Non-traditional isotopes as tracers of water-rock interactions in a complex karst aquifer: case preliminary study of Ljubljanica River, Slovenia

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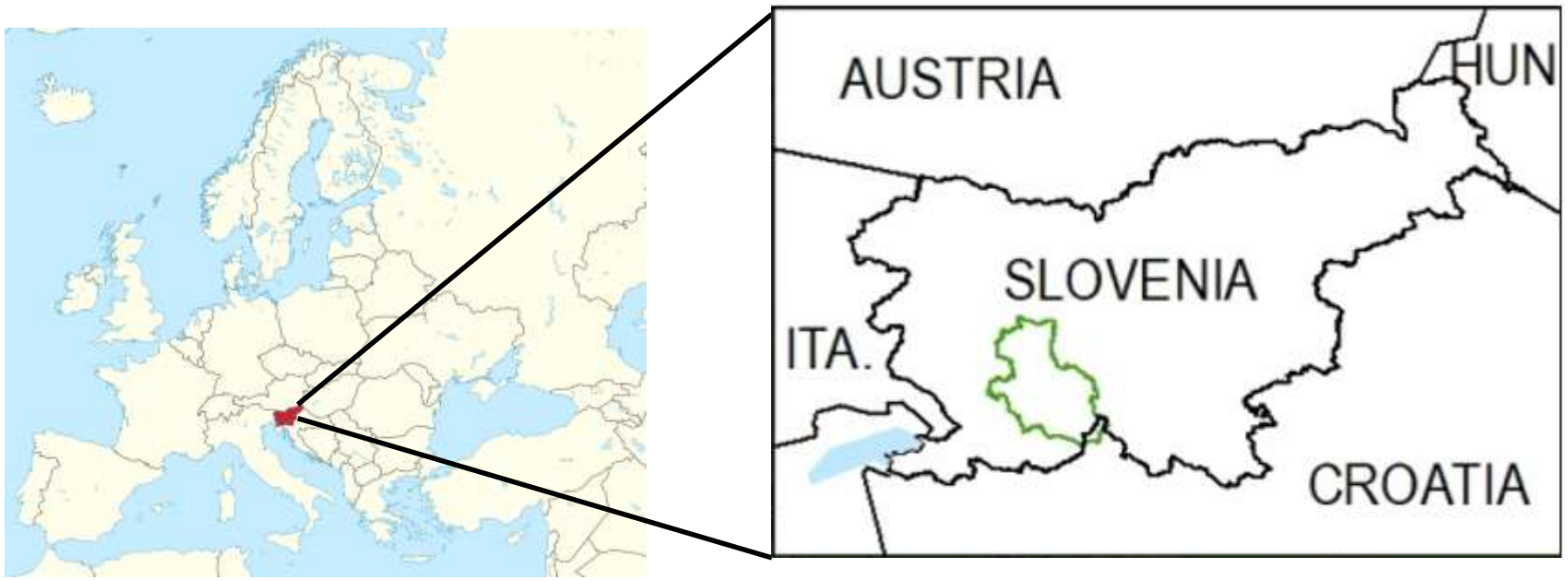
Karst aquifer

- a two-continuum medium: saturated matrix porosity drained by conduits
- contrast of several orders of magnitude in permeability between matrix and conduits
- Temporally and spatially highly variable diffuse and concnetrated recharge, storge (epikarst, vadoze and phreatic zone) and flow type (diffuse and along conduits)
- Important freshwater resources in many parts of the world, so quantitative understanding of their hydrological functioning is necessary for their management and exploitation

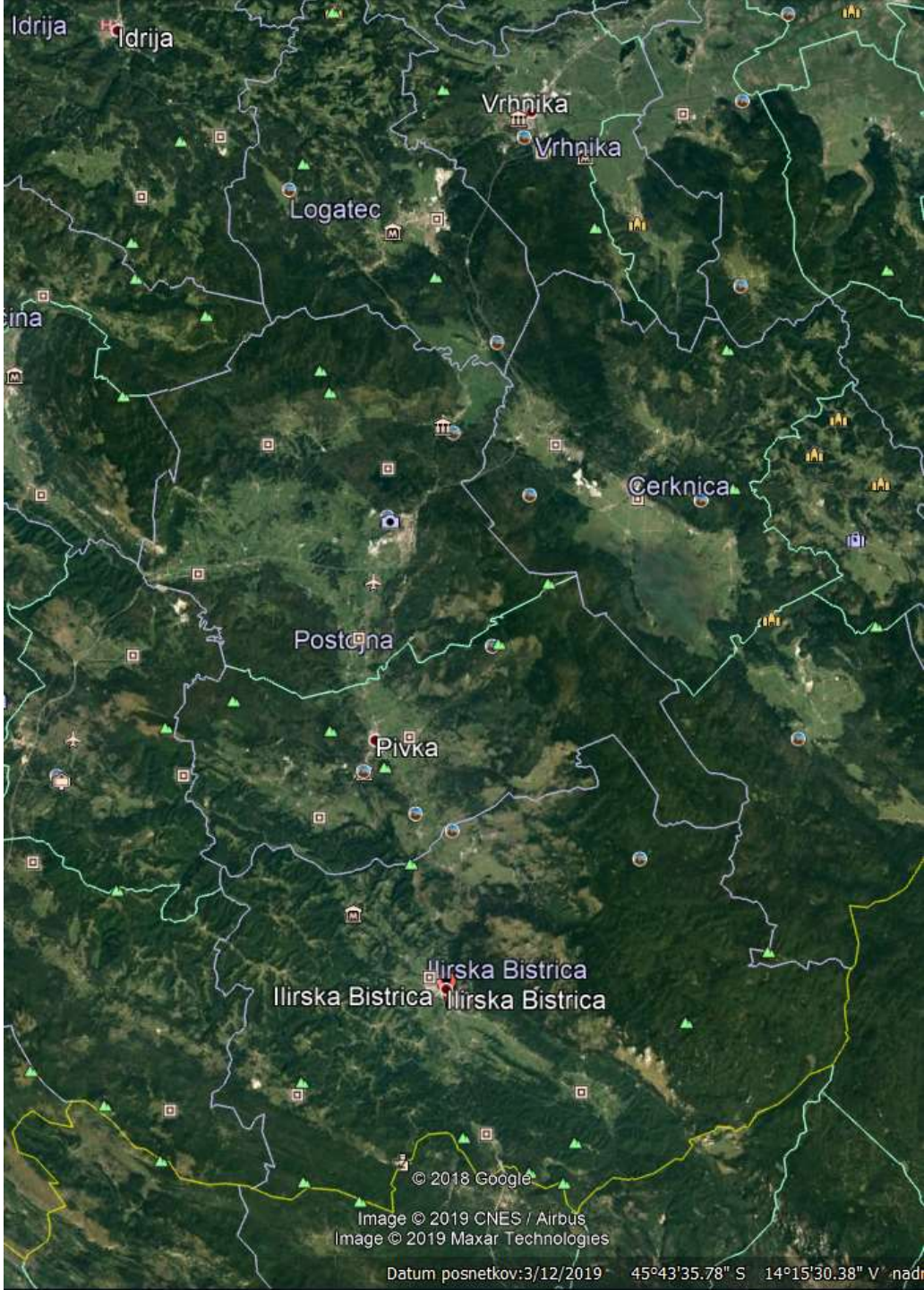
Ljubljanica aquifer



- Important groundwater body in SW Slovenia
- Identification of hydrological behaviour using stable isotopes of water (Rusjan, J. Hydrol. 577, 2019, 123956)
- Hydrochemistry and isotopic composition of solutes (DIC, Mg, Sr, U) to explore the biogeochemical processes and to validate the hydrological model

