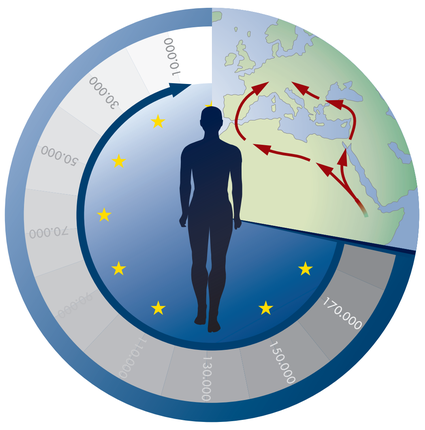

Stable isotopes in loess-palaeosol sequences from the Carpathian Basin

Methodological challenges and palaeoenvironmental implications

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Introduction

Stable isotope analyses of loess bulk organic matter are a powerful tool to reconstruct past vegetational patterns. Especially carbon isotopes ($\delta^{13}C_{org}$) were frequently used to investigate the palaeodistribution of C3- and C4 plants. These investigations are helpful to gain insights about the palaeoclimatic conditions.

In order to obtain reliable results for stable carbon isotope analyses, two main requirements must be met:

- complete decalcification of the sample and
- reproducibility of the applied method.

Here, we present methodological tests on both of these requirements for two loess-palaeosol sequences (LPS) in the Carpathian basin, Semlac and Irig. We discuss the palaeoclimatic implication of these findings on future and past studies of stable isotopes. We also discuss the potential of stable nitrogen isotopes ($\delta^{15}N$) as a powerful proxy for palaeoenvironmental reconstruction.

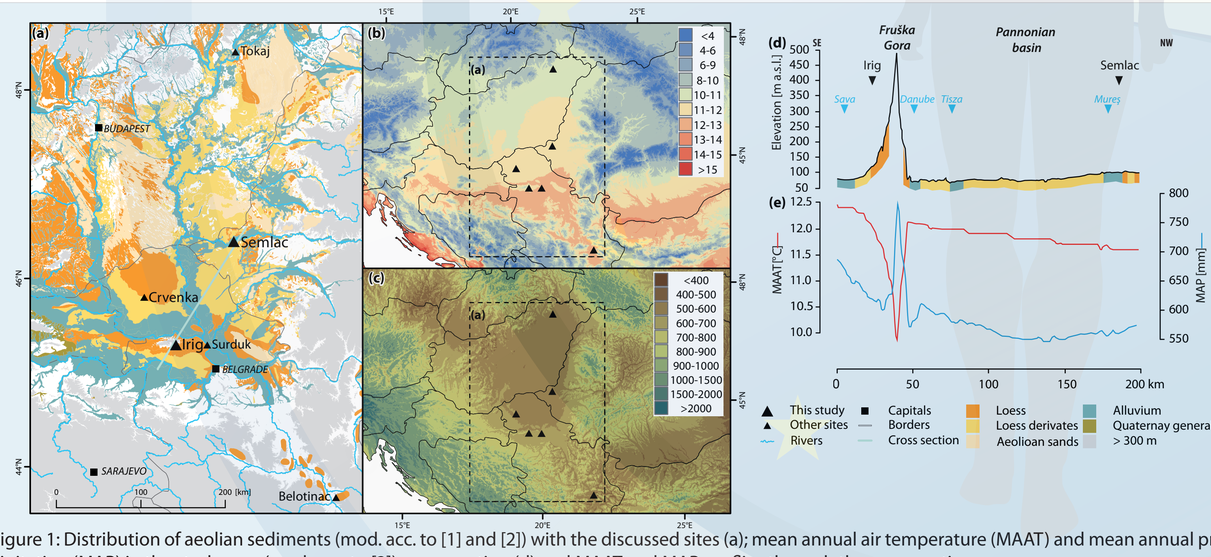

Figure 1: Distribution of aeolian sediments (mod. acc. to [1] and [2]) with the discussed sites (a); mean annual air temperature (MAAT) and mean annual precipitation (MAP) in the study area (mod. acc. to [3]); cross section (d) and MAAT and MAP profiles through the cross section.

