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DISTRIBUTION OF HYDROGEN, OXYGEN AND CARBON ISOTOPES IN THE ATMOSPHERE OF CROATIA AND SLOVENIA*

Ines KRAJCAR BRONIĆ¹, Polona VREČA², Nada HORVATINČIĆ¹, Jadranka BAREŠIĆ¹,
and Bogomil OBELIĆ¹

Ruder Bošković Institute, Zagreb, Croatia¹, Jožef Stefan Institute, 1000 Ljubljana, Slovenia²

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Monitoring of isotope distribution in the atmosphere included isotopes ²H, ³H and ¹⁸O in precipitation, and ¹³C and ¹⁴C in atmospheric CO₂. This paper presents the results of atmospheric monitoring over Croatia and Slovenia over the last few years.

Monthly precipitations in Zagreb and Ljubljana had been collected since 1976 and 1981, respectively. Between 2000 and 2003 monitoring also included seven stations along the Adriatic coast. Tritium activity in precipitation shows seasonal variations that were most pronounced inland (at the continental stations Zagreb and Ljubljana) and were the smallest in the south Adriatic (Komiža and Dubrovnik). Mean annual tritium activity decreases from the north to the south Adriatic coast. Seasonal variations in δ²H and δ¹⁸O in precipitation follow the temperature variations at the sampling stations.

Atmospheric CO₂ was collected in Zagreb and Plitvice as a composite monthly sample. Both Δ¹⁴C and δ¹³C showed seasonal variations. The mean annual ¹⁴C activities in Zagreb had been decreasing after the peak reached in the 1960s, and for the last three years the mean ¹⁴C activity (Δ¹⁴C) remained about 30 ‰.

KEY WORDS: *atmosphere, CO₂, ¹³C, ¹⁴C, ²H, ³H, ¹⁸O, precipitation, stable isotopes, tritium*

Atmospheric water vapour and carbon dioxide are important greenhouse gases that play a major role in regulating global climate (1). Natural water and carbon cycles can be studied by monitoring isotopic composition of water and atmospheric CO₂. Isotopic composition of a water molecule is characterised by the content of stable isotopes oxygen-18 (¹⁸O) and deuterium (²H) and the radioactive isotope tritium (³H), while CO₂ is characterised by the content of the carbon isotopes (stable isotope ¹³C and radioactive isotope ¹⁴C). Knowledge about the seasonal and spatial distributions of these isotopes in the atmosphere is of great importance for studying the processes of atmospheric circulation (1, 2) and climate changes

with palaeoclimatic implications, as well as in isotope hydrology (3) and in predictions of climate trends.

The Laboratory for Measurements of Low-level Radioactivity of the Ruđer Bošković Institute has been measuring radioactive isotopes ³H and ¹⁴C in various types of samples for more than 35 years and stable isotopes ²H, ¹³C, and ¹⁸O are measured in the Department of Environmental Sciences of the Jožef Stefan Institute. Both laboratories are taking part in international environmental and atmospheric monitoring programmes. A part of monitoring results has been presented at the previous symposia of the Croatian Radiation Protection Association (4-7) and this paper brings the new findings of isotopic

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composition in the atmosphere (water and CO_2) monitored over Croatia and Slovenia from 2000 to 2004. These results are compared with the previous long-term data (8).

SAMPLING AND MEASUREMENTS

Monthly precipitation samples at stations in Zagreb and Ljubljana had been collected continuously since 1976 and 1981, respectively. The stations have been a part of the international network for monitoring isotopic composition of precipitation, Global Network for Isotopes in Precipitation (GNIP), which was established by the International Atomic Energy Agency (IAEA) and World Meteorological Organisation (WMO) in 1963 (9). In 2000-2003, the sampling of monthly precipitation also included seven stations along the Adriatic coast of Croatia and Slovenia (10, 11) and in 2003 Plitvice Lakes National Park in Croatia.

Monthly samples of atmospheric CO_2 had been collected in Zagreb since 1985 and in Plitvice Lakes since 2003. Samples were collected by exposing to the open atmosphere about 100 mL of saturated carbonate-free sodium hydroxide solution in a tray protected by a wire-mesh. After one month exposure the sample was obtained as sodium carbonate.

