A first Holocene leaf wax isotope-based paleoclimate record from the semi-humid to semi-arid south-eastern Caucasian lowlands

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ABSTRACT: The Holocene paleoclimate of the Caucasus region is rather complex and not yet well understood: while existing studies are mainly based on pollen records from high-altitude and humid lowland regions, no records are available from the semi-humid to semi-arid south-eastern Caucasian lowlands. Therefore, this study investigated compound-specific δ13C and δ2H isotopes of leaf wax biomarkers from Holocene floodplain soils in eastern Georgia. Our results show that the leaf wax δ2H signal from the paleosols mostly reflects changes in the moisture source and its isotopic composition. Depleted δ2H values before ~8 cal ka BP change towards enriched values after ~5 cal ka BP and become again depleted after ~1.6 cal ka BP. This trend could be caused by Holocene changes of the isotopic compositions of the Black and eastern Mediterranean Sea, and/or by varying contribution of both moisture sources linked with the North Atlantic Oscillation. The leaf wax δ13C signal from the paleosols directly indicates varying local water availability and drought stress. Depleted δ13C values before ~8 and after ~5 cal ka BP indicate wetter local conditions with higher water availability, whereas more enriched values during the middle Holocene (~8 until at least 5 cal ka BP) indicate drier conditions with increased drought stress. © 2020 The Authors. Journal of Quaternary Science Published by John Wiley & Sons Ltd.

KEYWORDS: Caucasus region; compound-specific isotopes; floodplain soils; Holocene paleoclimate; leaf wax biomarkers

Introduction
The mid-latitudinal eastern Mediterranean and Caucasus region is expected to suffer increasingly and massively from droughts and climate change with accompanied socio-economic consequences over the next decades (Seager et al., 2014). Located at the transition zone between the mid-latitude Westerlies, the subtropical high-pressure systems and the Indian Summer Monsoon system (ISM), the region is a key location for understanding former and future large-scale changes in atmospheric circulation patterns and their underlying mechanisms (Djamali et al., 2010; Roberts et al., 2011; Joannin et al., 2014; Fig. 1). However, Holocene climate variability for the region remains controversial: for instance, high-resolution and well-dated regional Holocene climate records have been derived from stable δ18O isotopes from lake carbonates (Roberts et al., 2001, 2008; Stevens et al., 2001) and speleothems (Badertscher et al., 2011; Cheng et al., 2015). Depleted δ18O isotopes in most of those records during the early Holocene were classically interpreted to document more humid conditions and/or a shift in the timing of precipitation. In contrast, based on pollen and macrofossil records from regional lake sediments, several authors suggest a dry early Holocene (Bottema, 1986; Wright et al., 2003; Djamali et al., 2010; Messager et al., 2013; Joannin et al., 2014).

