Isotope Fractionation of Long Term Precipitation Averages in Ljubljana (Slovenia)

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Received: November 20, 2003 **Accepted:** December 22, 2003

Abstract: Variations of isotope fractionation in precipitation are described and the evaluation of obtained data is presented. The results express the seasonal changes of stable oxygen and hydrogen isotope composition, the tritium activity, temperature and vapour pressure in correlation to amount of rain and indicate the over ten years long period of climatic changes. The importance of knowledge about oxygen and hydrogen stable isotope fractionation processes to changes of climate is explained on the example of precipitations in Ljubljana during more than 15 years. The mean of 1332 mm of rain per year is found, the average measured temperature was 10.03 °C and 9.95 mbar of vapour pressure defined mean humidity. The weighted means in precipitations were calculated for $\delta^{18}O$ (-8.73 ‰) and for δD (-73.6 ‰). These made possible the evaluation of relevance of isotope fractionation in the climatic studies.

Keywords: precipitation, climatic changes, isotope composition, oxygen, tritium, temperature, Ljubljana

Introduction

Precipitations are the starting point of many interaction reactions that take place at the surface and underground. They consist of hydrogeochemical and biogeochemical processes and are involved in most of Earth's crustal events. They are indicators of climatic conditions too. Therefore the geochemical characteristics of meteoric water as well as it infiltration was studied very carefully (Rayleigh, 1896; Dansgaard, 1964; Epstein et al., 1970; Majzoub, 1971) long ago. The isotope methods are very successful (Edwards & Fritz, 1986; Ferronsky, 1983; Pezdič et al., 1996). Basic stable isotope correlation roles of water were defined more then 40 years ago by Craig (1961). International Atomic Energy Agency in Vienna has established a worldwide net of meteorological stations to collect rainwater for δD, $\delta^{18}O$ and T analysis as well as for temperature, water vapor pressure and precipitation amount measurements (IAEA, 1981, 1990, 2003). Gat (1981), Yurtsever & Gat (1981), Rozansky et al. (1992, 1993), Eriksson et al. (1983) evaluated these measurements to a great extent. Ljubljana has been a member of the IAEA worldwide precipitation net since 1981.

Geographical and climatic conditions

Slovenia lies in the southern part of Central Europe, more precisely at the juncture between the Alpine, Pannonian as well as in the Mediterranean climate diversities, with

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semi humid conditions. The most of rainwater precipitate from the western front waves that has source above the northern Atlantic Ocean. The southern part of area is significantly influenced by Mediterranean climate, while sometime continental climate influences reach Slovenia from the Russian plain too. So, the climate in Slovenia can be considered as a diversity of the most of Central European climate conditions. Ljubljana (14° 21' 42" E and 45° 53' 29" N, at altitude of 300 m, with ten years mean temperature 10.0 °C and 1332 mm of precipitation) is in the middle of these events. So, the importance of discussed data and conclusions from Ljubljana hydrometeorological station can be at least of Central European dimensions.

EXPERIMENTAL

Meteorological data (amount of precipitation, temperature and water vapor pressure) were obtained from the Environmental Agency of Slovenia (Agencija RS za okolje). Temperature and water vapor pressure were measured three times per day and averages have been calculated. The total month precipitations were collected in nontransparent plastic bottles. From the homogenized water samples for stable isotope and tritium analysis have been collected.

The δD and $\delta^{18}O$ were measured at the Jožef Stefan Institute, Ljubljana, and tritium (T) at the Ruđer Bošković Institute in Zagreb (HORVATINČIĆ ET AL., 1986). δD and $\delta^{18}O$ were analyzed on the Varian MAT 250 Mass spectrometer with modified standard methods (PEZDIČ, 1991, 1999) using oxygen exchange reaction with CO_2 to measure $\delta^{18}O$ and reduction of water on the hot zinc (490 °C) to obtain and measure hydrogen isotope composition. Tritium (T) was measured with a proportional counter (HORVATINČIĆ ET AL., 1986).

