

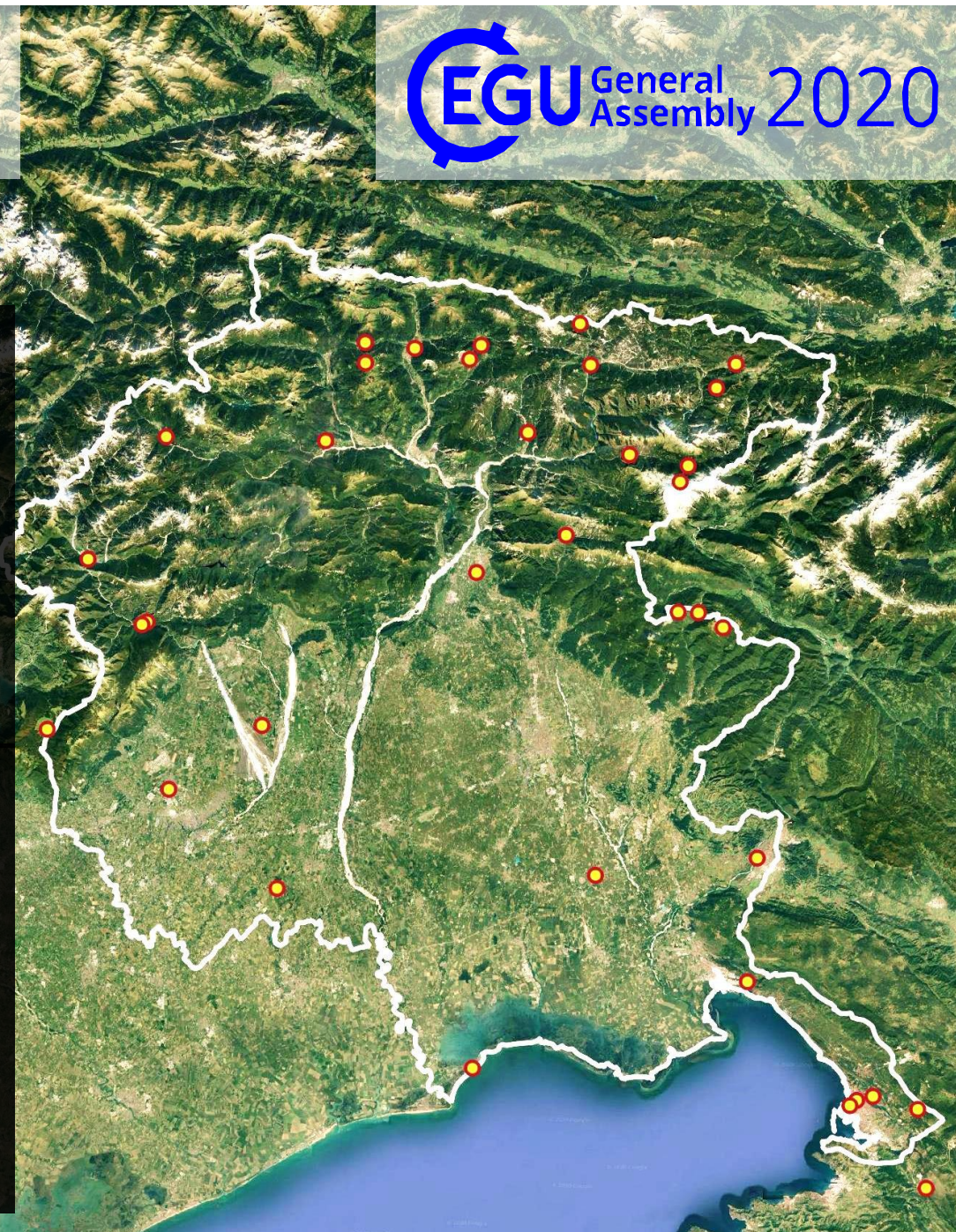
Interannual analysis of high spatially-resolved $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data in precipitation across North-East Italy

Masiol M.¹, Zannoni D.², Stenni B.¹, Dreossi G.², Zini L.³, Calligaris C.³, Karlicek D.³, Michelini M.³, Flora O.³, Cucchi F.³, Treu F.³

1. Dept. Environmental Sciences, Informatics and Statistics, Università Ca' Foscari Venezia

2. CNR-ISP, Venice, Italy

3. Dept. Mathematics and Geosciences, Università degli Studi di Trieste, Italy



Motivation

The **Friuli Venezia Giulia (FVG)** region exhibits among the **highest annual precipitation rates in Italy** and presents high-quantity, high-quality **groundwater resources**, today seriously threatened by anthropogenic pressures.

A comprehensive understanding of the **regional hydrogeological cycle** is therefore required, including the reconstruction of the isotopic composition of precipitation.

However, **data are still sparse** and/or incomplete, especially for $\delta^2\text{H}$ and D-excess.

