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Biomarkers in modern and buried soils of semi-desert and forest ecosystems of northern Iran

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In Northern Iran mean annual precipitation and vegetation vary significantly over short distance from a semi-desert to a forest biome. These ecosystems likely responded differently on past climate changes. We here aim at i) testing the applicability of biomarkers (leave-derived n-alkanes, their stable carbon isotope composition, and C and N stable isotopes of soil organic matter) in loess-derived soils to identify and differentiate past ecosystems, and ii) elucidating the variability of these biomarkers in palaeosols. We sampled modern topsoils and palaeosol horizons within an ecological gradient covering a range in mean annual precipitation from 200 to 750 mm from the Kopet Dag semi-desert to the Hyrcanian forest on the footslopes of the Alborz Mountains. C_{org}, N, $\delta^{13}C_{org}$, $\delta^{15}N$, and n-alkanes (and their compound-specific $\delta^{13}C$) were analyzed to characterize organic matter composition and sources. In modern soils a systematic increase in C_{org} and N was observed with precipitation. The $\delta^{15}N$ decreased from about 6 to 4‰ pointing to systematically more degraded organic matter in semi-desert soils. The leave-wax specific ratio of $(nC_{31} + nC_{33})/(nC_{27} + nC_{29})$-n-alkanes was >1 for semi-desert soils and <1 for the forest ecosystem. The $\delta^{13}C_{org}$ showed no systematic trend in this gradient. In loess and palaeosol profiles, contents of C_{org}, N and n-alkanes dropped about a factor 10 compared to modern soils. The n-alkane ratio and $\delta^{15}N$ ratios remained on comparable levels as did the compound-specific $\delta^{13}C$ in n-alkanes. However, bulk $\delta^{13}C_{org}$ was altered from about −27 in modern soil to −23‰ in loess-palaeosols. Systematically higher C_{org} and N values were observed in palaeo-topsoils compared to loess and subsoil. Stable C isotopes varied rather unsystematically within loess-palaeosol sequences, while $\delta^{15}N$ revealed trends within palaeosols, however, in contrasting directions with palaesol depth. The (temporal) average n-alkane ratio for all palaeosol horizons of one site systematically followed the modern precipitation gradient indicating that in all periods of soil formation a climatic gradient developed.

1. Introduction

The Quaternary is characterized by strong climate changes on orbital and sub-orbital time-scales. The amplitudes and magnitudes of climate change and their impact on specific ecosystems are not completely understood. In Northern Iran, numerous cycles of climate change were archived in loess-palaeosol sequences (Kehl, 2010). Loess of Northern Iran occurs along a precipitation gradient reaching from the Turkmen steppe to the Alborz foothills and encompassing an increase in mean annual precipitation (MAP) from 200 to 750 mm within 100 km from north to south (SWRI, 2000). According to this gradient, semi-desert, steppe, and forest ecosystems occur in the region. Assuming that this gradient also existed in the Pleistocene, this region allows studying the response of these ecosystems on climate change within a few kilometres.

Loess-palaeosol sequences in Northern Iran cover up to 6 major cycles of soil formation and loess deposition, indicating climate change (Kehl, 2010). These loess-soil sequences show a close

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correlation to changes in pollen composition of Lake Urmia (Djamali et al., 2008) and Lake Van (Pickarski et al., 2015), located in northwestern Iran and Turkey, and representing one of the most detailed and extensive climate records of the area. Leroy et al. (2013) investigated Holocene vegetation history in the north-eastern foothills of the Alborz Mountains and the Caspian Sea. Up to know it is not clear how biomarkers in palaeosols correlate to these records and if additional information about palaeovegetation distribution can be determined.

The analysis of organic matter archived in such loess and palaeosol horizons allows the reconstruction of past vegetation (e.g. Bai et al., 2009; Schatz et al., 2011; Zech et al., 2013), e.g. if forests or grasslands were abundant. Determining whether soil organic matter composition changed characteristically along the modern precipitation gradient and whether these changes may be traced in organic matter archived in palaeosol is part of the present study.