The activity concentrations of radioactive isotopes ^3H and ^{14}C were measured using gas proportional counters with methane as the counting gas. For ^3H measurement, methane was obtained in the reaction of water with Al_4C_3 at 150°C (12). Tritium activity concentration is expressed in Bq L^{-1} , which corresponds to the so-called Tritium Unit (TU, $1 \text{ TU} = 0.12 \text{ Bq L}^{-1}$), often used in hydrological applications by IAEA (9). For ^{14}C measurement, sodium carbonate was dissolved by HCl, and the obtained and purified CO_2 was then catalytically converted to methane. The results of ^{14}C activity concentrations are expressed as $\Delta^{14}\text{C}$ (in ‰), i.e., as a deviation from ^{14}C activity in the undisturbed atmospheric equilibrium that equals 0.226 Bq g^{-1} of carbon (13).

Stable oxygen and hydrogen isotopes were measured on a Varian MAT 250 mass spectrometer. The isotopic composition of oxygen ($\delta^{18}\text{O}$) was determined by the equilibration of CO_2 with water samples (14), and the isotopic composition of hydrogen ($\delta^2\text{H}$) was measured on H_2 generated by reduction of water over hot chromium (15). Results are

reported as $\delta^{18}\text{O}$ and $\delta^2\text{H}$, i.e., as relative deviations in per mil (‰) from the V-SMOW standard. Measurement reproducibility of duplicates was better than ± 0.1 ‰ for $\delta^{18}\text{O}$ and ± 1 ‰ for $\delta^2\text{H}$.

Isotopic composition of sodium carbonate ($\delta^{13}\text{C}$) was determined on CO_2 collected after reaction of sample with 100 % H_3PO_4 on a continuous flow Europa 20-20 ANCA-TG stable isotope mass spectrometer. Results are expressed as relative deviations in per mil (‰) from the V-PDB standard. Measurement reproducibility of duplicates was better than ± 0.2 ‰.

RESULTS AND DISCUSSION

Tritium

Figure 1 shows tritium activity concentration in monthly precipitation measured at continental stations in Zagreb, Ljubljana, and Plitvice, and at the north-Adriatic stations in Portorož, Kozina, and Malinska. All

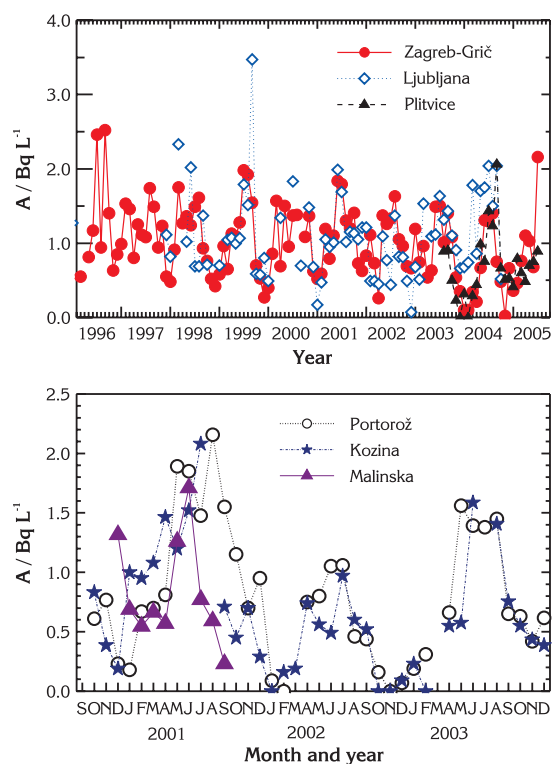


Figure 1 Tritium activity concentration in monthly precipitation at the continental stations in Zagreb, Ljubljana, and Plitvice in 1996-2005, at the north Adriatic stations in Portorož, Kozina, and Malinska in October 2000 – December 2003.

stations show similar seasonal variations, typical for the continental stations of the Northern Hemisphere (1): ³H activity shows maximum in early summer (about 2.2 Bq L⁻¹ during last several years), and minimum in winter, which approaches the natural tritium activity concentration of the atmosphere before atmospheric thermonuclear bomb-tests (1949-1963). Seasonal variations in 1976-1990 (5, 6, 8) were much more pronounced, and average annual ³H activity in precipitation decreased continuously after the maximum reached in 1963 (9). Our records show that in Zagreb in 1976 the lowest ³H activity was 3.0 Bq L⁻¹ and the highest 22.6 Bq L⁻¹, with the mean 14.3 Bq L⁻¹. In 1984 the lowest and the highest activities were 1.0 Bq L⁻¹ and 5.0 Bq L⁻¹, respectively, with the mean 2.5 Bq L⁻¹. In 1995 they were 0.6 Bq L⁻¹ and 2.8 Bq L⁻¹, respectively, with the mean 1.6 Bq L⁻¹. For the last decade, the average tritium activity concentration in inland Croatia and Slovenia has kept around 1 Bq L⁻¹ and has not shown any significant decrease.

