Comparative isotope hydrological characterization of the elements of the water cycle in two continental catchments: Koppány (Hungary) and Ledava (Slovenia) streams

István Gábor Hatvani[1], Zsolt Jolánkai[2], Adrienne Clement[2], Bence Decsi[2], Máté K. Kardos[2], Zsolt Kozma[2], József Deák[3], Sonja Lojen[4], Radmila Milačič[4], Polona Vreča[4] and Zoltán Kern[1]

[1]Institute for Geological and Geochemical Research, HUN-REN Research Centre for Astronomy and Earth Sciences, 1112 Budapest, Hungary
[21]Department of Sanitary and Environmental Engineering, Faculty of Civil Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3., H-1111 Budapest, Hungary
[3]GWIS Ltd., Hungary
[4] Department of Environmental Sciences, Jožef Stefan Institute (IJS), 1000 Ljubljana, Slovenia

Budapest, Hungary | **2024**

INTRODUCTION

The specific isotopic signatures of atmospheric processes such as evaporation, condensation, and deposition in precipitation are then imprinted in terrestrial water bodies, allowing the application of isotopic data to hydrological studies (Gat et al., 2001).
Interpretation of changes in the stable oxygen ($\delta^{18}O$) and hydrogen (δ^2H) isotopic signatures of catchment waters have proved to be useful tracers for identifying hydrological source areas/flow paths under different flow conditions and estimating catchment residence times (Rodgers et al., 2005).

This study explores the preliminary results of a targeted monitoring approach at a Hungarian and a Slovenian catchment which aims to enhance the understanding of contaminant pathways, quantify particulate transport and delineate surface versus subsurface contributions to fluxes in the catchment scale water cycle.

AIM

Obtain a preliminary isotope hydrological picture of two comparable watersheds in Central Europe.

MATERIALS & METHODS

Site description

The Hungarian catchment is located in SW Hungary covering the larger part of the Koppány Stream catchment above Tamási. It is hilly, ca. 660 km² catchment with a significant (~78%) agricultural share and extended undisturbed forests (~20%). The mean annual precipitation is 630 mm yr^{-1}. The Ledava catchment is a cross-border area (HU / SI (1940 km²)). It is hilly to lowland agricultural area, covered by 20 % of forest, the mean annual precipitation is 798 mm yr^{-1}.

Dataset

To characterize the water cycle components in both catchments the $\delta^{18}O$ and δ^2H were measured in precipitation, river and subsurface (shallow and deep groundwater) water from 2022onward on a bi-weekly to monthly basis. Regarding precipitation monthly bulk precipitation was collected.
The isotopic composition of water, i.e. δ^2H and $\delta^{18}O$ expressed in ‰, was determined using a water-H_2 (platinum – Pt) and water-CO_2 equilibration technique at the Jožef Stefan Institute. Measurements were carried out on a dual inlet isotope ratio mass spectrometer Finnigan MAT DELTA plus. The results were normalized to VSMOW/SLAP using the LIMS program. The overall uncertainties are estimated to be less than 1‰ and 0.05‰ for δ^2H and $\delta^{18}O$ respectively.

RESULTS & DISCUSSION

1. General stableisotope hydrological observations

- Considering the relative vicinity and similar climatic characteristics of the studied Koppány (HU) and Ledava (SI) catchments (Fig. 1) the range of the measurements of stable isotopic composition of precipitation is similar (Fig. 2: PRC_KO, PRC_LND).
- River- and subsurface water stable isotopic composition variability is explicitly smaller compared to that of precipitation.

River Water

- Koppány catchment
  - the stable isotopic composition of river water seems to be slightly more negative at the Törökkoppány (RIV_TK) site compared to the Tamási (RIV_TS). In contrast, the stable isotopic composition of subsurface water is more depleted in heavy isotopes than that of surface water and precipitation, most explicitly in the case of deep groundwater.
- Ledava catchment
  - RIV water tends to be less negative compared to the mean value of precipitation (Fig. 2A).
  - upstream at Polana (RIV_PLN) slightly higher $\delta^{18}O$ and δ^2H values are observed compared to Čentiba (RIV_CNT).

