Influence of climate change and human activities on the organic and inorganic composition of peat during the Little Ice Age (El Payo mire, W Spain)

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Abstract

The study of environmental change during the Little Ice Age (LIA) offers a great potential to improve our current understanding of the climate system and human-environment interactions. Here, a high resolution multiproxy investigation of a Mediterranean mire from central-western Spain, covering the last ~700 years, was used to reconstruct peat dynamics and land use change to gain further insights into their relationship with LIA climate (temperature and moisture). To accomplish this, concentrations and accumulation rates of major and minor lithogenic (Si, K, Ti, Rb, and Zr) and biophilic (C and N) elements, as well as humification indices (UV-Absorbance and Fourier Transform Infrared Spectroscopy - FTIR) and pollen and non-pollen palynomorphs were determined. Peatland dynamics seems to have been coupled to changes in solar irradiance and hydrological conditions. Our results point to wetter conditions after the mid-16th century, although with high intra-annual fluctuations. At the late 18th century, when solar activity was systematically higher than before, peat carbon accumulation rates (PCAR) showed a continuous increase and the humification indices suggest a change towards more humified peat. Enhanced soil erosion occurred at ~AD 1660-1800 (SE1), ~AD 1830-1920 (SE2) and ~AD 1940-1970 (SE3), although a minor increase in Si fluxes was also detected by ~AD 1460-1580. All phases coincided with higher abundances of fire indicators, but the changes recorded during the ~AD 1460-1580 event and SE1 coincide with the Spörer and Maunder minima, so a climatic influence on soil erosion cannot be discounted. Changes in the sources of mineral matter to the catchment between ~AD 1550 and ~AD 1650 and since the mid 17th century were likely related to modifications of tree cover and/or variations in wind strength.

1. Introduction

Palaeoenvironmental reconstruction of climate and land use changes using peatlands is important to improve our current understanding of the climate system and human-environment interactions. Knowledge of the long-term ecological dynamics of peatlands is essential to assess possible responses and feedbacks of these carbon-rich ecosystems to climate change and natural disturbance (Yu, 2006). Peatland dynamics, as well as carbon accumulation in peatlands, is a function of the balance between primary production of living plants and decomposition of the organic remains, both being controlled by climate and other environmental factors. Climate during the Holocene has generally favoured peat accumulation and has maintained a large carbon sink (Turunen, 2003), but the rate of carbon accumulation has never been constant. Well known intra-Holocene climate shifts, like the so-called Medieval Climate Optimum or the Little Ice Age, offer a great opportunity to test controls on carbon accumulation. Temperature plays a dominant role in carbon dynamics although, despite much research, a consensus has not yet emerged on the temperature sensitivity of soil carbon decomposition [for review on the topic see: (Davidson and Janssens, 2006)]. Increasing temperature favours organic matter decay and consequently carbon release to the atmosphere. However, temperature also exerts a strong influence on primary productivity, which is crucial for carbon sequestration. In northern peatlands, hydrological changes are also known to play an important role in carbon storage (Charman et al., 2009; Klein et al., 2013; Loisel and Garneau, 2010). They can be natural but also human induced by drying, burning or other mechanisms of peat degradation. Thus, peatland dynamics at various temporal scales result from complex and nonlinear relationships with temperature and moisture conditions (Yu et al., 2001). Discerning these links is important for understanding the past and future carbon cycle. In this sense, the study of carbon dynamics on a wide range of peatlands is required. Much research has been done in boreal and Northern peatlands (e.g. Frolking and Roulet, 2007; Gorhan and Gorham, 1991; Loisel and Yu, 2013; Ovenden, 1990; Packalen and Finkelstein, 2014; Turunen, 2003; Turunen et al., 2001; Vitt et al., 2000; Yu et al., 2003; Yu, 2006, 2012) but Mediterranean wetlands still remain relatively understudied (e.g. Rodríguez-Murillo et al., 2011).

The Little Ice Age (LIA) is normally defined as a recent period of generalized mountain glacier expansion and is conventionally framed between the 16th and 19th centuries, a period during when European climate was variable but frequently cooler (Grove, 1988; Mann, 2002). However, the timing and global character of the Little Ice Age is still a matter of debate (e.g. Bertler et al., 2011; Bradley et al., 2003; Diaz et al., 2011; Mann et al., 2009, 1999). Most multiproxy palaeoenvironmental studies, based on evidence of cooling, and earliest evidence of glacier expansions, place the start of the LIA to ~AD 1300-1400, after the end of the Medieval Climate Anomaly (MCA). Grove, (2004) defines the LIA as beginning in the 13th or 14th century and culminating between the mid-16th and mid-19th centuries. Changes in orbital cycles, solar and volcanic activity, as well as the thermohaline circulation have been proposed as the major causes behind it (Crowley and Kim, 1996; Lean et al., 1995; Rind and Overpeck, 1993; Robock, 2000; Stuiver et al., 1997).

Climatic deterioration at the LIA, besides altering peatland dynamics, is considered to have increased dust deposition in ombrotropic peatlands in Sweden (de Jong et al., 2007) and Poland (De Vleeschouwer et al., 2009). Massa et al., (2012) also detected increased Ti concentrations in Greenlandic lakes during this climatic event; although

Silva-Sánchez et al. (2015), failed to find increased mineral content in Greenlandic peat during the LIA. In most European settings, where long histories of human pressure are common, human-induced soil erosion through the use of fire for the creation of pastureland and cropland, appears to be more relevant than climate forcing (e.g. Hölzer and Hölzer, 1998; Martínez Cortizas et al., 2005; Silva-Sánchez et al., 2014). However, the interplay between climate and human activity makes it difficult to determine any climatic influence over soil erosion (Ballantyne, 1991; Foster et al., 2000; Fuchs, 2007). In the last few decades, erosion has became one of the most significant environmental problems worldwide (Grimm et al., 2002; Lal, 1990; Montgomery, 2007; Pimentel, 2006; Wilkinson and McElroy, 2007), particularly in areas having a seasonal climate and a long history of human pressure like the Mediterranean region (García-Ruiz et al., 2013). Palaeoenvironmental reconstructions from these environments might provide valuable information about how ecological systems have changed over time and how these changes have affected soil erosion processes. Contrasting palaeoenvironmental information about human activities and climate with historical evidence of social change allow global interpretations about socio-ecological systems.

Several investigations undertaken in the Iberian Peninsula revealed the imprint of the LIA. Evidence has been found in geomorphological studies of glacier fluctuations (e.g. Grove, 2001; González Trueba et al., 2008), dendroclimatological reconstructions (e.g. Büntgen et al., 2008) and palaeoenvironmental studies of natural archives such as alluvial terraces (e.g. Benito et al., 2003b; Gutiérrez-Elorza and Peña-Monné, 1998; Thorndycraft and Benito, 2006), marine (e.g. Abrantes et al., 2005; Bernárdez et al., 2008; Desprat et al., 2003; Diz et al., 2002; González-Álvarez et al., 2005; Martins et al., 2005; Nieto-Moreno et al., 2013) or lake sediments (e.g. Julià et al., 1998; Martín-

Puertas et al., 2008; Morellón et al., 2012; Valero Garcés et al., 2008; Valero-Garcés et al., 2006). Because of the geographical distribution of peatlands in Iberia, the LIA has been primarily recorded in the Northern areas -i.e. Eurosiberian bioclimatic region (e.g. Martínez-Cortizas et al., 1999; Gil García et al., 2007; Ortiz et al., 2008; Schellekens et al., 2011; Silva-Sánchez et al., 2014; Castro et al., 2015). Here, we present a high resolution multiproxy study of a Mediterranean mire covering the last ~700 years. Major and minor lithogenic (Si, K, Ti, Rb, and Zr) and biophilic (C and N) element concentrations and accumulation rates, humification indices obtained by UV-Absorbance and Fourier-transform infrared spectroscopy (FTIR) and pollen and non-pollen palynomorph records are combined. The main objectives are: 1) to analyse peat dynamics in terms of carbon accumulation and peat decay and relate it to climate (temperature and moisture) changes during the Little Ice Age, 2) provide evidence of soil erosion and establish their relationship with climate and human activity and 3) get insights in mineral matter sources and its possible drivers.

2. Material & Methods

2.1. *Study area and sampling*

El Payo mire (Figure 1) is a fen located in the Gata Range, at 1000 m a.s.l, near to a small stream and surrounded by elevations above 1400 m a.s.l. The peatland is very close to the Pass of Santa Clara, which connects the provinces of Cáceres and Salamanca. This area constitutes a contact zone between Precambrian shales and slates and the granitic materials, which define the Jalama Pluton. Large amounts of colluvial debris has accumulated above them (IGME, 1982). The monthly average temperature is 11.3˚C and annual rainfall reaches 1263 mm, so the area isincluded in the supramediterranean bioclimatic belt and has a humid ombroclimate (Peinado Lorca and Rivas-Martínez, 1987). Moreover, due to prevailing winds coming from the Southwest, there is an Atlantic influence.

