Reconstructing Quaternary vegetation history in the Carpathian Basin, SE Europe, using n-alkane biomarkers as molecular fossils

Problems and possible solutions, potential and limitations

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Abstract:

Over the recent years there has been increasing fossil charcoal and malacological evidence from loess-palaeosol sequences in the Carpathian (Pannonian) Basin that call into question the traditional paradigm of treeless full glacial palaeoenvironments. In order to contribute to this discussion we focus on plant-derived n-alkanes and evaluate their potential to serve as biomarkers for the reconstruction of vegetation history during the last glacial cycle. Recently published initial results show a strong degradation effect on the alkane pattern hindering the direct application of frequently used alkane ratios like nC31/nC27, which are in literature often used as vegetation proxies (grass vs. tree). In this paper we therefore introduce for the first time an end member model taking into account the different degree of organic matter (OM) degradation in soils/loess. The model is applied to the Crvenka loess-palaeosol sequence on the Bačka Loess Plateau (Vojvodina, Serbia) at the confluence of the Danube and Tisa Rivers. The results show grass dominance during the whole last glacial cycle. Some few trees likely contributed to the vegetation cover during glacial periods and during the Holocene, but not during the last interglacial and the Marine Isotope Stage (MIS) 3 interstadial. The reconstructed vegetation history is in agreement with previous malacological and charcoal findings as well as with climate and biome modelling

[Rekonstruktion der quartären Vegetationsgeschichte im Karpaten-Becken, Südost-Europa, mit Hilfe von n-Alkan Biomarkern als molekulare Fossilien: Probleme und mögliche Lösungen, Potenzial und Grenzen]

Zusammenfassung:

Seit einigen Jahren gibt es zunehmend Studien, die, basierend auf der Untersuchung von fossilen Holzkohlen und Schneckenschalen aus Löss-Paläoboden Sequenzen, die traditionelle Vorstellung von weitestgehend baumlosen Steppen im Karpaten-Becken während der letzten Kaltzeit in Frage stellen. Mit unseren Arbeiten versuchen wir anhand von Biomarkern einen Beitrag zu dieser Diskussion zu leisten und herauszufinden, welches Potenzial in der Untersuchung von Alkan Biomarkern für die Rekonstruktion der Vegetationsgeschichte während der letzten glazialen Zyklen steckt. Kürzlich veröffentlichte erste Ergebnisse weisen darauf hin, dass der Degradationsgrad der pflanzenbürtigen organischen Substanz einen starken Einfluss auf das Alkanmuster in Böden hat und dass der in der Literatur häufig verwendete Alkanquotient nC31/nC27 kein reiner Vegetations-Proxy ist, sondern auch maßgeblich die unterschiedliche Degradation widerspiegelt. In der vorliegenden Arbeit führen wir daher erstmals einen End Member Modellierungsansatz ein, bei dem der Degradationsgrad der organischen Bodensubstanz mit berücksichtig wird. Das Modell wird auf die Loess-Paläoboden Sequenz Crvenka auf dem Bačka Loess Plateau (Serbien) zwischen Donau und Theiss angewendet. Die so für den letzten Interglazial-Glazial-Zyklus rekonstruierte Vegetationsgeschichte bestätigt die Holzkohle- und Mollusken-Befunde und deutet auf Gras-Steppen während des letzten Interglazials und -stadials hin (Marine Isotopenstadien (MIS) 5 bzw. 3). Die Ergebnisse machen deutlich, dass Steppen während des gesamten letzten glazialen Zyklus vorgeherrscht haben. Für das letzte Interglazial und das Interstadial der Marinen Isotopen Stufe (MIS) 3 deuten die Biomarker Befunde auf reine Grassteppen hin. Dagegen prägten in den Glazialen vermutlich auch vereinzelte Bäume das Landschaftsbild einer "Taiga-Steppe". Die so rekonstruierte Vegetationsgeschichte steht im Einklang mit den Holzkohle- und Schneckenfunden, wie auch mit Ergebnissen von Klima- und Biom-Modellierungen.