Subsurface Waters

- Shallow groundwater $\delta^{18}O$ and δ^2H values perfectly fall in line with that of the river water, while the deep groundwater is more negative, nevertheless, in the Ledava catchment not as much as in the Koppány catchment.

2. Covariance of oxygen and hydrogen values at the two catchments

- In the Ledava catchment (Fig. 3A) all measured values fall on the modeled Local Meteoric Water Line (LMWL) of modern precipitation (Hatvani et a., 2023), in the meanwhile in the Koppány catchment the river water tends to follow a shallower slope (Fig. 3B).
  - Latter suggests evaporation effect
  - *Possible explanation*
    - the presence of numerous reservoirs on the Koppány, which significantly increase the water surface area,
    - this transition also means that the stream water is a mixture of the enriched reservoir water and rainwater.
  - Suggestion, to explore the stable isotopic composition of the reservoir waters in the Koppány catchment

- *Another striking difference* is that at the Koppány catchment the $\delta^{18}O$ and δ^2H values of deep groundwater are more negative than of the shallow (young) groundwater (Fig. 3B), indicating that deep groundwater infiltrated in a colder climate than today.

- Radiometric data (^3H and ^{14}C) collected from groundwater samples across the Koppány catchment indicated the oldest groundwaters are located next to the Koppány stream (Clement et al. 2023), providing a small amount of base-flow to the stream (Jolánkai et al., 2024).