Focusing on the Caucasus region, the Holocene climatic history is mainly based on pollen records that are either located at altitudes >1000 m a.s.l. in the Lesser and Greater Caucasus Mountains or in the humid western Caucasian Colchis lowlands (Fig. 1). In contrast, apart from some scattered and mostly incomplete pollen records with generally rather poor chronostratigraphic control, there are few paleoclimate records available from the semi-humid to semi-arid south-eastern Caucasian lowlands (Kvavadze and Connor, 2005; Connor and Kvavadze, 2009; Messager et al., 2013; Joannin et al., 2014). Instead, in recent years the Holocene landscape evolution of this region has mostly been investigated by fluvial-geomorphological studies (Furlani et al., 2012; von Suchodoletz et al., 2015; Ollivier et al., 2016; von Suchodoletz and Faust, 2018). However, those lowlands are densely populated today, and parts of these regions were also intensively settled since the Neolithic period (Furtwängler et al., 1998; Akhundov, 2004; Chataigner et al., 2014). The current climate of the Caucasus region is rather complex and often shows large gradients in precipitation and temperature over even small distances. This complexity is linked to the regional orography that is characterized by the Greater Caucasus in the north, the Lesser Caucasus in the south and the connecting north-south-running Likhi Range between those mountain ranges (Lydolph, 1977). Therefore, it can be expected that the paleoclimatic evolution of the semi-humid to semi-arid south-eastern Caucasian lowlands should have at least partly differed from that of the high-altitude and humid lowland regions that have been recently studied. Compound-specific δ2H and δ13C analyses of long-chain n–alkanes and/or n–alkanoic acids (≥C25) are novel and valuable proxies that complement pollen and δ18O isotopes on lake carbonates, and have increasingly been used to reconstruct paleoclimatic and paleohydrological changes (Aichner et al., 2010; Wirth and Sessions, 2016; Schäfer et al., 2018; Häggi et al., 2019). Long-chain n–alkanes and n–alkanoic acids are produced as leaf waxes in higher terrestrial plants. They serve as valuable biomarkers because they remain well
preserved in soils and sediments over millennia, due to their low water solubility and high resistance to degradation (Eglinton and Eglinton, 2008). The leaf wax δ2H signal is thought to reflect the isotopic signal of precipitation (Sachse et al., 2006), but various fractionation processes can occur from the moisture source to its fixation in the leaf waxes, such as source effects or evapotranspirative enrichment of soil and leaf water (Feakins and Sessions, 2010; Sachse et al., 2012; Kahmen et al., 2013). In the mid-latitudes, the isotopic signal of precipitation that is stored in the leaf wax δ2H signal is thought mainly to reflect the isotopic signal of the moisture source (Schemmel et al., 2016; Wirth and Sessions, 2016; Schäfer et al., 2018). In contrast, the leaf wax δ13C signal mainly reflects the vegetation composition of either C3 or C4 plants, with more depleted values for the former (−23 to −34‰) and more enriched values for the latter (−6 to −23‰) (Rommerskirchen et al., 2006). If only C3 plants are dominant, variations of the δ13C signal are mainly controlled by mean annual precipitation (MAP) and mean annual temperature (MAT), and reflect on local water availability and drought stress (Dietendorf and Freimuth, 2017). Therefore, using the climatic information from the two leaf wax isotopes enables leaf wax-based paleoclimatic records to be established that directly incorporate the isotopic signal of precipitation and reflect local water availability.

This study presents the first leaf wax isotope-based paleoclimatic reconstruction from the semi-humid to semi-arid south-eastern Caucasian lowlands. We investigated compound-specific δ2H and δ13C isotopes of leaf wax n-alkanes and n-alkanolic acids from a fluvial sediment-paleosol sequence (FSPS) along the upper Alazani River located within the southern foothills of the Greater Caucasus in eastern Georgia. Previous investigations demonstrated that this FSPS is a valuable archive for paleoenvironmental reconstructions based on leaf wax n-alkanes (Bliedtner et al., 2018, 2020), but that the leaf wax signal should be divided into (i) a catchment signal that is stored in fluvial sediment layers, and (ii) an on-site signal that originates from local vegetation and had continuously formed in the paleosols during pedogenesis. Previous compound-class 14C dating of the leaf wax n-alkanes from the FSPS showed that only the leaf waxes from well-developed paleosols show ages close to the timing of sedimentation. In contrast, those from weakly developed paleosols and fluvial sediment layers show partly strong pre-agings, i.e. pre-date the timing of sediment deposition by up to thousands of years (Bliedtner et al., 2020). Therefore, this study only uses leaf wax δ2H and δ13C isotopes from intensively developed paleosols to robustly reconstruct former climatic conditions. By using this first leaf wax isotope-based paleoclimate record from the semi-humid to semi-arid south-eastern Caucasian lowlands, we aim to contribute to the controversial discussion of the Holocene environmental history of the eastern Mediterranean and Caucasus region.