Goals

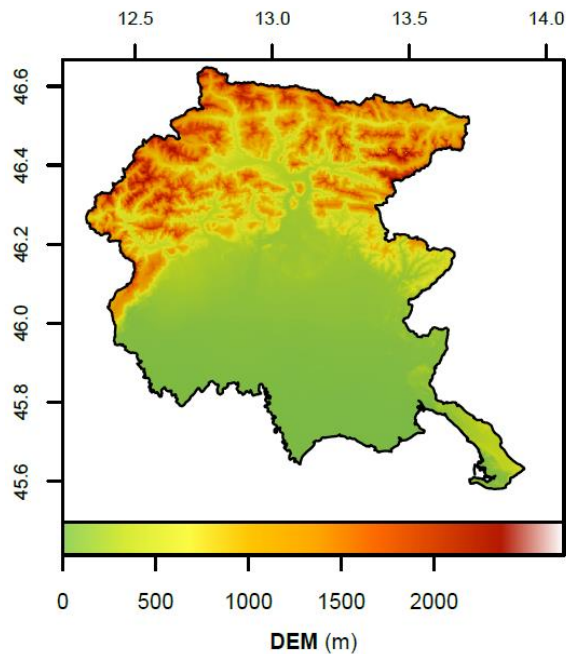
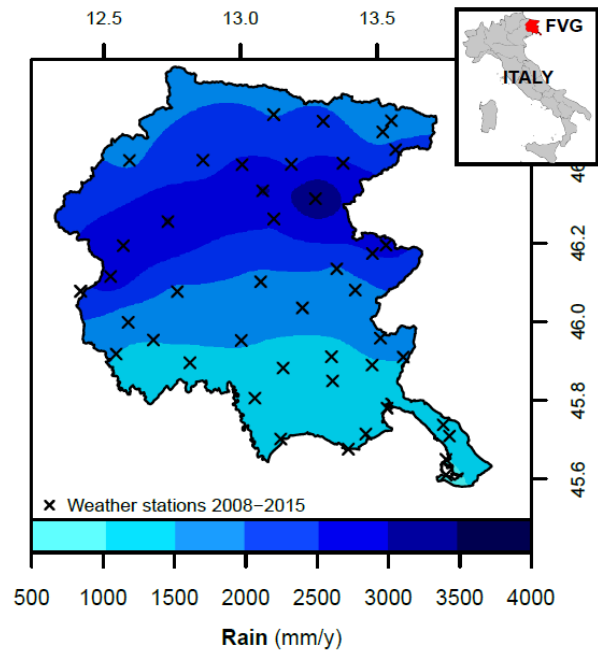
This study presents the isotopic composition of **2250 precipitation samples** collected **between 1984 and 2015** at **36 sites** across the FVG.

Objective **1**: analyze the spatial and seasonal variability of isotopic composition;

Objective **2**: quantify interannual trends and analyze their spatial distribution;

Objective **3**: investigate the spatial gradients of the local meteoric water lines;

Objective **4**: estimate the spatial distribution of $\delta^2\text{H}$, $\delta^2\text{H}$, deuterium excess and generate annual and seasonal maps.



Materials and Methods

Sites. 36 sites, almost all with a related weather station;

Altitude range: 14-1848 m;

Distance from the nearest coastline: 0 to 85 km.