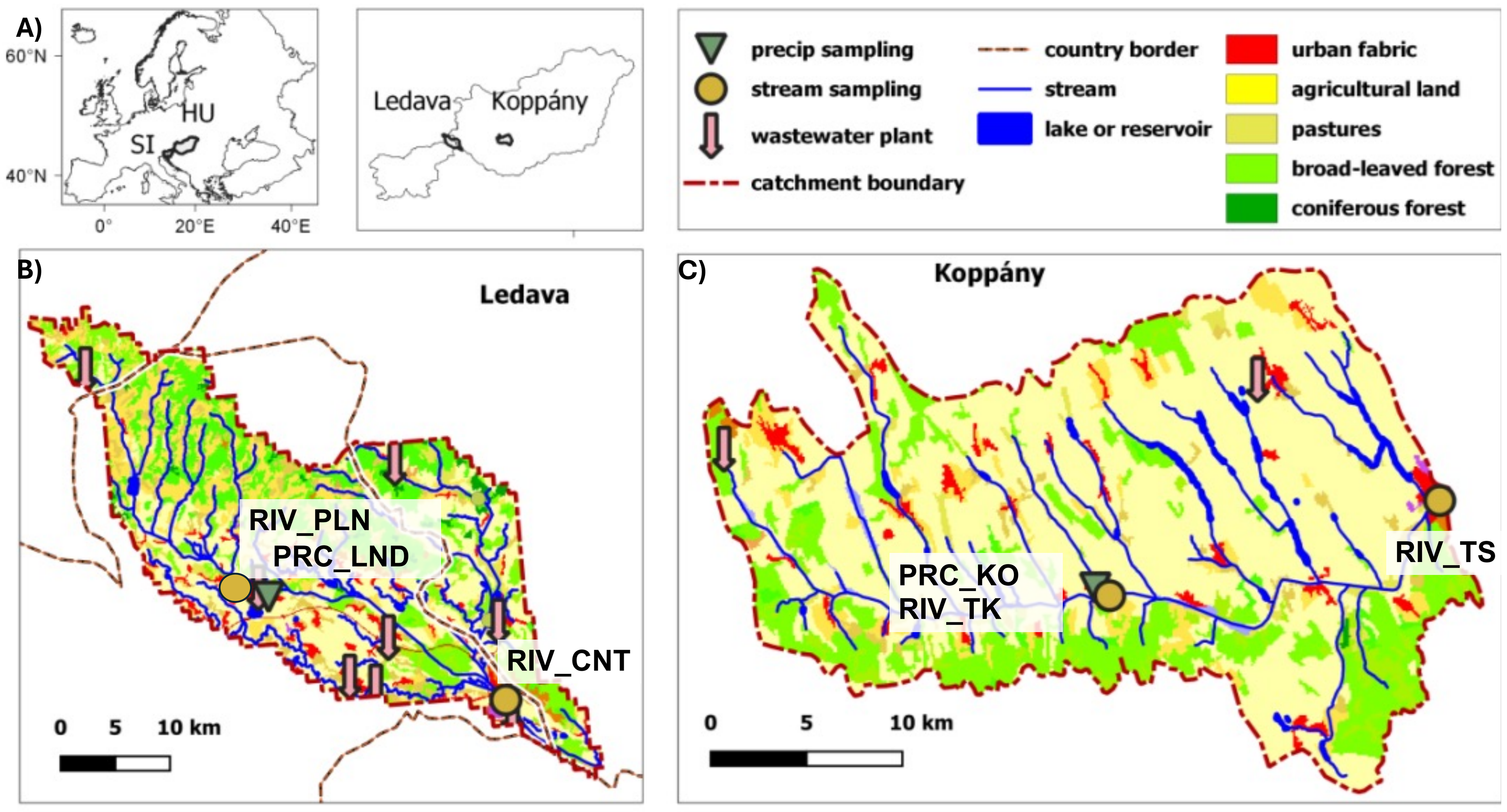

Figure 1: Location of studied catchments A) and monitoring sites in Slovenia (Rakičan (LND), Centiba (RIV_CNT) and Polana (RIV_PLN) B) and Hungary (Törökkoppány (RIV_TK) and Tamási (RIV_TS) C).