Characterization of soil organic matter is often approached by biomarker and stable isotope analysis. Biomarkers are characteristic remains of vegetation, which are stable for long periods of time (Schwark et al., 2002). For example n-alkanes from epicuticular leave waxes are often used to discriminate between soil organic matter from grass and forest vegetation (Bull et al., 2000; Sheldon and Tabor, 2009; Zech et al., 2013). Several studies showed that in tree and shrub leaves the n-alkanes nC_{27} and nC_{29} dominate (Schwark et al., 2002; Liu et al., 2005; Zech et al., 2012, 2013), whereas in grasses and herbs the n-alkanes nC_{31} and nC_{33} prevail. Stable carbon isotope composition in soil organic matter allows identifying contributions from C3 and C4-photosynthetically active plants (Farqhar et al., 1989). If the proportion of ^{13}C in soil organic matter increases, the input from C4 plants is higher, e.g. in the subtropics $\delta^{13}C$ is elevated compared to boreal forests (e.g. Bowen, 2010; Ladd et al., 2014). The stable nitrogen isotope composition ($\delta^{15}N$) in soil typically is between 5 and 0‰, the latter indicates high contributions of atmospheric N fixing organisms like e.g. cyanobacterias and lichen (e.g., Evans and Belnap, 1999 and references therein). Lichens and cyanobacteria may contribute high shares to the soil N pool in arid climates when other vegetation is missing (Belnap, 1995; Svirčev et al., 2013), hence the stable N isotope composition was successfully used for reconstruction of palaeoenvironments (Andreeva et al., 2013; Obreht et al., 2013; Gasiorowski et al., 2014). However, C and N isotope composition may be significantly altered by microbial degradation. This leads to the enrichment of the heavy isotopes ^{13}C and ^{15}N in soil horizons which exited their natural C and N cycling, as might be the case for palaeosols after loess coverage. Recently, also the $\delta^{13}C$ signature of n-alkanes (Liu et al., 2005; Wang et al., 2015) was used as a proxy for the proportion of C3 and C4 plants in lake sediments and palaeosols from China. Whether significant differences in soil n-alkane, stable C and N isotope composition, and the C isotope composition in leave wax-derived n-alkanes appear along a modern precipitation gradient and whether these can be recovered in palaeosol horizons shall be elucidated in this study.

This study aims at testing the applicability and sensitivity of C and N stable isotope ratios, n-alkane composition, and stable C isotope composition of n-alkanes as biomarkers for vegetation reconstruction in modern topsoils in an ecological gradient through Northern Iran. If this is assessed, the transferability of these biomarkers to palaeosol horizons will be checked with respect to the stability of the biomarker signals and their dependency on soil horizon specific differences. Finally, we aim at a preliminary reconstruction of palaeovegetation and palaeoenvironmental change since at least the last interglacial in four loess-palaeosol sequences in Northern Iran.

2. Materials and methods

2.1. Study areas and pedostratigraphy

The Northern Iranian Loess-Plateau forms a strongly dissected landscape with steeply sloping loess hills (Kehl, 2010). The loess deposits of the southern Caspian Lowlands form smooth hills covering the northward facing slopes of the Alborz mountain range.

The modern ecological conditions in Northern Iran are governed by a precipitation gradient. Accordingly, humidity increases from east to west and from north to south reaching from a semi-arid climate in the north with steppe-like vegetation to sub-humid climatic conditions with forest vegetation cover along the slopes of the Alborz Mountains (Fig. 1; e.g. Kehl et al., 2005; Khormali and Kehl, 2011; Khormali et al., 2012).

A modern soil transect representative for the ecological gradient and related changes in vegetation was sampled to test the suitability and power of biomarker signals for environmental reconstruction for the area under study (Fig. 1, Table 1). Eight modern soil profiles were prepared along the ecological gradient, the soils of which were classified as Entisols, Inceptisols, Mollisols and Alfisols (Table 1). The vegetation cover changed from grassland in the dry area (Hutan, Agh Band, Khaled Nabi) to dense shrub land (Yellibadragh) and forest (Agh Emam, Mobarak Abad, Gorgan, Neka) in the moist part of the ecological gradient. Modern soil profiles of Agh Emam, Mobarak Abad and Neka were located at the arable field margin. The soil samples were taken adjacent to the managed areas to minimize human impact.

Four loess-palaeosol sequences were studied (Table 1, Fig. 1):

- The profile of Agh Band is located in the westernmost part of the Northern Iranian Loess-Plateau and has at least 50 m thickness of loess deposits (for soil horizon classification, see Table S2).
- Nowdeh section is situated about 20 km southeast of Gonbad-e Kavus, in the vicinity of the Nowdeh River with loess deposits of 35 m thickness (for soil horizon classification, see Table S3).

Hitherto, chronological and palaeopedological studies on the Nowdeh and Agh Band sections were conducted by Kehl et al. (2005), Frechen et al. (2009) and Kehl (2010). According to the previous studies, Agh Band section has one palaeosol, likely related to interglacial soil formation probably during marine isotope stage (MIS) 5e or older (Frechen et al., 2009), whereas Nowdeh section hosts several palaeosols, probably correlated to MIS 3 to MIS 7 (Frechen et al., 2009; Khormali and Kehl, 2011).

- Mobarak Abad section is exposed in a deep road cut located on the northernmost ridge of the Alborz Mountains. In the loess deposits, about 40 m thick, at least six different palaeosols are intercalated, ranging from weakly developed CB horizons to strongly developed Bt horizons. Accumulation of secondary carbonates, pedogenic clay accumulation and Fe–Mn concretions are the most frequent pedological features in Mobarak Abad palaeosols. The palaeosols are separated by layers of yellowish brown loess showing several features of soil development including weakly developed sub-angular blocky structure, accumulation of secondary carbonates or Fe–Mn concretions (Shahriari et al., 2015) (for soil horizon classification, see Table S4).
- The Neka section is located on top of a deep limestone quarry about 10 km east of the City of Neka. The loess is divided by several palaeosol horizons. Loess deposits reach a thickness of approximately 20 m covering the foothills of the Alborz Mountains. Except of the first palaeosol, all palaeosols in Neka section have weakly to strongly developed Bt horizons

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