RESULTS AND DISCUSSION

Monthly averages of measured parameters. In Ljubljana, the isotope measurements of precipitation started in 1981. Presented data include the period from 1981 till 1996. Figure 1 shows some typical histograms of meteoric line dependence, variations of $\delta^{18}O$, tritium, temperature and partial vapor pressure. Distribution of δD vs. $\delta^{18}O$ is quite different for separate years. Also tritium shows an evident decrease (from 50 to 10 T.U.) during the period of decade. The monthly average temperatures range from -5 to 21 °C, with mean 10.03 °C and partial water vapor pressure varied between 5 and 18 mbar.

The typical years 1982, 1986 and 1994 are given as examples to present different climatic conditions in Ljubljana in last decades and consequently different characteristic isotope composition. Three correlations are given for individual year: δD vs. $\delta^{18}O$, month averages of 18-O, tritium, water vapor pressure (w.p.) and amount of precipitation per month. The symbols in Figures 1a, 1b and 1c mean as follow:

18-O	$\delta^{18}O$ – isotope composition of oxygen in water (‰)
Deuterium	δD – isotope composition of hydrogen in water (‰)
Tritium	tritium activity in T.U. (tritium units)
w.p.	water vapor pressure (mbar)
temper.	temperature in °C
precipitation	amount of precipitation per month

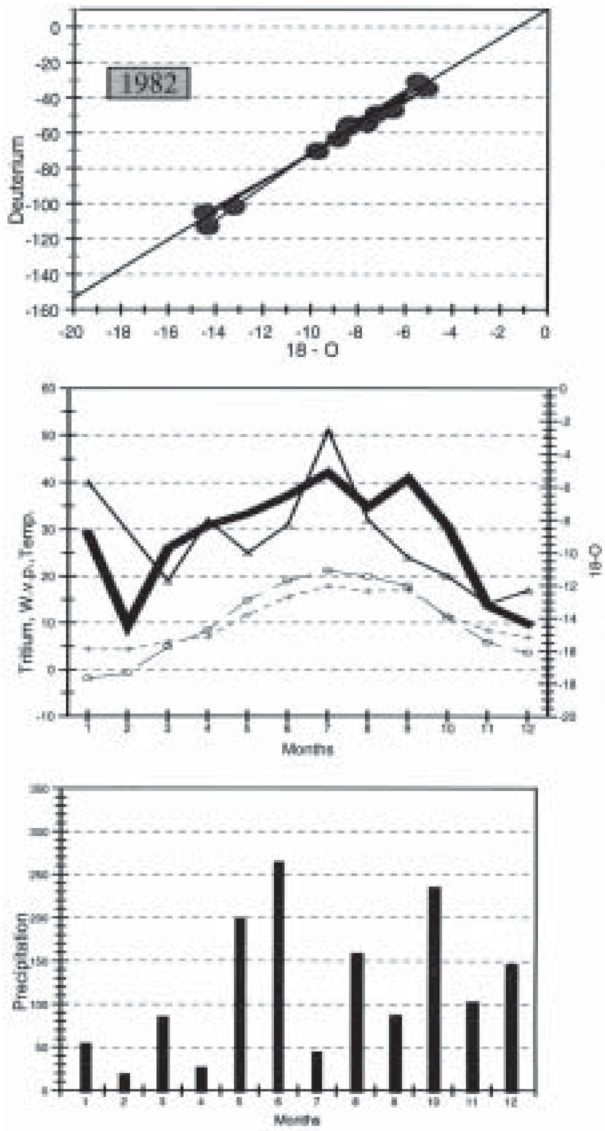

Figure 1a. Typical differences of the monthly averages of isotope composition, temperature, vapor pressure and precipitation amount in the year 1982 at the Ljubljana hydro-meteorological station. Meteoric line (large circles in first graph), $\delta^{18}O$ monthly averages (bold line), tritium month concentrations (normal line+triangle), water vapor pressure (thin line+plus) and temperature (thin line+crossline); monthly precipitation (columns in third graph).