Keywords:

Quaternary, Carpathian Basin, Loess, Palaeosols, Biomarkers, Alkanes, Palaeovegetation

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1 Introduction

Over the last few years, more and more attention has been focused on the loess-palaeosol sequences of SE Europe by Quaternary scientists aiming at establishing pedo-, magneto- and chronostratigraphies (Buggle et al. 2009; Fuchs et al. 2008; MARKOVIC et al. 2008; MARKOVIC et al. 2006) and at reconstructing palaeoenvironments and climate (MARKO-

vic et al. 2005; Markovic et al. 2007; Rudner & Sümegi 2001; Sümegi & Krolopp 2002; Willis et al. 2000; Zech et al. 2008a). Interestingly, there is increasing fossil charcoal and malacological evidence from loess-palaeosol sequences in the Carpathian Basin that call into question the traditional paradigm of a treeless full glacial palaeoenvironment. Hence, Willis & Andel (2004) ask "trees or no trees?" in the title of their publication and thoroughly review all the

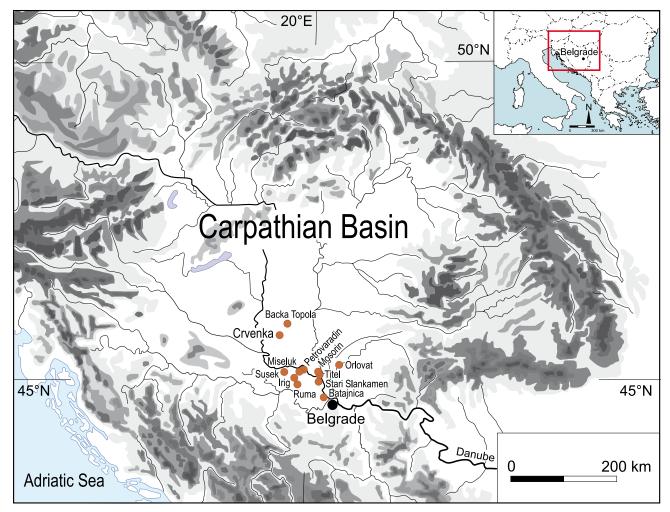


Fig. 1: Topographic map of the Carpathian Basin and the Vojvodina Province showing the geographic positions of the Crvenka and other loess exposures (MARKOVIC et al. 2008).

Abb. 1: Topographische Karte des Karpaten-Beckens und der Vojvodina Provinz mit der geographischen Lage der Loess-Paläoboden Sequenz Crvenka und anderer Loessaufschlüsse (MARKOVIC ET AL. 2008).

available fossil, genetic and palaeoclimatic evidence at that time. Although it was possible to find clear indicators for the presence of trees, the authors concluded that from the fossil evidence alone it is difficult to establish whether the proven trees grew in isolated pockets on an otherwise open tundra landscape, or in an open taiga forest. Potentially, biomarker studies, i.e. the searching for molecular fossil evidence in loess-palaeosol sequences using for example plant-derived n-alkanes, can contribute in the next years to a better understanding of the vegetation history in the Carpathian Basin.

n-Alkanes with 25 to 33 carbon atoms (nC25 – nC33) and a strong odd-over-even predominance (OEP) are important constituents of cuticular plant leaf waxes (Kolattukudy 1976). With the litter-fall they are deposited and stored in soils and sediments, for example in aeolian sediments, where they are assumed to be relatively resistant to biogeochemical degradation (Bourbonniere et al. 1997; Cranwell 1981). Furthermore, since different vegetation types reveal distinct alkane patterns and hence a so-called "chemical fingerprint", alkanes have the potential to serve as biomarkers. For instance, they are used to differentiate between autochthonous (lacustrine) and allochthonous (terrestrial) organic matter (OM) in lake sediments (Bourbonniere et al. 1997; Ficken et al. 2000; Mügler et al. 2008; Zech et al. 2008b), or to reconstruct vegetation changes, predominantly in terms of the

relative proportions of grasses and trees (Cranwell 1973; Schwark et al. 2002; Zech 2006). First n-alkane results for the Carpathian Basin presented by Zech et al. (2008a) indicate that the alkane pattern in soils and loess is not only strongly affected by the type of vegetation but also by OM degradation. In this paper we therefore propose a solution for this problem by establishing an end member model that (i) takes into account the degree of OM degradation and (ii) allows the differentiation of alkanes derived from grasses and herbs, versus alkanes derived from trees and shrubs. The model is applied to alkane results from the Crvenka loesspalaeosol sequence on the Bačka Loess Plateau, at the confluence of the Danube and Tisa Rivers. The potential and the limitations of the method are discussed.