Study area

We present isotope analyses for two LPS from the Pannonian basin; Irig (45°05'N/19°52'E) in the southern foothills of the Fruška Gora mountains in Northern Serbia and Semlac (46°7'N/20°57'E) from the flood plains of the Mureș river (Fig. 1 a+d) in Western Romania.

Despite their vicinity, the climate of both sites differ as Irig shows warmer and wetter conditions than Semlac (Fig. 1 b-e).

Methodological tests

To ensure reliable measurements of $\delta^{13}C$ of bulk organic matter of loess, we tested different acidification treatments: the wet chemical (WC) and the fumigation method (FM). The test shows that the fumigation method does not ensure complete decalcifiation on samples from LPS.

A test regarding the decalcification time for the WC method was conducted using the iron carbonate siderite ($FeCO_3$). It was shown that the pretreatment should be performed for four hours to ensure complete decalcification. This was tested against two hours for samples from Semlac.

The results were tested with a reproducibility test (Fig. 3). The $\delta^{13}C_{org}$-ratio was measured in replicate for samples from Semlac in order to determine the accuracy of the method. The test shows that especially samples with a low TOC content show a significant scatter that hinders reproducibility.

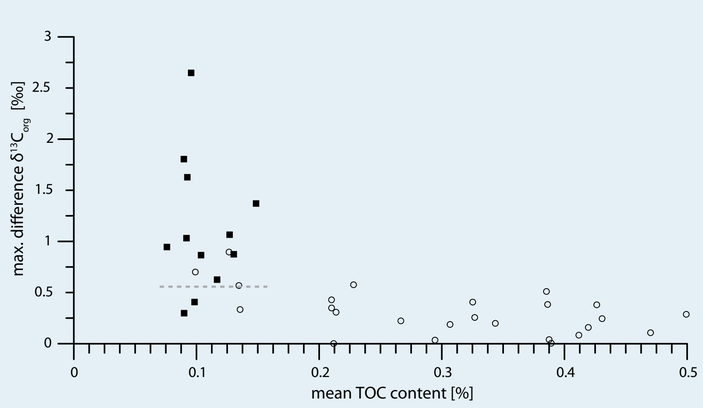

Figure 2: Reproducibilty of $\delta^{13}C$-measurements shown as the relation of total organic carbon (TOC) and the maximum difference of measuremtens of one sample each. The test was conducted with either five (squares) or two aliquots (circles). The mean maximum difference is 0.57‰ (grey dashed line), the maximum difference is 2.65‰.