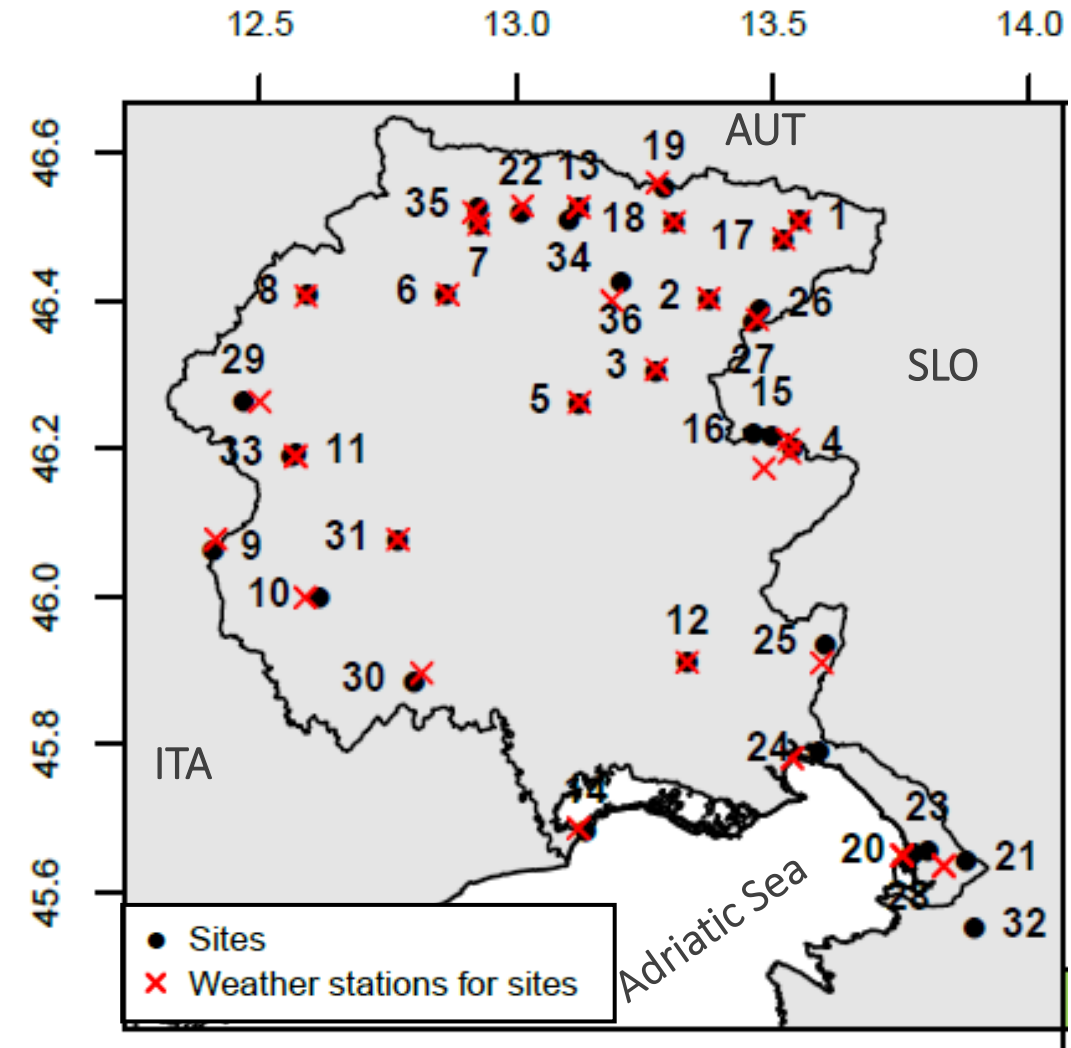
Timing. Most sites active during 2004-2015;

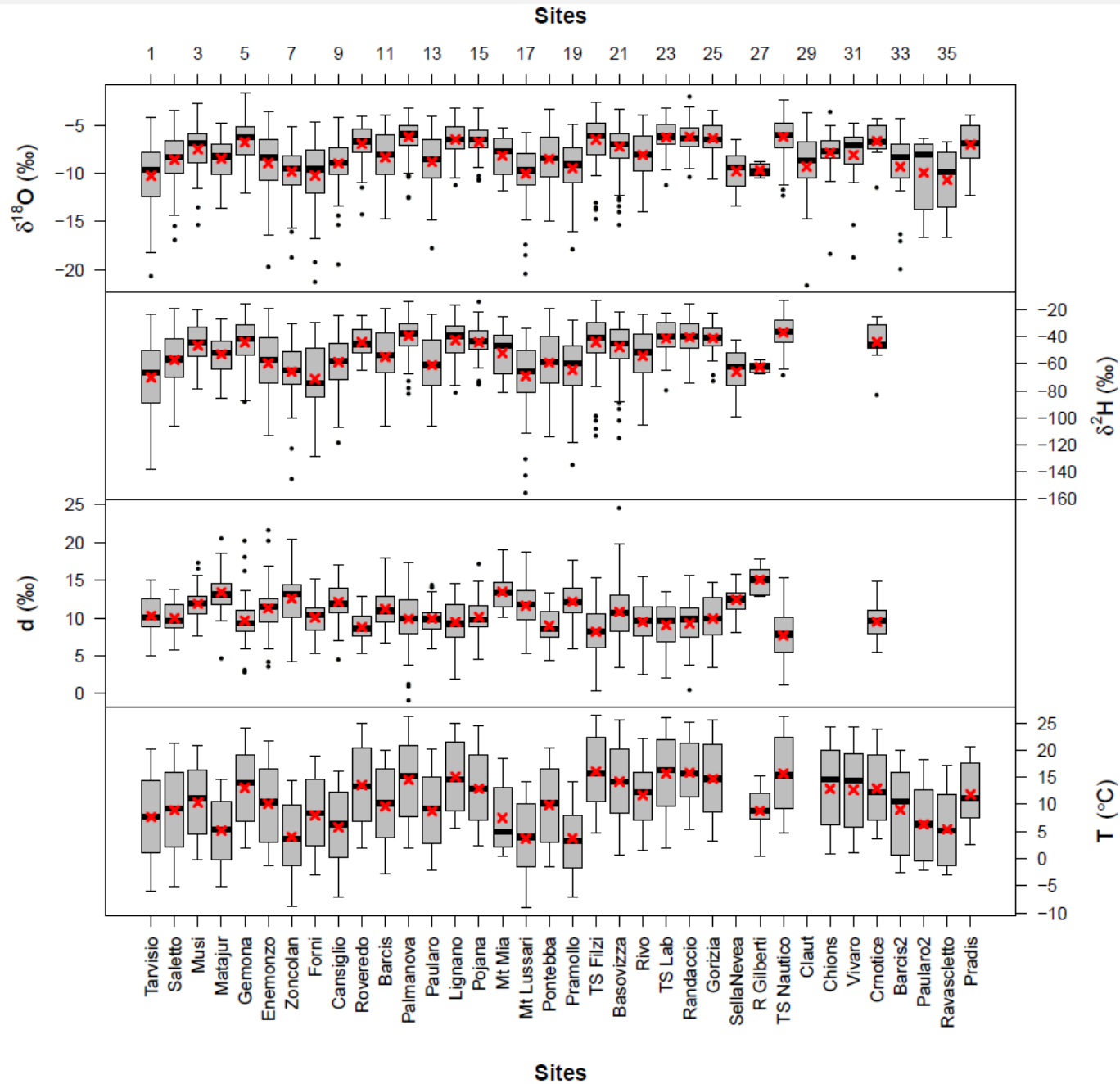
4 sites have $\delta^{18}\text{O}$ time-series longer than 9 years (starting in the 80s or 90s; ID 20, 21, 22, 28).