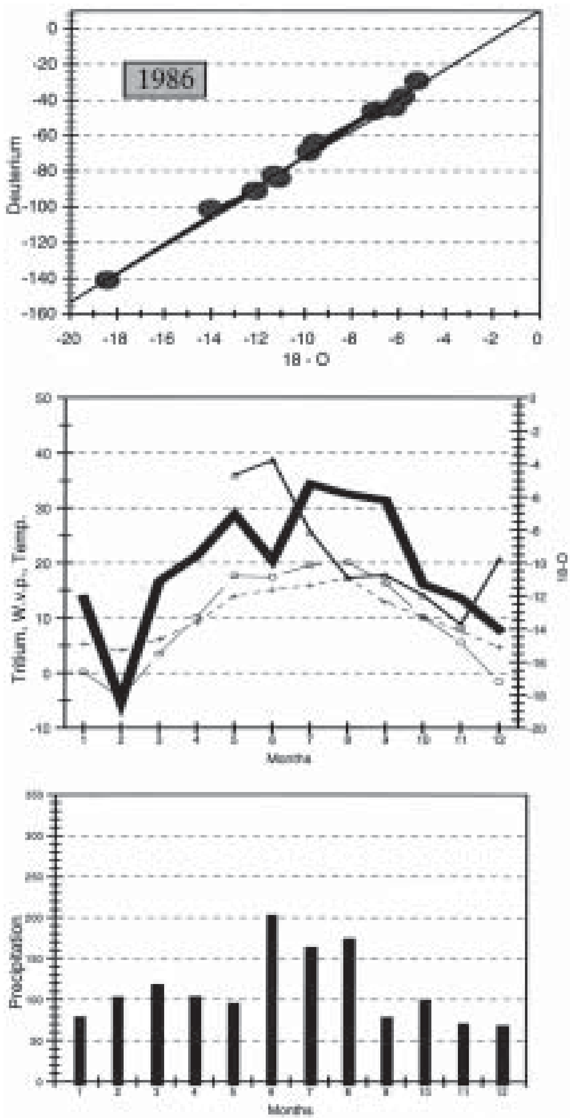

Figure 1b. Typical differences of the monthly averages of isotope composition, temperature, vapor pressure and precipitation amount in the year 1986 at the Ljubljana hydro-meteorological station. Meteoric line (large circles in first graph), $\delta^{18}O$ monthly averages (bold line), tritium month concentrations (normal line+triangle), water vapor pressure (thin line+plus) and temperature (thin line+crossline); monthly precipitation (columns in third graph).

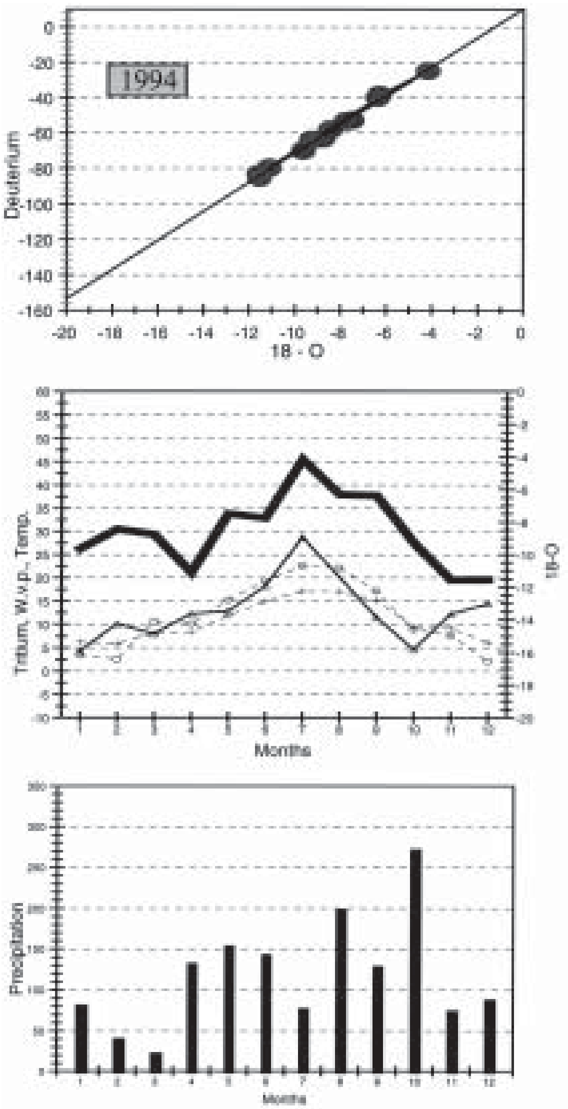

Figure 1c. Typical differences of the monthly averages of isotope composition, temperature, vapor pressure and precipitation amount in the year 1994 at the Ljubljana hydro-meteorological station. Meteoric line (large circles in first graph), $\delta^{18}O$ monthly averages (bold line), tritium month concentrations (normal line+triangle), water vapor pressure (thin line+plus) and temperature (thin line+crossline); monthly precipitation (columns in third graph).