Sampling stations in the central and south Adriatic (Zadar, Komiža, Dubrovnik) as well as the

station Zavižan on Mt Velebit show less pronounced seasonal variations (Figure 2), and their mean annual tritium activities are lower (0.39 Bq L⁻¹ in Dubrovnik and 0.75 Bq L⁻¹ in Zadar and Zavižan) than at the continental stations inland. Mean ³H activity in precipitation decreases along the Adriatic coast from the northwest to the southeast. Since the mean temperature increases in the same direction (10, 11) the decrease of tritium activity may be related to increased evaporation of seawater. Due to the effect of seawater evaporation, the correlation in tritium activity between any two central and south Adriatic stations is poor (correlation coefficient $r < 0.4$). Tritium activities measured at the inland and north Adriatic stations show good correlation ($r > 0.6$), while the correlation coefficient between Zagreb and other stations decreases in a southeast direction.

¹⁸O and ²H

Figure 3 shows the seasonal distribution of $\delta^{18}\text{O}$ in monthly precipitation for all sampling stations, including the long-term mean monthly $\delta^{18}\text{O}$ measured at the two GNIP stations (8). Seasonal variations with lowest values in winter (January) and highest in summer (July) reflect the temperature dependence of $\delta^{18}\text{O}$ in precipitation. Therefore, the largest differences between summer and winter $\delta^{18}\text{O}$ (13 ‰) are observed at the continental stations, where the differences in mean monthly air temperatures between July and January are also the largest (21 °C). Seasonal variations in mean monthly air temperatures (15.6 °C) and in $\delta^{18}\text{O}$ (8 ‰) are the smallest at the south Adriatic stations. At the altitude of 1594 m, the station Zavižan on Mt Velebit shows the lowest mean annual temperature (4.1 °C) and the lowest mean $\delta^{18}\text{O}$ (-9.3 ‰). Therefore, $\delta^{18}\text{O}$ in monthly precipitation correlates well with the mean monthly air temperatures for all sampling stations ($r > 0.7$ at all stations, Figure 4). However, the slope of $\delta^{18}\text{O}$ vs. T dependence is different for different stations, and it decreases as the mean annual temperature increases. The highest slope of the $\delta^{18}\text{O}$ vs. T relation was obtained for the station of Zavižan (0.37 ‰ per °C), followed by Zagreb (0.33 ‰ per °C) and Ljubljana (0.30 ‰ per °C), and finally the slope was the smallest for the south Adriatic stations (Dubrovnik, 0.15 ‰ per °C).

²H variations in monthly precipitation follow those of $\delta^{18}\text{O}$. Its values range from -127 ‰ to -20 ‰ at the inland stations and Zavižan, from -100 ‰ to -17 ‰ at the north Adriatic stations, and from -90 ‰ to 0 ‰

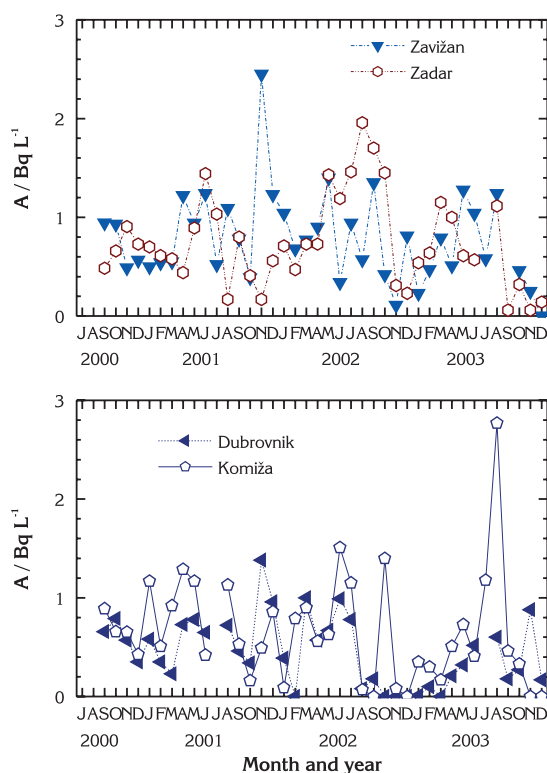


Figure 2 Tritium activity concentration in monthly precipitation in Zadar (central Adriatic) and Zavižan (Mt Velebit), and the south Adriatic stations (Dubrovnik, Komiža on the Island of Vis) in September 2000 – December 2003.