The vegetation is dominated by supramediterranean oak forests of *Quercus pyrenaica* enriched with many characteristic Atlantic elements (Peinado Lorca and Rivas-Martínez, 1987; Pulido et al., 2007). At lower altitudes distinct mesomediterranean oak forests are found on the slopes. Grazing activities have created areas of pasture and Scots pine (*Pinus sylvestris*) has also spread due to afforestation. At higher altitudes, the landscape is mainly composed of shrub communities consisting of *Echinospartum ibericum*, *Cytisus oromediterraneus*, *C. striatus* and *Erica australis*. Along watercourses, *Alnus glutinosa* grows, with isolated stands of *Betula alba*. The current vegetation on the mire is composed by species such as *Carex nigra, C. echinata, Molinia caerulea, Juncus acutiflorus, Erica tetralix, Genista anglica, Calluna vulgaris, Pedicularis sylvatica, Potentilla erecta, Drosera rotundifolia* and *Sphagnum* sp.

A core of 100 cm depth was obtained from the middle of the mire with a Russian core sampler of 5 cm diameter. The base, composed by sands and gravels, was reached. The core was then wrapped in plastic and stored under cold conditions until analysis.

2.2. *Radiocarbon dating and Chronology*

Five AMS (accelerator mass spectrometry) ^{14}C measurements were taken on bulk peat samples at the Uppsala (Ua) and *Centro Nacional de Aceleradores* (CNA) laboratories (Table 1) and used to produce an age depth model. Ages BP were calibrated using the IntCal13.14C curve (Reimer et al., 2013), while pM ages were calibrated with the postbomb_NH2.14C curve (Hua et al., 2013). The age depth model (Figure 2) was produced using Clam 2.2 software (Blaauw, 2010). The best fit was obtained applying a smooth spline solution. Confidence intervals of the calibrations and the age-depth model were calculated at 95% (2 σ). In the text ages are expressed as ca. yrs AD (i.e ~AD).

2.3. *Elemental analysis (concentrations and accumulation rates)*

Concentrations of major and trace lithogenic (Si, K, Ti, Rb, Zr) elements were determined using dispersive X-ray fluorescence with an EMMA-XRF analyser (Cheburkin and Shotyk, 1996). The instruments are hosted at the RIAIDT facility of the University of Santiago de Compostela. Carbon and N were measured with a LECO CHN-1000 analyser in the University of Santiago de Compostela using ethylenediaminetetraacetic acid (EDTA) as reference material. Quantification limits for Carbon and Nitrogen were 100 $\mu g \cdot g^{-1}$. As PY is a minerogenic mire it is possible to interpret changes in mineral matter fluxes as inorganic inputs from the soils of the catchment (i.e. soil erosion).

Accumulation rates were obtained by multiplying carbon concentration by dry bulk density and growth rate. Dry bulk density was calculated dividing dry mass (after drying peat samples for 24 hours at 105ºC) by wet sample volume, while the growth rate (cm/yr) was determined by the age depth model (provided by the Clam output).

2.4. *Humification -FTIR and UV-Absortion of NaOH peat extracts*

FTIR analyses and UV-Absorption of NaOH peat extracts (UV-Abs) were done on dried and milled peat samples at 1 cm contiguous intervals. ATR-FTIR spectral characterization was made using a Bruker IFS-66V FTIR spectrometer hosted at the RIAIDT facility of the University of Santiago de Compostela. Following Broder et al., (2012) a humification index (HI FTIR) was calculated as the ratio between peak intensities at 1630 cm^{-1} (aromatic C=C and asymmetric COO− group vibrations; i.e. lignin and other aromatics and aromatic or aliphatic carboxilates (Haberhauer et al., 1998) and 1035 cm^{-1} (C-O stretching and O-H deformation; i.e. polysaccharides (Artz et al., 2006)). UV-Absorption of the NaOH peat extracts was measured in the University of Santiago de Compostela following the conventional method of extracting the humic acid fraction from dried and milled peat samples using 8% NaOH and assessing the absorbance of the extract at 540 nm using a spectrophotometer (Blackford and Chambers, 1993).

2.5. Pollen analysis

Laboratory sub-sampling for pollen analysis was done at 2 cm contiguous intervals, resulting in a total number of 50 samples. The traditional pollen extraction method (Fægri and Iversen, 1989; Moore et al., 1991), with an initial wash with HCl, a NaOH wash and a final treatment with HF, was applied. A Thoulet solution was used for densimetric separation of pollen and non-pollen microfossils (Goeury and de Beaulieu, 1979). Pollen concentration was estimated by adding a *Lycopodium* tablet to each sample (Stockmarr, 1971). Pollen grains were identified with the help of different keys and atlases (Fægri and Iversen, 1989; Moore et al., 1991; Reille, 1992) and the reference collection of the Archaeobiology Laboratory of CSIC (Madrid). The identification of non-pollen palynomorphs (NPPs) is based on van Geel and Aptroot, (2006) and van Geel et al., (2003, 1989, 1981) and nomenclature follows Miola (2012).

Ferns, hydro-hygrophilous taxa and NPPs were excluded from the total pollen sum, (500 pollen grains minimum; 558 ± 29 pollen grains average) as they tend to be over represented (Wright and Patten, 1963). Data processing and graphic representation was performed with the help of the TILIA and TGView programs (Grimm 1992, 2004). Pollen assemblage zones have been determined with a cluster analysis using CONISS (Grimm, 1987). Microcharcoal have also been counted in the same slides used for pollen (Finsinger and Tinner, 2005; Tinner and Hu, 2003). Charcoal accumulation rate (CHAR) was finally calculated by dividing the concentration of microcharcoal by the deposition time of each sample.

3. Results

3.1. Chronology

Radiocarbon dates are shown in Table 1 and the age-depth model for the sequence is presented in Figure 2. Peat accumulation rate (AR) has varied considerably over the last 700 cal yr BP. It was initially low, 0.07-0.08 cm·yr^{-1}, and very constant between ~AD 1315 to ~1650 (equivalent to a deposition time [DT] of 13.4-11.7 yr·cm^{-1}). Then, peat growth increased gradually from ~AD 1650 to 1900 until it reached rates of ~0.33 cm·yr-1 (3.3 yr·cm^{-1}), staying stable around this point to the mire surface.

3.2. Geochemical record

3.2.1. Elemental analysis

Carbon concentrations progressively decrease from the base of the core to 60 cm. Above that depth, maximum carbon concentrations (36-45%) are reached in the upper (Figure 3). Nitrogen values remain fairly constant (mostly between 1.1 and 1.6%) although with minor fluctuations. Content is higher (2.0-2.4%) from 7 to 20 cm.

Concentrations of major and trace lithogenic elements (Si, K, Ti, Rb and Zr) show a common pattern of variation (Figure 3). Bilateral Pearson correlation coefficients (r) are statistically significant (α=0.01) ranging from 0.76 to 0.95. Minimum values occur between 60 and 19 cm and in the top 14 cm. From 60 cm to the base of the core, except for a short-lived decrease between 76 and 72 cm, lithogenic concentrations show high values. The lithogenic elements have low accumulation rates below 74 cm (Figure 3), although a minor increase from base line values can be found between 88 and 79 cm, particularly for Si, Rb and Zr. After that, three main increases – also from base line values- are apparent at: 55-72, 23-51 and 10-20 cm, the one nearest the mire surface having the highest values (44.5 and 1.2 g m^{-2} yr^{-1} for Si and K, and 200, 20 and 7.6 mg m^{-2} yr^{-1} for Ti, Rb and Zr respectively).

Peat carbon accumulation rates (PCAR) are highly constant from 100 to 60 cm (24.9±8.1 gC m^{-2} yr^{-1}), where they began to increase slightly. From 60 to 25 cm PCAR continuously increases (up to 167 gC m^{-2} yr^{-1}). After that they maintain more stable values (114.1 ± 29.3 gC m^{-2} yr^{-1}) although with a slightly decreasing trend.

3.2.2. Peat humification (HI FTIR and UV-Abs) and C/N ratio

HI FTIR and UV-Abs show the same pattern of variation, both decrease from the base of the core to 64 cm (1.07 to 0.55 and 0.48 to 0.27 respectively, Figure 3b), record high values from 64 cm to 19 cm (0.82-1.23 and 0.3-0.6 respectively) and lower values from there to the top of the core (Figure 3b). As with the humification indices, C/N ratio shows high values (25-38) between 64-19 cm, but also in the top 8 cm (around 28). Values in the section below 60 cm are low and rather constant (Figure 3b).

3.3. *Palynological record*

Betula, *Alnus*, *Quercus pyrenaica* and *Quercus ilex* are among the main arboreal pollen (AP) taxa (Figure 4). AP remains relatively high (23-78 %) in the whole sequence, but some arboreal taxa, like *Alnus* and *Betula*, show a more or less continuous decrease, being replaced by *Erica arborea* type, Poaceae, and cultivated trees like *Castanea*, *Olea* and *Pinus*. Among local taxa, Cyperaceae pollen and *Pteridium* spores are recorded continuously through the record.

Three major pollen assemblage zones were identified (Figure 4). PY 1 (78-100 cm; ~AD 1600-1330) is characterised by the highest percentages of AP (43-78 %; 64.7 ± 9.3), *Betula* being the dominant taxa. *Alnus* decreased continuously from the beginning of the record. *Erica arborea* type was well represented, increasing its presence nearly continuously, while Poaceae shows very constant low values. *Cerealia* and coprophilous fungi were recorded regularly. The transition from PY1 to PY2 is characterised by a sharp decrease in *Betula*. Poaceae and other herbs increase simultaneously. *Kretzschmaria deusta* (HdV-44; previously named *Ustulina deusta*) spores, whose fungus is a well known plant pathogen causing soft-rot of wood (van Geel and Andersen, 1988), occurs for the first time. Birch has been proven to be one of possible *Kretzschmaria deusta* host plants (Wilkins, 1934).