Materials and methods

Study area and climate setting

The investigated FSPS (42°02′17.7″N, 45°21′18.7″E) is located along the right bank of the upper Alazani River within the foothills of the Greater Caucasus in eastern Georgia ~60 km downstream of the river source. The site is located in the westernmost part of the semi-humid to semi-arid south-eastern Caucasian lowlands at an altitude of ~450 m a.s.l. (Fig. 1). The Alazani River originates from the southern slopes of the Greater Caucasus Mountains (Fig. 1), and the site-related catchment in that mountain range reaches altitudes up to 3700 m a.s.l. The river has its discharge maximum during spring and early summer (April–June) due to both snowmelt in the Greater Caucasus and the concomitant regional precipitation maximum (von Suchodoletz et al., 2018). At the nearest climate station from the FSPS ~10 km to the west, Akhmeta, MAP today is ~720 mm a−1 and MAT ~12.0°C (de.climate-data.org/location/28480/). Precipitation reaches its maximum during convective events in spring and early summer (Lydolph, 1977). Based on modeling results of Bowen and Revenaugh (2003), the hydrogen isotopic composition of precipitation at the investigated FSPS should have more depleted values of ~10% during the winter months and more enriched values of ~10% during the summer months (Fig. 2).
Precipitation and moisture in the Caucasus region between the Black Sea and Caspian Sea are related to a complex atmospheric pattern, but are mainly supplied by the year-round Westerlies (Stanev and Rachev, 1999; Martin-Benito et al., 2016). These advect moisture from the North Atlantic and recycled moisture from the continent (e.g. the Black Sea), although their intensity and location is controlled by the North Atlantic Oscillation (NAO) (Hurrell et al., 2003). During positive NAO phases, strengthened Westerlies penetrate over the Black Sea into the Caucasus region, bringing precipitation with more negative δ2H values. During negative NAO phases, the Westerlies are weakened and southerly storm trajectories bring precipitation from the eastern Mediterranean Sea with more positive δ2H values (Brittingham et al., 2019). While the NAO has its strongest influence in winter and spring, in the past the westerly circulation dynamics might have been more affected by the Siberian Anticyclone that is strengthened during winter and spring, and largely prevents moisture supply to the region during that time (Martin-Benito et al., 2016). Additionally, the Indian Summer Monsoon (ISM) plays an indirect role on regional precipitation during late spring and early summer by shifting the anticyclonic belt towards the north during periods of a strong ISM (Djamali et al., 2010). Strengthening/weakening of the different circulation systems had important impacts on regional precipitation and moisture availability during the Holocene (Djamali et al., 2010; Joannin et al., 2014).

**Analytical procedure**

Biomarker analyses were carried out at the Institute of Geography of the University of Bern, Switzerland. Free total lipids were extracted from ~40 g air-dried and sieved (<2 mm) soil/sediment samples using an accelerated solvent extractor (Dionex ASE 200) with dichloromethane (DCM)/methanol (MeOH) (9:1, v/v). The total lipid extract was separated over liquid extraction over silica pipette columns. Because of coeluting compounds, n-alkanes and n-alkanoic acids were further purified using coupled silver nitrate (AgNO3) – zeolite pipette columns. Compound-specific δ13C isotopes were measured on n-alkanoic acids, whereas compound-specific δ2H isotopes were measured on n-alkanes. Ideally, both isotopes should be measured at the same compound. However, we would expect that the n-alkanoic acids are comparable with the n-alkanes because both are derived from the same leaf waxes. Isotope measurements were performed on an IsoPrime 100 mass spectrometer that was coupled to an Agilent 7890A gas chromatograph (GC) via a GC5 combustion/pyrolysis interface. The GC5 operated in the combustion mode (CuO reactor) at 850 °C for δ13C analyses, and in the pyrolysis mode (chrome reactor) at 1000 °C for δ2H analyses. The GC was equipped with a 30 m fused silica column (HP5-MS, 0.32 mm x 0.25 μm), and the samples were injected splitless. Samples for δ13C and δ2H analyses were measured as triplicates. The analytical precision of the δ13C analyses was checked twice after six injections by an external standard mix with a certified isotopic composition

![Figure 2. Mean monthly temperature and precipitation composition of the nearest climate station (Akhmeta, climate-data.org) overlain with the modern modeled isotopic δ2H composition from the investigated site (Bowen and Revenaugh, 2003). ](image-url)
(Schimmelmann, C27, C29, C33), and the analytical error was below 0.2‰. As n-alkanoic acids were not corrected for their methyl group that was added during methylation, the carbon isotopic composition is reported in the delta notation as \( \delta^{13}C \). Therefore, the isotope values should be considered and interpreted as relative and not as absolute values. For \( \delta^{2}H \) analyses, the analytical precision was similarly checked by the external standard mix twice after six injections, and gave analytical errors below 3.5‰. The \( H_2O \)-correction factor was checked every 2 days, and gave stable values of 4.36 \( \pm 0.08 \). The hydrogen isotopic composition is given in the delta notation as \( \delta^{2}H \) against the Vienna Standard Mean Ocean Water (VSMOW).