2 Study Area and Pedostratigraphy

Large areas of the Carpathian Basin (Pannonian Basin) are covered with loess, often forming discontinuous plateau uplands between the alluvial plains of the Danube, Tisa, Sava and Tamiš Rivers. Close to the town Crvenka about 60 km northwest of Novi Sad in the Vojvodina Region (Serbia), a loess-palaeosol sequence of about 10 m thickness is exposed in a brickyard situated on the southwestern edge of the Bačka Loess Plateau (Fig. 1).

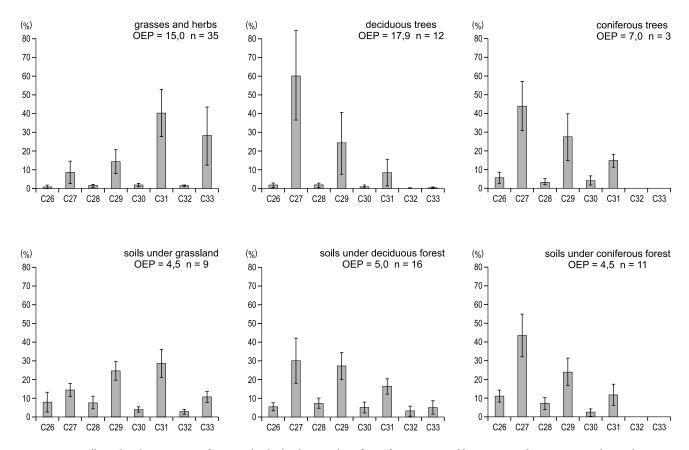


Fig. 2: Mean n-alkane distribution patterns from grasslands, deciduous and coniferous forests. OEP = odd over even predominance. Error bars indicate standard deviation. Based on data from Zech et al. (2008a) Marseille et al. (1999), Prügel (1994), Rommerskirchen (2006) and Rumpel & Wiesenberg (unpublished).

Abb. 2: Durchschnittliches n-Alkan Verbreitungsmuster von Grasland, Laub- und Nadelwald. OEP = odd over even predominance. Die Fehlerbalken kennzeichnen die Standardabweichung. Nach Daten von Zech et al. (2008a) Marseille et al. (1999), Prügel (1994), Rommerskirchen (2006) und Rumpel & Wiesenberg (unveröffentlicht).

Initial pedostratigraphical description and the first geochemical, grain-size and magnetic susceptibility results are provided by Markovic et al. (2008) and Zech et al. (2008a). According to these results, the Crvenka exposure contains a record of the last interglacial-glacial cycle with a ~2 m thick and clay-rich interglacial 'V S1' palaeosol (the prefix 'V' refers to the standard Pleistocene loess-palaeosol stratigraphy in the Vojvodina region (Markovic et al. 2008) exposed at the bottom of the sequence. The overlaying ~8 m thick 'V L1' loess contains an interbedded weakly developed interstadial palaeosol complex ('V L1S1') and the top of the loess-palaeosol sequence is capped by the Holocene/modern topsoil ('V S0').

3 Material and Methods

During a field campaign in November 2007, the Crvenka exposure was cleaned by digging and logging trenches about 1 m wide and 0.5 m deep. Sampling for biomarker analysis was conducted by taking mixed samples every 25 cm, resulting in totally 43 samples from the sequence. Additionally, 12 samples for luminescence dating were taken from the exposure. Manuscripts dealing with a detailed description of the stratigraphical/pedological/geochemical/magnetic features, as well as the luminescence dating are in preparation. At

the present state of research our chronostratigraphy for the Crvenka section is based on pedostratigraphic correlations to well dated sections of the region e.g. Surduk, Petrovaradin, Ruma (Fuchs et al. 2008; Markovic et al. 2005; Markovic et al. 2006), since the numerical dating results from Crvenka are not yet available.

In order to characterise the modern vegetation types with respect to their alkane pattern, mixed litter and topsoil samples were collected from several sites on the Fruska Gora Mountains about 10 km south of Novi Sad (mixed *Quercus sp. and Fagus sp.* forests) and from grasslands on the Titel Loess Plateau about 25 km east of Novi Sad (grass and herb vegetation) (Fig. 1).