During PY2 (78-24 cm; ~AD 1600-1925) *Betula* and *Alnus* increased in value although total AP is slightly lower (51-28 %; 41.9 ± 5.4) compared with PY1 (Figure 4). From 60 cm, some thermophilous cultivated taxa like *Castanea* and *Olea*, as well as coprophilous fungi, increased in abundance, indicating a possible climatic amelioration but also intensified human activity in the region. PY2 is characterised by a high increase in wetter conditions/shallow open water indicators (Figure 4). However, fungi associated with dry conditions also increased throughout the zone, albeit in much lower numbers, suggesting that intra-annual hydrological changes might have occurred. The transition from PY2 to PY3 is characterised by a sharp decrease in *Betula* and *Erica arborea* type and as Poaceae and other anthropozoogenous herbs increased. Simultaneosusly, *Cerealia* type increases suggesting cultivation was practised locally.

In PY3 *Betula* and *Alnus* have fallen to less than 5% (Figure 4). *Castanea* and *Olea* increased in value. *Pinus*, which has been used in recent afforestation schemes, as well as cereals (*Cerealia* and *Secale cereale*) also increased in representation. Anthropozoogenic taxa and coprophilous fungi, are also prominent. NPPs indicative of a change to eutrophic conditions also increased in this zone.

4. Discussion

4.1. Carbon accumulation, peat decay and their relation to temperature and moisture changes during the Little Ice Age

In the PY record, peat accumulation, as well as PCAR, seems to have been largely affected by the cooler conditions during the more rigorous times of the LIA. From the beginning of the record (~AD 1300) peat growth and PCAR were low, but at the end of the 18th century (~AD 1770), and coinciding with an increase in solar activity after the termination of the Maunder minimum (Figure 5a; Bard et al., 2000), they show a sizeable increase, the upward trend continuing until the present day. A longer and warmer growing season after the coldest period of the LIA might have favoured peat C accumulation by increasing net primary production. Similar results, recording decreased carbon accumulation during the LIA, had been found in a Swedish mire (between ~AD 1400-1800; Oldfield et al., (1997)) and in two peatlands, one from UK and one from Denmark (~AD 1300-1800 and ~AD 1490-1580, respectively; Mauquoy et al., (2002)). Increased C accumulation during warmer periods has also been found by Charman et al., (2013). They analysed an extensive data collection from Northern Hemisphere extratropical peatlands, concluding that carbon sequestration rate declined over the climatic transition from the Medieval Climate Anomaly (MCA) to the Little Ice Age. This probably happened as a consequence of lower LIA temperatures and other environmental factors which influence net primary production such as snow cover or cloudiness.

At ~AD 1760-1930 peat humification indices (UV-Abs and HI FTIR ratio) increase suggesting a change towards more decomposed peat (Figure 5a). C/N ratios also show an increase in this peat section. Although changes in vegetation have been reported to influence the trends of UV-Abs (Caseldine et al., 2000; Yeloff and Mauquoy, 2006), C/N ratios (Bragazza et al., 2007; van Smeerdijk, 1989) and molecular composition of the peat (Schellekens and Buurman, 2011), the pollen record of the PY core does not support any abrupt change in peat vegetation at this time. High UV-Abs and HI FTIR values have been frequently related with increased peat decomposition (Blackford and Chambers, 1993; Blackford, 2000). Elevated C/N ratios are often interpreted, in northern peatlands, as the result of decreased peat decomposition because of carbon, the energy source for the microorganisms, is lost and nitrogen is kept as proteins (Kuhry and Vitt, 1996; Malmer and Holm, 1984). But high C/N ratios, coinciding with higher decomposition peat layers, have also been previously reported for Northwest Iberian (Pontevedra Pombal et al., 2004) and Scottish peatlands (Anderson, 2002).

The C/N ratio depends both on C and N contents, but in peatlands relative N variation tends to be larger, having thus a higher influence on the ratio. In the PY record, the correlation of C/N with C is 0.32 (r; $\alpha = 0.01$) whereas with N is -0.77 (r; $\alpha = 0.01$; larger with a polynomial function). Nitrogen concentration in peat can be affected by several environmental factors (Kravchenko et al., 1996). Favourable conditions for decomposition, such as higher temperatures after the Maunder minimum or dry wet/shifts, may result in increasing N mineralization (Kralova et al., 1992; Morecroft et al., 1992; Reddy and Patrick, 1986), increasing the potential for N loss. If the amount of mineralised N exceeds the demand by the biota on the peat surface, then N will be lost relative to C in the catotelm (Anderson, 2002) and the C/N ratio will increase. Moreover, despite carbon loss through anaerobic decomposition in the catotelm, as plant remains are decomposed, peat organic matter gets enriched in aliphatic and aromatic compounds (Buurman et al., 2006; Hammond et al., 1985; Hatcher et al., 1986; Stout et al., 1988) with a higher C concentration than those that are preferentially lost (as polysaccharides); so the C content of the material that remains is higher (as well as the C/N ratio). This is supported in the PY core (Figure 5a) by higher HI FTIR ratios, which suggest an accumulation of aromatic and aliphatic moieties and a loss of polysaccharides and an increase in C concentration after ~AD 1760. The positive or negative sign of the balance between carbon accumulation (through enhanced primary production) and carbon losses (through enhanced decomposition and DOC release) under a warming scenario has been subject of much debate (e.g. Davidson and Janssens, 2006; Dorrepaal et al., 2009; Frolking et al., 2014; Ise et al., 2008). In PY, although late 18th century warming led to a clear increase in carbon accumulation, it also favoured peat decomposition for the period ~AD 1760-1930. Similarly, at ~AD 1580-1650, and also coinciding with a rise in solar activity [i.e. the brief period of climate amelioration between the Spörer and Maunder minima], C/N ratios and HI FTIR values (Figure 5a) point towards increased peat decomposition. A slight increase in C concentration can also be identified but, neither PCAR nor UV-Abs responded, highlighting the importance of relying in more than one proxy.

The hydrological regime, besides temperature, is thought to be a major forcing in peat dynamics. Enough moisture supply is needed for peat accumulation, while drier conditions may favour peat decomposition. Variations in NPP assemblage in the PY record support evidence of a wetter LIA in the Mediterranean, especially for the period after mid-16th century (Figure 5a). Wet indicators began to increase after ~AD 1550 and they show a sharper increase at ~AD 1720-1930. During the second phase a simultaneous increase in drier indicators suggests that high intra-annual hydrological fluctuations also occurred, especially at ~AD 1740-1760 and ~AD 1870-1940 when dry NPPs are more prominent (Figure 4). This chronology is coherent with other studies in Mediterranean Spain. Figure 5a shows the comparison of our NPP proxy data and previous reconstructions of variations in humidity in Mediterranean Spain. The best agreement is found for the record of Barriendos Vallve and Martin-Vide, (1998), who reconstructed flood periods based on historical documentation describing events on the Mediterranean coast of the Iberian Peninsula. Reconstruction from Taravilla lake record (Moreno et al., 2008), located in the Tagus headwaters, also resembles the one presented here from PY favourably, except that the wet periods they found at ~AD 1420 and ~AD 1540 do not have any equivalence at PY using the proxies determined. Benito et al., (2003a), who undertook a spatial-temporal analysis of documentary flood data collected for the Tagus basin (Central Spain), also identified the ~AD 1550-1670 event in the PY record, but not the ~AD 1770-1930 one, which seems to have occurred slightly earlier in their reconstruction. Research on river flooding, lake levels, marine sediments and studies on documentary sources in Mediterranean Iberian Peninsula (e.g. Fletcher and Zielhofer, 2013; Nieto-Moreno et al., 2013; Morellón et al., 2012; Moreno et al., 2008, 2012; Roberts et al., 2012; Valero Garcés et al., 2008; Benito et al., 2003a) have shown that the LIA, although with fluctuations, was generally wetter in comparison with the Medieval Warm Period. The PY records wetter conditions especially after 16th century and it is in agreement with numerous other studies (Barriendos Vallve and Martin-Vide, 1998; Benito et al., 2003a, 2003b; López-Sáez et al., 2009; Morellón et al., 2012; Moreno et al., 2008; Valero-Garcés et al., 2008), although even for this period droughts may have occurred intermittently.

Hydrological fluctuations in the Northern Hemisphere are thought to be highly influenced by the North Atlantic Oscillation, and ultimately forced by changes in solar activity. But the correlation between solar activity and NAO fluctuations has varied over time. (Kirov and Georgieva, 2002) indicated a negative correlation between solar activity and NAO. But, more recent studies (Trouet et al., 2009) indicate the existence of a positive forcing. According to them, a persistent positive NAO occurred during the Medieval Climate Anomaly and a clear shift to weaker NAO conditions occurred during the Little Ice Age. A negative (positive) state of the NAO would generate wetter (drier) conditions in the Mediterranean (at least in the west; Roberts et al. (2012)). In the PY record, the variations in NPP assemblages are consistent with changes in NAO reconstruction (Figure 5a -NAOms; Trouet et al. (2009)), with the wetter conditions of the LIA occurring synchronously with the weakest NAO.

