

# Insight into uranium isotopic composition of Ljubljana River catchment

Leja Rovan<sup>1,2</sup>, Ljudmila Benedik<sup>1,2</sup>, Marko Štok<sup>1,2</sup>

<sup>1</sup>Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia

<sup>2</sup>Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

Contact: leja.rovan@ijs.si



## Introduction:

Uranium (U) isotopic composition data in freshwaters environment in continental areas with predominantly carbonate lithology provide informations about the water composition and redox conditions in a karstic aquifer.

With the help of advanced analytical tools, such as is multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), we can achieve accurate and precise U isotopic composition in environmental samples at very low concentration.

Karstic aquifer of Ljubljana river has numerous springs and sinks, which provide interesting study area for analyzing redox sensitive U and its ability to identify and to quantify carbonate precipitation in freshwaters.

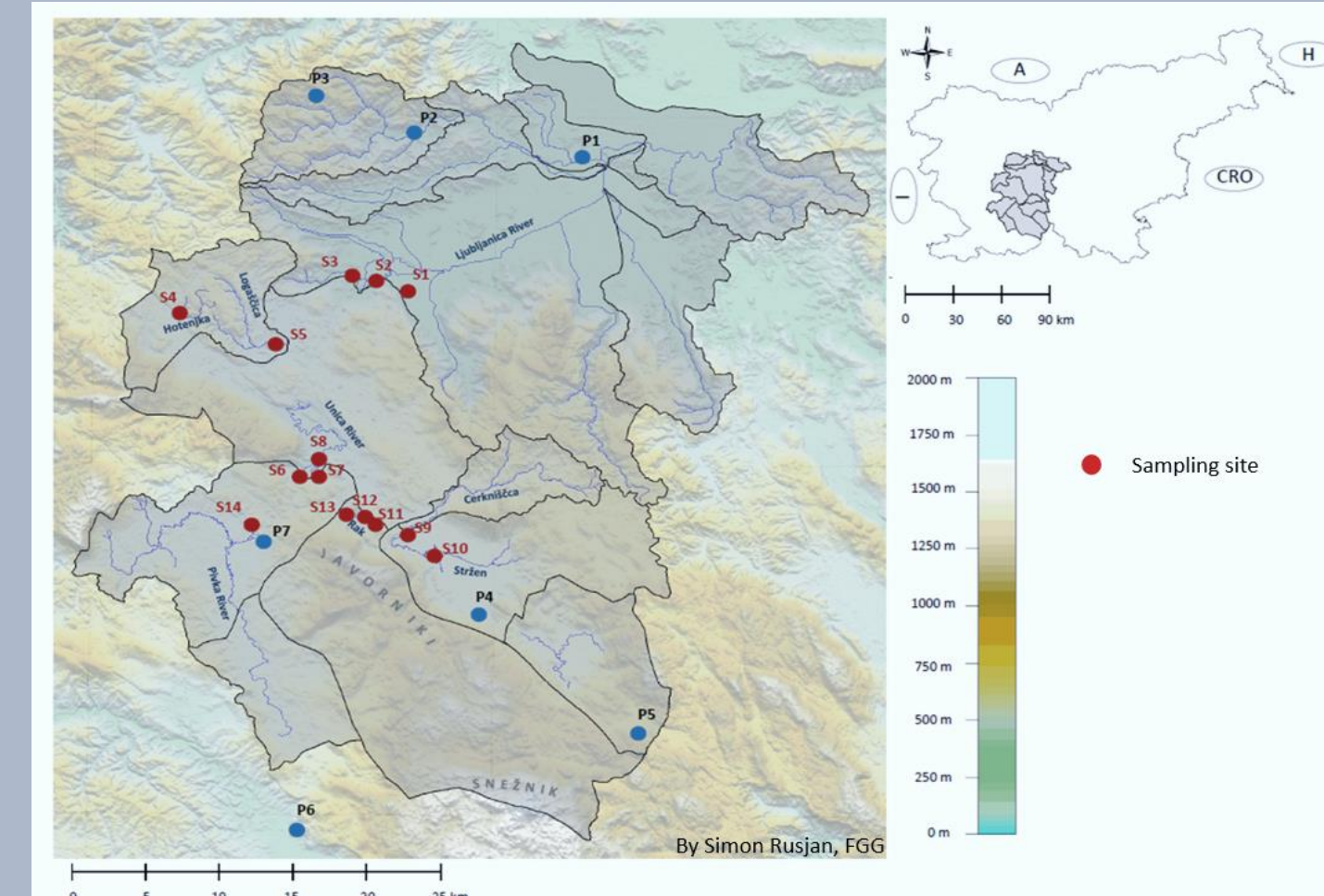


Figure 1: Map of the examined area of Ljubljana catchment and locations of the sampling sites with additional locations of rain collectors.