The "Meteoric line" was constructed by Craig (1961) who established the correlation between $\delta^{18}O$ and δD with the theoretical values: $\delta D = 8 \cdot \delta^{18}O + 10$. In natural conditions constants values are very near to Craig's. The real meteoric line ($\delta D = S \cdot \delta^{18}O + d$) for particular region is calculated for each individual year (IAEA, 1990), and examples for Ljubljana precipitations (Figure 1) have "S" and "d" values as follows:

1982 $\delta D = 8.38 \cdot \delta^{18}O\ (\pm 0.30) + 11.08\ (\pm 3.20)$
1986 $\delta D = 8.25 \cdot \delta^{18}O\ (\pm 0.21) + 11.19\ (\pm 2.73)$
1994 $\delta D = 8.38 \cdot \delta^{18}O\ (\pm 0.22) + 10.62\ (\pm 1.68)$

Obtained constants indicate that climate influences of the Mediterranean vs. continental type are different for individual years. These data enable us to evaluate the yearly averages and weighted means for the entire period.

Yearly weighted means and averages. Because the sampling and data acquirement period lasted 15 years, the statistical treatment was quite possible. The oxygen isotope composition has a weighted mean of -8.73 ‰, but the data ranged from -9.72 to -7.65 ‰, which means for 2 ‰. Two cycles can be observed. Tritium content was decreasing over the whole period from 30 to 10 T.U., what did not permit to use the tritium activity as a natural geochronological parameter. The problem was solved with a correction line constructed by PEZDIČ ET AL. (1998). Temperature and so partial water vapor pressure slightly increased from 8.6 to 11.8 °C, what in the wider world dimension means a large change, which can change climate – and it is so in Slovenia and southern Central Europe (Figure 2 a. and b.).

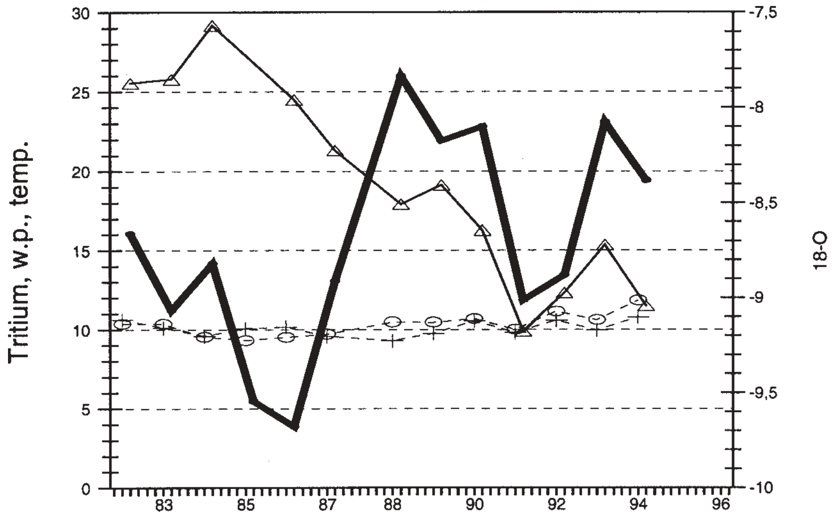

Figure 2. Twelve years variations of several parameters in precipitation at the Ljubljana Hydrometeorological station. a.) oxygen isotope compositions, tritium content, partial vapor pressure and temperature. (Tritium units are in T.U., water vapor pressure (w.p.) is in mbars and temperature is in °C, 18-O is in ‰); $\delta^{18}O$ monthly averages (bold line), tritium month concentrations (normal line+triangle), water vapor pressure (thin line+plus) and temperature (thin line+crossline); monthly precipitation (columns in third graph).