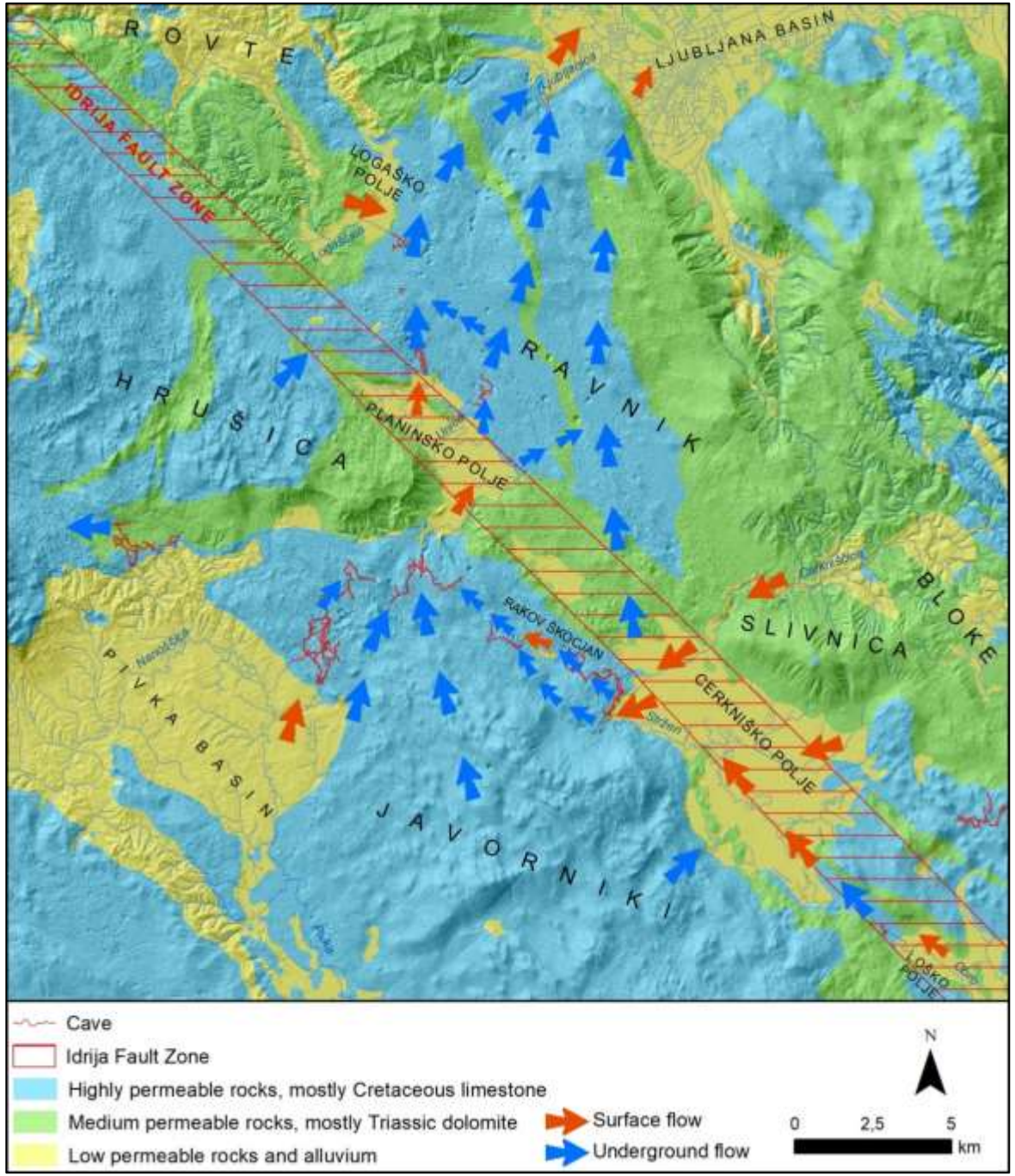
Ljubljanica catchment

- Important drinking water resourceS
- Intensively karstified, surface streams sinking underground several times
- Surface approx. 1880 km^2, altitude gradually decreasing from S to N (≈ 1800 – 300 m a.s.l.)
- Annual precipitation >2000 to 1400 mm, decreasing from S to N
- Climate: Cfb (oceanic) except in mountaneous part in the south (boreal)
- Mountains covered with forest, flood plains pastures, no intensive agriculture