### Optimal method settings for U analysis on the Nu plasma II with Aridus II™

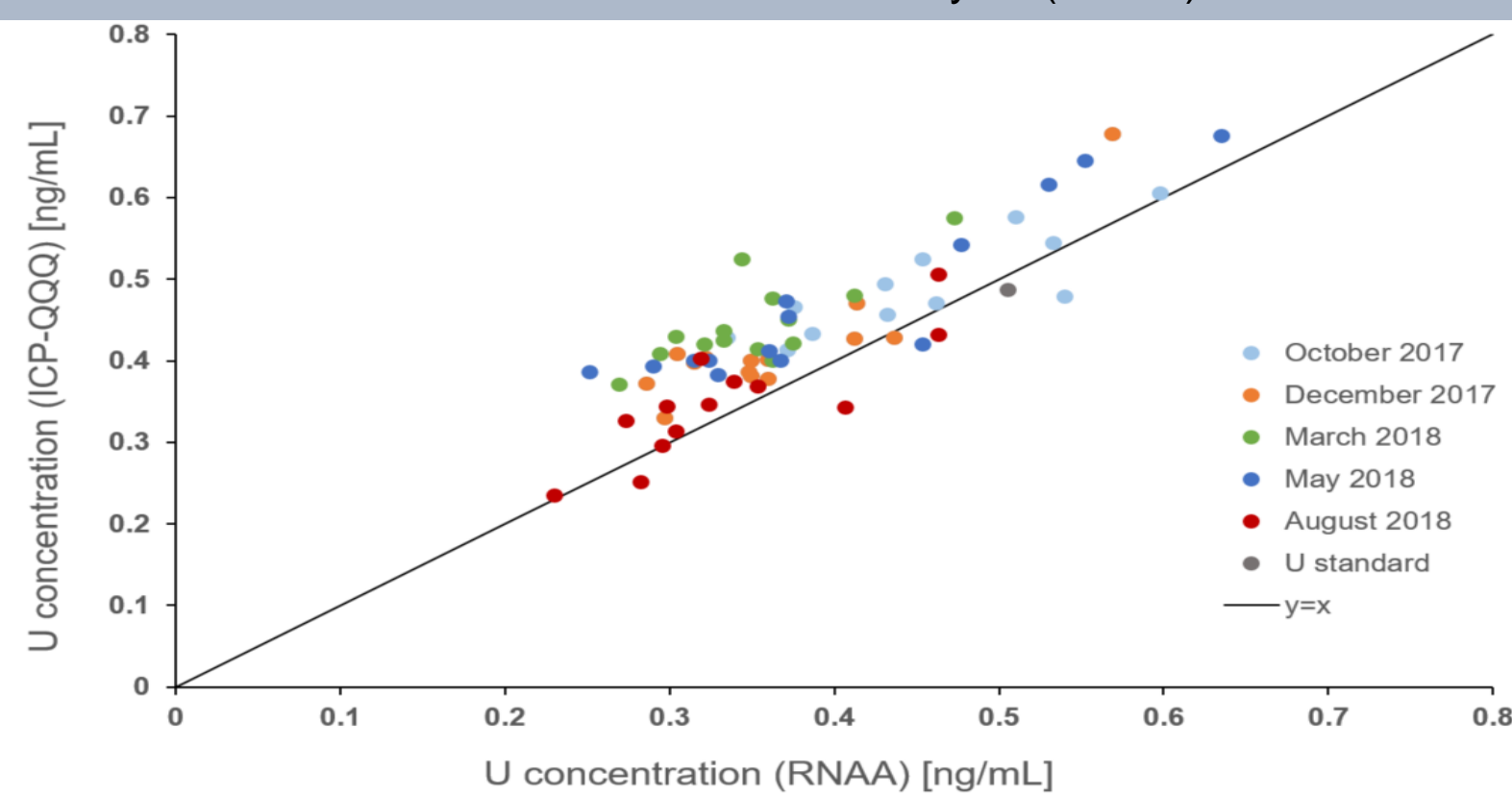
Cup configuration	<sup>234</sup> U(IC0) - <sup>235</sup> U(L5) - <sup>238</sup> U(L2)
Cycles / blocks	10 cycles / 6 blocks
Integration time	30 s (zero-ESA) ; 4 s (sample)
Magnet delay time	2 s
Transfer time	150 s
Wash time – 2 % HNO <sub>3</sub>	120 s
Analytical concentration	5 ng/mL
Sensitivity	~ 3 – 4 V for 5 ng/mL
Total analysis time	14 min / sample
Mass bias correction with standard-sample bracketing method.	

## Results

### Uranium concentration in water samples

- Mass spectrometric vs radiometric method

Figure 2: Comparison of U concentration in water samples, measured with triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ) and with radiochemical neutron activation analysis (RNAA).