Peatland carbon accumulation rates (PCAR) are controlled by the difference between production and decomposition, which is affected by local and climatic factors including hydrology and temperature (Klein et al., 2013). In the PY record, there was an adequate moisture supply during periods of increased temperature after the late 18th century, which might have triggered the increase in carbon accumulation. At the same time, warmer temperatures and seasonal drought might be behind increased peat decomposition. Higher values of dry indicators at ~AD1740-1760 and ~AD 1870-1940 (suggesting at least some seasonal drought) seem to have affected neither carbon accumulation nor peat decomposition. According to (Charman et al., 2013), although an adequate moisture supply is necessary for the presence of peat, above a threshold of moisture availability the effect on carbon accumulation is secondary relative to growing season temperature and light conditions.

4.2. Soil erosion, dust sources and its relation with climate and human activity

Although without any apparent increase in soil erosion, probably because of the high arboreal cover, ever since ~AD 1300, carbonicolous fungi, charcoal influx and coprophilous fungi in the PY mire indicate the use of fire and grazing (Figure 5b). Historical evidence indicates that the Gata Range experienced intense social and population changes during the LIA. After the early 13th century, the Gata Range no longer was considered a frontier between the Castilian and Muslim kingdoms, so intense efforts were made to repopulate the range (Blanco-González et al., 2015; Clemente Ramos and de la Montaña Conchiña, 1994; Martín Martín, 1985). Also in the

13th century, the development of *La Mesta*, a powerful association of sheepherders of the medieval Crown of Castile (Ezquerra Boticario and Gil Sánchez, 2008), took place. Palynological research in the Central System indicates that from the Iron Age to the Early Middle Ages, anthropic activities were still sporadic and mainly located in the lowlands, but from the Feudal Period onwards, when *La Mesta* transhumance system took place, they spread into the high-mountains (López-Sáez et al., 2014). Livestock herds were transhumant, moving to and from pastures in the kingdom according to the season through protected and defined cattle trials (Abel-Schaad and López-Sáez, 2012; Abel-Schaad et al., 2014; López-Merino et al., 2009; López-Sáez et al., 2009). The main tracks (*Cañadas Reales*) took most of large herds over long distances on well-defined itineraries, joining wintering areas in the South with summering areas in the North. ,.In the Mediterranean basin livestock movements between landscapes with complementary ecologies were widespread phenomena. They ocurred in the Iberian and the Italic Peninsulas, as well in Southern France and in the Balkans (Pascua Echegarai, 2012). Besides main tracks, smaller subsidiary routes, where trips were shorter, were also common. One of these routes passed nearby the PY mire. Based upon increases in coprophilous fungi (Figure 5b), cattle passage might have been higher at ~AD 1330-1400 and at ~AD 1500-1580. Increased charcoal influx/carbonicolous fungi indicate that the use of fire was common during this time. By ~AD 1460-1580, a first, slight increase in the fluxes of lithogenic elements (Figure 5b) occurred roughly coinciding with the ~AD 1500-1580 increase in grazing pressure indicators, but also with the Spörer minimum. By then, soil erosion intensity was still limited. Tree cover was high (being arboreal pollen ~70%), but some taxa, like *Alnus*, showed a continuous decrease from the beginning of the PY record (~AD 1300), most likely linked to its use as livestock feed.

After that, three major periods of enhanced soil erosion (SE1: ~AD 1660-1800, SE2: ~AD 1830-1920 and SE3: ~AD 1940-1970 (Figure 5b) seem to have occurred associated with increases in the use of fire to create agriculture and pasture land, although at times climatic influence cannot be discarded.

During SE1 (~AD 1660-1800) Si, K, Ti, Rb, and Zr fluxes increased. Silicon, and to a lesser extent Zr, Rb and K fluxes peak during the Maunder minimum (Figure 5b), which may indicate a possible climatic influence on mineral matter inputs, through enhanced soil erosion. SE1 also coincides with a rise in charcoal influx indicating an active use of fire. But, it is not until ~AD 1720, after the Maunder minimum, when *Cerealia* and coprophilous fungi doubled in value, reinforcing the climatic interpretation of the Si enrichment during SE1 and suggesting that in this mountainous location a possible connection between the development of cultivation and pasture and ameliorated climatic conditions exists.

Throughout SE2 (~AD 1830-1920), new efforts appear to have been made in order to favour grazing activities through the use of fire. The increase in *Quercus ilex* may indicate a proliferation of *dehesas* in the lowlands (Figure 4). *Dehesas* (*montados* in Portugal) are *Quercus ilex* dominated woodland-pastures with important ecological and cultural functions on the Iberian Peninsula. This traditional land-use system evolved as an adaptation to poor soils and adverse rainfall that cannot support intensive agriculture. Cultivation of arboreal species such as *Castanea* and *Olea* occurred at the same time. This intensification of human activities in the range are chronologically framed by the rise of liberal policies in the early decades of the 19th century, that led to the confiscation of large areas of land to councils and the Church and the dissolution of *La Mesta* (Merino Navarro, 1976). The first *Olea* plantations were planted at the beginning of the 16th century (Figure 4) by encouragement of the Order of Santiago and Emperor Carlos due to an olive oil shortage (Maldonado Santiago, 2005). According to some sources (Ezquerra Boticario and Gil Sánchez, 2008) the spread of *Olea* at the beginning of the 19th century (Figure 4) was related with an increase in the value of olives, but due to its coincidence with increased solar activity it might be very likely that climate also played an impact on this trend. According to the records of most lithogenic elements and dust flux, SE2 seem to have been lower and more fluctuating than the previous phase. Rubidium and Ti fluxes show the highest increases, while other lithogenics keep values more similar to their background levels. A change in lithogenic sources might explain this pattern, and this is discussed further in the text. Moreover, the dissolution of *La Mesta* in 1836 favoured the interests of local stockbreeders against large landowners, which resulted in further grazing intensification, showed by the increase of coprophilous fungi (Figure 5b). The latter seem to be a general pattern for central and western Central System (Abel-Schaad et al., 2014; López-Sáez et al., 2014).

SE3 (~AD 1940-1970) is the most severe erosion episode recorded in the last seven hundred years in the PY mire catchment. Maximum values in charcoal influx and carbonicolous fungi indicate that fire was again used to transform the landscape (Figure 5b). Further increases in *Cerealia* and coprophilous fungi and the anthropogenic and anthropozoogenic herb assemblages indicate a more intensive land use. During this time, grazing activities reached the highest intensity of the whole record. Assuming that the imprint provided by the passage of herds would be characteristically lower compared with that produced by the presence of local livestock, the area was no longer a livestock track, but became pasture land for local stockbreeders, especially in summer time. Riparian trees, like *Alnus* and *Betula*, are reduced to isolated stands along watercourses.

In 1938 a General Plan of afforestation promoted short cycle tree plantations at a national level (Ximénez de Embún and Ceballos, 1939). As a consequence, *Pinus* afforestation plantations were very prominent. In the study area, *Pinus sylvestris* was the favoured species as it grows better at these altitudes. In lower areas *P. pinaster* was also planted on a large scale. These plantations were mainly created in treeless areas, especially on pastureland, but also on shrublands. The pollen record shows an intense decrease of grasslands during this period. Decreases in *Cistus* type and *Erica arborea* type pollen percentages are also detected in PY pollen record. To some extent, the decrease in other taxa like *Betula* and *Alnus*, may have also been linked to the spread in *Pinus* afforestation and other human transformations of the landscape in the last couple of decades.

A coupling between soil erosion and tree cover during historical times has been detected in many records from European peatlands (e.g. Chapman, 1964; Hölzer and Hölzer, 1998; Kempter and Frenzel, 1999; Martínez Cortizas et al., 2005). In the PY mire, the creation of cropland, pastureland and fruit tree plantations, often associated with *Betula* and *Alnus* clearance, promoted soil exposure in the catchment leading to increased dust fluxes to the peatland. However, it is surprising that the large decrease in *Betula* (and *Alnus*) percentages between ~AD 1550 and ~AD 1650 were not accompanied by any noticeable impact on lithogenic fluxes. Anyway, despite the lack of response in net mineral inputs to the mire, coinciding with *Betula* and *Alnus* decreases (~AD 1550-1650 and from the mid ~AD 1700s) there was an increase in the Ti/Zr ratio (Figure 5b) , pointing to a change in dust sources associated to changes in the forest stand near the peatland. Titanium is enriched in fine soil fractions (i.e. clay) compared to Zr (Schuetz, 1989; Taboada et al., 2006) so an increase in Ti/Zr values indicate the arrival of smaller grain size material. This can happen with a change in wind strength (Fábregas Valcarce et al., 2003; Martínez Cortizas et al., 2002) but also, which appears to be the case, because a change in tree cover would modify the potential source areas (Kempter and Frenzel, 1999).The exact cause of the reduction of *Betula* and *Alnus* between at ~AD 1550-1650 is difficult to ascertain. On one hand, there is a simultaneous increase in anthropozoogenic perennial pasture and coprophilous fungi, pointing towards clearances related with the creation of pastureland for grazing (in this case without the use of fire) (Figure 5b). There is also evidence of cereal cultivation, but without any noticeable increase compared to previous times. On the other hand, the presence of *Kretzschmaria deusta* (HdV-44), known from birch carr deposits (van Geel, 1978), is a pathogen of broadleaved trees including *Betula* and *Alnus* (van Geel and Andersen, 1988). It causes soft-rot on living trees and it can continue to decay wood after the host tree has died, making *K. deusta* a facultative parasite. Thus, even though grazing was probably favoured (intentionally or not) to some extent, tree disease may have also played an important role in *Betula* and *Alnus* decline.