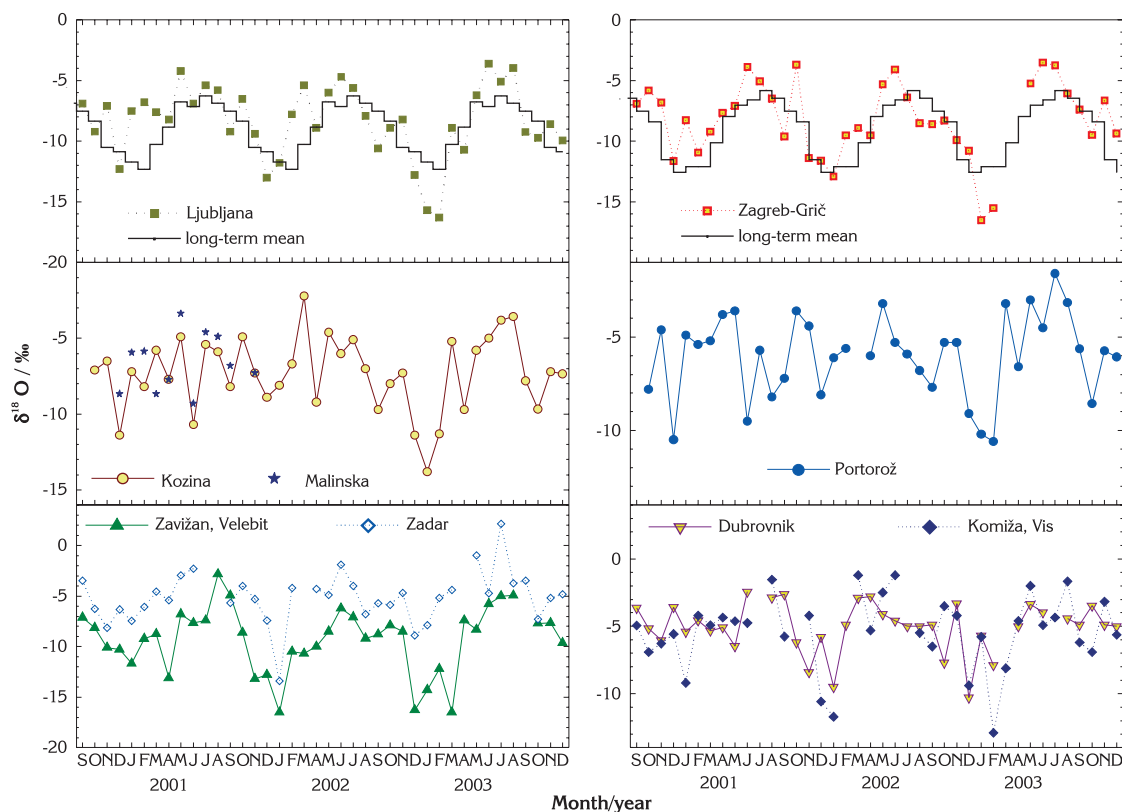


Figure 3 $\delta^{18}\text{O}$ in monthly precipitation between September 2000 and December 2003. Long-term mean monthly values are shown for stations in Zagreb and Ljubljana.

at the south Adriatic stations. Therefore, the range of $\delta^2\text{H}$ values is determined by seasonal changes in the air temperature. Mean annual $\delta^2\text{H}$ increases along the coast from the northwest (-50 ‰) to the southeast (-33 ‰).