Sampling. Monthly-to-seasonal frequencies using rain gauges built to prevent evaporation processes.

Analytical. Analysis of $\delta^{18}\text{O}$ (2250 samples), $\delta^2\text{H}$ and D-excess (1367 samples) mostly using IRMS (with $\text{CO}_2\text{-H}_2/\text{water}$ equilibration method); ~10% samples analyzed with CRDS.

QA/QC and data consistency. Comparable sampling, analytical procedures and analytical precision through the entire sampling campaign. Good agreement between IRMS and CRDS.





Data overview

Isotopic composition. Single samples :

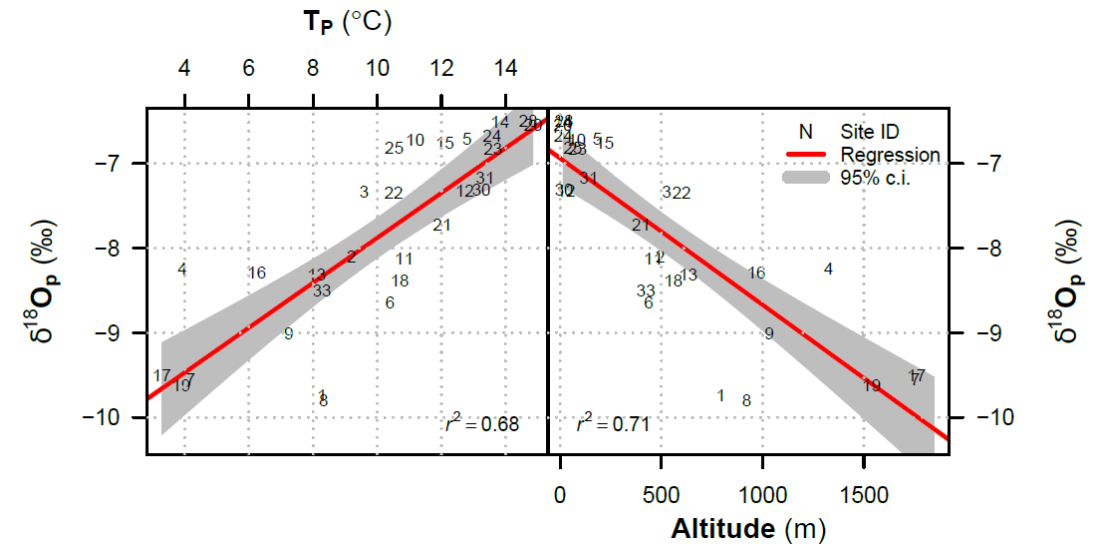
$\delta^{18}\text{O}$ -21.6‰ to -1.7‰;

$\delta^2\text{H}$ -155‰ to -13‰;

D-excess (d) -0.9‰ to 24.6‰.

Weather. Single sample average air temperature: -9/+26°C.

Significant temperature and altitude effects; the amount effect is negligible.