Sample preparation of the n-alkanes was carried out at the University of Novi Sad, Serbia, and at the University of Bayreuth, Germany, using a modified method after Zech & Glaser (2008). Free lipids were extracted with methanol/toluene (7/3) using Soxhlet apparatus and subsequently concentrated using rotary evaporation. The lipid extracts were purified on silica-alox columns (2g of each, 5% deactivated). n-Alkanes were eluted with 3*10 ml hexane/toluene (85/15). Quantification was performed on an HP 6890 gas chromatograph equipped with a flame ionisation detector (FID). 5α -Androstan and Hexatriacontane (nC36) were added as internal and recovery standards, respectively.

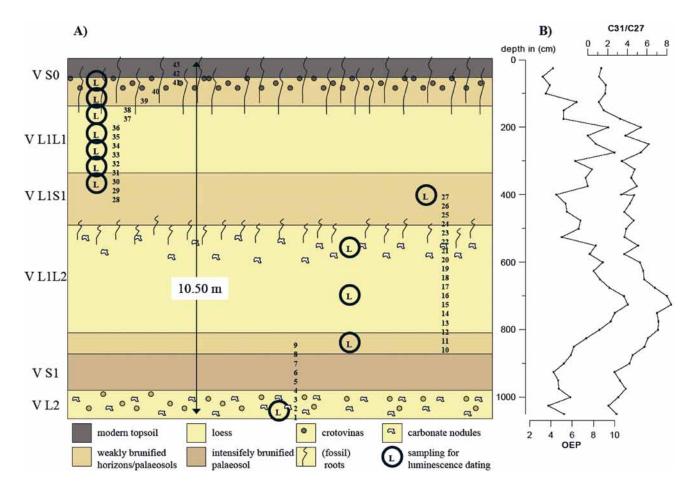


Fig. 3: A) Pedostratigraphy and sampling scheme for the Crvenka loess-palaeosol sequence (from Zech et al. 2008a). B) Depth functions for the OEP and the alkane ratio C31/C27.

Abb. 3: A) Pedostratigraphie und Probenentnahmeschema für die Loess-Paläoboden Sequenz Crvenka (nach Zech et al. 2008a). B) Tiefenfunktion für OEP und das Alkan-Verhältnis C31/C27.

4 Results and Discussion

4.1 n-Alkane distribution patterns of modern vegetation and soils

The n-alkane patterns obtained from the litter and topsoil samples collected from mixed *Quercus sp.* and *Fagus sp.* forests on the Fruska Gora Mountains and samples from grasslands on the Titel Loess Plateau are in agreement with findings in the literature. In order to increase our data set for the end member modelling, we additionally implemented data from Marseille et al. (1999), Prügel et al. (1994), Rommerskirchen et al. (2006) and Rumpel & Wiesenberg (unpublished).

Firstly, the fresh biomass reveals a strong odd-over-even predominance (OEP, Fig. 2) with mean values of 15.0, 17.9 and 7.0 for grasses and herbs, deciduous trees and conifers, respectively, where

$$OEP = (C27+C29+C31+C33)/(C26+C28+C30+C32).$$

Hence, high OEP values are typical for fresh undegraded cuticular plant leaf waxes. In comparison, lower OEP values (< 5) are characteristic for the topsoils (Fig. 2) and are often interpreted in terms of OM degradation. Secondly, it is strik-

ing that the alkane patterns of respective litter and topsoils are not identical, but become more balanced, i.e. for instance the ratios C31/C27 approach the values 1. This might be attributed to either an input of microbial or root biomass or to biodegradation (Wiesenberg et al. 2004).

In spite of these variations, it is valid that in forest litter and forest soils the n-alkanes C27 and C29 dominate, whereas in grasslands the alkanes C31 and C33 are more abundant (Fig. 2). These results explain why alkane ratios are used as tool to differentiate between forest and grassland vegetation in palaeoenvironmental studies (Cranwell 1973; Schwark et al. 2002; Zech 2006; Zhang et al. 2006).

