni mensili di precipitazioni atmosferiche nel centro urbano di Bologna nell'arco di quattro anni dal Marzo 1996 al Marzo 2000. I campioni sono stati analizzati per la composizione isotopica dell'idrogeno e dell'ossigeno, ed i risultati confrontati con dati di letteratura relativi a precipitazioni mensili raccolte nella parte periferica della città dall'Agosto 1997 e l'Agosto 2001. Le rette meteoriche δ^2H-$\delta^{18}O$ per i due siti differiscono significativamente sia per pendenza sia per intercetta, con valori minori rispettivamente del 12% e del 9‰ (unità-δ) nel centro urbano. L'eccesso medio pesato di deuterio è anch'esso inferiore del 2‰ (unità-δ) nel centro urbano rispetto alla periferia. L'insieme dei parametri indica che la composizione isotopica delle precipitazioni studiate è apprezzabilmente influenzata da processi d'evaporazione secondaria nell'atmosfera durante la caduta al suolo.

Key words: *Precipitation; Stable isotopes; Secondary evaporation; Bologna*

Introduction

Recently, a comprehensive study on the isotope composition of precipitation of Italy was carried out by Longinelli and Selmo (2003), who published a nationwide oxygen isotope composition map. The study includes a station at Bologna, located at the CNR campus in a suburban area to the NW of the city. The campus is about 3.3 km from the Department of Earth and Geo-Environmental Sciences within the historic, completely urbanized

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centre of the city. At the department, mean monthly precipitation samples were collected from March 1996 to March 2000, along with individual precipitation from March 1996 to April 1997. These samples were analyzed for major chemistry, sulfur isotope composition of aqueous sulfate, and hydrogen and oxygen isotope compositions of water. Data on chemistry and sulfur isotopes were already published (Panettiere *et al.*, 2000), and the other ones are reported and discussed in the present paper.

The main purpose of the paper is to compare our results with those of Longinelli and Selmo (2003), in order to verify the existence of isotopic effects on rain drops due to secondary evaporation during their falling through an atmosphere that should be heavily influenced by the city, and in which the rain drops may behave as "gliders" supported by ascending warm air bubbles especially during summer. This phenomenon is known to occur in dry environments or during hot and dry seasons (e.g. Clark and Fritz, 1997). However, as far as we know, it has not been documented in atmospheric precipitation on cities.

The city of Bologna and climate

Bologna is a densely populated and busy city at the foot of the Apennine ridge to the south and in front to the Po River plain to the north, at an elevation of 54 m a.s.l. Its total surface is of about 141 km^2. The most urbanized part is about 30 km^2 wide, with the historic centre covering about 7 km^2.

The climate can be classified as subtropical humid (Pinna, 1977), with pluviometric maxima normally in spring and autumn. During the period of survey, mean monthly air temperature reaches values as low as 2.5 °C during winter and as high as 26.3 °C during summer, with annual mean values of 13.2 to 14.9 °C (AER-ARPA, 1996-2000).

Sampling and analyses

Monthly rain water was collected within a plastic bottle adapted with a funnel and added with vaseline oil to prevent evaporation. Individual rain water was sampled by means of a polyethylene sheet. Reported mean monthly air temperature data are from the G. Marconi airport meteorological station, about 6 km far from the sampling site.

The hydrogen and oxygen isotope compositions (expressed in δ^2H and $\delta^{18}O$ units, in permil, relative to V-SMOW standard) were determined respectively by reaction of water with metallic zinc at 440 °C (Coleman *et al.*, 1982) and by water-CO_2 equilibration at 25 °C (Epstein and Mayeda, 1953), then submitting H_2 and CO_2 to mass spectrometric analysis. The standard deviation (1σ) of runs was within ± 0.1‰ for oxygen and ± 1‰ for hydrogen.

Results and discussion

The analytical results and relevant meteorological data for monthly precipitation are reported in Table 1.