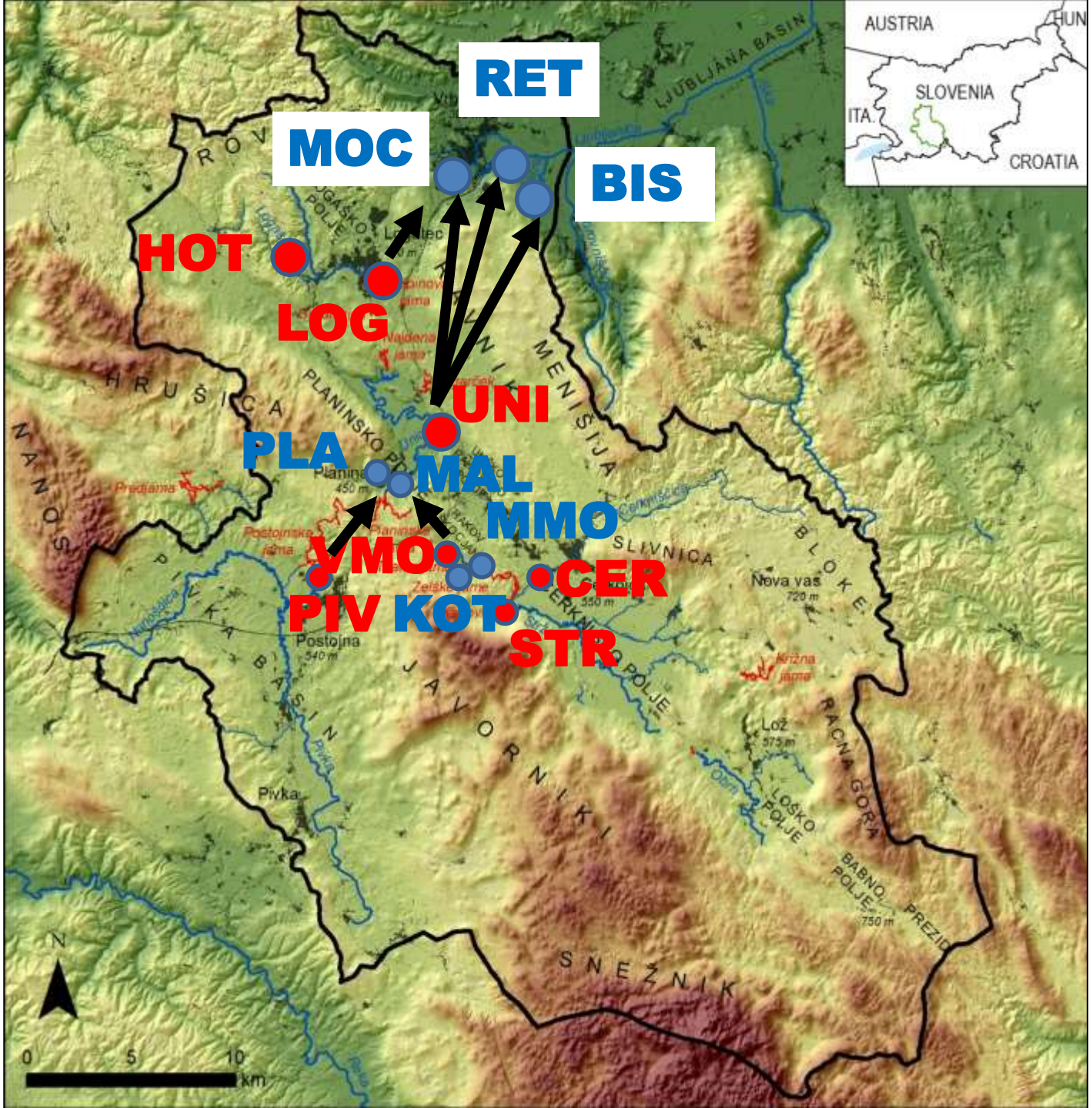


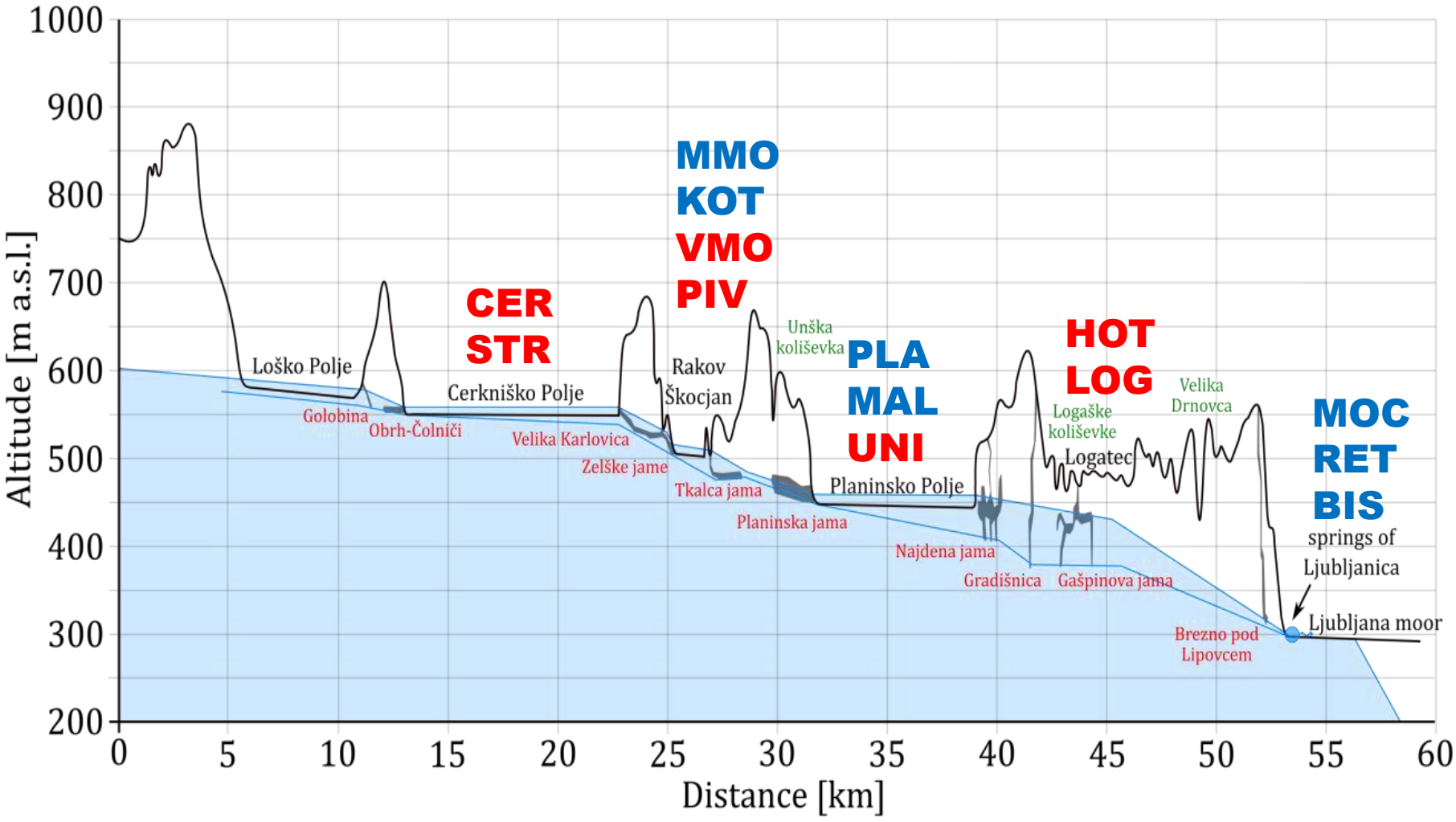
Lithology: limestone, dolomite,

siliciclastic rocks



Ljubljanica karst catchment




1000
900
800
700
600
500
400
300
200
Altitude [m a.s.l.]
0
5
10
15
20
25
30
35
40
45
50
55
60
Distance [km]
Loško Polje
Golobina
Obrh-Čolniči
Cerkniško Polje
CER
STR
Velika Karlovica
Zelške jame
Rakov
Škocjan
MMO
KOT
VMO
PIV
Tkalca jama
Unška
koliševka
PLA
MAL
UNI
Planinsko Polje
Planinska jama
Najdena jama
Gradišnica
Gašpinova jama
HOT
LOG
Logaške
koliševke
Logatec
Velika
Drnovca
MOC
RET
BIS
springs of
Ljubljanica
Ljubljana moor
Brezno pod
Lipovcem

What was known on hydrology

Highest level: streams at Cerkniško polje (CER, STR) are recharged from NW (dolomite area)

2. level: Rak creek (MMO, KOT, VMO) shall be recharged mainly from Cerkniško polje (STR, CER)

3. level: Malenščica spring (MAL) is recharged mainly from STR & CER and Rak creek (VMO), little or no connection to Pivka river (PIV), while Unica spring (PLA) is recharged from Rak stream (VMO)

Lowest level: main Ljubljanica springs (MOC, RET, BIS) are recharged from Unica (UNI) and Logaščica & Hotenka (HOT, LOG) in variable fractions

Study 2016-2018: identifying the hydrological hydrological behaviour using stable water isotopes (Rusjan et al. 2019)

Regular analyses of precipitation and surface & groundwater in the catchment area

Some seasonal and spatial patterns were identified in contrasting hydrological conditions (base flow *vs.* high discharge)

Sources of precipitation are difficult to define because of mixing of Mediterranean and Atlantic precipitation with local moisture, but the precipitation isotope patterns were recognized in the $\delta^{18}O$ and $\delta^{2}H$ values of sources and sinks (Krklec et al. 2018)

Mean transit times (MTT) were calculated for main conduits and tributaries, ranging from 0.33 to 0.72 years

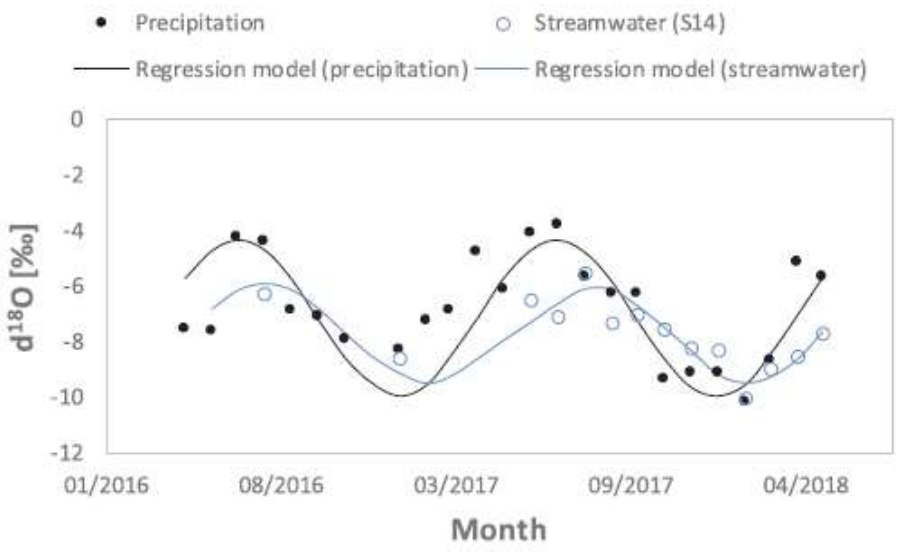
The fraction of young water for the entire catchment was 0.28, meaning that about ¼ of the total discharge is younger than 2.3 months

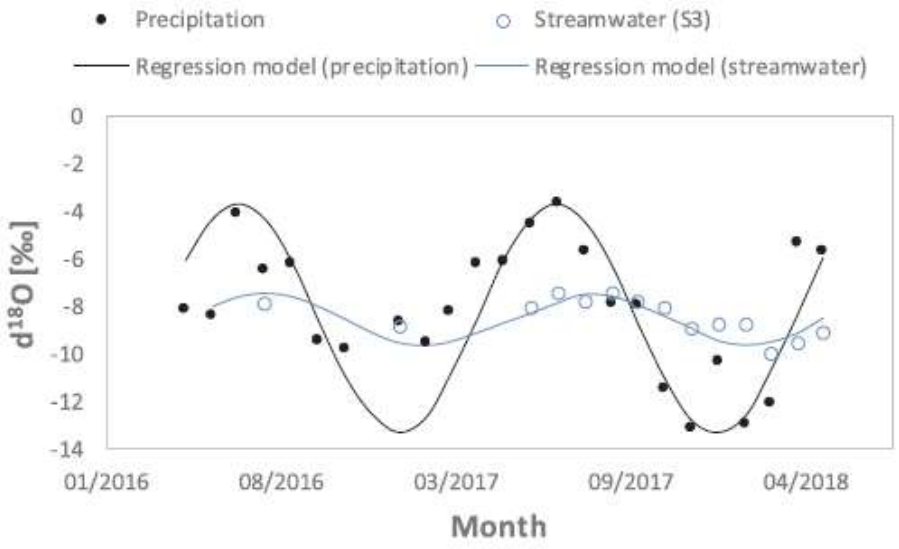
Can new isotope tracers validate the model and support interpretation of groundwater flow and mixing?