The long term "Meteoric line" for Ljubljana was calculated from monthly as well as from yearly weighted means for oxygen and hydrogen correlation. The monthly average line has following constants:

$\delta D = 8.19 \bullet \delta^{18}O\ (\pm 0.24) + 10.66\ (\pm 2.19)$ (Pezdič, 1991)

which fits very well to the worldwide (over 200 stations) "Meteoric line" calculated by Yurtsever & Gat (1981) and Rozanski et al. (1992):

$\delta D = 8.17 \bullet \delta^{18}O\ (\pm 0.08) + 10.55\ (\pm 0.64)$ (Yurtsever et al.)
$\delta D = 8.17 \bullet \delta^{18}O\ (\pm 0.07) + 11.27\ (\pm 0.65)$ (Rozanski et al.)

On the other hand the yearly means are shifted from the standard meteoric line:

$\delta D = 8.83 \bullet \delta^{18}O + 16.15$

It is quite difficult to interpret these differences, but because there are variations in single year's line for "S" from 8.08 to 8.38 and for "d" from 9.57 to 11.19, it is possible that the Mediterranean climate effect is more expressed in the yearly means. There is also the possibility that long term weighted means shift the calculated line.

Of the same interest is also the dependence between precipitation yearly sums and yearly mean $\delta^{18}O$ data. It is seen that there are two correlations expressed. The majority of data

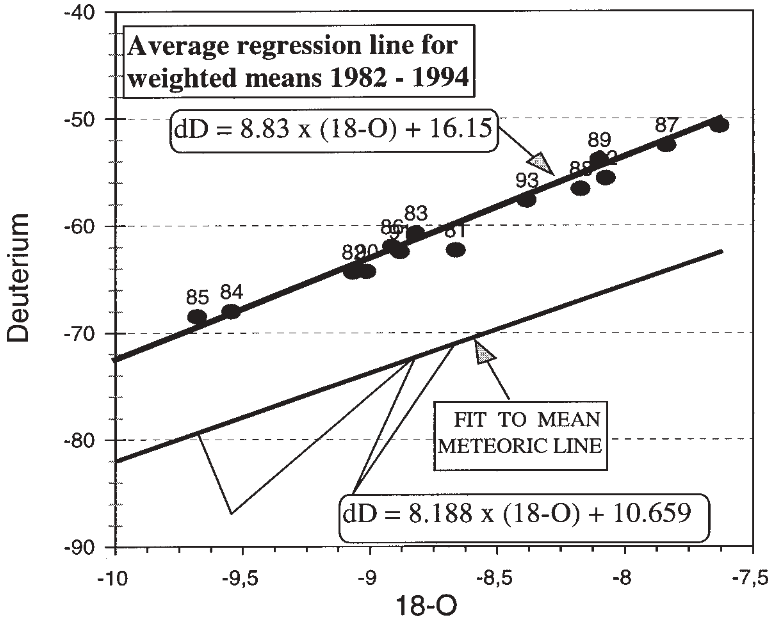

Figure 3. Incongruity between the standard "Meteoric line" $\delta D = 8.188 \bullet \delta^{18}O + 10.659$ for Ljubljana (1982-1994) and the Average regression line calculated from weighted yearly means of precipitations ($\delta D = 8.83 \bullet \delta^{18}O + 16.15$).

fit to main regression line, but the rest of results represent dry years, and so there is the reason for difference. Statistically the regression is highly significant. Perhaps it can't represent all climatic conditions, but for the region with mixing climate from the continental to the Mediterranean, it is an effective parameter.

The temperature function as dependence to $\delta^{18}O$ is calculated for the whole period.

$$\delta^{18}O = 0.25 (\pm 0.06) \cdot T + 10.78 (\pm 1.52)$$

The calculated temperature fits very well to the measured one.