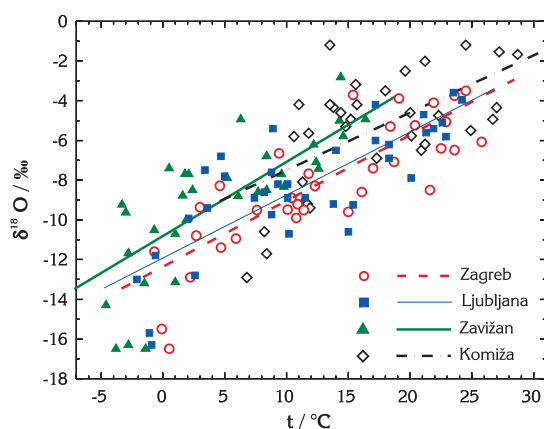


Figure 4 Relation between $\delta^{18}\text{O}$ in monthly precipitation and the mean monthly air temperature. Symbols: monthly data, lines: regression lines.

The relation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ on the global scale can be described by the so-called Global Meteoric Water Line (GMWL), whereby $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ (16). However, the $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ relation for local precipitation may differ from the GMWL. For example, Local Meteoric Water Line (LMWL) for Zagreb is $\delta^2\text{H} = 7.7 \delta^{18}\text{O} + 4.5$ ($r = 0.98$, $n = 270$). LMWLs for the south Adriatic stations have lower slopes (< 7) and intercepts (< 5) due to higher temperatures and possible evaporation of raindrops (3, 10, 11), but the correlation is still very good ($r > 0.9$).

^{14}C and ^{13}C

^{14}C activity ($\Delta^{14}\text{C}$) in the atmospheric CO_2 shows seasonal variations at the sampling sites in Zagreb and Plitvice in 2000-2004 (Figure 5); in the winter it is lower than in the summer as a consequence of fossil fuel combustion mainly for heating. Fossil fuels (charcoal, oil) do not contain ^{14}C , and their $\delta^{13}\text{C}$ content is depleted (more negative) when compared to that of the atmosphere, so the use of fossil fuels increases CO_2 concentration in the atmosphere, but

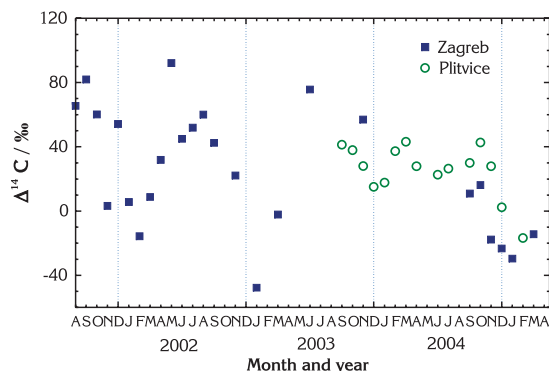


Figure 5 ^{14}C activity ($\Delta^{14}\text{C}$) of the atmospheric CO_2 in 2002-2005 in Zagreb and Plitvice Lakes.

decreases the concentration of ^{14}C ($\Delta^{14}\text{C}$) and changes the atmospheric $\delta^{13}\text{C}$ towards more negative values. In Zagreb, monthly $\Delta^{14}\text{C}$ ranges between -30‰ in the winter and $+92\text{‰}$ in the summer, and in Plitvice between 0‰ and $+50\text{‰}$. Lower winter $\Delta^{14}\text{C}$ values in the atmosphere of highly populated city of Zagreb indicate local contamination with fossil fuels. Mean annual $\Delta^{14}\text{C}$ in the last 3 years was about 30‰ , which is close to the natural ^{14}C activity ($\Delta^{14}\text{C} = 0\text{‰}$) of the atmosphere before thermonuclear bomb-tests and other anthropogenic influences (2, 7, 8). Anthropogenic activities after the World War II led to an increase in the atmospheric $\Delta^{14}\text{C}$ activity that reached a maximum of almost 1000‰ in 1963. After the atmospheric test ban treaty in 1963, mixing of the atmosphere with other carbon reservoirs (oceans and terrestrial biosphere) led to a decrease in the atmospheric ^{14}C activity (2).

$\Delta^{14}\text{C}$ in the atmosphere had continuously been decreased since our measurement started (8); in 1986 the lowest $\Delta^{14}\text{C}$ in Zagreb in the winter was 120‰ and the highest in the summer was 232‰ (mean annual value 172‰), while in 1995 the corresponding $\Delta^{14}\text{C}$ values were 35‰ and 147‰ with the mean 88‰ .