Hydrogen and oxygen isotopes

δ^2H vs $\delta^{18}O$: slope, δ^2H-intercept and deuterium excess

As shown in Fig. 1, the δ^2H-$\delta^{18}O$ meteoric water line inclusive of all the monthly samples (hereafter HCWL) shows a correlation coefficient R^2 of 0.92, a slope of 6.68 and an intercept of -1.76‰. When samples with negative deuterium excess "d" (defined as δ^2H-8 $\delta^{18}O$; Dansgaard, 1964) are excluded, the slope and intercept of the new linear relation (hereafter HDWL) increase respectively to 7.33 and 4.22‰, and the R^2 improves to 0.95. Both meteoric lines differ significantly from the GMWL of Rosanski *et al.*, (1993), that has a slope of 8.20 and an intercept of 11.27‰. In Europe, the HCWL line is comparable with that reported by Clark and Fritz (1997) for the Vienna weather station (s = 7.1; i = -1.4‰), in keeping with the common temperate continental climate of Vienna and Bologna, with warm, sunny summers and cold winters.

HCWL differs substantially from that of Longinelli and Selmo (personal communication; hereafter indicated as LSWL), whereas the agreement is good for the HDWL. The monthly samples with "d" < 0 (n = 4) refer to spring (May) to summer (June and August) rains (Fig. 2), with rainfall of 21.4 to 61.2 mm and air temperature

TABLE 1
Isotopic composition of monthly precipitation in the urban centre of Bologna

Month/Year	δ^2H (‰)	$\delta^{18}O$ (‰)	"d" (‰)	Rainfall (mm)	T (°C)
March 1996	-65.0	-9.51	11.1	43.6	7.2
April	-43.2	-6.43	8.2	80.6	13.4
May	-49.0	-6.89	6.1	63.2	18.1
June	-47.6	-5.82	-1.0	61.2	22.3
July	-34.2	-4.82	4.4	5.8	23.3
August	-29.6	-5.03	10.6	44.6	22.8
September	-48.0	-7.55	12.4	62.2	16.1
October	-49.4	-7.66	11.9	158.6	13.8
November	-64.6	-9.17	8.8	81.2	10.2
December	-49.7	-7.76	12.4	123.6	3.8
January 1997	-83.0	-11.85	11.7	76.6	3.9
February	-49.0	-6.93	6.4	17.0	6.3
March	-65.4	-9.58	11.2	32.0	10.9
April	-77.5	-10.25	4.5	25.0	11.3
May	-36.7	-5.88	10.3	22.0	18.7
June	-46.4	-6.44	5.1	74.0	22.3
July	nd	-4.85	nd	20.4	24.6
August	-33.2	-5.46	10.5	14.6	24.8
September	-43.5	-6.86	11.4	8.0	21.5
October	-37.5	-6.08	11.1	32.3	13.9
November	-72.6	-10.17	8.8	131.5	8.4
December	-72.0	-10.61	12.9	46.1	4.2
January 1998	-64.2	-8.91	7.1	32.3	4.5
February	-48.2	-6.56	4.3	21.9	8.2
March	-68.6	-11.05	19.8	39.2	8.5
April	-37.4	-5.12	3.6	45.0	13.5
May	-48.0	-6.52	4.2	94.6	17.6
June	-31.7	-3.23	-5.9	39.2	23.5
July	-41.8	-5.71	3.9	38.5	26.3
August	-31.8	-2.87	-8.8	21.4	25.3
September	-37.8	-5.63	7.2	113.0	20.0
October	-34.0	-5.54	10.3	69.2	14.8
November	-62.3	-9.32	12.3	18.0	7.4
December	-87.2	-12.30	11.2	71.5	2.5

TABLE 1
continued...