Other example of decoupling between tree cover and soil erosion happened in recent times, as high lithogenic accumulation rates were detected during the spread of *Pinus* afforestations at El Payo. Recent soil erosion inputs in minerotrophic peatlands, despite increased tree afforestation in the catchment, seem to be a wider process as evidence of this has also been found for example in North West Spain (e.g. Silva-Sánchez et al., 2014).

5. Conclusions

Climate change during the Little Ice Age was one of the main drivers of environmental change, at different scales, in the Mediterranean mountain sector where the PY mire is located. It affected peatland dynamics, which varied considerably through the period seemingly in response to changes in solar irradiance and hydrological conditions. Changes in PCAR in the PY core are consistent with previous research, which indicates enhanced carbon accumulation in peatlands during warmer periods. From ~AD 1770 (when solar activity is systematically higher than before) PCAR showed a continuous increase pointing to enhanced carbon accumulation probably due to higher primary productivity associated with warmer conditions. Moreover, at ~AD 1770-1930, despite evidence of increased wetter conditions - at least seasonally -, FTIR and UV-Abs humification indices indicate a change towards more humified peat. The fact that there was an adequate moisture supply during periods of increased temperature after the late 18th century might have triggered the increase recorded in carbon accumulation, whereas warmer temperatures and seasonal drought might be behind increased peat decomposition. This research indicates that under a warming scenario Mediterranean mountainous peatlands might have a positive net carbon accumulation, at least, if enough water supply is maintained.

Three major periods of enhanced soil erosion occurred at ~AD 1660-1800 (SE1), ~AD 1830-1920 (SE2) and ~AD 1940-1970 (SE3), although a minor increase in Si fluxes was already detected by ~AD 1460-1580. Although the latter one and SE1 happened during the Spörer and Maunder minima, all phases coincided with increases in fire indicators. According to this, fire, applied as a tool of land use change (e.g. to promote pastureland in detriment of shrubland), seems to have strongly influenced soil erosion and mineral influx to the mire. Increased soil erosion was not always accompanied by forest decline. Nevertheless, changes in woodland vegetation (*Betula* and *Alnus*) were coeval with changes in chemical indicators of dust sources (the Ti/Zr ratio), although changes in wind strength may have also influenced the origin of the dust that reached the mire.

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Figure captions

Figure 1. Location map of El Payo mire.

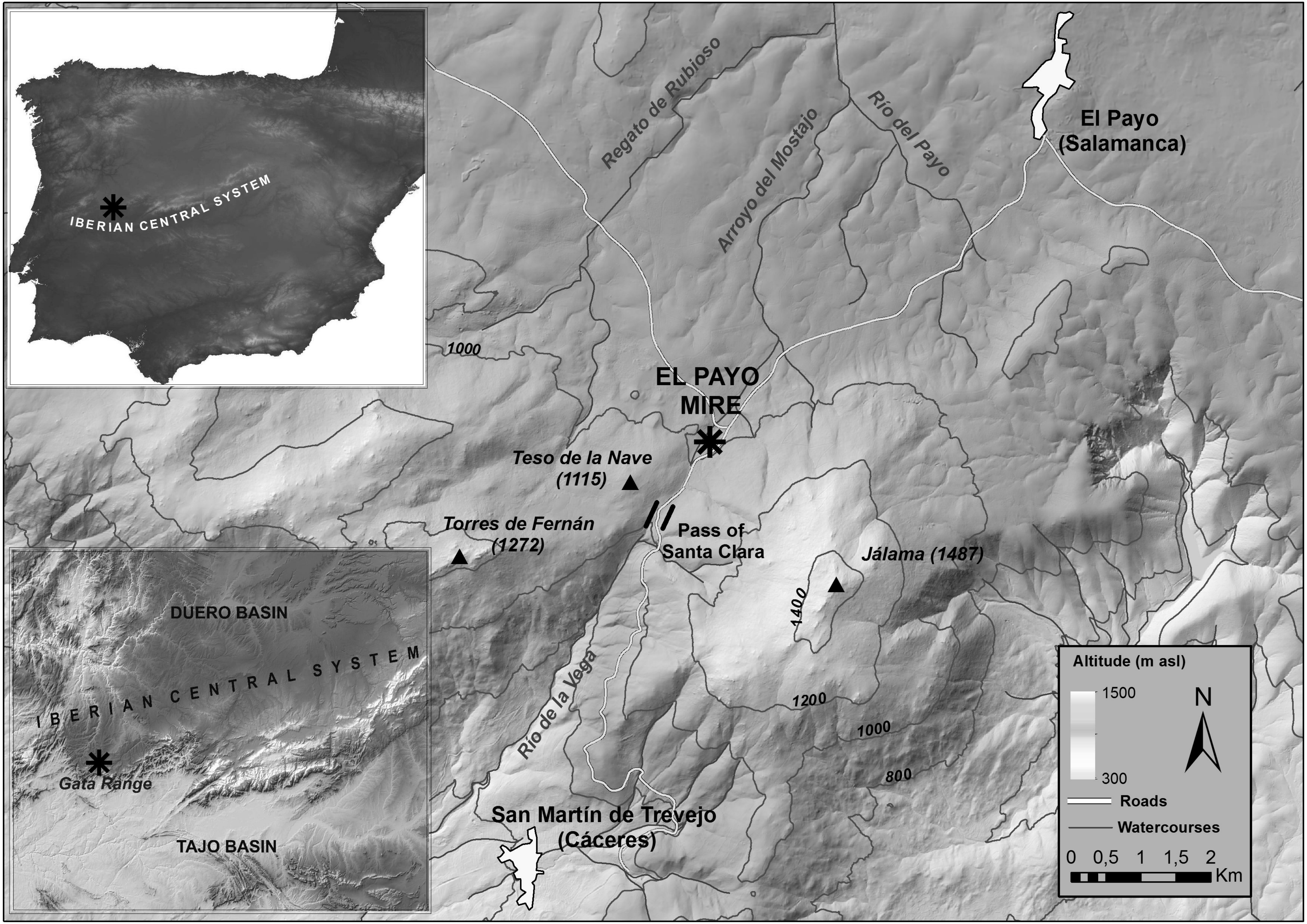
Figure 2. Age depth model of the PY core. Blocks in the radiocarbon ages represent the 95% confidence level in radiocarbon dates calibration, and the grey-shaded area the highest density ranges.

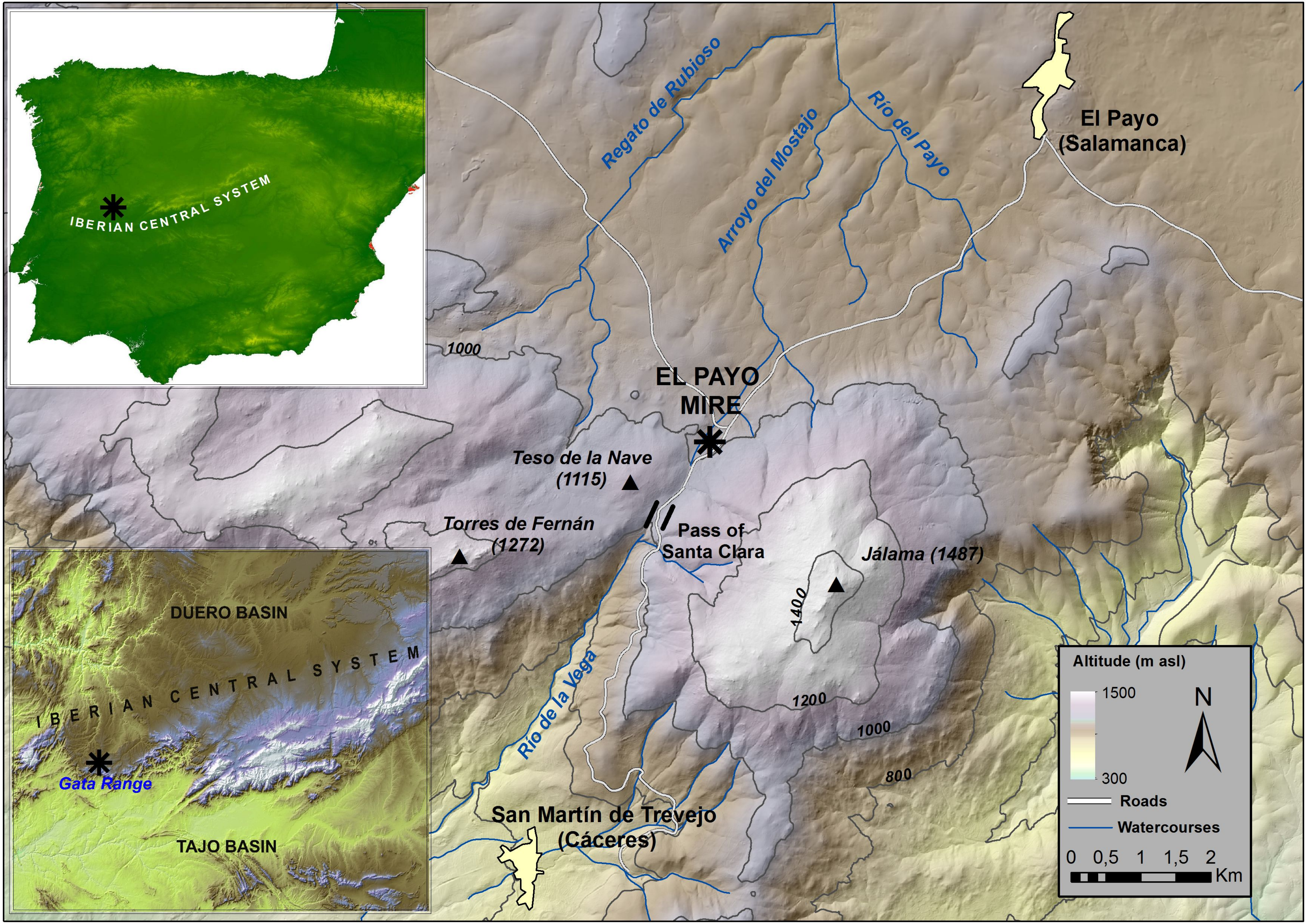
Figure 3. A) Vertical trends in the elemental composition of organic (C, N) and lithogenic elements (Si, K, Ti, Rb, Zr) in the PY core expressed as % and as accumulation rates. For accumulation rates (PCAR, Si AR, K AR, Ti AR, Rb AR and Zr AR) dashed lines connect measured values and solid line represents the smoothed trends. Vertical dashed lines: mean values at the base of the core. Horizontal dashed bars: minor and major (SE1, SE2 and SE3) soil erosion events; B)vertical trends in organic matter decomposition proxies: C/N ratio and humification indexes (HI FTIR and HI UV-Abs).