Measured $\delta^{13}\text{C}$ values in the same samples of atmospheric CO_2 ($\delta^{13}\text{C}$ in the range from -28‰ to -22‰) are much lower than the usual $\delta^{13}\text{C}$ of the atmospheric CO_2 (-8‰), which can be due to the sampling procedure, *i.e.*, sampling of the air on a highly alkaline medium (17). However, seasonal variations of $\delta^{13}\text{C}$, with lower $\delta^{13}\text{C}$ in the winter, corroborate our belief that fossil fuel combustion affects the atmospheric CO_2 isotopic composition.

CONCLUSIONS

Our results have given us an idea about the natural temporal and spatial distribution of isotopes

constituting the water molecule (^2H , ^3H , ^{18}O in precipitation) and CO_2 molecule (^{14}C and ^{13}C in atmospheric CO_2). The data present current status of these isotopic parameters of the atmosphere.

The studied area is relatively small, but rich in variety of geographic and climatic properties, making it possible to study the influence of different parameters (air temperature, amount of precipitation, altitude, seawater evaporation) on the atmospheric isotopic composition. The obtained data can be used as input data for modelling water and CO_2 cycles in natural environment, or as natural (local) markers of groundwater in different regions of Croatia and Slovenia. In addition, the obtained isotopic data have an important application in meteorological and climatologic studies, especially in the areas where air masses of different origin mix, such as the Adriatic coast where the air masses of the western Atlantic and southeastern Mediterranean mix. The monitoring of different isotopes in the atmosphere can also help in the investigations of anthropogenic influence on the atmospheric composition and may reveal increased activities of ^3H and ^{14}C that might be caused by regular operation of various nuclear facilities or by nuclear accidents.

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Sažetak

RASPODJELA IZOTOPA VODIKA, KISIKA I UGLJIKA U ATMOSFERI HRVATSKE I SLOVENIJE

Praćenje izotopnog sastava atmosfere uključuje praćenje izotopa ²H, ³H i ¹⁸O u oborinama te ¹³C i ¹⁴C u atmosferskom CO₂. U ovom su radu prikazani rezultati takvog monitoringa u atmosferi iznad Hrvatske i Slovenije za razdoblje 2000. – 2004., koji su uspoređeni s podacima dugogodišnjeg monitoringa izotopnog sastava atmosfere u Zagrebu.

Mjesečne oborine u Zagrebu i Ljubljani skupljaju se od 1976., odnosno 1981. godine. U razdoblju 2000. – 2003. skupljale su se mjesečne oborine i na 7 postaja duž jadranske obale. Koncentracija aktivnosti tricija u oborinama pokazuje sezonske varijacije koje su najizraženije na kontinentalnim postajama (Zagreb, Ljubljana), a najmanje na postajama južnog Jadrana (Komiža, Dubrovnik). Prosječna godišnja koncentracija aktivnosti tricija opada od sjevera prema jugu jadranske obale. Sezonske varijacije δ²H i δ¹⁸O u oborinama slijede sezonske promjene srednje mjesečne temperature te su određene korelacije između mjesečnih δ¹⁸O u oborinama i srednjih mjesečnih temperatura za sve postaje.

Atmosferski CO₂ skuplja se u mjesečnim intervalima na postajama u Zagrebu i na Plitvičkim jezerima. Opažene su sezonske varijacije u koncentraciji obaju ugljikovih izotopa, tj. u Δ¹⁴C i δ¹³C, zbog povećane potrošnje fosilnih goriva (nafta, ugljen) tijekom zimskih mjeseci. Srednje godišnje aktivnosti ¹⁴C u atmosferskom CO₂ na području Zagreba pokazuju stalan pad aktivnosti nakon maksimalnih vrijednosti šezdesetih godina prošlog stoljeća (koje su bile uzrokovane atmosferskim nuklearnim eksplozijama). Tijekom posljednje 3 godine srednja godišnja ¹⁴C aktivnost (Δ¹⁴C) iznosi oko 30 ‰.

KLJUČNE RIJEČI: *atmosferski CO₂, ¹³C, ¹⁴C, ²H, ³H, ¹⁸O, oborine, stabilni izotopi, tricij*

REQUESTS FOR REPRINTS:

Ines Krajcar Bronić, Ph. D.
Ruđer Bošković Institute
Bijenička c. 54, HR-10000 Zagreb, Croatia
E-mail: krajcar@irb.hr