Month/Year	δ^2H (‰)	$\delta^{18}O$ (‰)	"d" (‰)	Rainfall (mm)	T (°C)
January 1999	-55.9	-8.11	9.0	36.9	4.4
February	-102.8	-13.66	6.5	65.7	4.8
March	-42.2	-6.29	8.1	41.5	10.4
April	-48.7	-7.33	9.9	72.7	14.1
May	-42.0	-3.99	-10.1	46.1	20.0
June	-48.0	-6.38	3.0	70.4	23.1
July	-49.9	-6.65	3.3	8.9	25.3
August	-27.4	-4.98	12.4	83.2	25.9
September	-43.4	-7.16	13.9	89.1	22.3
October	-33.2	-6.50	18.8	73.2	16.0
November	-79.6	-11.97	16.2	221.7	6.9
December	-87.7	-12.30	10.7	75.3	2.9
January 2000	-59.7	-9.83	18.9	16.5	2.5
February	-37.2	-5.47	6.6	4.8	6.7
March	-32.2	-5.19	9.3	41.4	10.6

of 20.0 to 25.3 °C. They locate away to the right of the HCWL line, this being expected when falling raindrops undergo substantial secondary evaporation and related isotopic effects. These features concur to suggest that precipitation in the suburban site is not significantly influenced by secondary evaporation effects, even if sampled not so far from the centre of the city.

The secondary evaporation process works mainly during hot (dry) seasons and particularly on light rains. As a consequence, it determines the lowering of the slope and the δ^2H-intercept of the local meteoric line, as well as the "d" value of the rain sample (e.g. Clark and Fritz, 1997). This is clearly manifest in the plot of Fig. 3, where monthly precipitation with average monthly air temperature ≥20 °C defines an evaporation trend with slope and intercept much lower than those of the line fitting the precipitation with lower air temperature. The correlation is low, as the secondary evaporation effects recorded in the precipitation depend on the air temperature and humidity, as well as on rainfall.

The overall amount weighted means of the monthly samples are -54.9‰ for δ^2H, -8.0‰

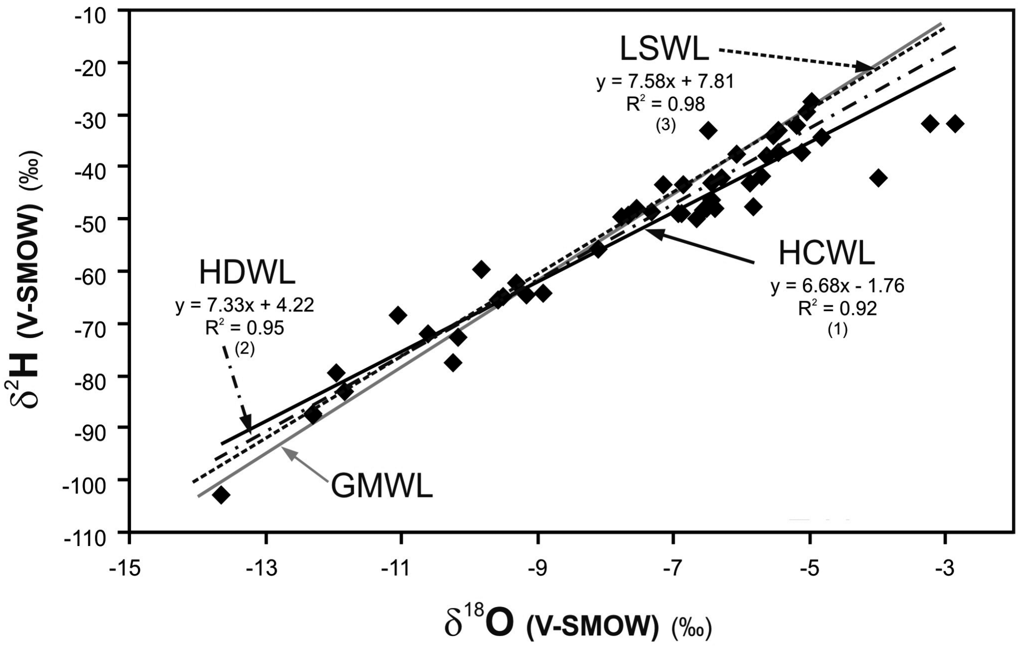

Fig. 1 – Meteoric water lines from this work, interpolating all data (HCWL solid line; equation 1), or excluding samples with negative deuterium excess (HDWL dotted-dashed line; equation 2). Both lines are compared with that (LSWL dotted line; equation 3) obtained for the suburban precipitation at Bologna from 1998 to 2001 (A. Longinelli, personal communication; see also Longinelli and Selmo, 2003). The Global Meteoric Water Line (GMWL; Rosanski *et al*., 1993) is also shown.