- Water sample concentrations of U varied from 0.23 to 0.68 ng/mL.
- Results obtained by ICP-QQQ are higher than results obtained by RNAA, but comparable and are within measurement uncertainties.

## Conclusions:

- The objective of this study was to check possible U fractionation in freshwaters environment in continental areas with predominantly carbonate lithology, with the help of MC-ICP-MS.
- Results of U isotopic composition from different sampling campaigns show variations for some sampling sites between sampling campaigns and between samples and natural uranium standard.
- Study provide a good groundwork for further researching to identify and quantify the extents of authigenic carbonate formation as C sink.

## Methodology

### Study area

- Ljubljana catchment
- Karstic aquifer

### Sampling

- Water samples (1L)
- In-situ physicochemical parameters (pH, Eh, conductivity)
- Filtration

### Measurement

- ICP-QQQ and RNAA → U concentration
- MC-ICP-MS → U isotopic composition



### Optimization of sample preparation

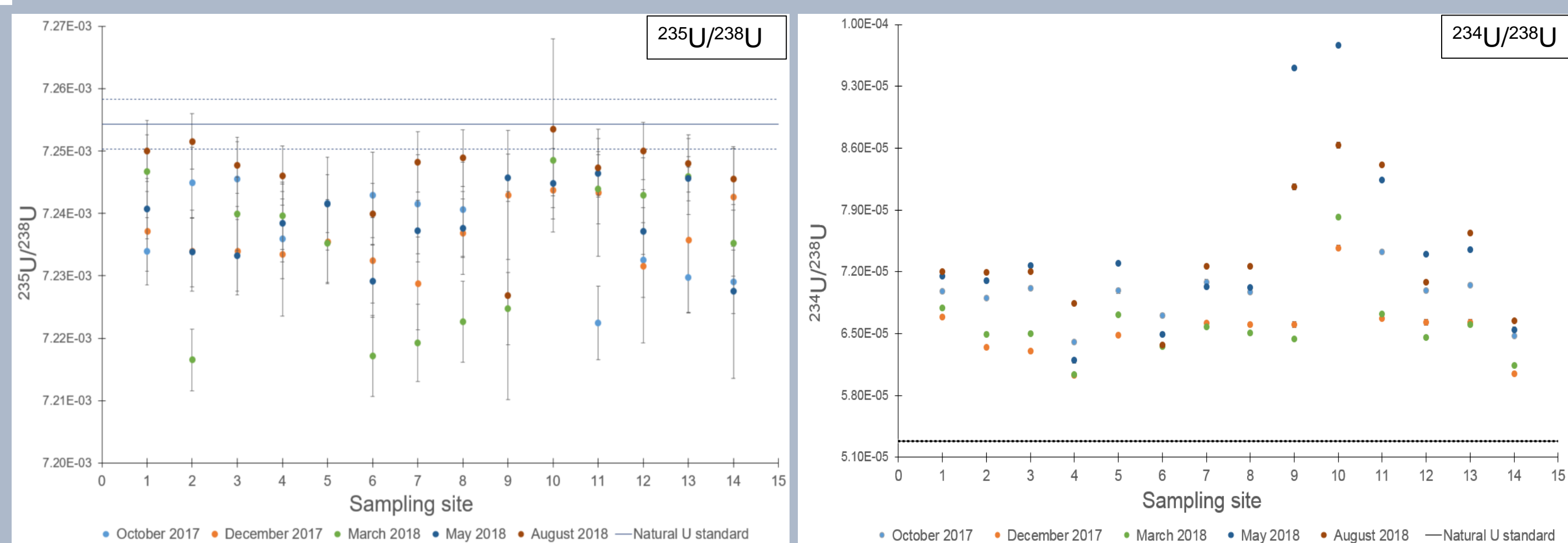
- Pre-concentration → Fe(OH)<sub>3</sub> co-precipitation
- Separation → UTEVA®



### Uranium isotopic composition in water samples

- <sup>235</sup>U/<sup>238</sup>U & <sup>234</sup>U/<sup>238</sup>U

Figure 3: <sup>235</sup>U/<sup>238</sup>U and <sup>234</sup>U/<sup>238</sup>U isotope ratios (absolute values) from five sampling campaigns in water samples of karstic aquifer and certified natural U standard value with the expanded uncertainty (k=2).



- Clear deviation of U isotopic composition between water samples and natural U standard (CRM 145).
- Small (important) variations between sampling sites and different seasons for <sup>235</sup>U/<sup>238</sup>U.
- <sup>234</sup>U enrichment in water samples → elevated values compared to natural U standard.
- Different sampling campaigns show significant variations between seasons for <sup>234</sup>U/<sup>238</sup>U (December, March & October, May, August).