### Results

Leaf wax-derived \( n \)-alkanes and \( n \)-alkanoic acids were present in all the analysed samples. The concentrations of the most abundant compounds (C29 and C31 for \( n \)-alkanes, C28 and C30 for \( n \)-alkanoic acids) were sufficient to perform compound-specific isotope analyses. The obtained isotope values can be found in the Supporting Information. \( \delta^{2}H \) values of the \( n \)-alkanes from the uppermost parts of Ahb6, Ahb5, Ahb4, Ahb1 and Ah that were used for paleoclimatic interpretations ranged from \(-176.0 \pm 1.7\) to \(-145.5 \pm 1.8\)% for C29, and from \(-184.6 \pm 1.4\) to \(-154.4 \pm 1.0\)% for C31. \( \delta^{13}C \) values of the \( n \)-alkanoic acids of the uppermost parts of Ahb6, Ahb5, Ahb4, Ahb1 and Ah ranged from \(-32.3 \pm 0.2\) to \(-30.4 \pm 0.2\)% for C28, and from \(-32.8 \pm 0.1\) to \(-29.6 \pm 1.6\)% for C30 (Fig. 3B). \( \delta^{2}H \) and \( \delta^{13}C \) isotopes from the lower parts of intensively developed paleosols, less intensively developed paleosol Ahb2 and fluvial sediment layers that were not used for paleoclimatic interpretations showed a similar range to those from the uppermost parts of intensively developed paleosols, and are shown in Fig. 3B.

### Discussion

The \( \delta^{2}H \) signal

In the investigated FSPS, the leaf wax \( n \)-alkane \( \delta^{2}H \) signal from the uppermost parts of Ahb6, Ahb5, Ahb4, Ahb1 and Ah shows distinct changes of \(-30\)% through the sequence, with more depleted values in Ahb6, Ahb5 and Ahb4 that had developed before \(-5\) cal ka \( BP \), a more enriched value in Ahb1 that had developed after \(-3\) cal ka \( BP \), and again a more depleted value in
the recent soil Ah that had formed after ~1.6 cal ka BP (Fig. 4A). Similarly, depleted leaf wax $\delta^2$H values during the early Holocene are reported from the Neor peat mire in northern Iran (Sharifi et al., 2015; Fig. 4C), and they are paralleled by depleted $\delta^{18}$O values in Mediterranean lakes (Roberts et al., 2008; Fig. 4D). These studies interpret the observed values as indicating increased precipitation during the early Holocene, that led to wetter conditions. Likewise, the distinct enrichment of the leaf wax $\delta^2$H signal after ~5 cal ka BP in our record could classically be interpreted in terms of decreased precipitation amount and/or temperature changes, i.e. with wetter/warmer conditions before 5 cal ka BP and drier/colder conditions thereafter.

However, interpreting leaf wax $\delta^2$H can be complicated by different fractionation processes. Besides precipitation amount and temperature changes these processes potentially influence the leaf wax $\delta^2$H signal. Leaf wax $\delta^2$H values largely reflect the isotopic composition of the plant’s source water that is taken up by the plants via the soil water and mainly consists of infiltrating precipitation (Sachse et al., 2012). It has been assumed that the leaf wax $\delta^2$H signal is mainly formed during the time of leaf formation and the following 30 days, and that the rest of the growing season has just a minor influence (Sachse et al., 2010; Kahmen et al., 2011; Tipple et al., 2013). However, residual moisture from late winter snowfall can also still be stored in the soils and thus potentially contributes to the plant’s source water with more depleted $\delta^2$H values (Wirth and Sessions, 2016; Fig. 2). Therefore, the isotopic composition of the source water is a mixture of directly precipitation-derived soil water and of residual water from late winter snowfall. For our investigated site in the south-eastern Caucasian lowlands, the current isotopic composition of the plant’s source water should represent that of the period between March and May because the start of the growing season coincides with the period of main precipitation during spring and early summer that is linked to convective events (Lydolph, 1977; Fig. 2). It is therefore possible that former changes in the timing of the precipitation maximum could explain the observed $\delta^2$H pattern in our record: a shift of the precipitation maximum towards early spring with precipitation more depleted in $\delta^2$H