Figure 4. Palynological summary diagram of the PY core. Anthropozoogenic perennial pastures: Apiaceae, Brassicaceae, *Campanula*, Caryophyllaceae, Fabaceae undiff., Liliaceae undiff., Rosaceae undiff., Scrophulariaceae; Anthropozoogenic nitrophilous communities: *Anthemis*, Chenopodiaceae, *Galium*, *Plantago*, *Rumex*, *Urtica dioica* type; Anthropogenic nitrophilous communities: *Aster* type, Cichorioideae, *Erodium*, *Geranium*; Dry indicators: *Pleospora* (HdV-3B), HdV-10, *Byssothecium circinans* (HdV-16C), HdV-63 (van Geel and Aptroot, 2006; van Geel, 1978); Wet/Open water indicators: HdV-18, Spermatophores of Copepoda (HdV-28), HdV-65, HdV-92 (Bakker and van Smeerdijk, 1982; Ellis, 1971; Mighall et al., 2006; van Geel, 1978); Eutrophic indicators: HdV-123, HdV-124, HdV-181 (Bakker and van Smeerdijk, 1982; Pals et al.,

1980; van Geel, 1978). Shaded areas represent a x5 exaggeration. CONISS: Constrained incremental sum of squares.

Figure 5. A) variations in indicators of peatland dynamics and climate. PCAR, C/N, HI FTIR, UV-Abs variations and wet/Open water vs. dry non pollen palynomorphs (NPPs) variations the PY core plotted against Solar activity reconstruction by Bard et al., 2000, several paleoflood reconstructions on Mediterranean river or lake basins (Barriendos and Martín-Vide, 1998; Benito et al., 2003; Moreno et al., 2008) and NAOms reconstruction by Trouet et al., 2009. Vertical ligth grey bars: Spörer and Maunder minimums in solar activity; horizontal mid grey bars: increases in wet-open water NPP; horizontal dark grey bars: increases in dry NPP; B) variation in indicators of soil erosion, fire incidence and human activity. Ti and Si AR; Charcoal AR; Carbonicolous fungi*: *Gelasinospora* (HdV-1) and *Chaetomium* (HdV-7A); Coprophilous fungi*: *Cercophora* type (HdV-112), *Sporormiella* type (HdV-113), *Podospora* type (HdV-368) and *Sordaria* type (HdV-55A); Cerealia* and Ti/Zr and stacked diagram of tree, shrub and herb pollen sums. Ligth grey bars: Spörer and Maunder minimums in solar activity. Dashed bars: minor and major (SE1, SE2, SE3) soil erosion events. * Lighter lines shows a x5 exaggeration


IBERIAN CENTRAL SYSTEM
Regato de Rubioso
Arroyo del Mostajo
Río del Payo
El Payo
(Salamanca)
1000
EL PAYO
MIRE
Teso de la Nave
(1115)
Torres de Fernán
(1272)
Pass of
Santa Clara
Jálama (1487)
1400
DUERO BASIN
IBERIAN CENTRAL SYSTEM
Gata Range
TAJO BASIN
Río de la Vega
1200
1000
800
San Martín de Trevejo
(Cáceres)
Altitude (m asl)
1500
300
N
Roads
Watercourses
0
0,5
1
1,5
2
Km


IBERIAN CENTRAL SYSTEM
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IBERIAN CENTRAL SYSTEM
Gata Range
TAJO BASIN
Regato de Rubioso
Arroyo del Mostajo
Río del Payo
El Payo
(Salamanca)
1000
EL PAYO
MIRE
Teso de la Nave
(1115)
Torres de Fernán
(1272)
Pass of
Santa Clara
Jálama (1487)
1400
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800
Río de la Vega
San Martín de Trevejo
(Cáceres)
Altitude (m asl)
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300
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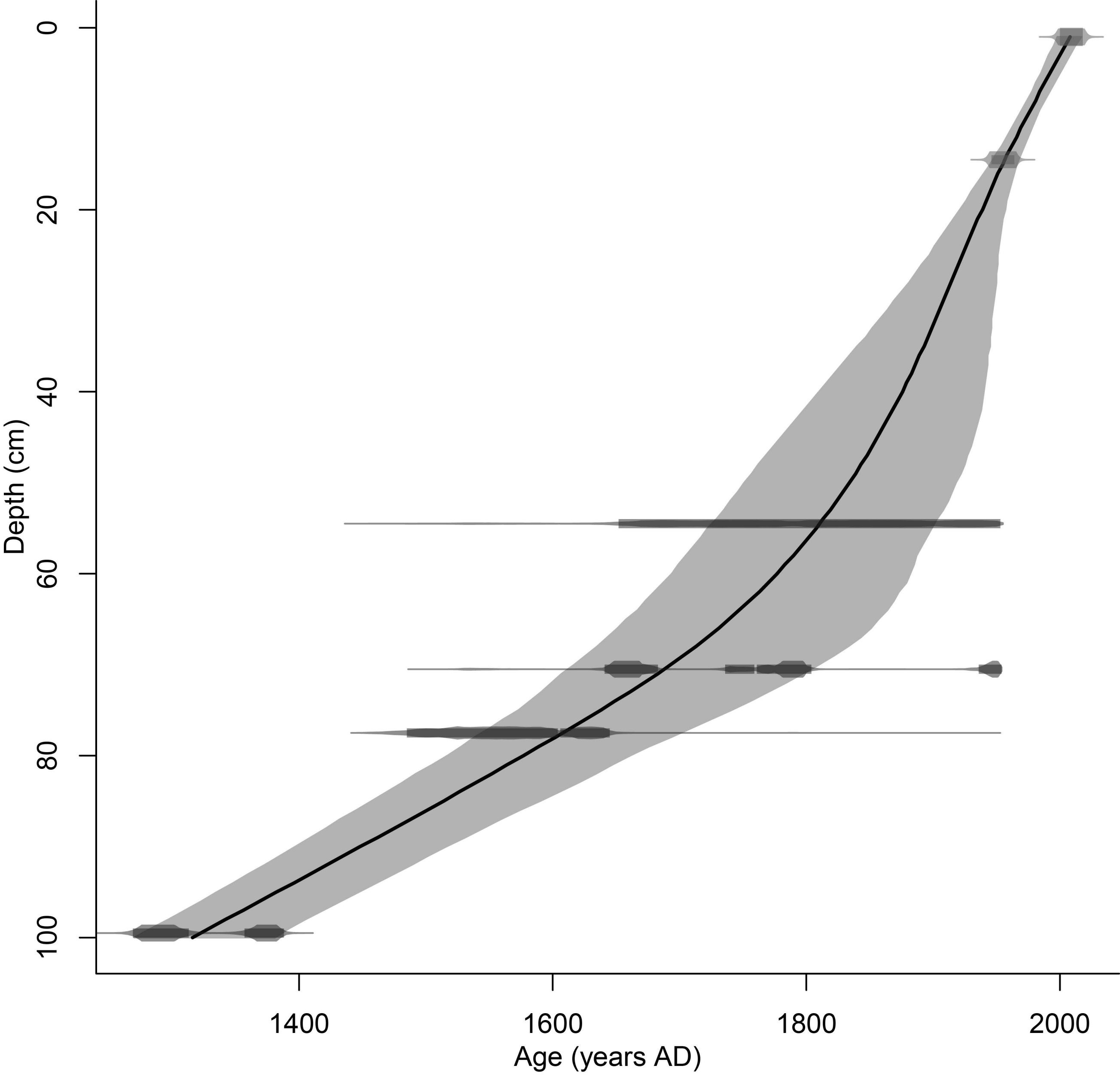
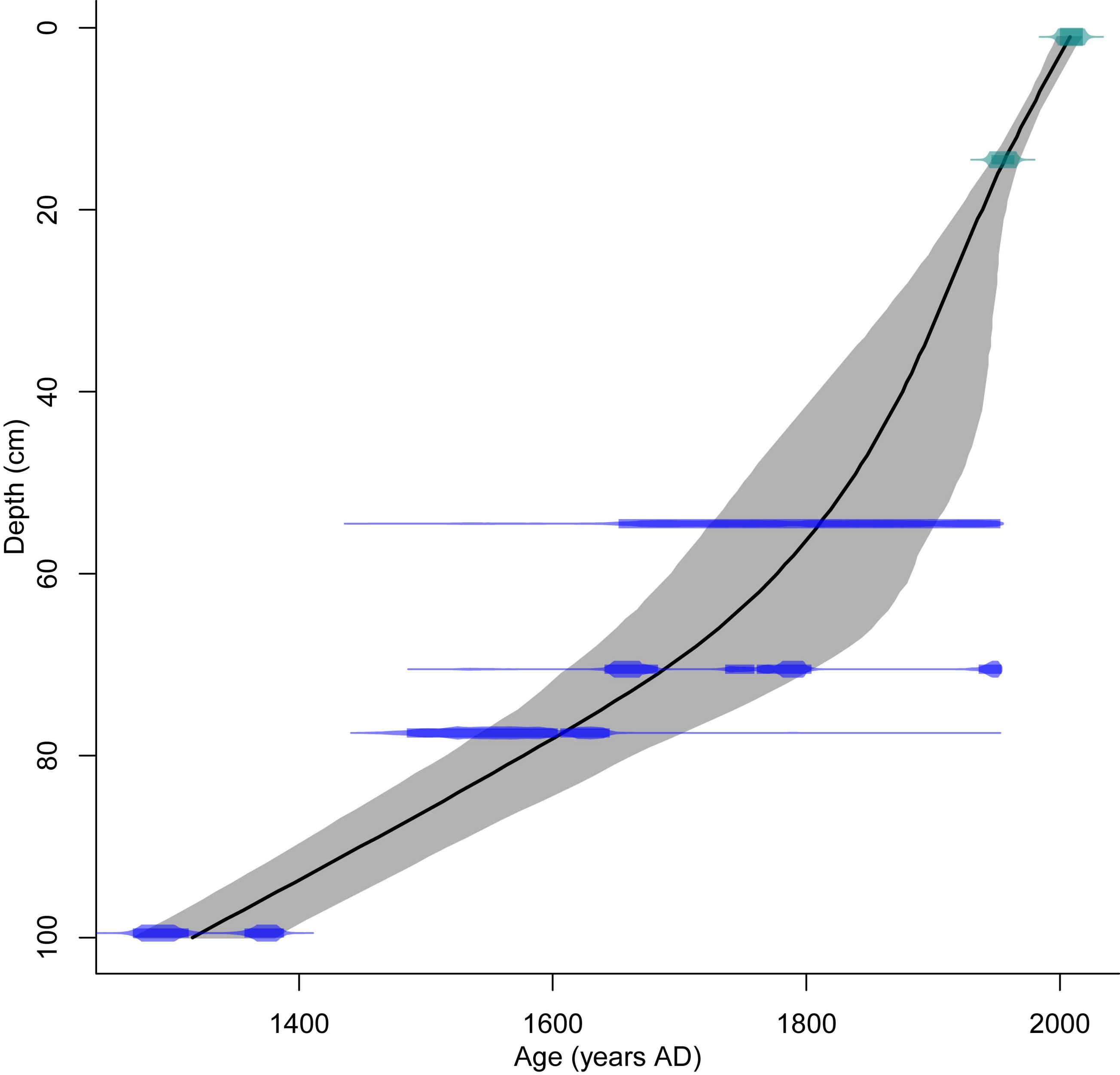
Roads
Watercourses
0 0,5 1 1,5 2
Km


