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Compound-specific δ^2H using analytical pyrolysis (Py-CSIA) for assessing source and processes of soil organic matter driven by climatic changes within a Mediterranean evergreen oak forest (*dehesas*)

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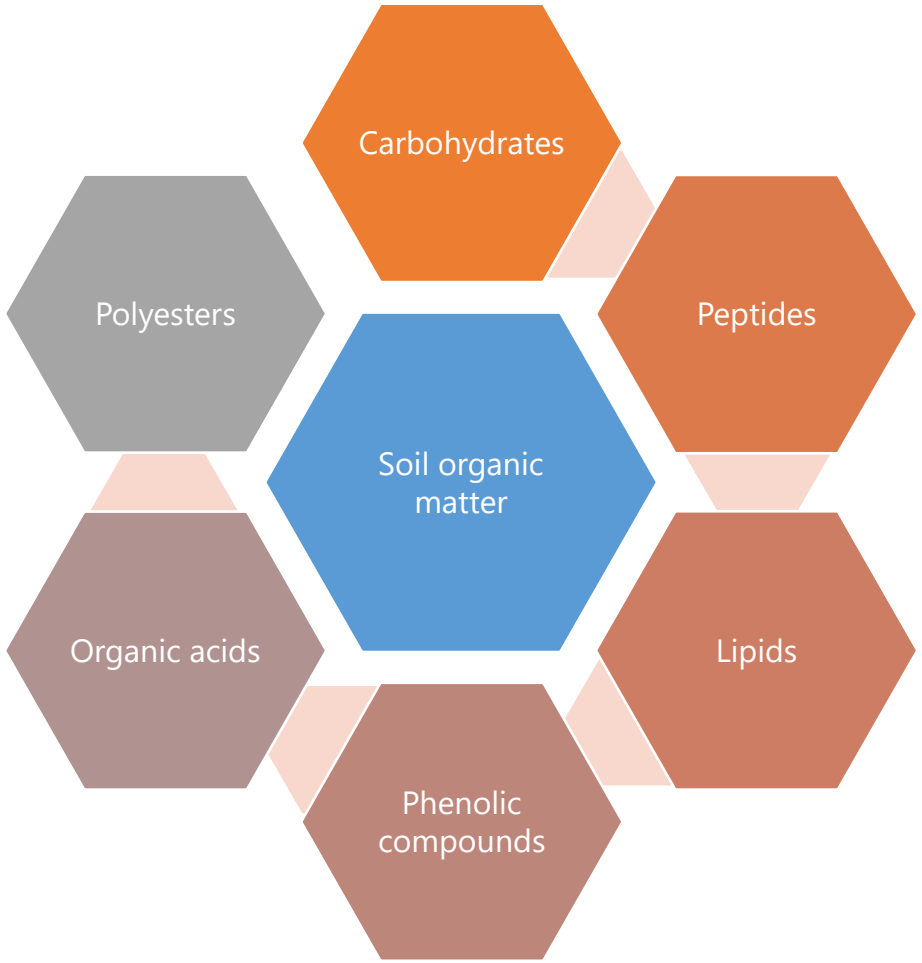
Highlights:
In this display, we describe and validate a methodology based on analytical pyrolysis for the direct measure of compound-specific H isotope composition (δ^2H) in soil samples. The technique combines Py-GC with a high-temperature conversion reactor and a continuous flow isotope ratio mass spectrometer (IRMS) (Py-GC-HTC IRMS).
According to the content showed in the following slides, we will bring novelty results in relation to the processes affecting the isotopic composition of non-exchangeable hydrogen exerted by climatic treatments on diverse SOM specific compounds.