Figure 4. Leaf wax $\delta^2$H and $\delta^{13}$C paleosol records (A,B) from the investigated FSPS at the upper Alazani river compared to (C) leaf wax $\delta^2$H from Neor peat mire (Sharifi et al., 2015), (D) $\delta^{18}$O of lake carbonates from Lake Eski Acigöl (Roberts et al., 2008), (E) $\delta^{18}$O from Sofular Cave (Fleitmann et al., 2009), (F) $\delta^{18}$O from Jelta Cave (Cheng et al., 2015), (G) the North Atlantic Oscillation index (NAO) (Olsen et al., 2012) and (H) average precipitation anomaly of Georgia (mm a$^{-1}$) that was mostly derived from pollen records in the Caucasian Colchis lowlands and higher altitudes of the Lesser and Greater Caucasus (Connor and Kvavadze, 2009). [Color figure can be viewed at wileyonlinelibrary.com]
and possibly greater contributions from late winter snowfall could have led to the more depleted values observed before 5 cal ka BP, whereas changes of the precipitation maximum to early summer could have resulted in the more enriched values after 5 cal ka BP with precipitation more enriched in δ18O (Fig. 2). However, regional/local changes in the timing of precipitation and the amount of residual moisture from late winter are difficult to quantify, and there are no regional records from the south-eastern Caucasian lowlands for direct comparison. Another possibility to explain isotopic enrichment of leaf wax δ18O could be soil water evaporation and transpiration from the leaves (Feakins and Sessions, 2010; Kahmen et al., 2013). However, the influence of evaporative enrichment on our leaf wax δ18O signal should be less important, because the δ18O signal is set at the beginning of the growing season when most of the precipitation is falling and evaporation is still quite low.

In contrast, of more importance in the mid-latitudes is the dependence of the isotopic composition of precipitation on the variable isotopic composition of the moisture source and varying transport pathways, resulting in a complex leaf wax δ18O signal (Schemmel et al., 2016; Wirth and Sessions, 2016; Schäfer et al., 2018). For the investigated FSPS at the southern foothills of the Greater Caucasus Mountains most moisture is delivered by the Westerlies (Fig. 1), and the intensity and location of which are controlled by the NAO. For the Armenian Lesser Caucasus, Brittingham et al. (2019) found a significant relationship between the NAO and δ2H and δ13C isotopes in precipitation: during positive NAO phases with strengthened and northward displaced Westerlies, isotopically depleted precipitation from the Black Sea is dominant, whereas due to weakened and southward displaced Westerlies isotopically enriched precipitation from the eastern Mediterranean Sea is brought during negative NAO phases. Therefore, our δ2H record might reflect a complex and mixed signal of the two different moisture sources and their isotopic changes throughout the Holocene. On the one hand, the observed leaf wax δ18O changes in our FSPS with depleted values during the early Holocene and more enriched values after ~5 cal ka BP mostly follow the progressive isotopic enrichment of the Black Sea surface water throughout the Holocene. This constant isotopic enrichment trend of the Black Sea surface water is indicated by a δ18O speleothem record from Sofular Cave in northern Turkey (Fleitmann et al., 2009; Badertscher et al., 2011). In this context, depleted δ2H values in the Black Sea during the early Holocene are explained by the absence of a connection with the Mediterranean Sea and the strongly increasing amount of isotopically depleted water from large European rivers during ice melt, as well as with an only slow progress of isotopic mixing of the large water body after the deglaciation. After ~9 ka BP, increasing inflow of δ18O-enriched Mediterranean Sea water slowly shifted the Black Sea surface water towards more enriched values (Fig. 4E). On the other hand, leaf wax δ13C changes in our FSPS could also indicate a change in the moisture source from the Black Sea to the eastern Mediterranean Sea due to changes in the position of the NAO. Unfortunately, changes in the position of the NAO during the early Holocene are not yet known. Interestingly, similar to the Black Sea the eastern Mediterranean surface waters were also isotopically depleted in δ18O during that period, as indicated by a speleothem record from Jefita Cave in the northern Levante (Cheng et al., 2015; Fig. 4F). This was caused by isotopically depleted inflow of the Nile River water (Almogi-Labin et al., 2009). Therefore, although the δ18O values of the eastern Mediterranean surface waters are generally more enriched compared to the Black Sea surface waters, we cannot exclude a possible higher contribution from this moisture source during the early Holocene. Subsequently, more enriched leaf wax δ18O values after ~5 cal ka BP in our FSPS correspond well to a negative NAO phase linked to a southward displacement of the Westerlies (Olsen et al., 2012; Fig. 4G). Thus, isotopically enriched precipitation might have been brought from the eastern Mediterranean Sea during the middle Holocene. Vice versa, the following distinct depletion of leaf wax δ18O in the recent soil Ah since ~1.6 cal ka BP might be explained by a positive NAO phase linked to a northward displacement of the Westerlies during that period, leading to a stronger Black Sea source (Olsen et al., 2012; Figure 4E,G).