0
20
40
60
80
100
Depth (cm)
1400
1600
1800
2000
Age (years AD)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Depth (cm)
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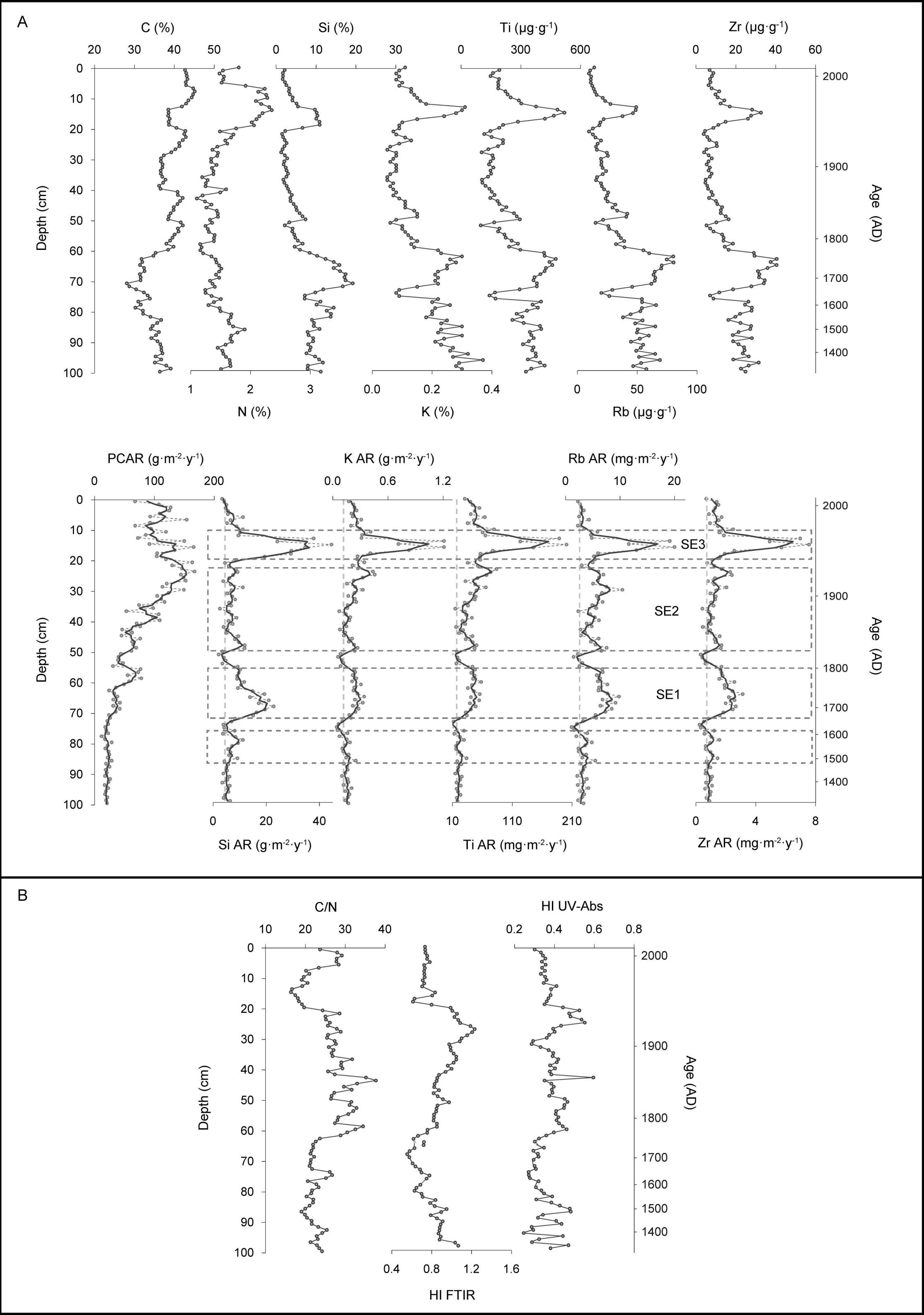
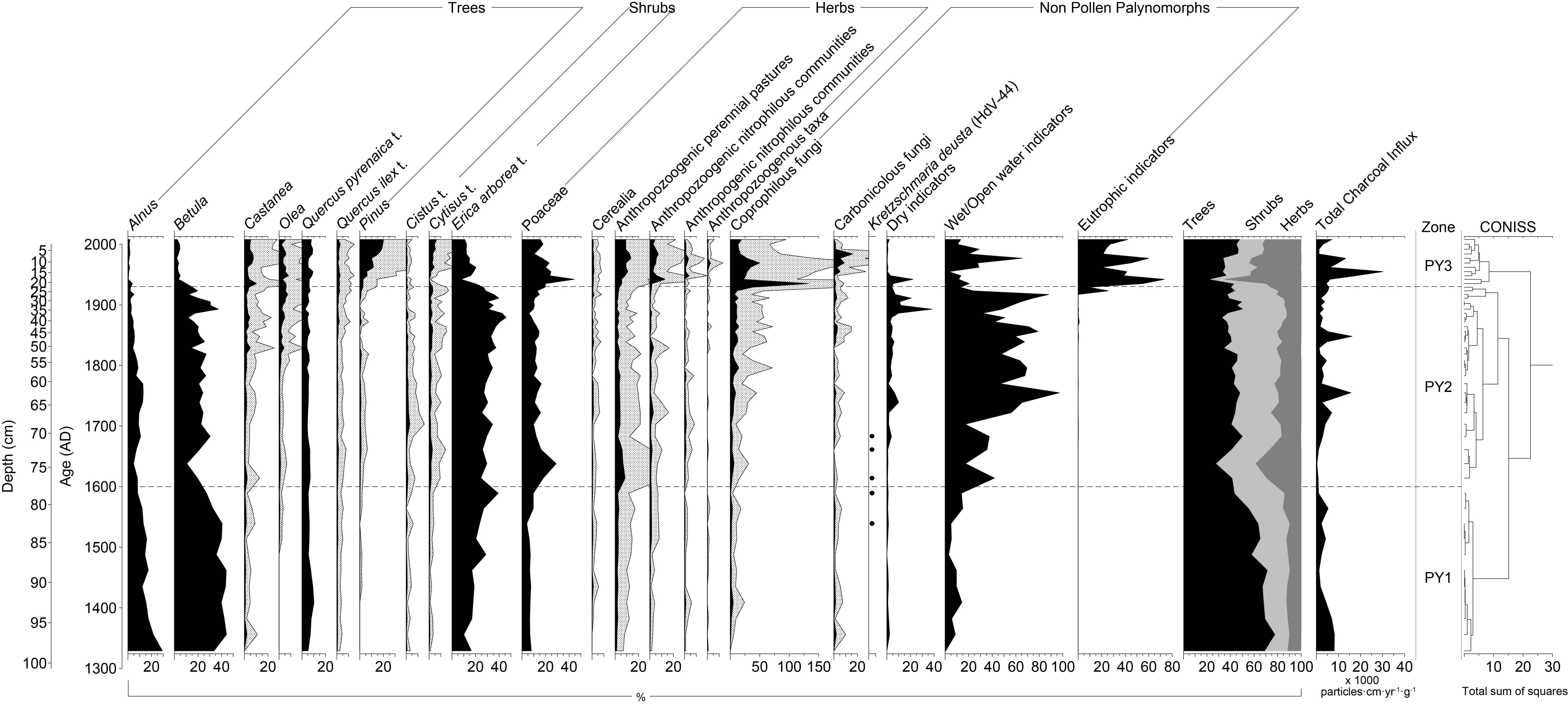
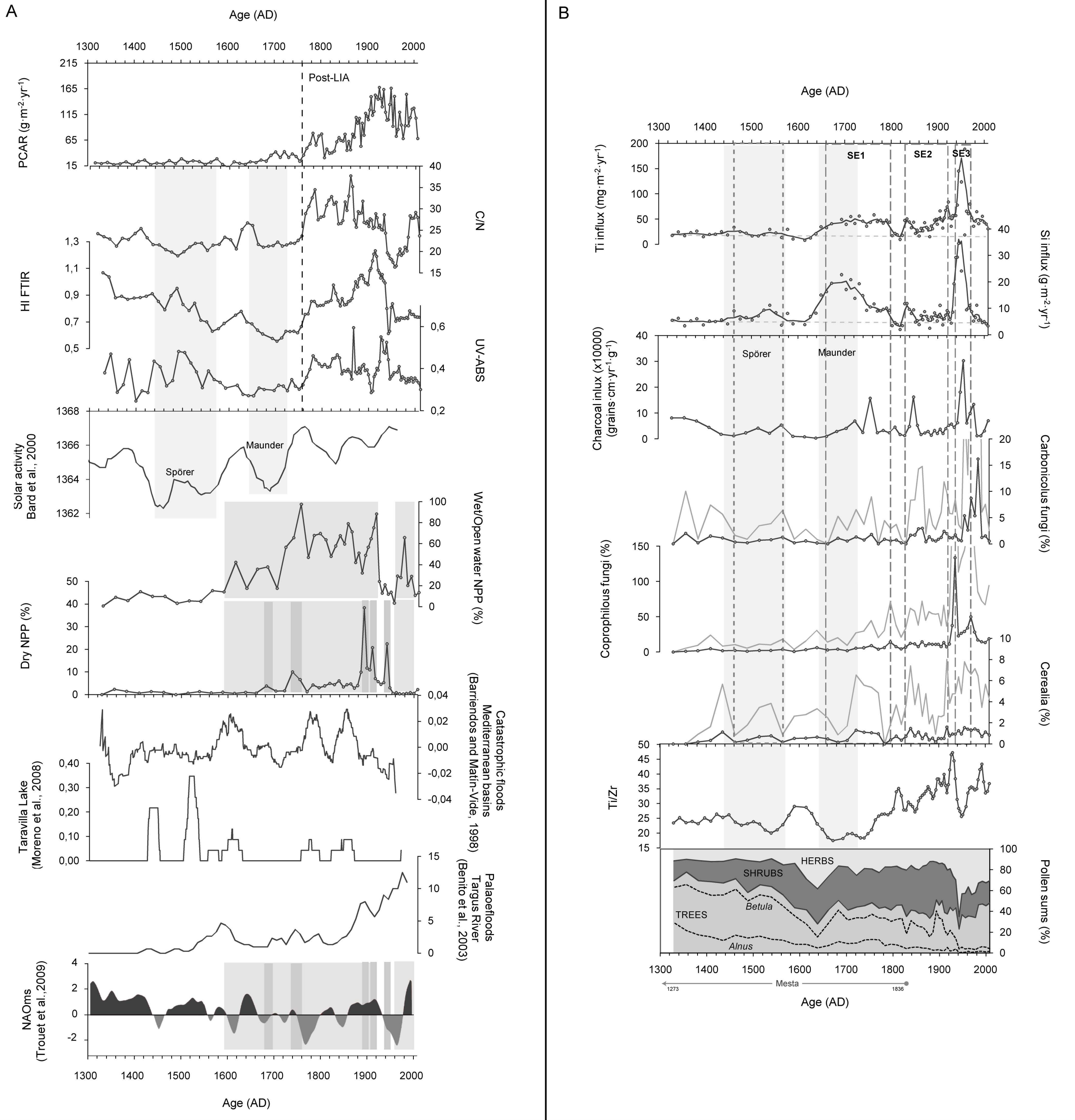
Age (years AD)