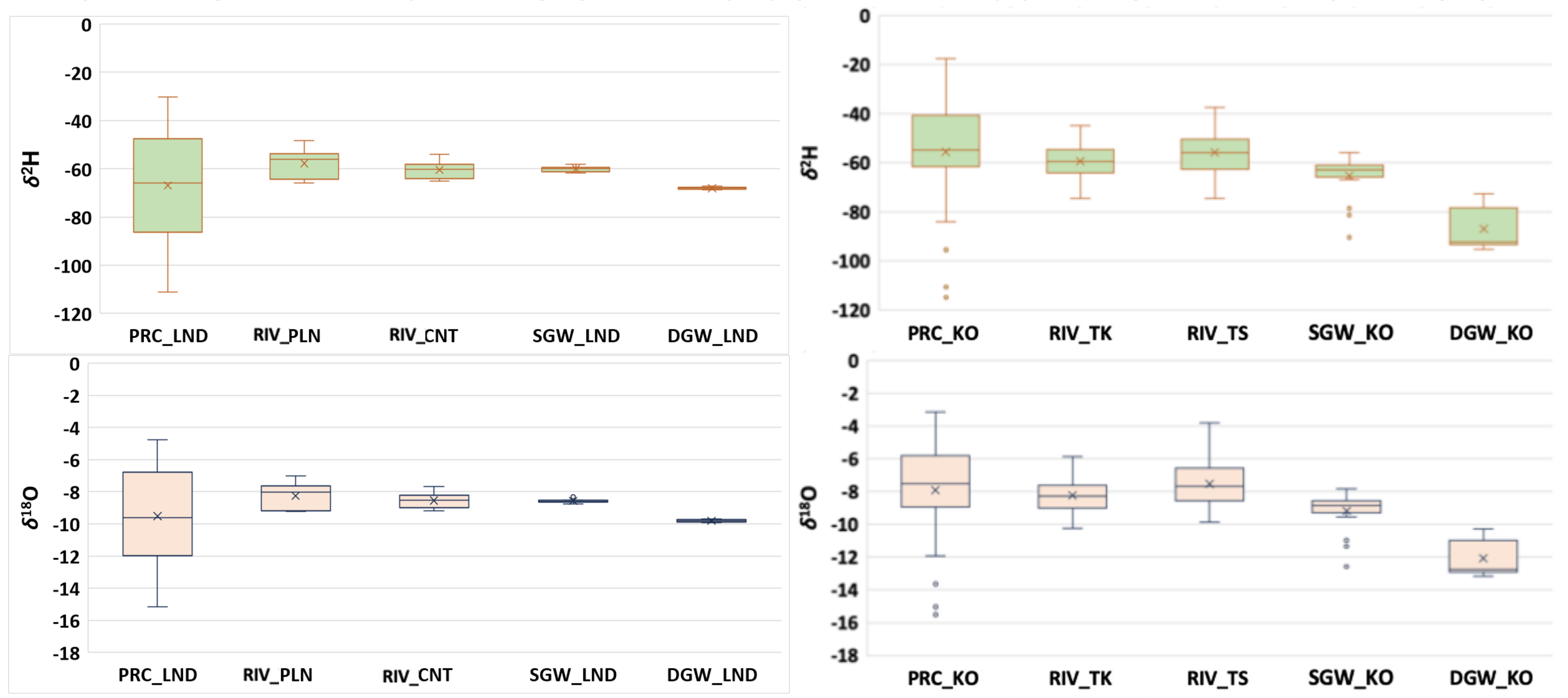

Figure 2: Box-and-whiskers plots of precipitation-river-subsurface water (shallow (SGW) and deep groundwater (DGW) at the sites are shown for the Ledava catchment (SI, left) and the Koppány catchment (HU, right). The boxes show the interquartile range and the black horizontal line in the middle of each box is the median value. The two upright lines represent the data within the 1.5 interquartile range (Kovács et al., 2012).

