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Comparison of monthly and daily isotopic composition of precipitation in south-western Slovenia

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Introduction

Precipitation is of major interest in the hydrologic cycle as it is the ultimate source of water to catchments. The terrestrial portion of the hydrologic cycle begins when the precipitation reaches the ground. Therefore, the understanding of the formation of precipitation, as well as knowledge of temporal and spatial variations in the amount and mode of precipitation are important for basin-wide balance studies. Similarly, understanding how isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) is controlled by the formation of precipitation and knowledge of the temporal and spatial variations in isotopic composition of precipitation are equally important. Within the Global Network of Isotopes in Precipitation (GNIP) organised by IAEA and WMO worldwide monitoring of isotopes in precipitation is performed. The GNIP database is thus extremely valuable for modelling of climatic changes as well as in hydrological and hydrogeological investigations.

Monitoring of isotopes in monthly precipitation has been performed at continental sampling station in Ljubljana (Slovenia) since 1981 within the GNIP (Vreča et al., 2006). In the framework of IAEA Co-ordinated Research Program "Isotopic Composition of Precipitation in the Mediterranean Basin in Relation to Air Circulation Patterns and Climate" the monitoring program was extended to two additional sampling stations in south-western, Mediterranean region of Slovenia in October 2000 (Vreča et al., 2005). In this study, we present 1-year long monthly, as well as daily records of isotopic composition in precipitation together with meteorological data from two stations in Slovenian Mediterranean region.

Sampling and analyses

Samples were collected from October 2002 till September 2003 at coastal station Portorož Airport (45°28’N, 13°37’E) and at station close to the coast in Kozina (45°36’N, 13°56’E). Monthly composite precipitation sample was collected in a rain gauge with diameter of 16 cm. Daily samples were collected in the morning after precipitation event in a rain gauge with a diameter of 54 cm. Meteorological data (precipitation amount and temperature) were obtained from the Environmental Agency of Republic of Slovenia for station at Portorož Airport, while for Kozina only data on precipitation amount were available.

The stable isotopic composition of water samples was measured on a dual inlet Varian MAT 250 mass spectrometer at the Jožef Stefan Institute and on a continuous flow Finnigan DELTA^{plus} XP mass spectrometer with a HEKAtech high-temperature oven at Institute of Institute of Water Resources Management (WRM). The oxygen isotopic composition ($\delta^{18}O$) was measured by means of the water-CO_2 equilibration technique, and the isotopic composition of hydrogen (δ^2H) was performed using H_2 generated by reduction of water over hot chromium. Measurement reproducibility of duplicates was better than ±0.05‰ for $\delta^{18}O$ and ±1‰ for δ^2H.

Results and discussion

Stable isotopic composition of precipitation varies considerably at both sampling stations. In monthly collected samples $\delta^{18}O$ values vary between –10.6 and –1.6‰ (mean -5.7‰) at Portorož Airport, and between –13.8 and –3.6‰ (mean -7.7‰) in Kozina. δ^2H values vary between –80 and –8‰ (mean -36‰)at Portorož Airport, and between –102 and –23‰ (mean -50‰)in Kozina. The highest values are observed at the coastal station at Portorož Airport and lower, due to continental and altitude effect, at Kozina. Obtained data fit very well to the Craig’s Global Meteoric Water Line (GMWL) however some deviations were observed in summer months at Portorož Airport and are probably a result of partial evaporation of raindrops (Table 1). *d-excess* values vary between 3 and 19‰ (mean 10‰) at Portorož Airport, and between 4 and 18‰ (mean 12‰) in Kozina. The lowest values were observed during May and August, respectively. The comparison of obtained stable isotopic data with precipitation amount showed no significant correlation. In contrast, significant correlation between stable isotopic data and air temperature was observed at Portorož Airport.

Table 1. Local meteoric water lines for Portorož Airport and Kozina.

Portorož Airport (monthly)	$\delta^2H = 7.4\ \delta^{18}O + 6.2$	r= 0.97
Portorož Airport (daily)	$\delta^2H = 6.7\ \delta^{18}O – 0.6$	r= 0.95
Kozina (monthly)	$\delta^2H = 7.8\ \delta^{18}O + 10.0$	r= 0.98
Kozina (daily)	$\delta^2H = 7.8\ \delta^{18}O + 7.9$	r= 0.98

Considerable daily variations in stable isotopic composition were observed during observation period. $\delta^{18}O$ values vary between –14.9 and +3.5‰ (mean -4.5‰) at Portorož Airport, and between –17.5 and +1.2‰ (mean -7.1‰) in Kozina. δ^2H values vary between –112 and +8‰ (mean -31‰) at Portorož Airport, and between –134 and +3‰ (mean -47‰) in Kozina. *d-excess* values vary between -20 and 27‰ (mean 5‰) at Portorož Airport, and between -16 and 26‰ (mean 10‰) in Kozina. Higher values were observed at the start of precipitation event and decreased during precipitation event. Obtained data fit well to the GMWL at Kozina while at Portorož Airport the influence of evaporation during extremely warm period (spring-summer 2003) is reflected in data below the GMWL (Table 1).

Furthermore, mean monthly amount-weighted isotopic composition was calculated from individual daily data and compared to results obtained for individual monthly samples (Table 2). The differences between both set of results could be attributed to:

1) difference in precipitation amount of monthly sample and daily collected samples (e.g. not all daily samples were collected in December 2002, January, March and April 2003);

2) position of sampling rain gauges (approx. 10-20 m apart);

3) different diameter of sampling rain gauges;

4) evaporation effect during extremely warm and dry year 2003 (e.g. July 2003 at Portorož Airport).

Table 2. Comparison of isotopic composition of monthly collected samples (m) and monthly isotopic composition calculated amount-weighted isotopic composition from individual daily data (wdm) at Portorož Airport and Kozina.

Month/ Year	Portorož Airport				Kozina			
	δ^2H_m (‰)	δ^2H_{wdm} (‰)	$\delta^{18}O_m$ (‰)	$\delta^{18}O_{wdm}$ (‰)	δ^2H_m (‰)	δ^2H_{wdm} (‰)	$\delta^{18}O_m$ (‰)	$\delta^{18}O_{wdm}$ (‰)

10/2002	-24	-30	-5.3	-5.8	-47	-47	-8.0	-7.8
11/2002	-25	-35	-5.3	-5.6	-45	-44	-7.3	-7.4
12/2002	-58	-36	-9.1	-5.7	-77	-86	-11.4	-12.2
1/2003	-68	-54	-10.2	-7.2	-102	-91	-13.8	-12.3
2/2003	-80	-76	-10.6	-10.9	-80	-77	-11.3	-11.4
3/2003	-17	-16	-3.2	-3.8	-23	-50	-5.2	-7.7
4/2003	-46	-39	-6.6	-4.8	-66	-68	-9.7	-9.5
5/2003	-20	-20	-3.0	-2.7	-34	-34	-5.8	-5.4
6/2003	-31	-32	-4.5	-4.3	-31	-33	-5.0	-4.9
7/2003	-8	-6	-1.6	-0.9	-25	-23	-3.8	-3.0
8/2003	-21	-21	-3.2	-2.8	-25	-20	-3.6	-2.1
9/2003	-30	-37	-5.6	-6.0	-45	-51	-7.8	-7.7

Conclusion

Comparison of monthly and daily isotopic composition of precipitation showed differences between both set of data and indicates the need for short-term determination of isotopic composition that would enable better understanding of the effect of changing meteorological conditions that are lost during long-term (e.g. monthly) collection of precipitation samples.

References

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