Motivation and objectives



- Carbon dynamics have been widely studied using the natural $^{13}C/^{12}C$ ratios: different turnover of soil organic pools [1].
- **Non-exchangeable hydrogen** are expected to follow the same dynamics as carbon in soil: is worth of study as an approach to estimate dynamic processes such as stabilization, mineralization, or biodegradation [2].
- The **total bulk soil**, composed of a mixture of non-exchangeable and exchangeable, organic and inorganic hydrogen, makes the hydrogen isotopic composition hard to determine [3].
- A prerequisite to reach this objective is to test the applicability of direct compound-specific H isotopic techniques (**Py-GC-HTC/IRMS**) for the determination of total non-exchangeable H in soil organic matter.

Experimental design

In April 2019, soil samples were taken from the 10 uppermost cm of soil in an experimental plot (under evergreen oak canopy), in collaboration with the project DECAFUN (CGL2015-70123-R). Sampling was conducted in Pozoblanco (Córdoba, SW Spain).

Two habitats:
- Under the canopy (tree)
- Open

Four climatic treatments:
1. Warming (W)
2. Control (C)
3. Drought (D)
4. Warming + dry (W+D)

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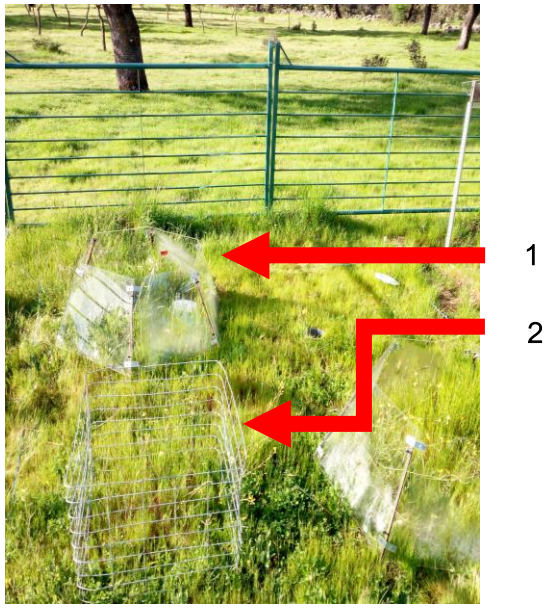

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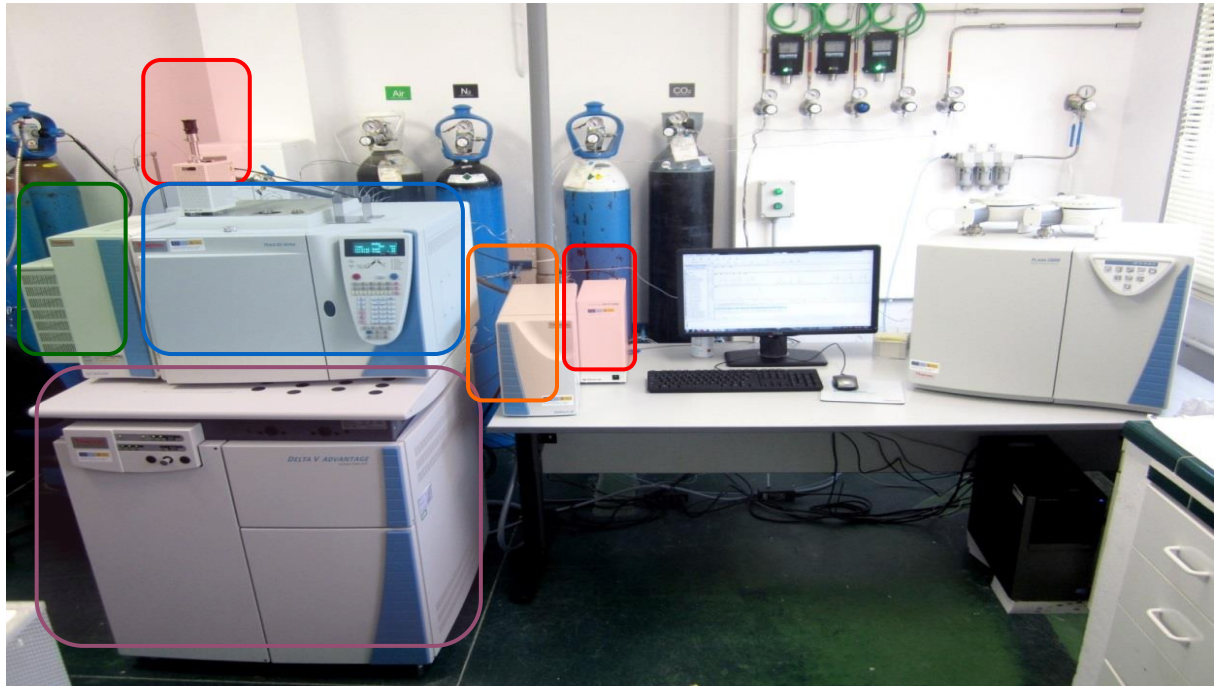
Lab equipment