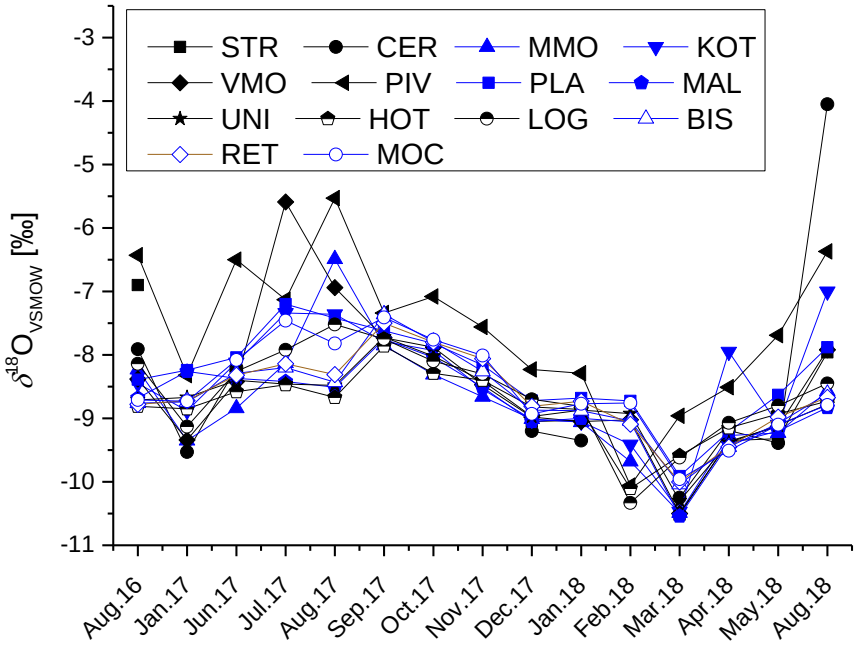
Methods

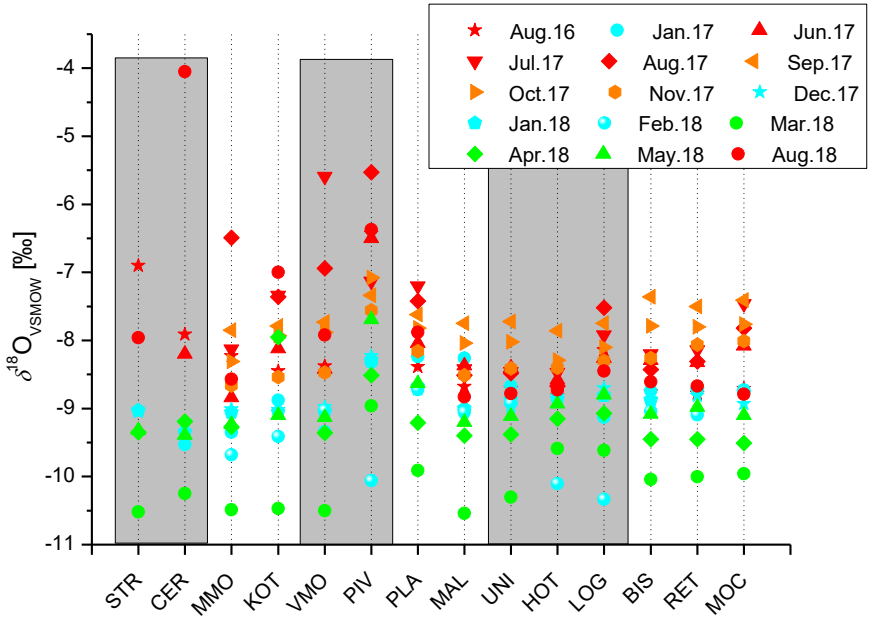
Analyses:

- $\delta^{13}C$ of DIC; $\delta^{18}O$ and $\delta^{2}H$ of water and precipitation
- Hydrochemistry: alkalinity, major and trace elements (QQQ ICP-MS)
- Non-traditional isotopes: Sr ($^{87/86}Sr$, $\delta^{88/86}Sr$), U ($^{234/238}U$, $\delta^{238}U$), (^{26}Mg), analysis by Nu Plasma MC-ICP-MS
    - Sr: separation on Sr-resin (SRM984)
    - U: separtion on UTEVA resin (CRM 112a)