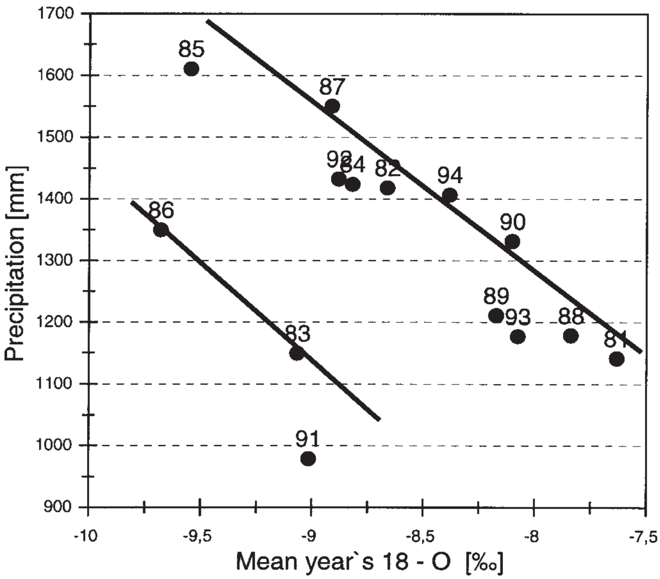

Figure 4. Dependence between mean yearly precipitation and weighted yearly means of oxygen stable isotope composition. Two regression lines can be calculated in the evaluated period of 15 years.

CONCLUSIONS

According to the data explained above the following main conclusions can be reached:

- The calculated monthly means "Meteoric line" of the period 1981 to 1996 for Ljubljana is very close to that representing by the worldwide meteoric stations.
- The meteoric line calculated from yearly means (n=13) differ from that of the weighted month means, having "S" = 8.83 and "d" = 16.15. It is evidently seen that yearly means for oxygen varied from -9.7 to -7.65 ‰ and show significant dependence to the humidity. Weighted mean for the whole period is -8.73 ‰ for oxygen and -60.6 ‰ for hydrogen.
- The yearly average tritium content decreased from the beginning of study from 30 to 10 T.U., while temperature increased from 8.6 to 11.8 °C. Especially the temperature increase of more than 3 °C affect the climate.

- The monthly mean meteoric line is similar to the worldwide one, while the yearly means regression line (Figure 3) indicate a positive shift from the standard meteoric line (Craig, 1961). It is probably due to the Mediterranean climate effect expressed to a greater extent as it is seen in the worldwide dimensions.
- The correlation between yearly amounts of precipitation against weighted means of oxygen isotope composition is evident (n=13) and only 3 points are not fitted to the main regression line. But there is explanation - they belong to years with especially dry conditions.

Acknowledgements

Many thanks to Silva Perko and Zdenka Trkov for appropriate collecting of water samples and exact measurements of stable isotope composition at J. Stefan Institute. Thanks to Nada Horvatinčić and Ines Krajcar-Bronić for tritium data, which took place within the scientific co-operation between the Ruđer Bošković Institute and the Jožef Stefan Institute. It is also my honour to thanks the staff of the Hydrometeorological Survey (now Environmental Agency) of Slovenia for the precipitation amount data, as well as for temperature and water vapor pressure data used in the present paper.

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Izotopske spremembe v povprečnih dolgoletnih padavinah (Ljubljana, Slovenija)

Povzetek: Prikazano je spreminjanje izotopske sestave v padavinah in opisana obdelava dobljenih podatkov. Rezultati kažejo sezonske spremembe izotopske sestave kisika in vodika, aktivnosti tritija, temperature in parcialnega tlaka vodne pare (vlažnost) glede na količino padavin in nakazujejo dolgo letne (več kot deset let) klimatske spremembe. Pomembnost poznavanja procesov izotopske frakcionacije stabilnih izotopov kisika in vodika pri spreminjanju klime je obrazložen na primeru padavin v Ljubljani za obdobje več kot 15 let. Tu je na leto padlo povprečno 1332 mm padavin, koncentracija tritija je bila 17,5 T.U., povprečna petnajstletna temperatura je bila 10,03 °C in vlažnost 9,95 mbar. Srednje vrednosti so bile izračunane še za d^{18}O (-8,73 ‰) in dD (-73,6 ‰). Vse to je omogočilo opredeliti pomembne lastnosti izotopske frakcionacije pri študiju klimatskih sprememb.

Ključne besede: padavine, spremembe klime, izotopska sestava, kisik, tritij, temperatura, Ljubljana