Py-GC/MS: structural information

A conventional Py-GC/MS system (pyrolyzer F. Labs 2020i) + Agilent MSD 6890N

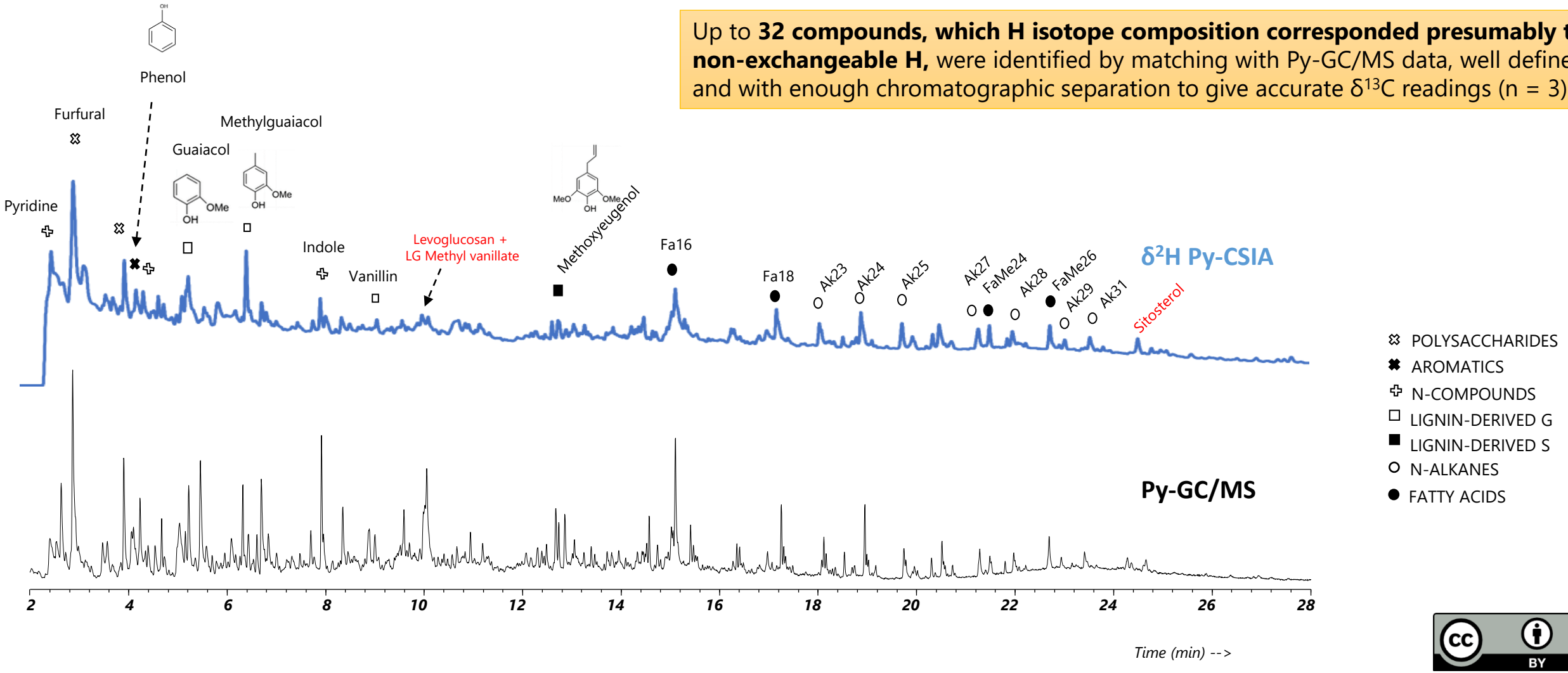
Py-GC-C/TC-IRMS: isotopic information ($\delta^{13}C$, $\delta^{2}H$, $\delta^{18}O$, $\delta^{15}N$)