4.2 n-Alkane ratios from the Crvenka loess-palaeosol sequence

Recently, we tried a tentative palaeovegetational reconstruction for the Crvenka loess-palaeosol sequence based on alkane ratios (Zech et al. 2008a). In fact, for instance the ratio C31/C27 varies widely between ~1 and 8.5 (Fig. 3B), with maxima characterising the loess units 'V L1L1' and 'V L1L2'. One may be tempted to interpret these variations in terms of grass-forest vegetation changes having occurred during the last glacial cycle. However, we rejected this idea, because (i) studying modern litter and respective topsoils indicates

that the ratio C31/C27 is prone to degradation effects (Fig. 2) and because (ii) C31/C27 correlates highly significantly with the OEP (R = 0.87, Fig. 3B), the latter having the potential to serve as degradation proxy. Hence it is likely, that most of the C31/C27 variations in the Crvenka dataset are caused by degradation rather than by vegetation changes. Eventually,

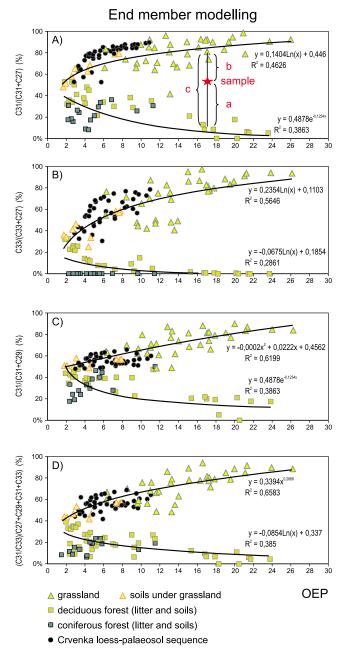


Fig. 4: End member modelling for the alkane ratios A) C31/C27, B) C33/C27, C) C31/C29 and D) (C31+C33)/(C27+C33). Trend lines were fitted to the data sets (own data and data from literature, see above) from modern grasslands and forests, respectively, describing 'degradation lines'. An estimated percentage contribution of tree-derived alkanes to a palaeosol sample can be calculated by the ratio a/c.

Abb. 4: End Member Modell für die Alkan-Verhältnisse A) C31/C7, B) C33/C27, C) C31/C29 und D) (C31+C33)/(C27+C33). Die Trendlinie wurde an die Datensätze von rezentem Grasland und Wäldern angepasst (eigene Daten und Literaturdaten, s. oben) und beschreibt eine Degradationslinie. Der Anteil von Alkanen in einer Paläobodenprobe, die von Bäumen stammen, kann aus dem Verhältnis A/C berechnet werden.

all biomarker-based reconstructions of vegetation changes have to be considered with caution unless it can be guaranteed that the organic matter is highly preserved throughout the whole archive (e.g. lake sediments) or a pronounced forest dominance (C31/C27 <1) alternated with a pronounced grass dominance (C31/C27 >1). In spite of this apparent impact of degradation on alkane ratios, we are aware of no published attempts to correct alkane biomarker results for this effect, neither qualitatively nor quantitatively, when using alkane ratios as vegetation proxies.

4.3 End member modelling – accounting for the degradation effect

As a result of OM degradation the originally high C31/C27 ratios in grasses and herbs decrease during decomposition and formation of soil OM (Fig. 2). This can be plotted as 'degradation line', using the OEP as proxy for degradation and plotting both fresh litter and topsoil samples from modern grasslands (Fig. 4A). Note that the ordinate is given as the proportion of C31 to the sum of C31 and C27 in percent and not as ratio of C31/C27. A degradation line can also be plotted for the litter and topsoils from forest sites, thus allowing a simplified description of the alkane ratio changes during degradation of OM derived from trees and shrubs.

Loess-palaeosol samples that were formed purely under one of these two vegetation types (end members) should plot on or close to the 'degradation lines'. Samples that were formed under a mixed vegetation should plot in-between the degradation lines (Fig. 4A). The percentage contribution of grasses and herbs versus trees and shrubs to the total content of fossil plant alkanes in a loess or palaeosol sample can be determined in two steps:

Firstly, using the OEP of the sample, the respective alkane ratio end members for grassland versus forest are calculated by means of the functions describing the 'degradation lines'.

Secondly, using the end members obtained for a certain sample, the % contribution of the two vegetation types is estimated by means of a two component mixing equation. Accordingly the quotient a/c gives the % alkane contribution of grasses and herbs, whereas the quotient b/c gives the % alkane contribution of trees and shrubs (Fig. 4A).