In summary, for the leaf wax δ18O changes in our FSPS from depleted values during the early Holocene towards more enriched values after ~5 cal ka BP and back to more depleted values after ~1.6 cal ka BP, we propose that these most probably reflect changes in the moisture source and/or isotopic changes of the respective moisture source throughout the Holocene. Moreover, the influence of the moisture source probably overprinted local climatic controls of our δ18O signal. A similar isotopic enrichment in leaf wax δ2H between the early Holocene and ~3 cal ka BP is also shown by Sharifi et al. (2015) for the Neor peat mire (Figs 1 and 4C). Although these authors compared their observed trend with δ18O changes in tropical East African lakes and interpreted them in terms of precipitation amount, we suggest that their mid-latitude leaf wax δ18O record might also reflect changes in the isotopic composition of the moisture source, i.e. varying influences of the eastern Mediterranean and Black Sea.

The δ13C signal

Looking at the δ13C record from our investigated FSPS, this signal shows distinct changes of ~3‰ throughout the sequence: depleted values are seen in Ahb6 that had developed before ~8 cal ka BP, more enriched values in Ahb5 and Ahb 4 that had developed during the middle Holocene between ~7 and 5 cal ka BP, and again more depleted values in Ahb1 and the recent soil Ah that had formed after ~3 cal ka BP (Fig. 4B). All leaf wax δ13C values are in a range typical for C3 plants so that no vegetation shifts towards C4 plants obviously occurred during the observed period. Therefore, the leaf wax δ13C signal can be interpreted in terms of local water availability and drought stress, because MAT and MAP are the most prominent fractionation factors in this case (Diefendorf and Freimuth, 2017). Furthermore, changes in atmospheric CO2 are also not likely to have influenced fractionation in δ13C, because this effect is more important on glacial-interglacial timescales but negligible during the pre-industrial Holocene (Schubert and Jahren, 2012; Schäfer et al., 2018). The interpretation of δ13C signals from C3 plants in terms of changing water availability is mainly based on the fact that water availability has a strong influence on the plant’s stomatal conductance. This factor regulates CO2 diffusion with the ambient atmosphere and thus influences carbon fractionation during plant photosynthesis (Farquhar et al., 1989; Kohn, 2010). Because photosynthesis lasts for the whole growing season, water availability and drought stress should influence δ13C constantly over this period, i.e. the δ13C signal encompasses the total growing season from spring until autumn. Leaf wax δ13C values in our investigated FSPS indicate that the early Holocene before ~8 cal ka BP was wetter than today, followed by a drier middle Holocene between ~7 and at least 5 cal ka BP. Subsequently, wetter conditions than today prevailed again until at the latest 1.6 cal ka BP, and afterwards it became drier again. Those findings oppose the only so far existing Holocene precipitation record for the Caucasus region by Connor and Kvatadze (2009).
(Fig. 4H). That record indicates that a large part of the Holocene was generally wetter than today, with the wettest conditions found during the middle Holocene and relatively drier conditions before and after. This difference could have two possible explanations: (i) the precipitation reconstruction of Connor and Kvavadze (2009) is mainly based on pollen records from the humid western Caucasian Colchis lowlands and higher altitudes of the Lesser and Greater Caucasus, whereas only a few incomplete records with generally rather low chronostatigraphic resolution were included from the semi-humid to semi-arid south-eastern Caucasian lowlands (where our record is located and where pollen records are generally scarce). (ii) Regional pollen-based precipitation reconstructions in the Caucasus region have generally to be treated with caution, because pollen and δ¹³C lake carbonate records do not agree with each other especially for the early Holocene: dominating non-arboreal pollen indicate a pronounced dry early Holocene, contrasting with depleted δ¹⁸O values from lake carbonates suggesting wetter conditions during that time (Wright et al., 2003; Roberts et al., 2008; Djamali et al., 2010). Possible explanations for this obvious discrepancy are overprinting of the climate signal in δ¹³C lake carbonates by the isotopic composition of the moisture source, whereas different explanations are suggested for delayed regional reforestation compared with Europe as indicated by the pollen records. Possible explanations for the latter are changes in precipitation seasonality, intensified regional human land use and/or an intensified ISM (Wright et al., 2003; Djamali et al., 2010). If intensified human land use with pastoralism, wood cutting and landscape burning (Djamali et al., 2010) led to increased input of non-arboreal pollen to regional sediment archives during the early Holocene, then paleoprecipitation reconstructions from such records that suggest more arid conditions during that period are not reliable. 