A double-shot/micro-furnace pyrolyzer (Frontier Laboratories, model 3030iD)
Gas chromatographer (Trace Ultra GC system)
Individual volatile pyrolysis products separated by GC are directed to GC-Isolink System with combustion (C and N) and pyrolysis (H or O) micro-furnaces.
Coupled to isotope ratio mass spectrometer, IRMS (Thermo Delta V Advantage) via a ConFlo IV univ interface unit

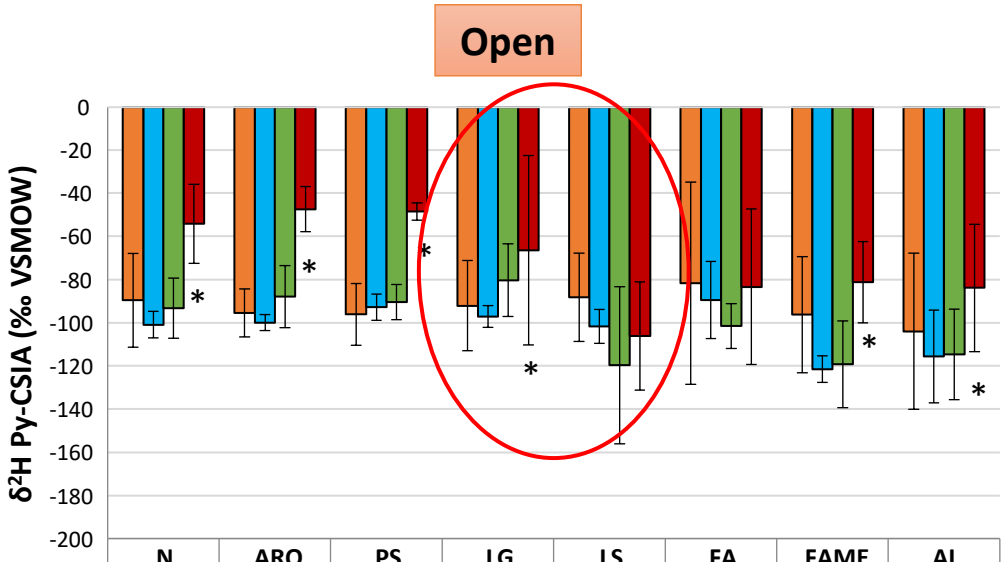
Py-GC-HTC-IRMS was externally calibrated prior to any analysis, using standard mixtures C4 for n-alkanes (n-C_{16} to n-C_{30}), obtained from the Stable Isotope Laboratory (Schimmelmann, Indiana University) http://arndt.schimmelmann.us/compounds.html
The values obtained were accepted when fitting accordingly to a straight line ($R^2 > 0.99$).