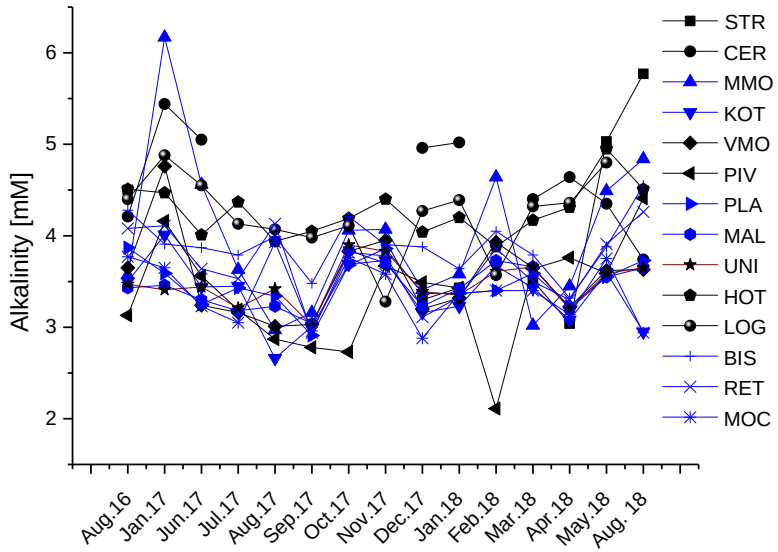


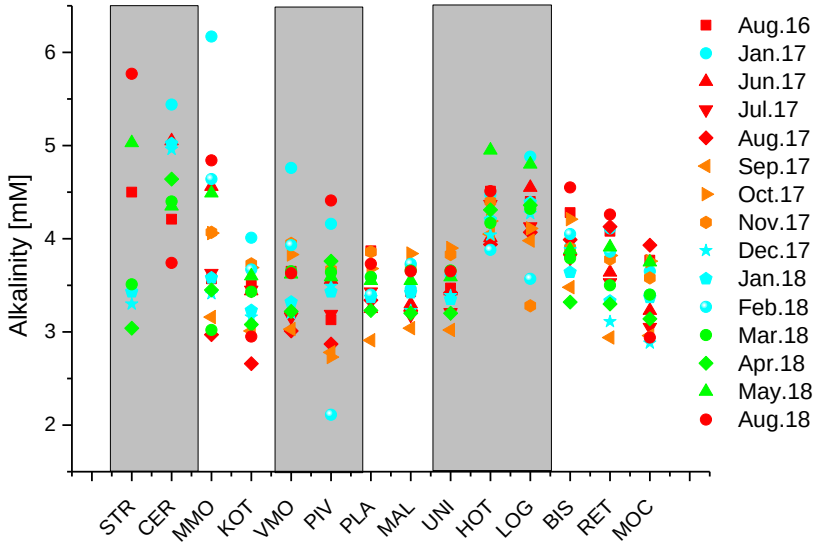


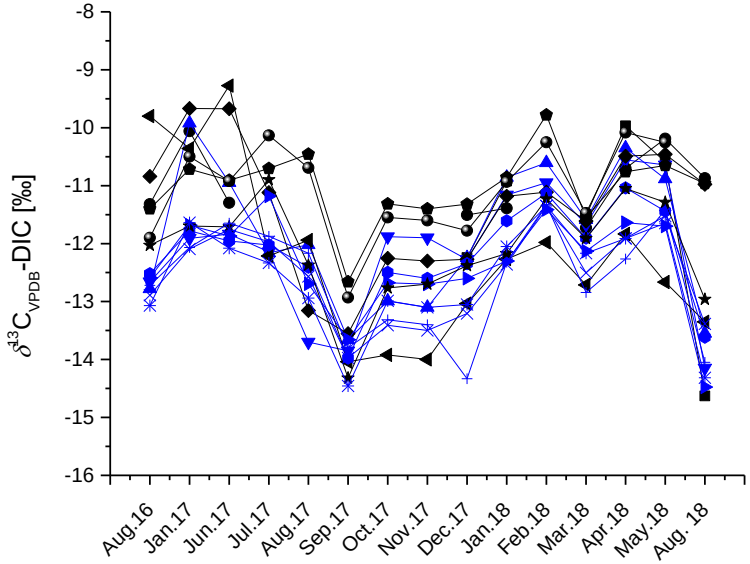


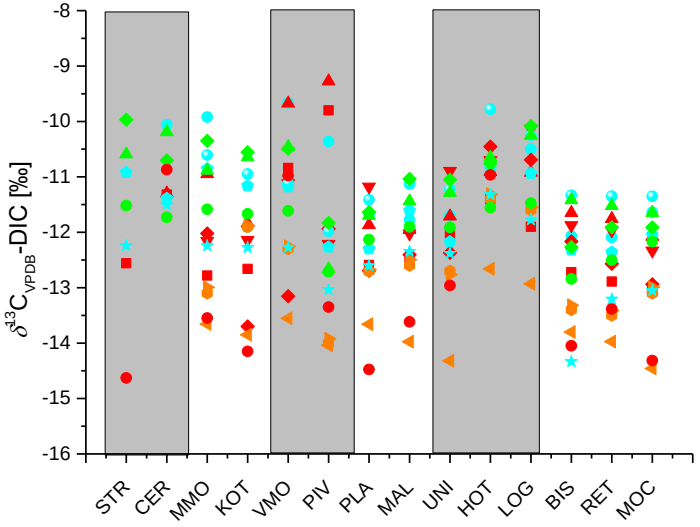


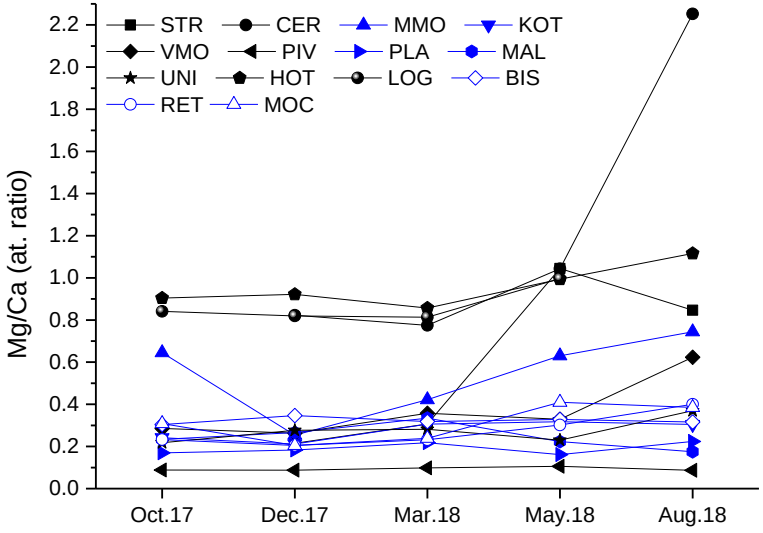
from Rusjan et al. 2018

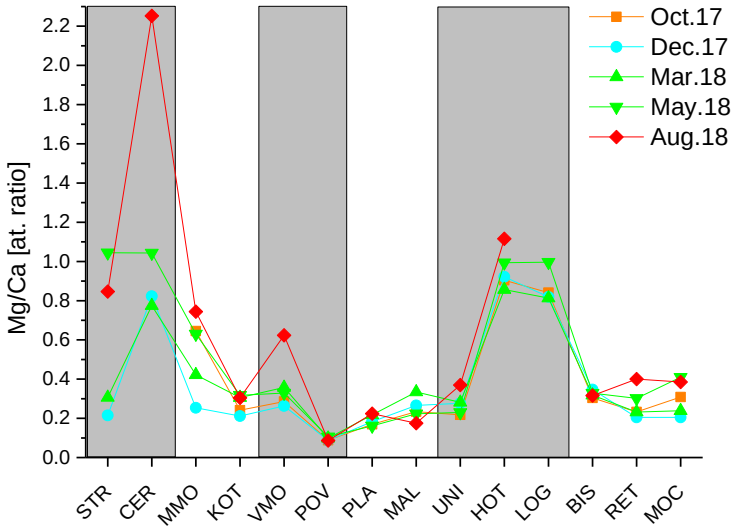

Alkalinity [mM]
2
3
4
5
6
Aug.16
Jan.17
Jun.17
Jul.17
Aug.17
Sep.17
Oct.17
Nov.17
Dec.17
Jan.18
Feb.18
Mar.18
Apr.18
May.18
Aug. 18
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC

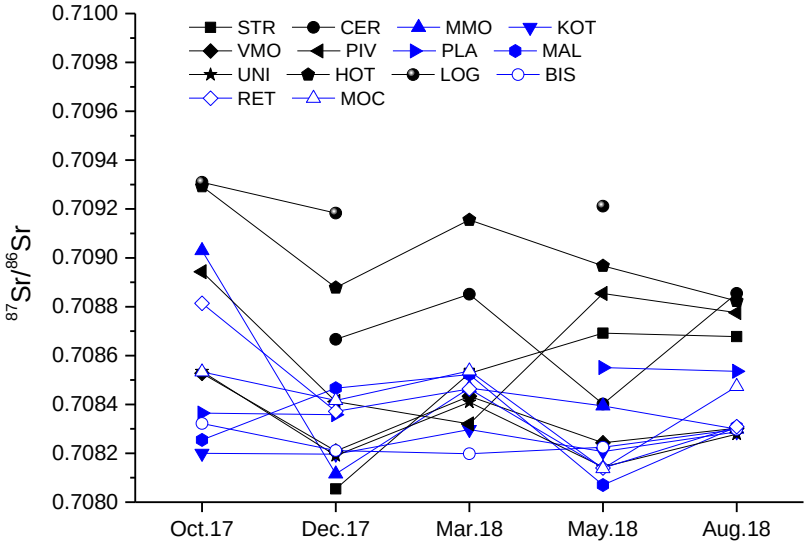

Alkalinity [mM]
2
3
4
5
6
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
Aug.16
Jan.17
Jun.17
Jul.17
Aug.17
Sep.17
Oct.17
Nov.17
Dec.17
Jan.18
Feb.18
Mar.18
Apr.18
May.18
Aug.18

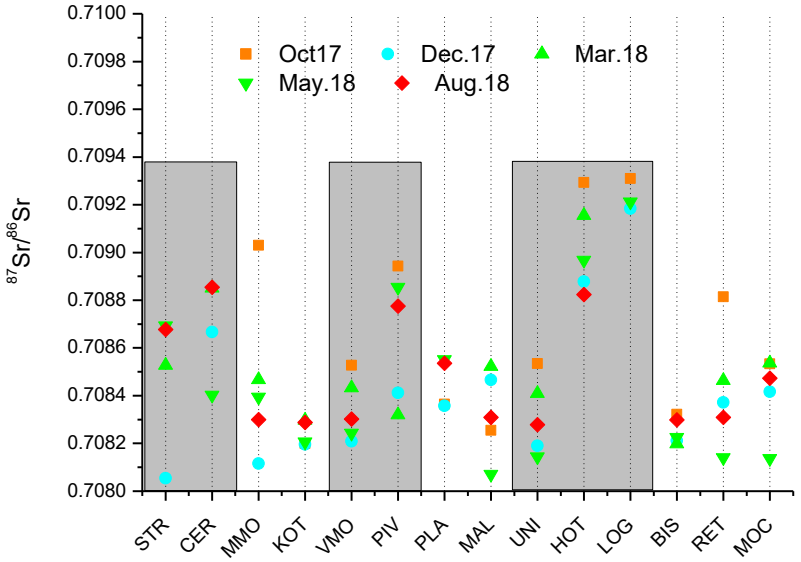

δ13CVPDB-DIC [‰]
-8
-9
-10
-11
-12
-13
-14
-15
-16
Aug.16
Jan.17
Jun.17
Jul.17
Aug.17
Sep.17
Oct.17
Nov.17
Dec.17
Jan.18
Feb.18
Mar.18
Apr.18
May.18
Aug. 18

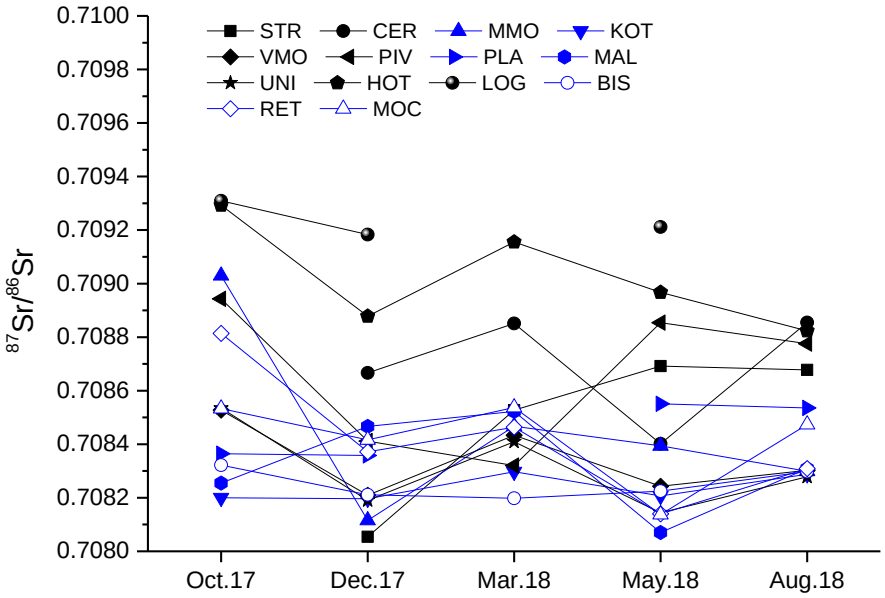

δ13CVPDB-DIC [‰]
-8
-9
-10
-11
-12
-13
-14
-15
-16
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC

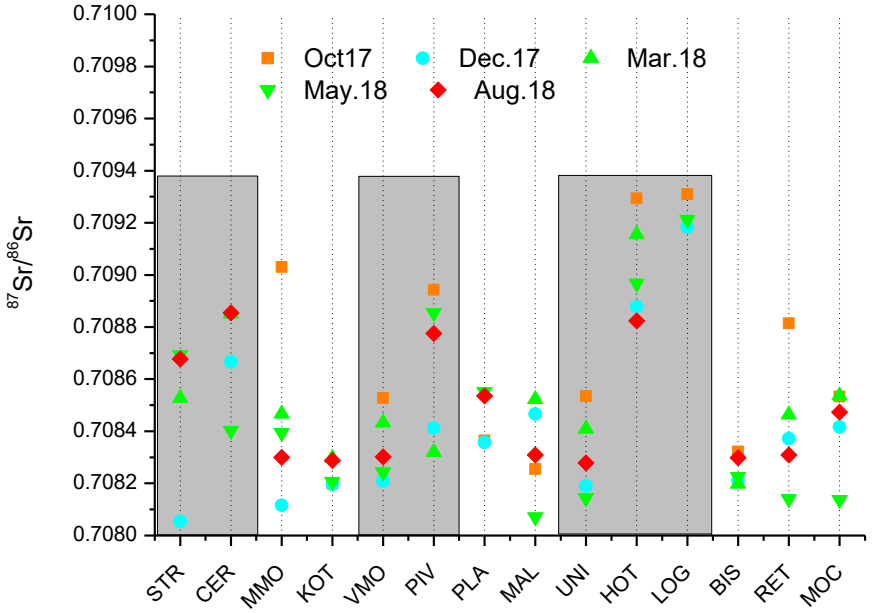

STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
Mg/Ca (at. ratio)
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct.17
Dec.17
Mar.18
May.18
Aug.18
Mg/Ca [at. ratio]
STR
CER
MMO
KOT
VMO
POV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC


STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
87Sr/86Sr
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct17
Dec.17
Mar.18
May.18
Aug.18
87Sr/86Sr
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC


STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
$^{87}Sr/^{86}Sr$
0.7100
0.7098
0.7096
0.7094
0.7092
0.7090
0.7088
0.7086
0.7084
0.7082
0.7080
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct17
Dec.17
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May.18
Aug.18
$^{87}Sr/^{86}Sr$
0.7100
0.7098
0.7096
0.7094
0.7092
0.7090
0.7088
0.7086
0.7084
0.7082
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STR
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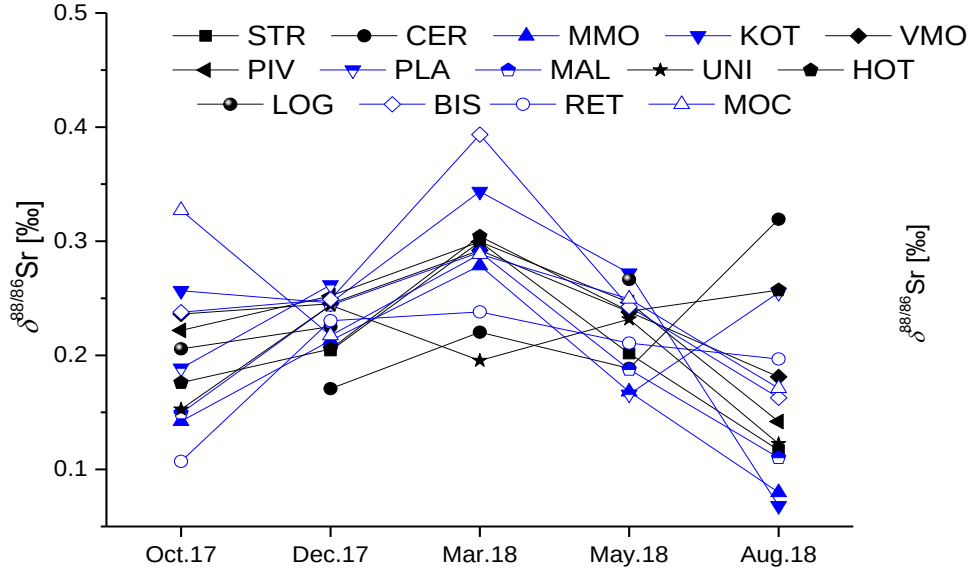
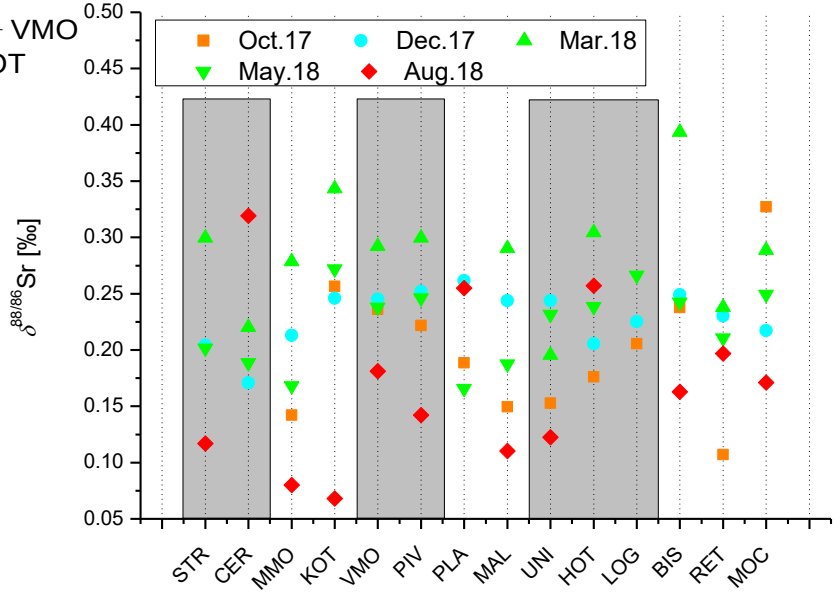
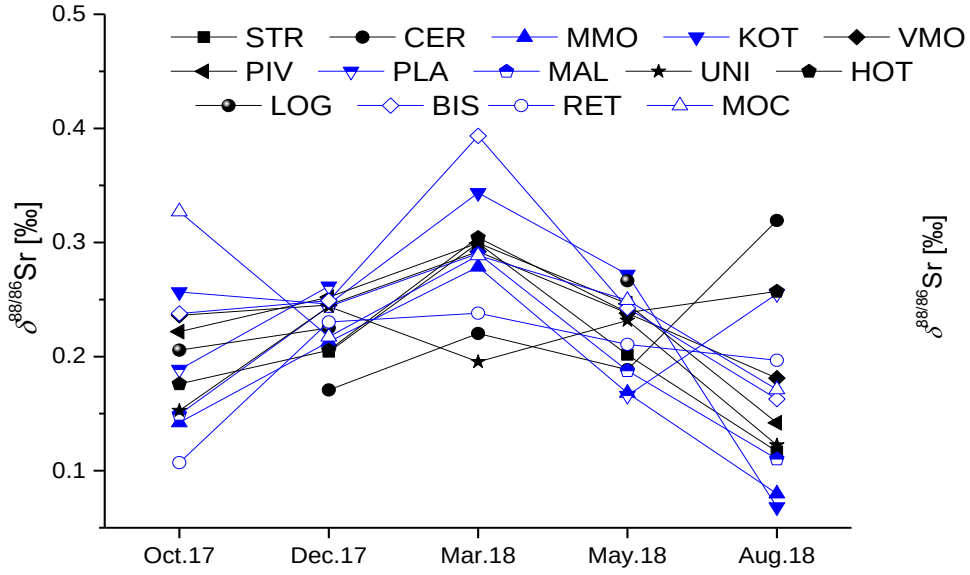
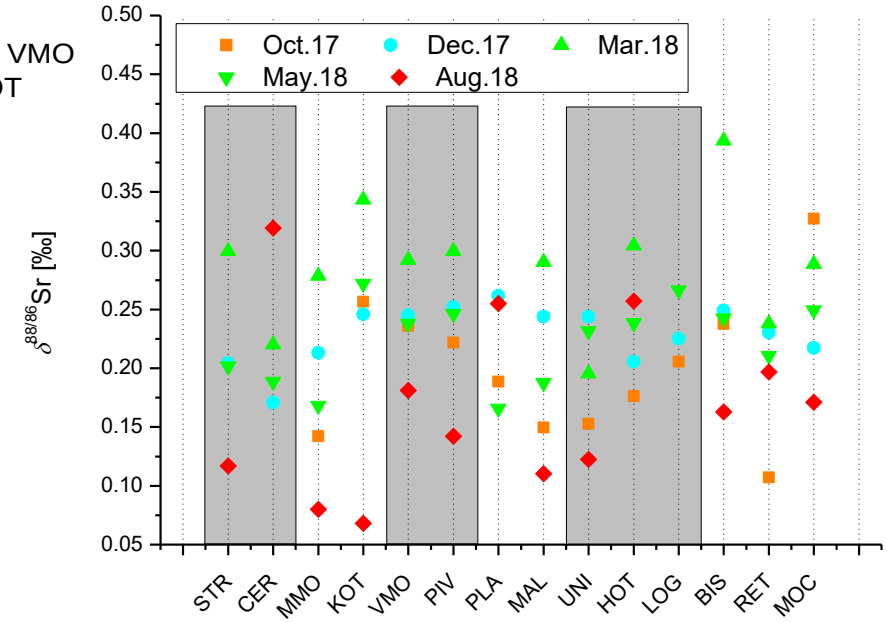
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC


STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
$\delta^{88/86}Sr$ [‰]
0.5
0.4
0.3
0.2
0.1
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct.17
Dec.17
Mar.18
May.18
Aug.18
$\delta^{88/86}Sr$ [‰]
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC


STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
δ88/86Sr [‰]
0.5
0.4
0.3
0.2
0.1
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct.17
Dec.17
Mar.18
May.18
Aug.18
δ88/86Sr [‰]
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
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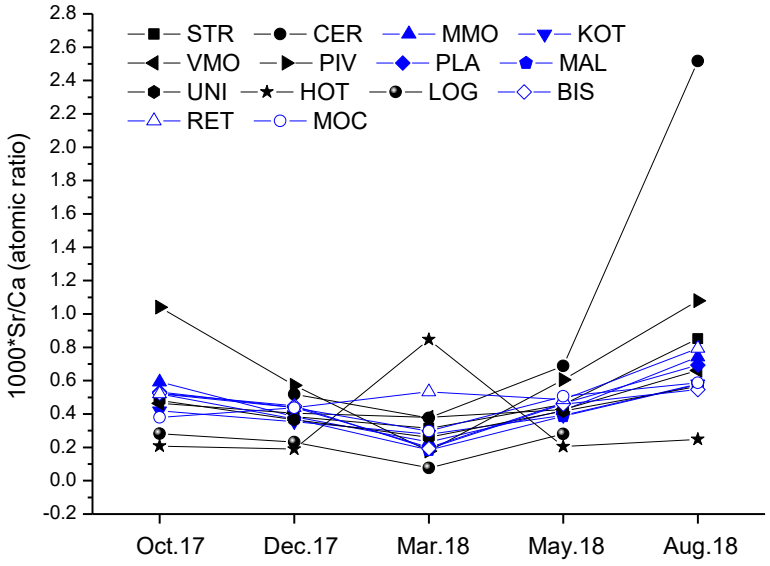
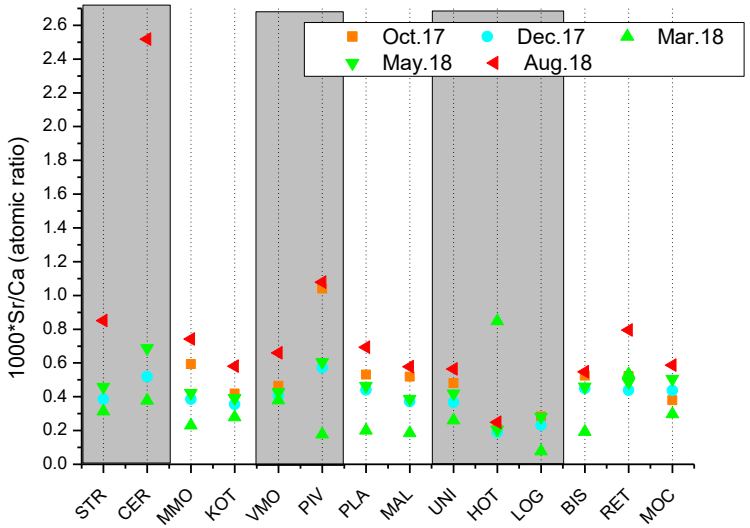
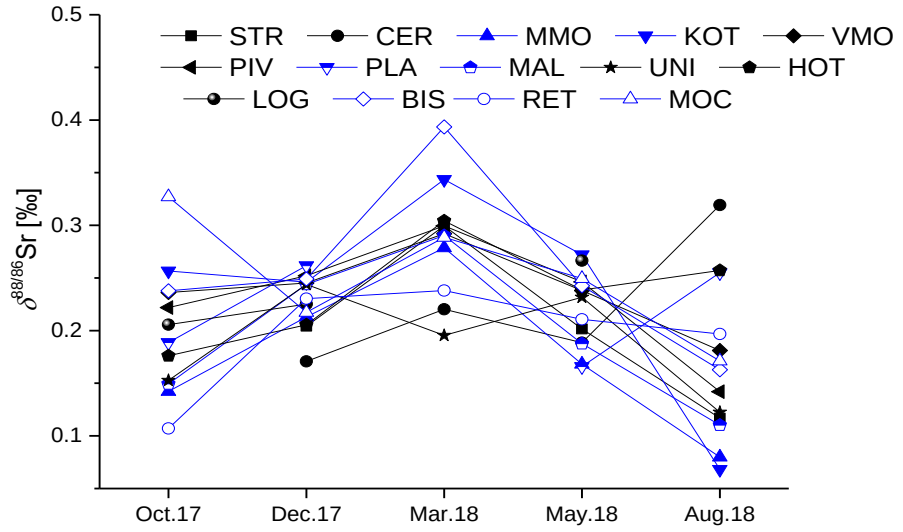
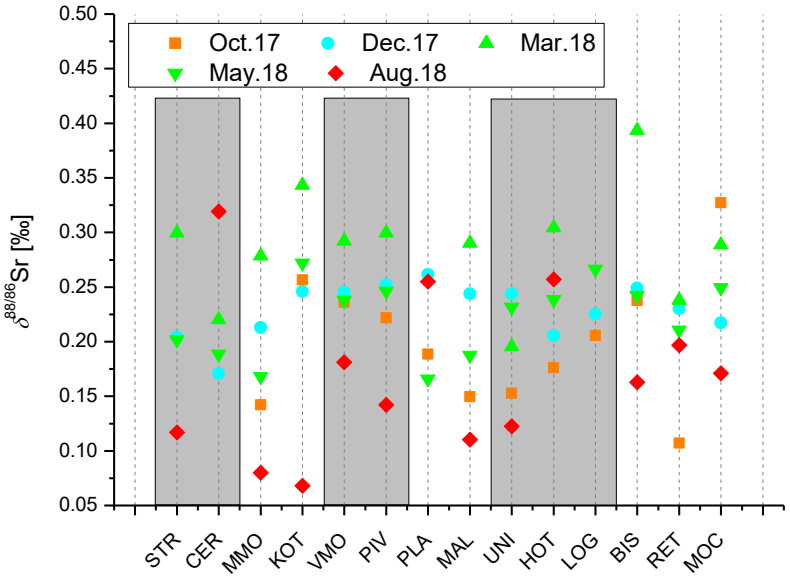
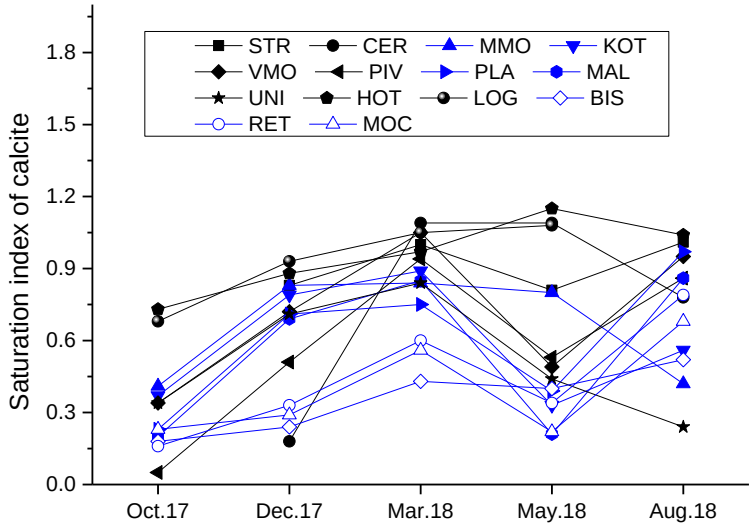
HOT
LOG
BIS
RET
MOC