A
C (%)
Si (%)
Ti (µg·g-1)
Zr (µg·g-1)
N (%)
K (%)
Rb (µg·g-1)
Depth (cm)
Age (AD)
PCAR (g·m-2·y-1)
K AR (g·m-2·y-1)
Rb AR (mg·m-2·y-1)
Si AR (g·m-2·y-1)
Ti AR (mg·m-2·y-1)
Zr AR (mg·m-2·y-1)
SE3
SE2
SE1
B
C/N
HI UV-Abs
HI FTIR
Depth (cm)
Age (AD)


Trees
Shrubs
Herbs
Non Pollen Palynomorphs
Alnus
Betula
Castanea
Olea
Quercus pyrenaica t.
Quercus ilex t.
Pinus
Cistus t.
Cytisus t.
Erica arborea t.
Poaceae
Cerealia
Anthropozoogenic perennial pastures
Anthropozoogenic nitrophilous communities
Anthropogenic nitrophilous communities
Anthropozoogenous taxa
Coprophilous fungi
Carbonicolous fungi
Kretzschmaria deusta (HdV-44)
Dry indicators
Wet/Open water indicators
Eutrophic indicators
Trees
Shrubs
Herbs
Total Charcoal Influx
Zone
CONISS
Depth (cm)
Age (AD)
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
2000
1900
1800
1700
1600
1500
1400
1300
PY3
PY2
PY1
20
20 40
20
20
20
20
20 40
20 40
20
20
50 100 150
20
20 40
20 40 60 80 100
20 40 60 80
20 40 60 80 100
10 20 30 40
x 1000
particles·cm·yr⁻¹·g⁻¹
10 20 30
Total sum of squares
%


A
Age (AD)
1300 1400 1500 1600 1700 1800 1900 2000
PCAR (g·m⁻²·yr⁻¹)
215 165 115 65 15
Post-LIA
C/N
40 35 30 25 20 15
HI FTIR
1,3 1,1 0,9 0,7 0,5
UV-ABS
0,6 0,4 0,2
Solar activity
Bard et al., 2000
1368 1366 1364 1362
Spörer
Maunder
Wet/Open water NPP (%)
100 80 60 40 20 0
Dry NPP (%)
50 40 30 20 10 0
Catastrophic floods
Mediterranean basins
(Barriendos and Matín-Vide, 1998)
0,04 0,02 0,00 -0,02 -0,04
Taravilla Lake
(Moreno et al., 2008)
0,40 0,30 0,20 0,10 0,00
Palaeofloods
Targus River
(Benito et al., 2003)
15 10 5 0
NAOms
(Trouet et al.,2009)
4 2 0 -2
1300 1400 1500 1600 1700 1800 1900 2000
Age (AD)
B
Age (AD)
1300 1400 1500 1600 1700 1800 1900 2000
SE1
SE2
SE3
Ti influx (mg·m⁻²·yr⁻¹)
200 150 100 50 0
Si influx (g·m⁻²·yr⁻¹)
40 30 20 10 0
Spörer
Maunder
Charcoal inlux (x10000)
(grains·cm·yr⁻¹·g⁻¹)
40 30 20 10 0
Carbonicolus fungi (%)
20 15 10 5 0
Coprophilous fungi (%)
150 100 50 0
Cerealia (%)
10 8 6 4 2 0
Ti/Zr
50 45 40 35 30 25 20 15
Pollen sums (%)
100 80 60 40 20 0
HERBS
SHRUBS
TREES
Betula
Alnus
1300 1400 1500 1600 1700 1800 1900 2000
1273
Mesta
1836
Age (AD)