Chromatographic results

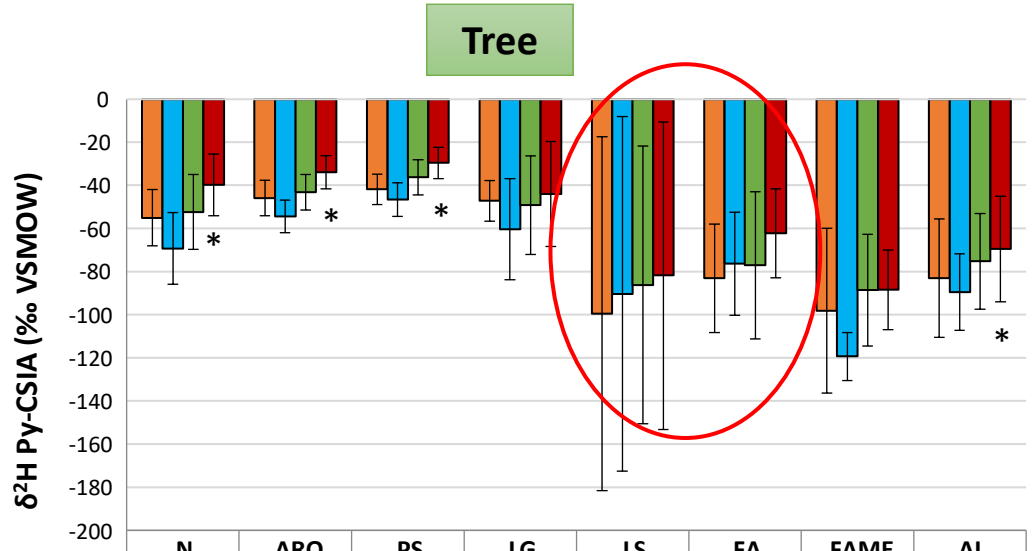
Up to **32 compounds, which H isotope composition corresponded presumably to non-exchangeable H,** were identified by matching with Py-GC/MS data, well defined and with enough chromatographic separation to give accurate $\delta^{13}C$ readings (n = 3).



δ^2H CSIA according to SOM compounds



	N	ARO	PS	LG	LS	FA	FAME	AL
OPEN * CONTROL	-89.57	-95.48	-96.10	-92.13	-88.25	-81.67	-96.26	-103.96
OPEN * WARMING	-100.89	-99.93	-92.74	-97.06	-101.70	-89.43	-121.47	-115.58
OPEN * DRY	-93.25	-87.94	-90.34	-80.31	-119.68	-101.55	-119.34	-114.61
OPEN * W+D	-54.13	-47.41	-48.37	-66.39	-106.15	-83.41	-81.23	-83.87



	N	ARO	PS	LG	LS	FA	FAME	AL
TREE * CONTROL	-55.06	-45.90	-41.79	-47.20	-99.53	-83.05	-98.18	-82.98
TREE * WARMING	-69.27	-54.41	-46.68	-60.42	-90.32	-76.27	-119.33	-89.53
TREE * DRY	-52.35	-43.27	-36.28	-49.24	-86.22	-77.09	-88.54	-75.25
TREE * W+D	-39.80	-33.91	-29.60	-44.06	-81.81	-62.19	-88.50	-69.47