for $\delta^{18}O$ and 9.1‰ for "d". All these values are significantly lower than those reported by Longinelli and Selmo (2003), i.e. -48.8‰ for δ^2H, -7.5‰ for $\delta^{18}O$ and 11.3‰ for "d". In particular, the "d" value is lower by 2.2‰, thus testifying that the raindrops falling in the centre of the city are appreciably affected by secondary evaporation compared to those in the more verdant and air open suburban site. In addition, the "d" turns to 10.7‰ if the samples with negative "d" values (6% of the total rainfall) and June to August samples (14% of the total rainfall; air temperature 22.3 to 26.3 °C) are excluded from the computation, thus approaching the "d" value obtained in the suburban site. The slope and intercept (s = 7.5, i = 5.9) of the corresponding δ^2H-$\delta^{18}O$ relation also increase further on relative to the all samples' line (cf. Fig. 1). On an annual basis, secondary evaporation effects were highest in 1998, this corresponding to the highest amount weighted mean δ^2H and $\delta^{18}O$ values, the lowest weighted mean "d" value, and the highest spring-summer to autumn-winter rainfall amount ratio (Table 2). The enhanced evaporation effects on 1998 rains match with a comparatively hotter summer, as well as a slightly higher mean annual temperature (14.9 °C), compared to 1997 (14.5 °C) and 1999 (14.4 °C).

Table 2

Annual amount weighted means of shown parameters and annual meteoric lines of studied monthly precipitation

Year	δ^2H ‰	$\delta^{18}O$ ‰	RR	"d" ‰	meteoric δ^2H-$\delta^{18}O$ lines slope	intercept
1997	-63.1	-8.87	0.5	8.1	7.85	8.23
1998	-48.9	-6.90	1.4	6.5	5.81	-9.36
1999	-56.6	-8.81	0.7	10.9	7.15	1.75

RR = spring-summer to autumn-winter rainfall amount ratio (mm/mm). "d" = amount weighted mean of deuterium excess

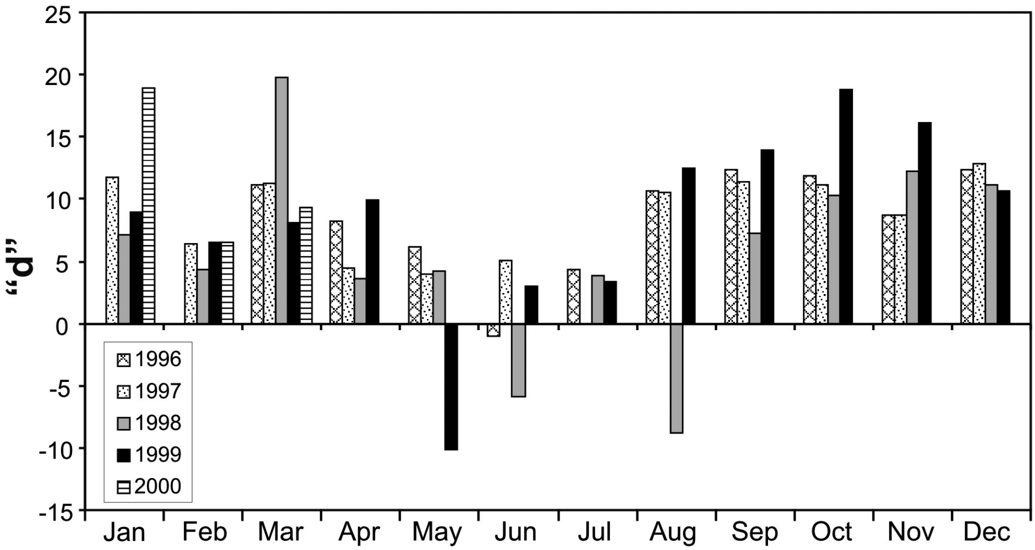

Fig 2 – Monthly weighted mean deuterium excess values in precipitation from March 1996 to March 2000.