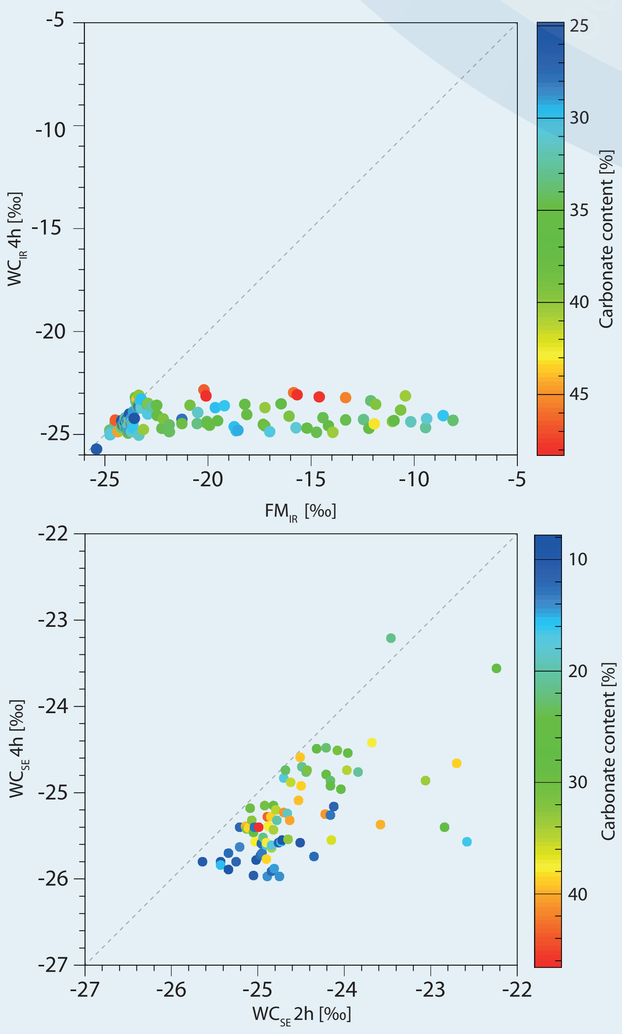

Figure 3: $\delta^{13}C_{org}$-compositions after fumigation treatment (FM_{IR}, x-axis) and wet chemical treatment for four hours (WC_{IR} 4h), y-axis) on the samples from Irig. The colours represent the carbonate content of each sample. The grey line represents the 1:1 relation between methods/treatments, hence identical results. The stronger a sample deviates from the line, the higher are the differences between the two compared pre-treatment methods. The area left of the grey dashed line indicates an increase due to the WC-treatment, the area right of the line indicates a decrease.

Figure 4: $\delta^{13}C_{org}$-compositions after wet chemical treatment for two (WC_{SE} 2h, x-axis) and four hours (WC_{SE} 4h), y-axis) on the samples from Semlac. The colours represent the carbonate content of each sample. The grey line represents the 1:1 relation between methods/treatments, hence identical results. The stronger a sample deviates from the line, the higher are the differences between the two compared pre-treatment methods. The area left of the grey dashed line indicates an increase due to the WC-treatment, the area right of the line indicates a decrease.

Methodological challenges

1 The methodological tests show...

- that both acidification method and time have a significant influence on the results of $\delta^{13}C$-analyses

2 The reproducibility test shows...

- that especially samples with a low TOC content are prone to reproducibility issues
- that the scatter of one sample can exceed 10% of the measured $\delta^{13}C$-ratio

3 We suggest...

-to disregard the fumigation method as a pre-treatment for samples from loess-palaeosol sequences

- a wet chemical acidification for four hours to obtain complete decalcification for comparable samples
- individual methdological tests before each stable isotope study
- individual reproducibility tests with a sub-sample set for each stable isotope study