The most accurate results can be expected for samples with high OEP values, whereas accuracy should decrease with decreasing OEP values due to the converging degradation lines (Fig. 4A). Accuracy is furthermore limited by the scattering of the modern dataset. Furthermore, it should be mentioned that there is not only an interspecie variability of the alkane pattern producing the scattering around the degradation lines, but also an innerspecie variability. The latter can be caused by leaf and needle aging (Prügel et al. 1994) as well as by environmental stress (Shepherd & Griffiths 2006). Due to the scattering, modelling can result in negative percentage values for tree- or grass-derived alkanes (Fig. 5). However, this does not indicate that the idea of the model is wrong or invalid. It rather points to the limitation of the model to incorporate interspecie and innerspecie variability within grasslands and forests, respectively. In order to check the robustness of our end member model, we calculated the model not only with C31/C27, but additionally also for

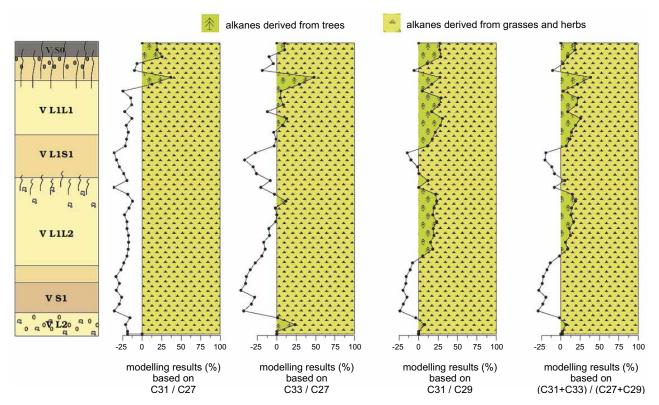


Fig. 5: Modelling results for the alkane ratios C31/C27, C33/C27, C31/C29 and (C31+C33)/(C27+C29). Although the observed variations could potentially be explained with inter- and innerspecie variability in grasslands, the contribution of some few trees to the alkane patterns during glacials and during the Holocene cannot be excluded. This latter scenario is supported by charcoal and malacological findings as well as by climate modelling results.

Abb. 5: Ergebnisse der Modellierung der Alkan-Verhältnisse C31/C27, C33/C27, C31/C29 und (C31+C33)/(C27+C29). Obwohl die gemessenen Variationen potenziell durch artspezifische Variabilitäten innerhalb der Graslandvegetation erklärt werden könnten, ist das Auftreten von Bäumen während der Glaziale und im Holozän durch das gezeigte Alkanmuster nicht auszuschließen. Letztere Annahme wird durch den Nachweis von Holzkohle und malakofaunistischen Funden ebenso bestätigt, wie durch die Resultate von Klimamodellen.

several other alkane ratios like C33/C27 (Fig. 4B), C31/C29 (Fig. 4C) and (C31+C33)/(C27/C29) (Fig. 4D).

4.4 Reconstruction of vegetation and climate history recorded in the Crvenka loess-palaeosol sequence

Fig. 4 depicts that most of the 43 loess-palaeosol samples from Crevenka plot close to the grass 'degradation lines' for all four illustrated alkane ratios. This finding proves that grassland dominated the study area throughout the last glacial cycle. On the one hand, within the methodological uncertainties of the end member model, the alkane biomarkers alone can not be cited as evidence for the occurrence of trees. On the other hand, it can not be concluded that trees did not contribute at least partly to the observed scattering of the Crvenka samples. Hence, given that the modelling results for all alkane ratios show similar shifts (Fig. 5) and aiming at contributing to the question "trees or no trees?", the alkane biomarker results may serve as one testimony amongst others.

According to the modelling results illustrated in Fig. 5, trees disappeared entirely at the beginning of the last interglacial and grassland prevailed during the formation of the 'V S1' palaeosol. Climatically, these findings can be interpreted in terms of warm steppic conditions with pronounced dry summer seasons. During MIS 4, when loess deposition started again ('V L1L2'), plant-derived OM is much better preserved (high OEP, Fig. 3) and alkane biomarkers indi-

cate that some few trees contributed to the vegetation cover (Fig. 5). This is in disagreement with the traditional suggestion of treeless cold steppic environments during cold and dry glacial conditions. For the 'V L1S1' interstadial palaeosol, correlated tentatively with the MIS 3, the modelling results suggest that trees retreated, presumably because the summer seasons were again too dry to support them. Trees only immigrated again during MIS 2, with the onset of further loess deposition ('V L1L1'). Both MIS 2 and the Holocene, the latter being represented by the 'V So' soil, have experienced several major fluctuations in the proportion of trees to the vegetation cover at the study site. The brunified subsoil horizon of 'V So' reveals a marked re-expansion of pure grassland (Fig. 5). Probably, this reflects warmer climatic conditions with lower net precipitation in the Early-to Mid-Holocene. This interpretation is supported by the climate modelling results of Kutzbach & Guetter (1986) for the continental interiors of Eurasia between 30 and 60 ° N.