UNIVERSITÀ
DEGLI STUDI DI TRIESTE



Università
Ca' Foscari
Venezia

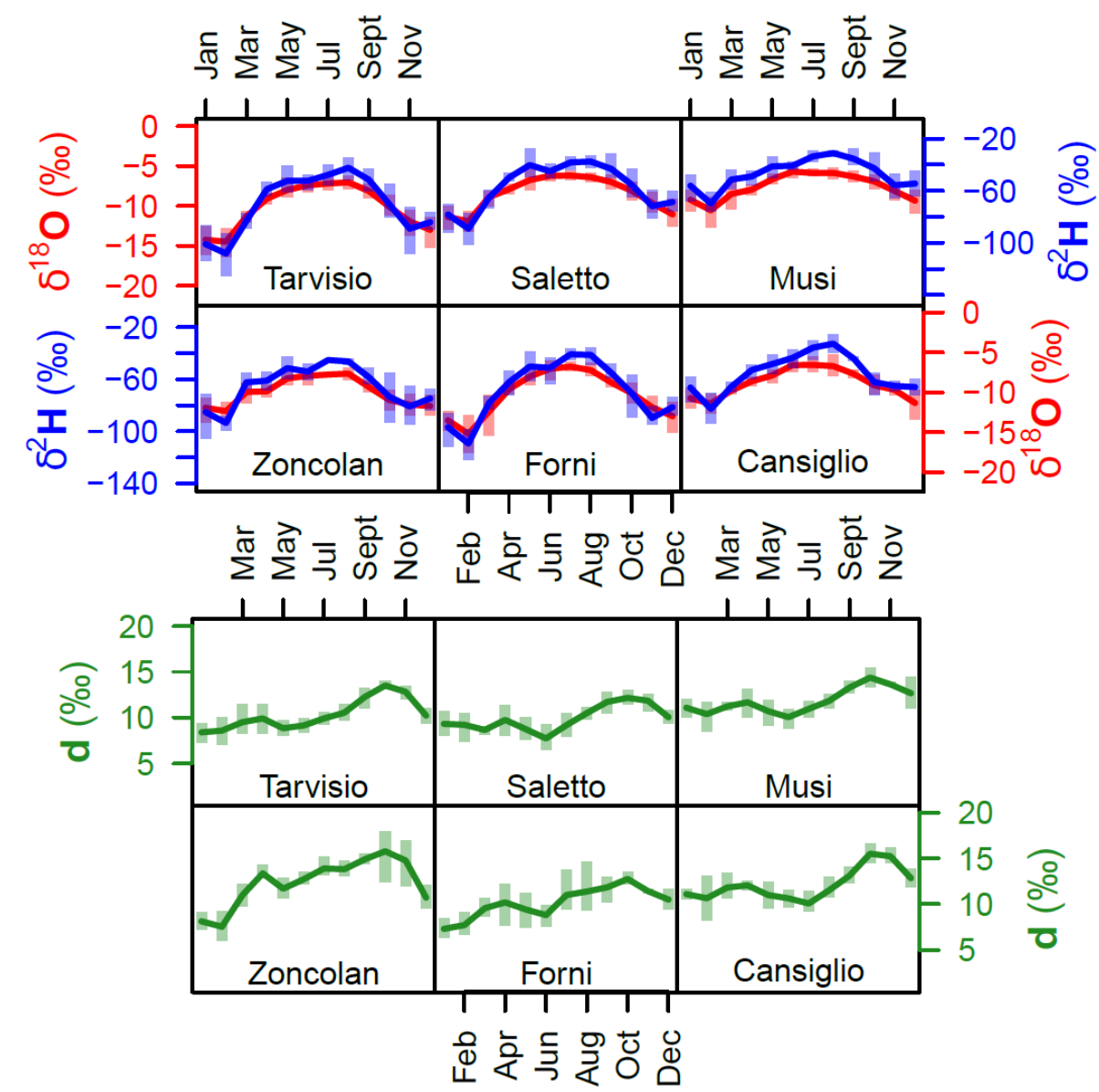
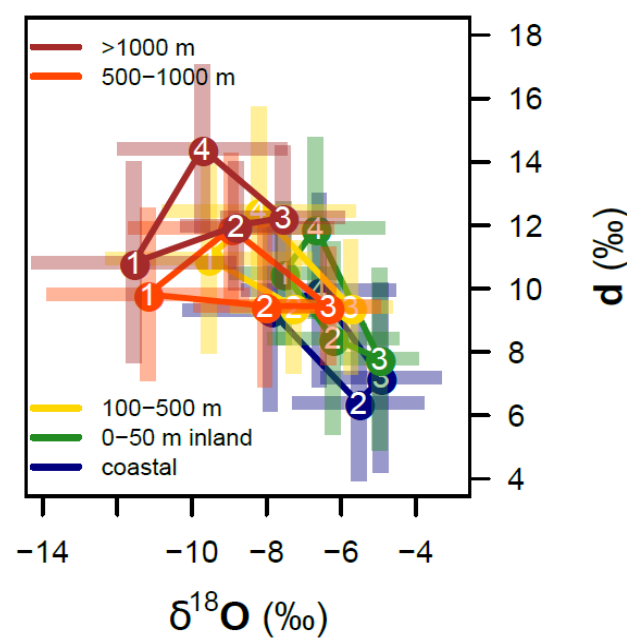


4

Seasonal variations

Seasonality: the more $\delta^{18}\text{O}$ - and $\delta^2\text{H}$ -depleted samples in winter. Weaker seasonal effect on D-excess, generally higher values in autumn.