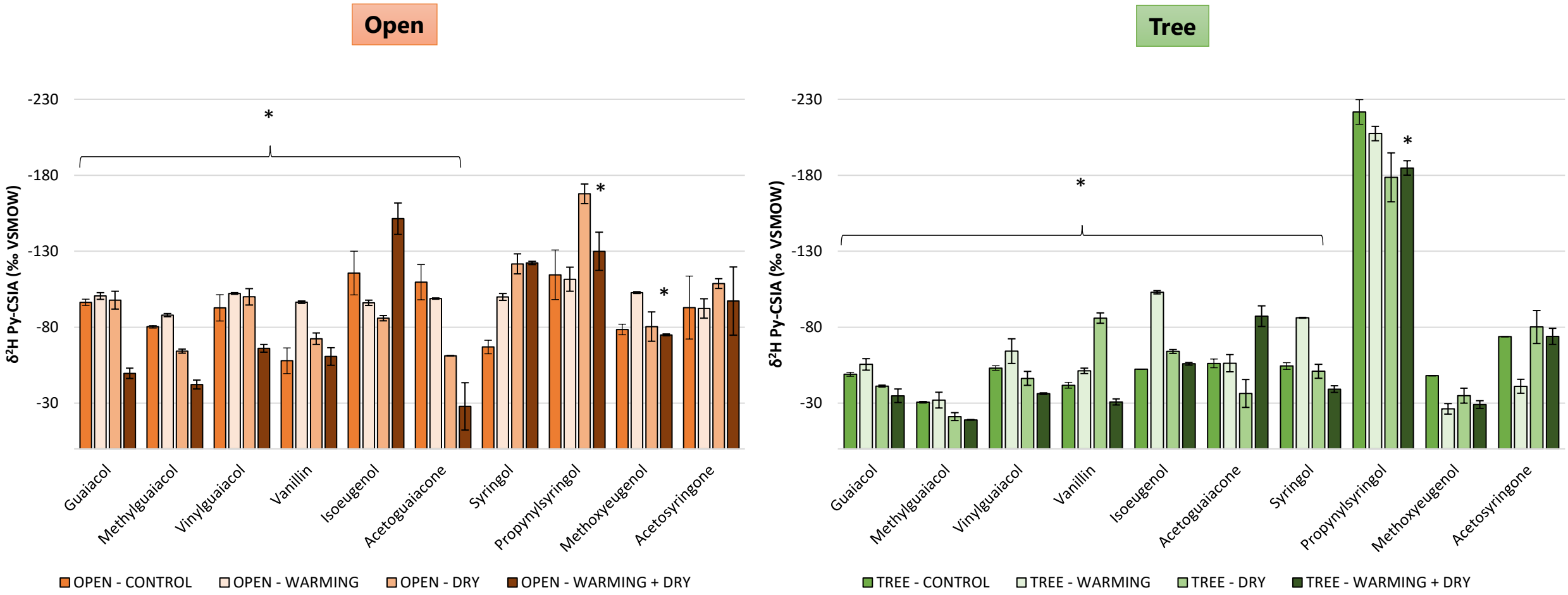
ANOVA at $p<0.05$. "*" indicates significant differences comparing treatments within a same compound family

Significant differences are reportedly driven by the differences in habitat: **more depleted δ^2H values were found in SOM produced in the open pasture than under the tree canopy, in all compounds except for FAME.**

Within each habitat, the climatic treatment that showed remarkable statistical differences among all were the **combination of warming + dry (W+D)**

These isotopic shifts were more pronounced in open pasture than under the tree canopy, especially for lignin-derived units.

