Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Tritium and stable isotope variations in precipitation of Croatia and Slovenia

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Monitoring of isotope composition (^{2}H, ^{3}H, ^{18}O) of monthly precipitation at Zagreb (Croatia, 157 m a.s.l.) and Ljubljana (Slovenia, 299 m a.s.l.) has been performed since 1976 and 1980, respectively (Krajcar Bronić et al., 1998) within the Global Network for Isotopes in Precipitation (GNIP) organized jointly by the Isotope Hydrology Section of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). The GNIP network includes also monitoring of meteorological data (amount of precipitation, mean air temperature, mean atmospheric water vapour pressure) on monthly basis (IAEA, 2004). The type of climate at the two stations is continental, with yearly amount of precipitation of 883 mm (yearly mean for 30-year period) and 1394 mm, and mean yearly temperature 11.4°C and 9.8°C, in Zagreb and Ljubljana, respectively.

Within the IAEA Co-ordinated Research Program "Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate" the network has been extended to several stations along the Adriatic coasts of Croatia and Slovenia in the period between September 2000 and December 2003: Portorož-Airport (2 m a.s.l., 13.1°C, 911 mm) and Kozina (497 m a.s.l., 1511 mm) in Slovenia, and in Croatia Malinska on Krk Island (1 m a.s.l., 14.8°C, 1306 mm), Zadar (5 m a.s.l., 15.9°C, 937 mm), Komiža on Vis Island (6 m a.s.l., 17.6°C, 706 mm), Dubrovnik (52 m a.s.l., 17.2°C, 1092 mm), and Zavižan on Mt. Velebit (1594 m a.s.l, 4.3°C, 2113 mm/year). The sampling sites are characterized by different types of climate (continental and Mediterranean, or mixing influence) and the corresponding mean monthly temperatures and mean yearly precipitation amounts for the same period are given above in parentheses. The lowest mean tem-

perature and highest amount of precipitation were recorded at Zavižan. Marine stations at southern Adriatic show higher mean temperatures than the continental stations, while at the North Adriatic mean temperature lies between the continental and marine values.

Long-term tritium records for stations Zagreb and Ljubljana show that in the past mean yearly tritium activity concentration in precipitation continuously decreased after reaching a global atmospheric maximum in 1963 due to thermonuclear bomb-tests in mid-20th century (Krajcar Bronić et al., 1998). The observed seasonal variations are typical for the continental stations of the Northern Hemisphere with winter minima approaching in the last years the natural pre-bomb tritium level (≤0.4 Bq/L). Maxima are observed in early summer, and reach presently up to 2.1 Bq/L. The seasonal variations in the last decade were less pronounced than in the period 1976 – 1990. Thus, mean yearly tritium concentrations in Zagreb and Ljubljana precipitation during the last decade are ~1.1 Bq/L.

Tritium activity distribution at the north Adriatic coast is similar to that at the continental stations, showing just slightly lower mean values. Seasonal variations at maritime stations of mid-Adriatic and especially of south-Adriatic 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 - mean tritium activities in precipitation in Zadar, Komiža and Dubrovnik are equal to 0.75 Bq/L, 0.70 Bq/L and 0.46 Bq/L, respectively. Tritium distribution pattern and the mean tritium concentration at Zavižan (0.78 Bq/L) are closer to those of the Mediterranean stations in the vicinity than to those of the continental stations. Tritium activity concentrations in monthly precipitation at all three stations in Slovenia vary seasonally from ≤0.4 to 2.2 Bq/L and are typical for the continental stations of Northern Hemisphere.

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‰ in $\delta^{18}O$ at stations Zagreb and Ljubljana), compared with the maritime stations (*e.g.*, 11.6‰ and 8‰ at stations Komiža and Dubrovnik, respectively) due to larger temperature differences in summer and winter. At the high-altitude station Zavižan on Mt. Velebit the two types of climate, the Mediterranean and the cold continental one, 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 (seasonal variations in $\delta^{18}O$ equal to 13.7‰).

Correlation of $\delta^{18}O$ with mean monthly temperature is good for all stations. The long-term (1976-2001) slope of the correlation line for Zagreb is 0.3‰ $\delta^{18}O$ per °C. Similar values are obtained for north- and mid-Adriatic stations, while for the south-Adriatic stations the slope is 0.15‰ $\delta^{18}O$ per °C. For the coldest Zavižan station the slope is 0.4‰ $\delta^{18}O$ per °C.

The correlation between $\delta^{18}O$ and $\delta^{2}H$ is very good for each station and obtained data fit well to the "Global Meteoric Water Line", $\delta^{2}H = 8\ \delta^{18}O + 10$. Some deviations were observed in summer months and are probably a result of partial evaporation of raindrops. However, a detailed inspection shows that the slope is higher (close to 8) for the continental stations and Zavižan, while the maritime stations have smaller slope (about 7). The mean values of deuterium excess ($d = \delta^{2}H - 8\ \delta^{18}O$) are also different: 13 for Zavižan, ~7.5 for Zagreb and Ljubljana, and between 7 and 9 for mid- and south-Adriatic stations. Higher monthly values of *d*-excess (above 12) were also occasionally observed and can be attributed to precipitation from the Mediterranean Sea.

As the station differ in their altitudes, it is possible to estimate the so-called altitude effect for the region. For the continental stations the decrease of 0.37‰ $\delta^{18}O$ per 100 m altitude difference is obtained, while for the stations in the coastal region (including Zavižan) the decrease is 0.26‰ $\delta^{18}O$ per 100 m altitude difference.

The presented data shows present-day temporal and spatial distribution of tritium and stable isotopes ^{2}H and ^{18}O in precipitation of a relatively small area rich in climatic diversity. The data can be used in various applications, such as climatology and hydrology.

Acknowledgement The work performed under the IAEA Research Contracts RC11265 and RC11267, the Project 0098014 by the Ministry of Science, Republic of Croatia, and the project of bilateral co-operation "Isotopes in precipitation" between Croatia and Slovenia.

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