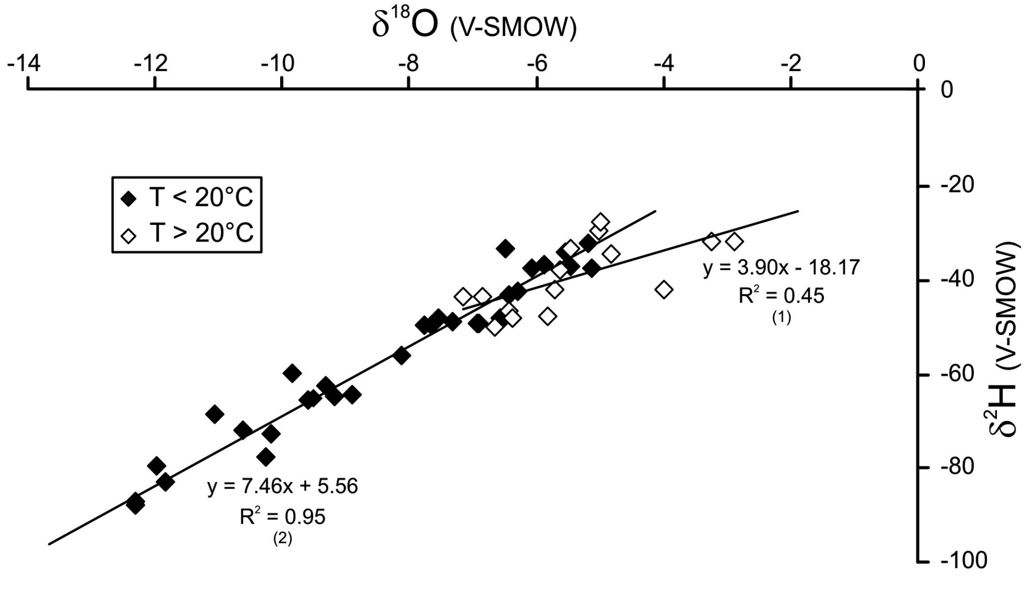

Fig. 3 – Isotopic relations for monthly precipitation from March 1996 to March 2000 distinguished on the basis of mean monthly air temperature higher (equation-1) or lower (equation-2) than 20 °C.

Samples of individual precipitation between March 1996 and April 1997 show a good δ^2H-$\delta^{18}O$ relationship (s = 7.4, i = 5.3, R^2 = 0.95). The relation appears to be only a slightly affected by secondary evaporation. When disjointed, the data on autumn-winter samples distinguish from the spring-summer ones (Fig. 4). The latter include two rains with negative "d" in May and August, and fit a correlation line with lower slope and δ^2H-intercept; the distinction persists also excluding the two samples (s = 7.6, i = 6.0, R^2 = 0.97), thus suggesting that the spring-summer rains suffered appreciable secondary evaporation effects, especially samples with "d" ~ 0‰ or lower in May to August. When compared with the mean monthly samples in the same period, the obtained relation is very good (R^2 = 0.95; Fig. 5), even including the samples with "d" < 0‰. The latter samples (a monthly and two individuals) arrange to the right of the relation and seemingly fit an evaporation path.

δ^2H and $\delta^{18}O$ time-variations in monthly samples

As expected (e.g. Clark and Fritz, 1997), the two parameters show clear-cut and totally synchronous seasonal variations, with highest and lowest values normally in summer and winter, respectively (Fig. 6). Anomalously high δ-values in February 1997, February 1998 and January to March 2000 cannot be related to temperature effects, but rather to amount effects, as they correspond to normal air temperatures (see Table 1) but anomalously low rainfalls (Fig. 6).