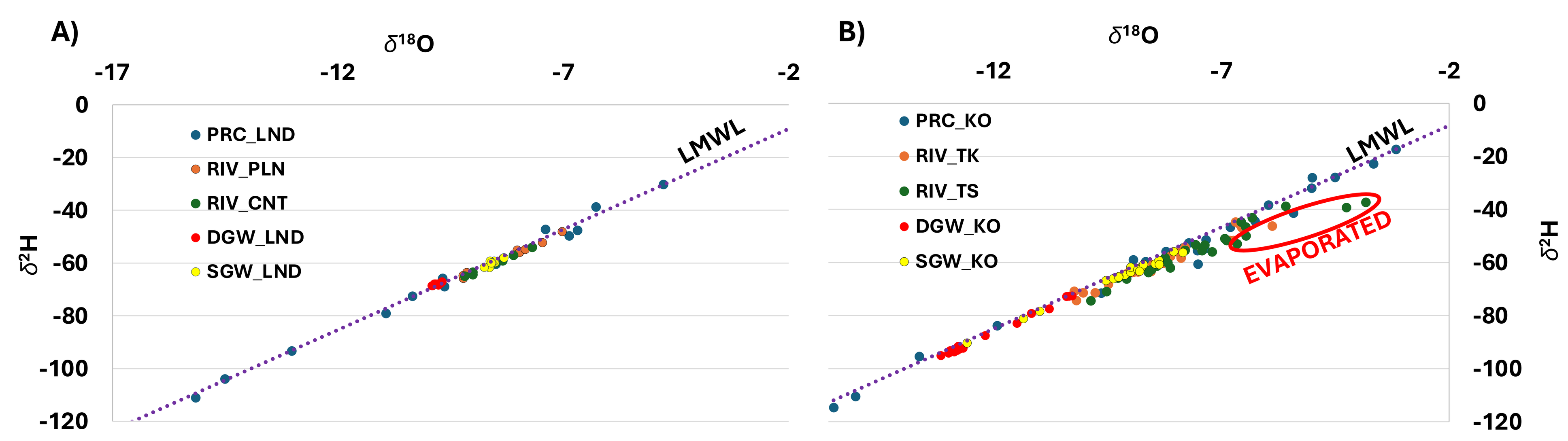

Figure 3: $\delta^{18}O$ - δ^2H crossplot of the precipitation (PRC), river water (RIV) ,-subsurface water (shallow (SGW) and deep groundwater (DGW) for the Ledava catchment A) and the Koppány catchment B). The modelled modern Local Meteoric Water Line (Hatvani et al., 2023) is shown for both catchments for reference.

CONCLUSIONS & OUTLOOK

Conclusions

- Two catchments were analyzed with similar characteristics, however striking isotope hydrological differences were observed in the catchment-scale water cycle.
- The Ledava stream $\delta^{18}O$ and δ^2H values fit nicely to the meteoric waterline in the $\delta^{18}O$ - δ^2H crossplot, while in the Koppány, evaporation is observed (Fig. 3B: red ellipse).
- Subsurface water $\delta^{18}O$ and δ^2H values fit to the LMWL in both catchments
  - However, the deep groundwater has a more negative mean values than its shallow counterpart.
  - difference is much more characteristic in the case of the Koppány, likely due to the older age (pre-Holocene) of the groundwater there; supported by the preliminary radiometric ages (Clement et al., 2023).

Outlook

Next steps include the incorporation of the above results in the catchment emission model with a special focus on nitrate contamination as soon as the nitrate-$\delta^{15}N$ become available. Key limitations are, monitoring is still ongoing, thus at this stage empirical analyses were conducted, statistical tests will follow to explore the similarities and differences.

SELECTED REFERENCES

Clement A, Deák J, Decsi B, Hatvani IG, Jolánkai Zs, Kern Z, Kardos KM, Kozma Z, Palcsu L, Lojen S, Milácic R, Vreca P., 2023. Implementation Of A Monitoring Program To Track Pollutant Transport Processes In A Pilot Catchment In Hungary. In: Kalicz, P. et al. (eds.) HydroCarpath 2023 Hydrology of the Carpathian Basin: Abstracts of the Conference. Sopron, Hungary : Soproni Egyetem Kiadó 53 p. pp. 49-49. Paper: P29.
Gat, J.R., Mook, W.G., Meijer, H.A., 2001. Environmental isotopes in the hydrological cycle. International Atomic Energy Agency, Paris.
Hatvani, I.G., Smati, A.E., Erdélyi, D., Szatmári, G., Vreča, P., Kern, Z., 2023. Modeling the spatial distribution of the meteoric water line of modern precipitation across the broader Mediterranean region. Journal of Hydrology 617, 128925.
Jolánkai, Zs., Kardos, M.K., Decsi, B., Kozma, Zs., Deák, J., Clement, A., 2024. Tracking nitrogen load patterns in a meso-scale hilly watershed using surface and subsurface monitoring. 19th Carpathian Basin Conference For Environmental Science. Debrecen.
Kovács J, Tanos P, Korponai J, Székely IK, Gondár K, et al., 2012. Analysis of water quality data for scientists. In:Voudouris K, Voutsa D, editors. Water Quality Monitoring and Assessment. Rijeka: Tech Open Access Publisher,. p. 65–90.
Rodgers, P., C. Soulsby, S. Waldron (2005): Stable isotope tracers as diagnostic tools in upscaling flow path understanding and residence time estimates in a mountainous mesoscale catchment. Hydrol. Process. 19, 2291–2307. doi.org/10.1002/hyp.5677

ACKNOWLEDGEMENTS

The research presented herein was supported by the National Research, Development, and Innovation Office (OTKA project grant number SNN 143868). The authors also acknowledge the financial support received by the Slovenian Research Innovation Agency (ARIS) for project N1-0309 and research programme P1-0143.