Groups of sites by altitude and continentality: the more elevated and continental are the sites, the lower $\delta^{18}\text{O}$ and higher D-excess (d) values are measured; this relationship is observed during all the seasons except winter, which shows almost constant D-excess values.

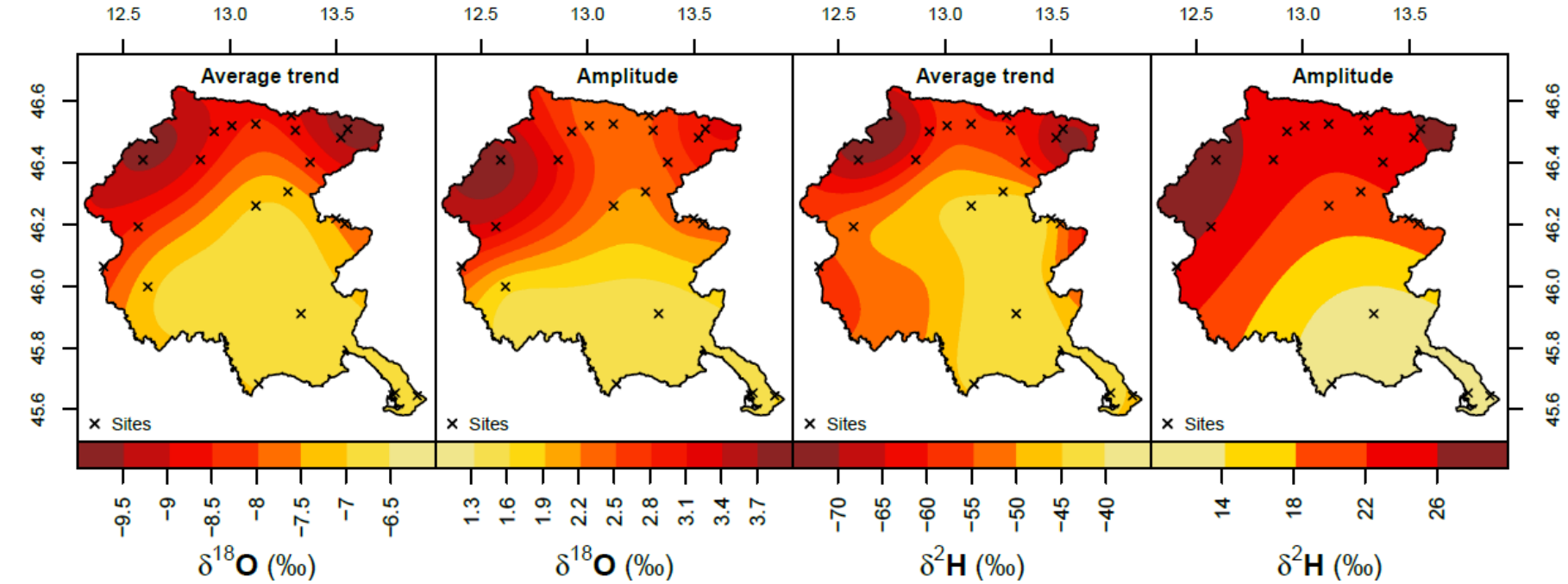
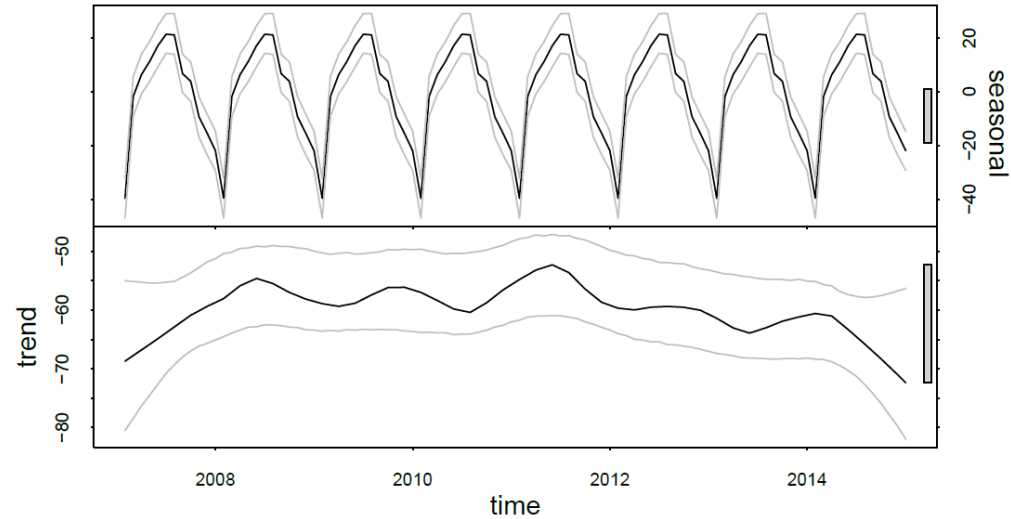


De-trended seasonal patterns by STL

Quasi-sinusoidal seasonal cycles found at all the sites for $\delta^{18}\text{O}$ - and $\delta^2\text{H}$. The shape of the seasonal component was less prominent at sites close to the coastline or located in the lower plain areas.

