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Abstract

Stable isotopes of water (^{18}O and ^2H) constitute a well-established technique to assess the origin and interactions of river waters with groundwater. The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in 8 monitoring points of the Pinios River Basin (PRB) ranged from -6.2 ‰ to -9.5 ‰ and from -40.2 ‰ to -61.3 ‰, respectively. The river water data showed a meteoric origin with air masses originating from the Atlantic Ocean and the Mediterranean Sea. However, *d*-excess values < +10 ‰ demonstrated influence from evaporation, particularly during summer. The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the PRB were significantly lower at the headwaters and increased downstream due to decreasing altitude. Highest average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were recorded during summer (-7.0 ‰ and -45.9 ‰, respectively) and lowest during winter (-7.8 ‰ and -49.7 ‰, respectively) due to temperature difference. Higher groundwater contribution was found upstream and before the river enters the deltaic plain.

Introduction

The Pinios River is the main river of the Pinios River Basin (PRB) that flows from its headwaters at Pindus mountains and through the Thessalian plain it discharges into Thermaikos Gulf, after forming a deltaic plain (Fig. 1). The climate is typical Mediterranean, but becomes more continental in the western part. The mean annual precipitation of ~700 mm is distributed unevenly in space (higher amounts at the western part) and time (higher amounts during autumn and winter). The PRB is covered mainly by alluvial deposits and Neogene sediments, whereas limestones and marbles host aquifers, which discharge through springs. Here, we present the preliminary findings of the systematic monitoring of the PRB for water isotopes (^2H and ^{18}O of H_2O) to better understand the dynamics in the basin. The monitoring was done under the framework of the International Atomic Energy Agency (IAEA) Global Network of Isotopes in Rivers (GNIR).



Methods and Materials

River water samples from the PRB were collected at 8 monitoring sites (Fig. 1) on a monthly basis in 2019–2021, following GNIR guidelines. The samples were analysed for stable isotope ratios ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) at the Isotope Hydrology Laboratory of the IAEA (Vienna, Austria) using a Los Gatos Research Liquid-Water Isotope Analyzer (TLWIA-912). The isotope values were expressed in delta (δ) units with a per mil (‰) notation relative to Vienna Standard Mean Ocean Water (VSMOW):

$$\delta_{\text{sample}} (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right) * 1000$$

where R_{sample} is the $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ ratio of the sample for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. The analytical uncertainty was ± 0.1 for $\delta^{18}\text{O}$ and ± 0.5 for $\delta^2\text{H}$. The “deuterium excess” or “*d*-excess” was calculated as follows:

$$d\text{-excess} (\text{‰}) = \delta^2\text{H} - 8 * \delta^{18}\text{O}$$

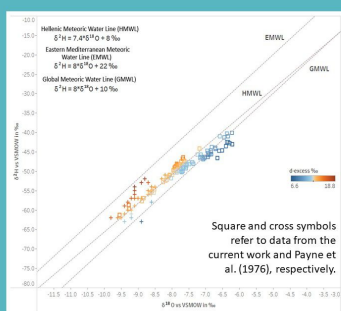


Fig. 2. $\delta^{18}\text{O}$ vs $\delta^2\text{H}$ plot depicting the river water samples.

Acknowledgments

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Results & Discussion (I)

- The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the PRB ranged on average from -6.2 ‰ to -9.5 ‰ and from -40.2 ‰ to -61.3 ‰, respectively. These values were similar but higher than those reported by Payne et al. (1976) for the western part of the basin.
- River water data showed a meteoric origin that was better explained by the Hellenic Meteoric Water Line (HMWL) (Fig. 2).
- Higher isotope values due to evaporation processes, particularly during the summer season, lowered the slope of the regression line.
- d*-excess values ranged between +6.6 ‰ and +15.6 ‰ showing precipitation originating from the Atlantic Ocean and the Mediterranean Sea (Fig. 2).
- The very low *d*-excess values were attributed to kinetic isotope effects due to evaporation.

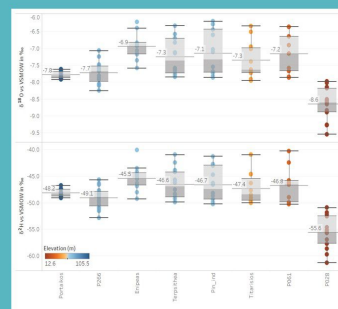


Fig. 3. Box plots of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values per site from headwaters (Portaikos) to the outlet (P028) of the PRB.

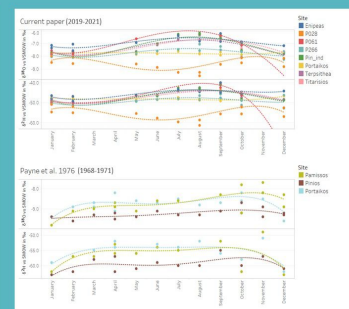


Fig. 4. Monthly evolution of water isotope values in the PRB.

Results & Discussion (II)

- The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the PRB were significantly lower at the headwaters and increased downstream due to altitude effect.
- The low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at river site P028 (-8.5 ‰ and -54.8 ‰, respectively) were attributed to groundwater influence of Ag. Paraskevi springs.
- The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in river waters showed a seasonal variation (Fig. 3) due to temperature effect.
- The temporal variation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values was lower in the river stations at the headwaters (Fig. 4) and higher towards the outlet. Low temporal variability of the river waters was attributed to higher contribution from groundwater, whereas the opposite to enhanced recharge from local precipitation.
- The river site P028 exhibited lower $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the summer (Fig. 4), due to increased contribution of baseflow from spring waters (groundwater) originating from an altitude of ~1,000 m based on the altitude- $\delta^{18}\text{O}$ gradient established by Payne et al. (1976) for the region.

Conclusions

The preliminary findings of the systematic monitoring of water isotopes in the PRB showed that river waters have meteoric origin, which was better explained by the HMWL, although evaporation processes were identified. The isotopic values ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) were significantly lower at the headwaters (Payne et al., 1976) and increased till the confluence with the Enipeas tributary due to altitude effect. More variable contributions of groundwater and recharge from local precipitation to the river were detected at its downstream part. Overall, the isotopic composition of the river showed a seasonal pattern due to temperature. Before the river enters the deltaic plain, an increasing contribution of baseflow during summer was identified.

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