Relation between $\delta^{18}O$, rainfall and air temperature

Rainwater $\delta^{18}O$ and local air temperature should show a good positive correlation, especially when annual mean values are compared (Dansgaard, 1964). At the monthly scale, deviations can often occur (e.g. Clark and Fritz, 1997). In Fig. 7a our monthly data conform reasonably to the expected relationship, with major anomalies during winter. In a binary plot, the resulting $\delta^{18}O$-temperature correlation (s = 0.245, i = -10.86‰, R^2 = 0.56) is close to the Yurtsever and Gat (1981)'s global one also based on monthly means (s = 0.338, i = -11.99‰), i.e. a 0.25‰/° C gradient may be approximated for the precipitation at Bologna. This gradient is comprised between those observed in continental (0.58‰/° C) and marine (0.17‰/° C) stations (Clark and Fritz, 1997 and references

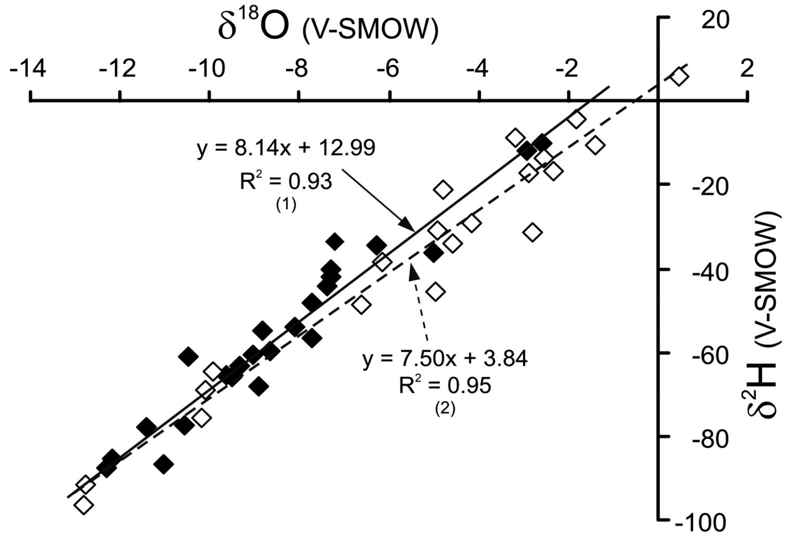

Fig. 4 – Isotopic relations for seasonally separated individual precipitation samples (autumn/winter = filled diamond and equation-1; spring-summer = open diamond and equation-2). The complete data set is available upon request from the corresponding author.

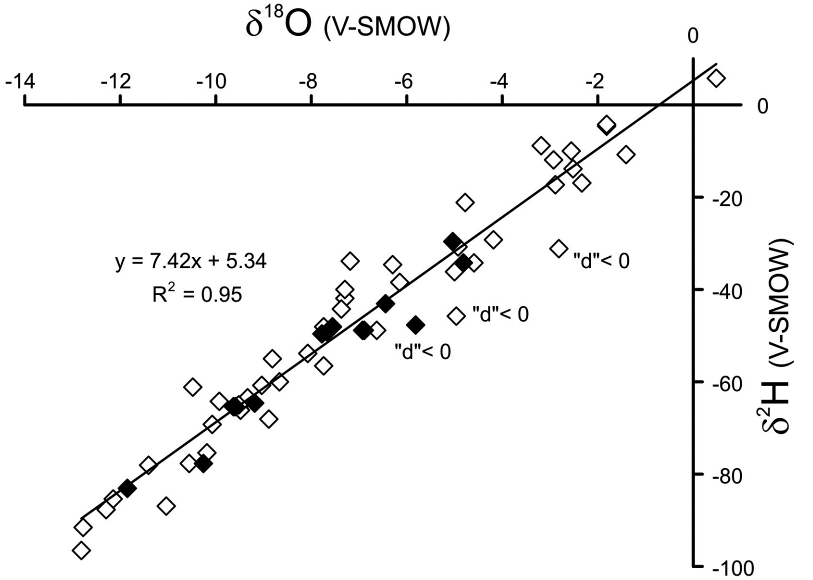

Fig. 5 – Relation between individual (open diamond) and monthly precipitation (filled diamond) from March 1996 to April 1997. Samples with deuterium excess "d" < 0‰ are identified. Line and equation refer to individual precipitation only.