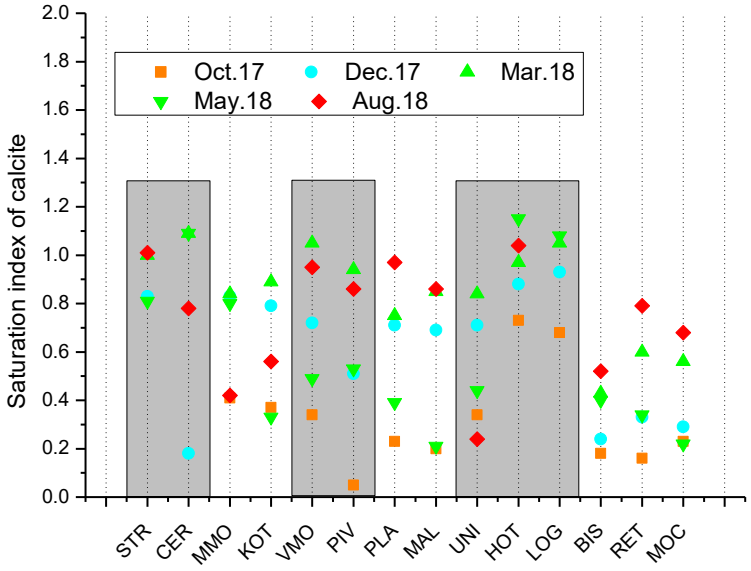

STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
1000*Sr/Ca (atomic ratio)
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
Oct.17
Dec.17
Mar.18
May.18
Aug.18

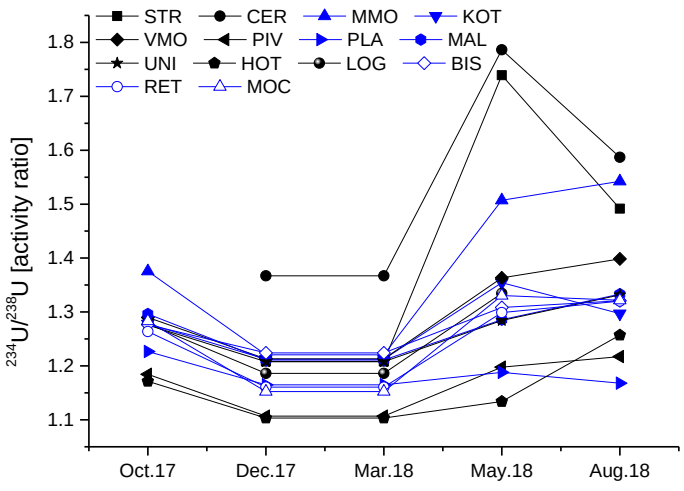

Oct.17
Dec.17
Mar.18
May.18
Aug.18
1000*Sr/Ca (atomic ratio)
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC

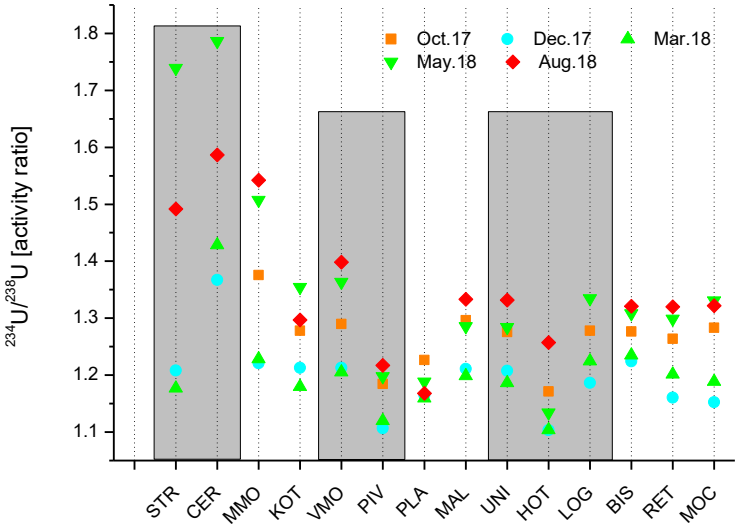

STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
δ88/86Sr [‰]
0.5
0.4
0.3
0.2
0.1
Oct.17
Dec.17
Mar.18
May.18
Aug.18

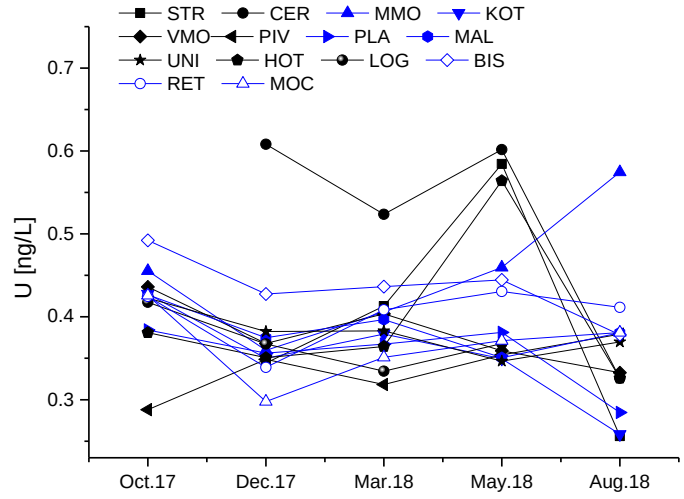

Oct.17
Dec.17
Mar.18
May.18
Aug.18
δ88/86Sr [‰]
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC


STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
Saturation index of calcite
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct.17
Dec.17
Mar.18
May.18
Aug.18
Saturation index of calcite
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC


STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC
234U/238U [activity ratio]
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
Oct.17
Dec.17
Mar.18
May.18
Aug.18


Oct.17
Dec.17
Mar.18
May.18
Aug.18
234U/238U [activity ratio]
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
STR
CER
MMO
KOT
VMO
PIV
PLA
MAL
UNI
HOT
LOG
BIS
RET
MOC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CER
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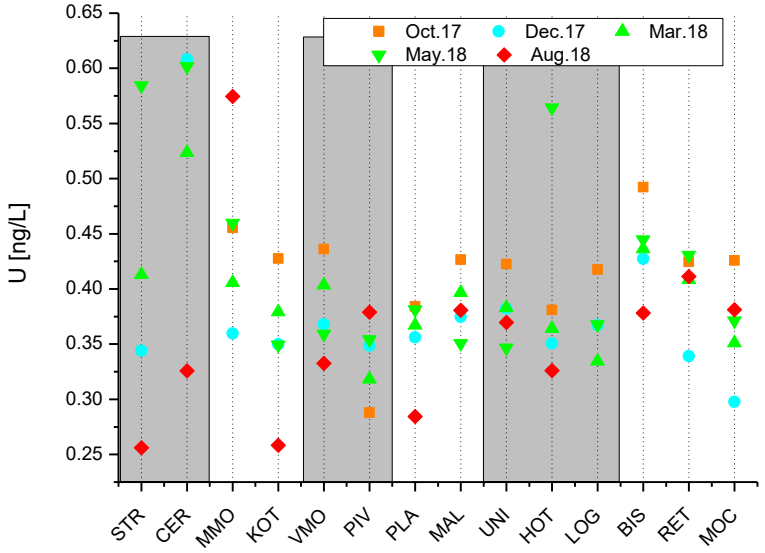
0.6
0.5
0.4
0.3
Oct.17
Dec.17
Mar.18
May.18
Aug.18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Dec.17
Mar.18
May.18
Aug.18
U [ng/L]
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0.60
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0.50
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0.35
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STR
CER
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Preliminary conclusions

- a LOT of work still to do…..

- $^{87/86}Sr$ was useful for interpretation of Mg concentrations and Mg/Ca ratios in the carbonate, while $\delta^{88/86}Sr$ provided information on the potential carbonate precpitation

- $^{234/238}U$ is the only parameter, which is consistently correlated with the discharge, so at the moment, it seems to be the best hydrological tracer for this fluviokarst system

…BUT many results are virtually inconclusive and need further investigation

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J1-9179 „Non-traditional isotopes as identifiers of authigenic carbonate“ 2018-2021