Both average trends and amplitudes showed gradients with increasing values at higher latitudes.

Weak de-trended seasonal patterns for D-excess.



Interannual trends

No statistically significant interannual trends were detected by the Mann-Kendall trend analysis and the Theil-Sen nonparametric estimator of slope analyzing the long time-series (>9 years of data).

Local meteoric water lines

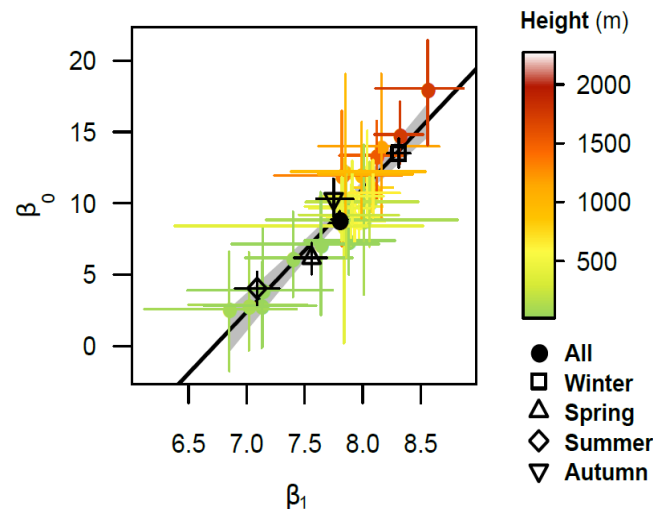
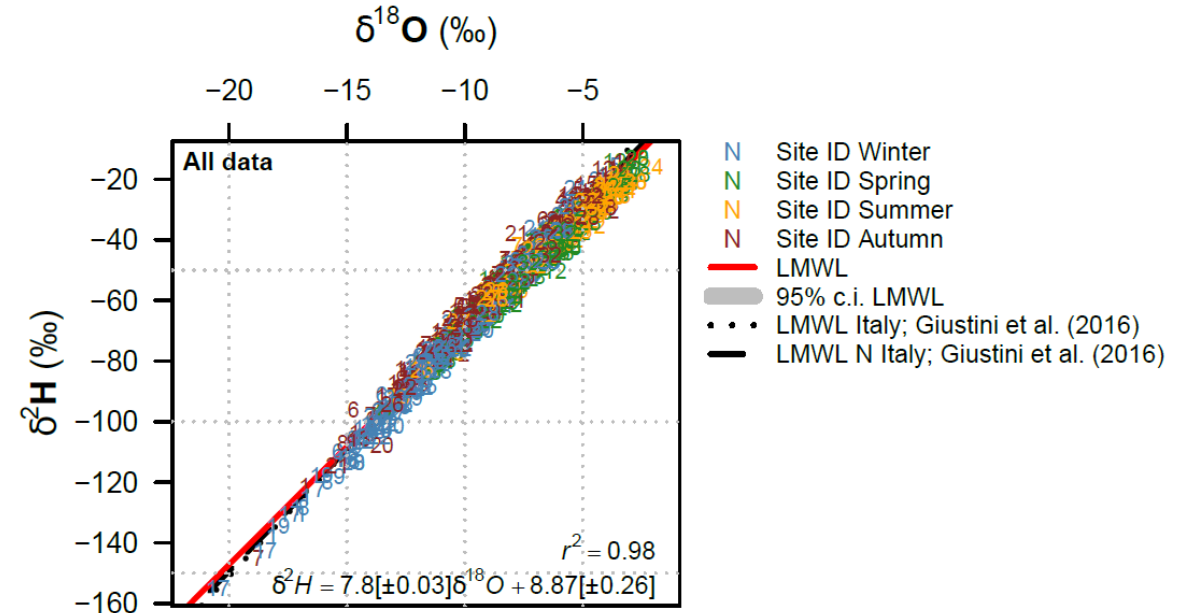
Computed on **all single samples** ($n=1365$, $r^2 = 0.98$):

$$\delta^2\text{H} = 7.8 [\text{CI } 7.7; 7.9] \cdot \delta^{18}\text{O} + 8.9 [\text{CI } 8.3; 9.4]$$

Precipitation-weighted yearly averages ($r^2 = 0.98$):