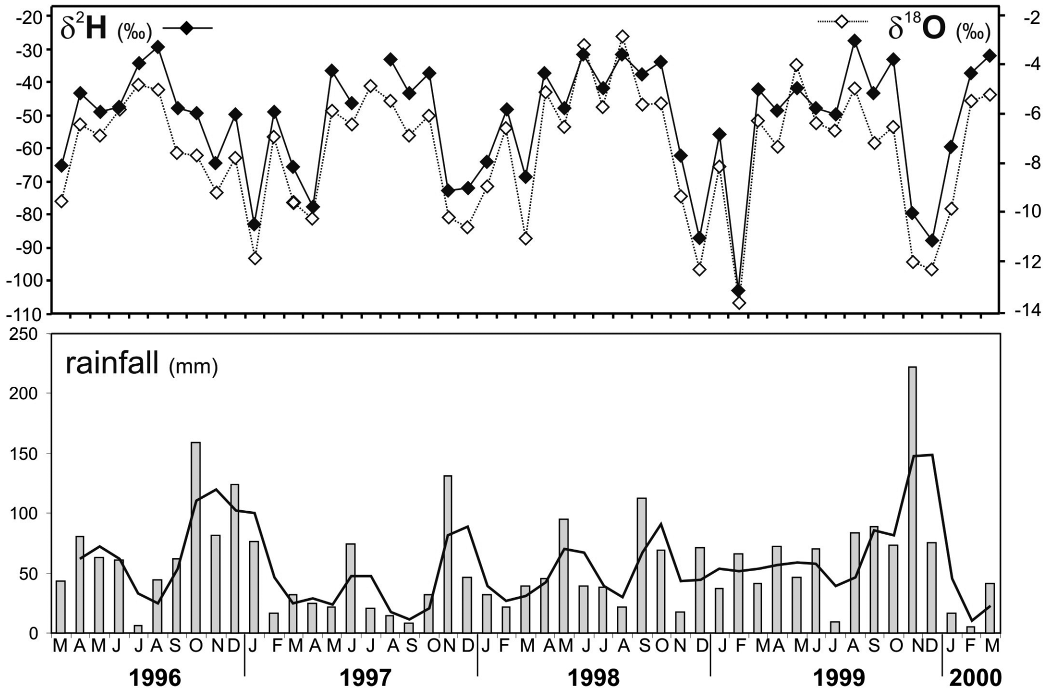

Fig. 6 – Seasonal hydrogen (filled diamond) and oxygen (open diamond) isotope variations in monthly precipitation, compared to the monthly rainfall seasonal variation and its moving mean.