δ^2H CSIA in lignin-derived compounds



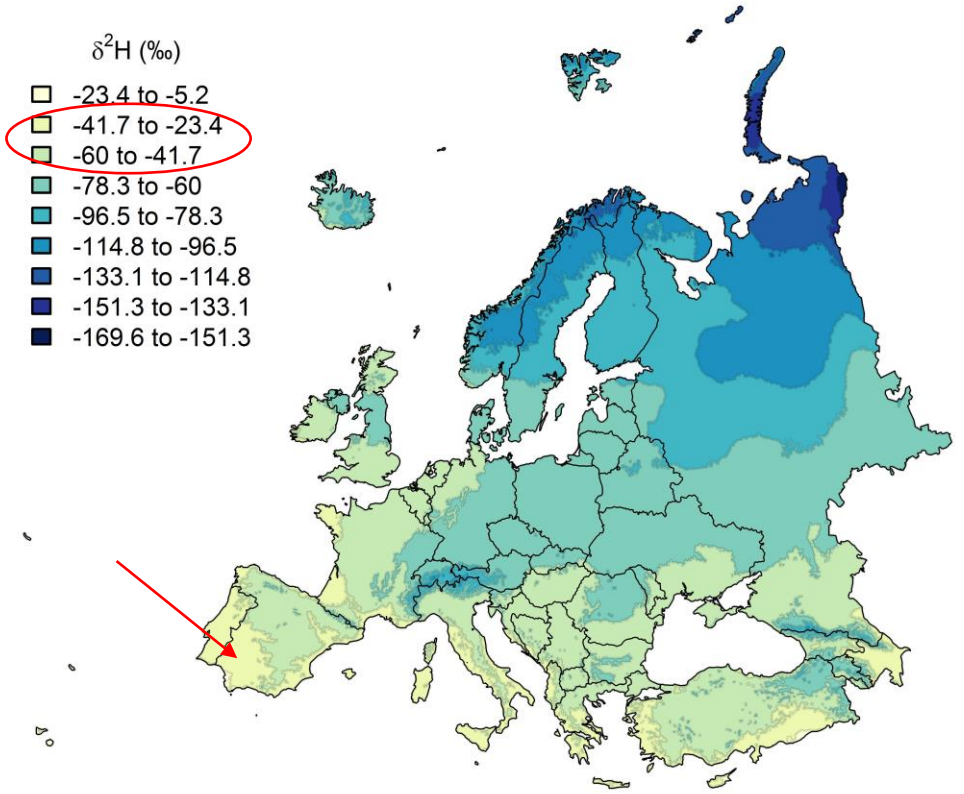
Lignin methoxyl groups from W+D treatment were enriched in ^2H relative to other climatic treatments.
Syringyl units are generally more depleted, especially under tree canopy, down to -230 ‰.
Differences in hydrogen isotope values are more marked in lignin-guayacil units (G).

δ^2H CSIA according to the geographical location

Average H isotopic composition of annual precipitation [4]

Average CSIA and bulk measurements ranged from -56 ‰ (maximum value found in tree) to -80 ‰ (minimum value found in open).

These data matched what is expected according to the average H isotopic composition of annual precipitation in Southern Spain (month of April).



Conclusion remarks

- Pyrolysis-compound-specific isotopic analysis (Py-CSIA) revealed the suitability for the direct measurement of non-exchangeable δ^2H in relevant soil organic matter specific components, including those from polysaccharides (cellulose/hemicellulose), lignin, lipid/waxes and peptide/protein derived compounds.
- The combination of warming and drought plays a major role in the δ^2H values, especially in open pasture.
- Lignin methoxyl groups of SOM may be considered a great biomarker that truly records δ^2H values according to the water availability and further changes driven by the climate.
- Measurement results of SOM from Southern Europe confirm that the isotopic composition of nonexchangeable H in soil is partly determined by the average isotopic composition of local precipitation-derived source water.
- This determination could be used for prediction models of carbon-hydrogen SOM dynamics.

Thanks for your “virtual” attention!
Would you like to know more?

Here you have some useful references:

[1] González-Pérez, J. A., San Emeterio, L. M., González-Vila, F. J., Domínguez-Núñez, M. T., and de la Rosa, J. M.: Direct soil organic matter compound specific δ13C analysis using pyrolysis (Py-CSIA): identification of biomarkers in a dehesa from Southern Spain, EGU General Assembly 2020, Online, 4–8 May 2020, EGU2020-19596, https://doi.org/10.5194/egusphere-egu2020-19596, 2020

[2] Paul, A., Hatté, C., Pastor, L., Thiry, Y., Siclet, F., & Balesdent, J. (2016). Hydrogen dynamics in soil organic matter as determined by 13 C and 2 H labeling experiments. Biogeosciences, 13(24), 6587-6598.

[3] Seki, O., Nakatsuka, T., Shibata, H., & Kawamura, K. (2010). A compound-specific n-alkane δ13C and δD approach for assessing source and delivery processes of terrestrial organic matter within a forested watershed in northern Japan. Geochimica et Cosmochimica Acta, 74(2), 599-613.

[4] Bowen, G.J., (2009). Spatial modelling of stable isotopes in water. Available at https://wateriso.utah.edu/waterisotopes/

More info about our project INTERCARBON

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