The alkane biomarker results presented above suggest that full glacial conditions in the Carpathian Basin were not generally characterised by treeless cold steppic environments Instead, rather open taiga forest prevailed even on the loess plateaus. This scenario is not only supported by other palaeoecoligical proxies like fossil charcoal and molluscs (SÜMEGI & KROLOPP 2002; WILLIS & ANDEL 2004; WILLIS et al. 2000), but also by modelling results (STAGE_3-PROJECT). Accordingly, the majority of the Carpathian Basin was not covered by steppes during the last glacial maximum (LGM),

but rather by evergreen taiga. Palaeoenvironmentally and –climatologically, one can conclude that in spite of lower precipitation levels than experienced today, reduced evapotranspiration due to lower temperature, and thus a higher net moisture budget, is responsible for sufficient water being available for trees to grow during glacial periods. Also the palaeoclimatic modelling results of Kutzbach & Guetter (1986) support this conclusion, suggesting that for the LGM, reduction of evaporation was a stronger influence on water availability than the associated decrease in precipitation, especially at 45–55°N. In contrast to the glacial conditions, during interglacial/–stadial periods seasonal summer dryness (higher temperature and evaporation combined with less summer precipitation) may have impeded the expansion of forests, at least on the loess plateaus.

Some preliminary conclusions concerning loess sedimentation during the last glacial cycle can be drawn from these findings. The loess plateaus in the Carpathian Basin were covered by vegetation capable to filter aeolian dust during the whole last glacial cycle. However, it seems that loess sedimentation did not depend crucially on the vegetation type, but rather on the dust supply originating from the glacial braided river systems during the glacial periods (Buggle et al. 2008; Smalley & Leach 1978). This supports the appellation 'Danube Loess' (name of the special session during the DEUQUA meeting 2008 in Vienna) for many of the aeolian sediments of the Carpathian Basin.

5 Conclusions and Outlook

In order to contribute to the discussion over "trees or no tress" (Willis & Andel 2004) in the Carpathian Basin during full glacial conditions, we investigated the alkane patterns of modern forests and grasslands, as well as those recovered from the Crvenka loess-palaeosol sequence on the southwestern edge of the Bačka Loess Plateau. Results from the modern study sites suggest (i) that the plant-derived alkane biomarkers have the potential to differentiate between OM derived from forests versus OM derived form grasslands; (ii) that the alkane ratios do not only depend on the type of vegetation but also on the degree of OM degradation. We therefore propose an end member model based on the alkane patterns of litter and topsoils from modern study sites that takes into account the degradation dependency (using the OEP as degradation proxy) of different alkane ratios.

The results for the Crvenka loess-palaeosol sequence firstly demonstrate the potential of the alkane biomarker method for terrestrial archives, where pollen are often intensively degraded. Secondly, they clearly show that grasses dominated the vegetation cover during the whole last glacial cycle. The accuracy of the model is limited by the scattering of the modern datasets for grasslands and forests. Nevertheless, the modelling results for different alkane ratios reveal similar and systematic shifts, which may have been caused by small and varying proportions of trees. Accordingly, pure grassland prevailed during the last interglacial and interstadial, whereas some few trees contributed to the soil OM during glacial periods and hence during loess deposition. This questions the traditional and palynologically derived paradigm of treeless full-glacial palaeoenvironments, but is in apparent agreement with charcoal and malacological findings

from the Carpathian Basin as well as with modelling results.

Ongoing work focuses on δD and $\delta^{18}O$ analyses in plant-derived biomarkers from loess-palaeosol sequences. Recently, we have established the respective method for $\delta^{18}O$ and demonstrated its potential to serve as climate proxy in modern litter and soils (Zech & Glaser 2009). Hence, water stress of plants, which we make responsible for Quaternary vegetation changes in our study area rather than cold temperatures, could be addressed more quantitatively in the future.

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