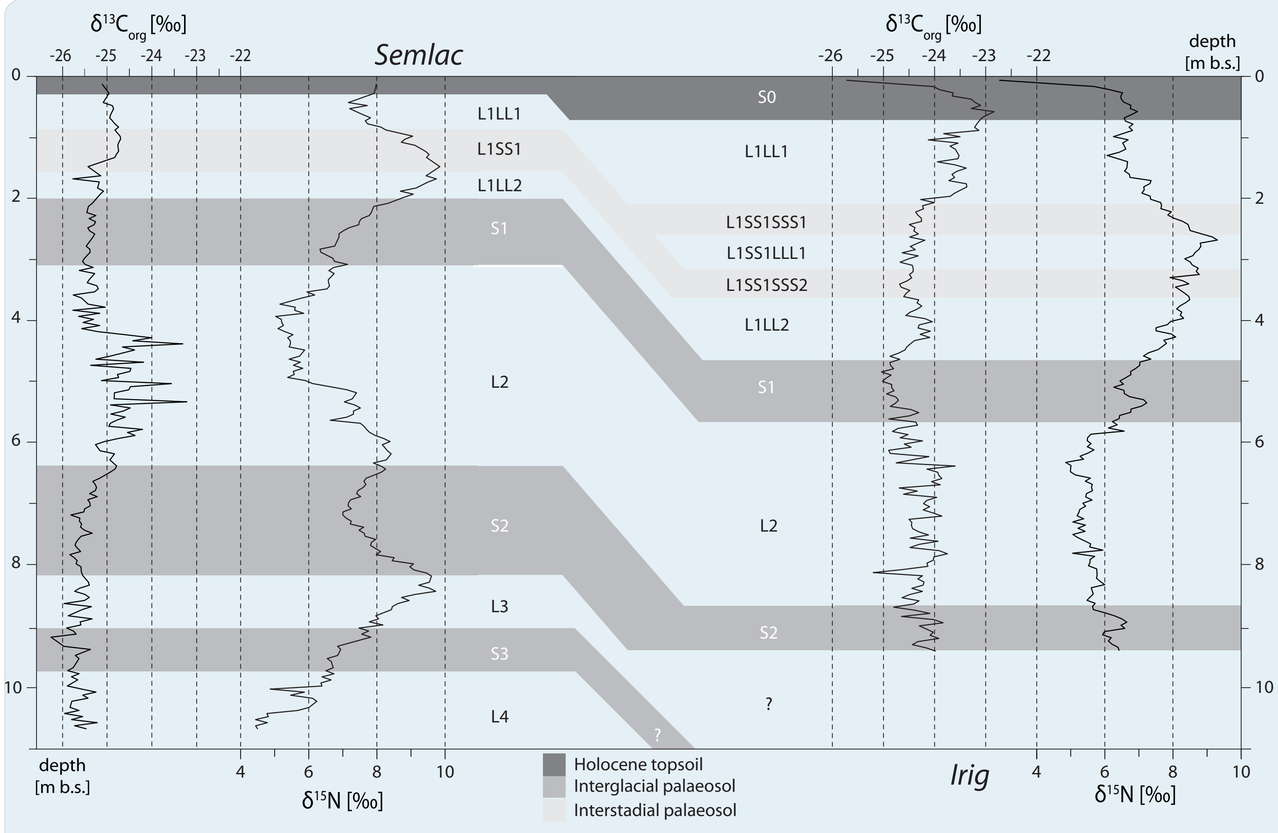

Fig. 5: Stable organic carbon ($\delta^{13}C_{org}$) and bulk nitrogen isotope ($\delta^{15}N$) compositions for Semlac (left panel) and Irig (right panel).

Palaeoclimatic implications

Our data show no dominance of C4-vegetation during the last two glacial cycles within the southern Carpathian Basin. The organic matter of both sections is mostly composed of C3-vegetation. This correspondents to other findings from isotopic studies on LPS in the area. The $\delta^{13}C_{org}$-ratios are slightly elevated compared to modern C3-vegetation, which can be explained by lower CO_2-concentrations during the Pleistocene. The values are higher in Irig compared to Semlac due to water availability.

The high scatter in the L2-loess, especially in Semlac, may be the result of allochtonous organic matter, deposited with the loess, or sample inhomogeneity.

The $\delta^{15}N$-ratios indicate higher productivity rates during times of enhanced pedogenesis, especially during the interstadials of the last glacial cycle. This may be an indicator for less precipitation during interstadials, compared to e.g. interglacial periods.

Conclusions

Our study stresses the importance of sample pre-treatment for stable carbon isotope studies. Complete decalcification must be ensured in order to obtain reliable results. We disregard the fumigation method as a suitable procedure, since this pre-treatment does not ensure sufficient carbonate removal. For the wet chemical acidiciation, we suggest a methodological test regarding the decalcification time before stable carbon isotope measurements.

The δ13Corg-ratios of the two study sites show no hints for a dominance of C4-vegetation during the middle to late Pleistocene. The δ15N-analysis shows higher bioactivity and producitivity in warmer periods of the Quaternary, especially the interstadials.

Affilations

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References

[1] Lehmkuhl et. (2018), JoM. [2] Haase et al. (2007), QSR.
[3] Karger et al. (2017), Sci. Data.

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