Overall, the regional paleoenvironmental picture of the region remains unresolved, and unfortunately there are no other δ¹³C records from the semi-humid to semi-arid south-eastern Caucasian lowlands for direct comparison. In a larger region δ¹³C records are limited to a few speleothems (Bar-Matthews et al., 1999; Fleitmann et al., 2009; Cheng et al., 2015).

Conclusions

This study presents the first leaf wax isotope-based paleoclimatic record from the semi-humid to semi-arid south-eastern Caucasian lowlands, based on compound-specific δ²H isotopes from leaf wax n-alkanes and δ¹³C isotopes from leaf wax n-alkanoic acids of Holocene floodplain soils in an FSPS from eastern Georgia. Our study led to the following conclusions:

- Although the leaf wax δ²H signal from the paleosols of the investigated FSPS could potentially be influenced by changes in the timing of precipitation, this signal is probably controlled by varying proportions of precipitation that is brought from the eastern Mediterranean and Black Sea and by variations in their isotopic compositions: depleted leaf wax δ²H values during the early Holocene change towards more enriched values after ~5 cal ka BP, and this trend follows the progressive δ¹⁸O enrichment of the Black Sea waters throughout the Holocene. However, it is also possible that more isotopically enriched precipitation from the eastern Mediterranean Sea was brought in the context of a negative NAO phase after the middle Holocene. Accordingly, a stronger dominance of isotopically depleted precipitation from the Black Sea could possibly also explain isotopically depleted δ²H values in the recent soil Ah that formed after ~1.6 cal ka BP, given that this change coincides with the shift towards a generally more positive NAO phase. Therefore, one has to be aware of this source effect when interpreting leaf wax δ²H (and water isotopes in general) in the mid-latitude eastern Mediterranean and Caucasus region, because it strongly overprints the isotopic fractionation by climatic parameters such as precipitation amount or temperature changes.

- In contrast, the leaf wax δ¹³C signal from the intensively developed paleosols of the FSPS can be interpreted in terms of local water availability and drought stress, and therefore seems to be a more reliable paleoclimatic indicator: more depleted values in δ¹³C before ~8 cal ka BP and after ~3 cal ka BP indicate wetter local conditions with higher water availability, whereas more enriched values during the middle Holocene (~8 until at least 5 cal ka BP) indicate drier conditions with increased drought stress for the local vegetation.

- Our findings partly oppose the existing paleoclimatic picture of the eastern Mediterranean and Caucasus region, i.e. both former pollen and stable isotope results. These discrepancies might be explained by a partly different palaeoclimatic evolution in the semi-humid to semi-arid south-eastern Caucasian lowlands compared with the neighbouring mountain or humid lowland regions.

Overall, leaf wax isotopes have great potential to reconstruct palaeoclimatic conditions in the semi-humid to semi-arid south-eastern Caucasian lowlands. During this study, they were applied to paleosols in a fluvial sediment sequence, but we have to note that our palaeoclimate reconstruction is only based on a low sample resolution due to the generally discontinuous nature of such sequences. Nevertheless, leaf wax isotopes could potentially also be applied to more continuous lake or peat sediments in the region that often allow higher chronological resolutions. Therefore, a larger application of these proxies could possibly help to disentangle the palaeoclimatic conditions for former cultures that had settled in the semi-humid to semi-arid south-eastern Caucasian lowlands since the Neolithic period, but could also contribute to a better understanding of the complex and still poorly understood palaeoclimatic history of the larger eastern Mediterranean and Caucasus region.

Data availability

Data are available in the Supporting Information.
Supporting information

Additional supporting information may be found in the online version of this article at the publisher’s web-site.

Acknowledgements. This project was financially supported by the Swiss National Science Foundation (project P00P2-150590). We thank two anonymous reviewers for their valuable and helpful comments on this paper.

Abbreviations. DCM, dichloromethane; FAME, fatty acid methyl ester; FSPS, fluvial sediment–paleosol sequence; ISM, Indian Summer Monsoon; MAP, mean annual precipitation; MAT, mean annual temperature; MeOH, methanol; NAO, North Atlantic Oscillation; SDI, Soil Development Index; TOC, total organic carbon; VSMOW, Vienna Standard Mean Ocean Water.

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