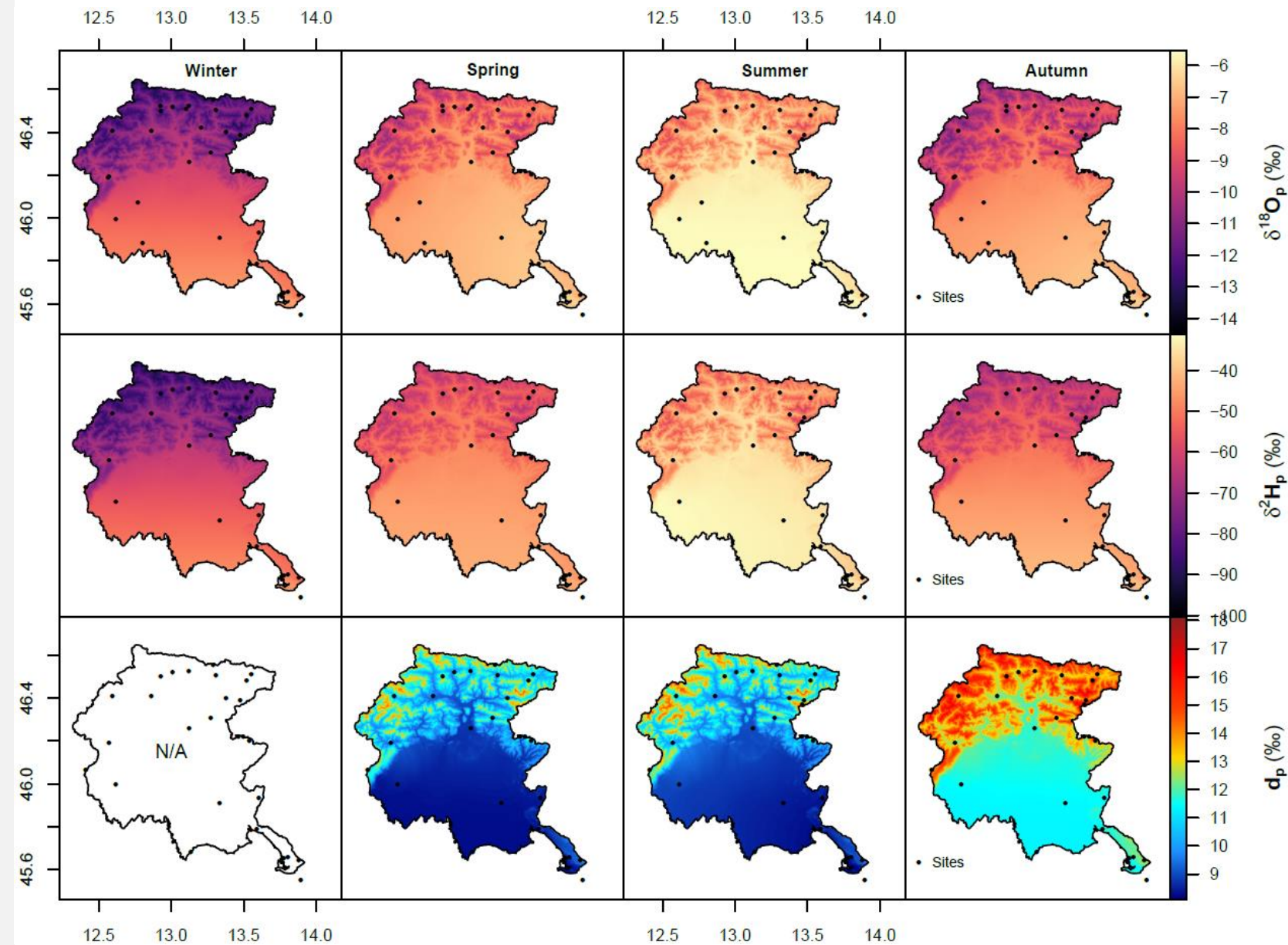
$$\delta^2\text{H} = 7.2 [\text{CI } 6.8; 7.6] \cdot \delta^{18}\text{O} + 4.5 [\text{CI } 1.6; 7.6]$$

LMWLs very similar to previous studies in North Italy.



A further regression analysis among slopes (β_1) and intercepts (β_0) of LMWLs showed a clear and strong relationship ($r^2=0.85$).

Intercepts increase quasi-linearly with the altitude for sites located $>\sim 500$ m, indicating that topography has an effect on non-equilibrium kinetic fractionation processes.



Mapping

A stepwise multiple linear regression model was applied to reconstruct the isotopic composition of precipitation at a regional scale.

This approach was able to explain 68-75% and 60-82% of variances for $\delta^{18}\text{O}_p$ and $\delta^2\text{H}_p$, respectively. The model failed to estimate D-excess during wintertime, while it was able to explain 50-79% of the variance during the remaining seasons. The RMSE are in the 0.5-1‰, 3.5-8.2‰ and 0.9-1.5‰ intervals for $\delta^{18}\text{O}_p$ and $\delta^2\text{H}_p$, and D-excess, respectively.




Thank You





Università
Ca' Foscari
Venezia



UNIVERSITÀ
DEGLI STUDI DI TRIESTE

Mauro Masiol, Barbara Stenni 

+39 041 234 8996 

mauro.masiol@unive.it; 

barabara.stenni@unive.it 