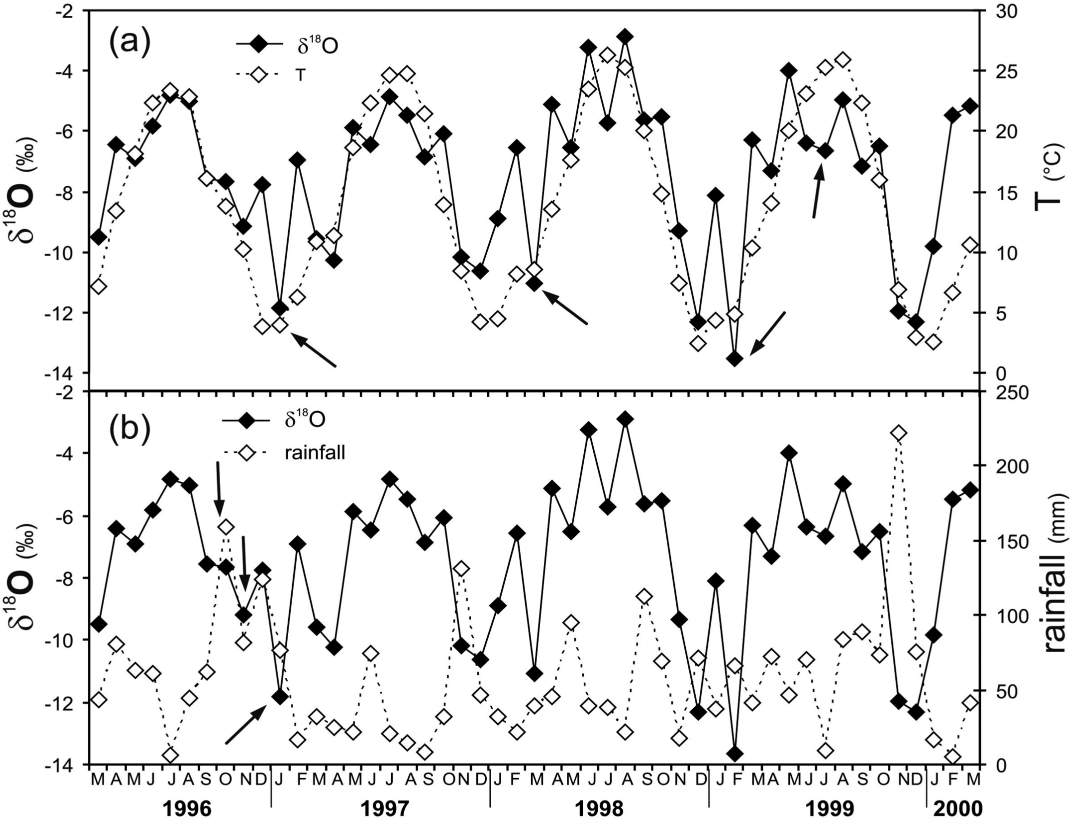

Fig. 7 – a) Comparison between the seasonal variation of the monthly mean oxygen isotope composition of precipitation (filled diamond) and monthly mean air temperature (open diamond). Arrows indicate major amount isotopic effects on precipitation, all but one during winter; b) seasonal variations of the monthly mean oxygen isotope composition of precipitation (filled diamond) and monthly mean rainfall (open diamond). Arrows indicate major anomalies relative to expected trends.

therein), in keeping with a mainly marine origin of the vapour originating the studied precipitation at Bologna.

The relation between $\delta^{18}O$ and rainfall is mostly negative (Fig. 7b), as expected when the amount effect on $\delta^{18}O$ is prevailing. However, disturbing factors can play a role, like provenance of the vapour (i.e. the distance of its source/s) and continental effects, this resulting in anomalous trends as manifestly recorded in December 1999.

CONCLUSIONS

Main conclusions that can be drawn out are:

1. Precipitation in the urban centre of Bologna undergoes appreciable isotopic effects due to secondary evaporation during falling. As a consequence, the resulting δ^2H-$\delta^{18}O$ meteoric line is notably different from that of precipitation in the peripheral part of the city in a verdant and air open site. The differences deal with all relevant parameters like $\delta^2H/\delta^{18}O$ slope, δ^2H-intercept and deuterium excess (“d”). The regression line for urban precipitation has slope and intercept lower respectively by 12% and 9.6‰ delta-units with respect to the sub-urban one. Also, the overall amount weighted mean “d” is lower by 2.2‰ delta-units in the urban site.

2. Spring-summer rain waters define an isotopic meteoric line that differs from that of autumn-winter precipitation, with significantly lower slope and intercept. Annual amount weighted means

reveal that secondary evaporation was particularly high during 1998, in keeping with a slightly higher annual mean temperature (14.9 °C) and a hotter summer. In 1998, all isotopic parameters were lower to much lower than in 1997 and 1999, this feature corresponding to a higher spring-summer to autumn-winter rainfall amount ratio.

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