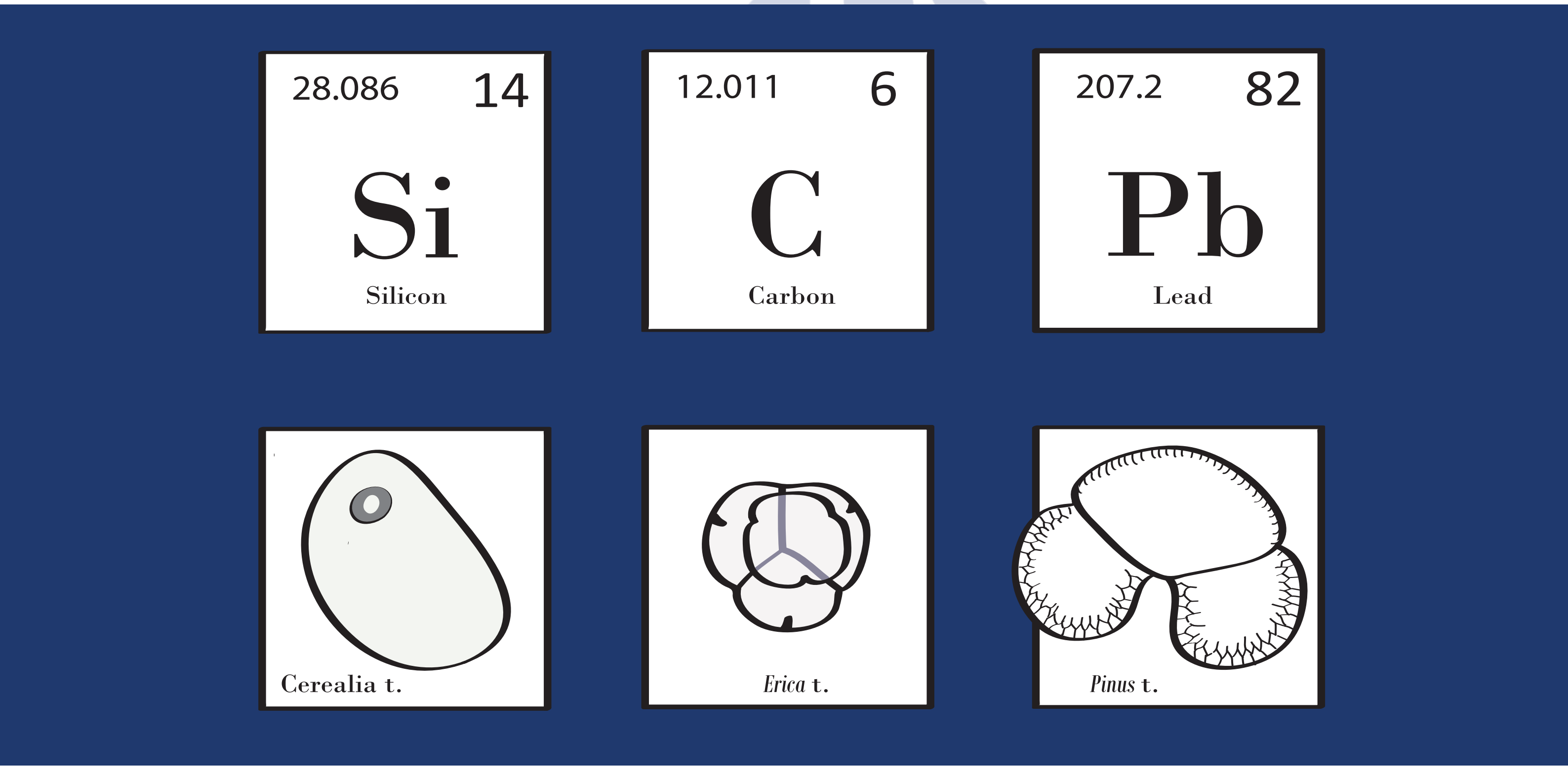
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

TESE DE DOUTORAMENTO - PhD THESIS

MODALIDADE DE COMPENDIO DE ARTIGOS - COMPILATION OF PUBLICATIONS

LATE-HOLOCENE ENVIRONMENTS RECONSTRUCTED FROM PEATLANDS: LINKING GEOCHEMISTRY AND PALYNOLOGY

Noemí Silva Sánchez



PROGRAMA DE DOUTORAMENTO EN MEDIO AMBIENTE E RECURSOS NATURAIS

FACULTADE DE BIOLOXÍA

SANTIAGO DE COMPOSTELA

2016

LATE-HOLOCENE ENVIRONMENTS RECONSTRUCTED FROM PEATLANDS: LINKING GEOCHEMISTRY AND PALYNOLOGY

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Santiago de Compostela, 2016

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DECLARAN:

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Santiago de Compostela, a 10 de Marzo de 2016.

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SYNTHESIS

The principal aim of the PhD work presented here is to explore how geochemistry and palynological approaches on peatlands, particularly when considered together, can help in the understanding of Holocene (the last ~11600 years) environmental changes. To achieve this general aim, different types of peatlands (ombrotrophic and minerothrophic), environments (boreal and temperate zones) and Holocene chronological intervals (although with special attention to the Late Holocene) have been studied. The focus has been on gaining insights into how different environmental stressors –such as climate and human activities– influenced past environments. In particular, the following processes have been addressed: 1) natural- and human-induced soil erosion and its relation with forest evolution and hydrological changes on wetlands; 2) changes in past climate and its relation with peat organic matter decomposition, vegetation and other aspects of the environment, including human activity, and paying special attention to the Little Ice Age period, and 3) trends in past atmospheric metal pollution and its possible link with changes in the tree cover. Within geochemistry, both physical (loss on ignition and density of the peat) and chemical (elemental composition, carbon and nitrogen stable isotope ratios, lead isotope ratios, peat humification and infrared spectroscopy) analyses were applied, whereas within palynology both pollen and non-pollen palynomorphs were considered. Because the inherent complexity in the functioning of natural systems is behind the interaction among different compartments of ecosystems (i.e., biosphere, lithosphere, hydrosphere and atmosphere), the combined use of geochemistry and palynology enabled us to obtain a more integrated overview of past environmental changes beyond what would have been possible by any of these disciplines independently. Knowing the past evolution of ecosystems at large enough temporal scales is crucial to understand their dynamic and functioning, hence, this knowledge should be considered when implementing present-day environmental policies.

Keywords: geochemistry, palynology, peatlands, palaeoenvironment, soil erosion, climate, lead pollution

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SÍNTESIS

El principal propósito del trabajo de doctorado que aquí se presenta es el de explorar cómo las aproximaciones geoquímicas y palinológicas en turberas, particularmente cuando se consideran conjuntamente, pueden ayudar a comprender los cambios ambientales del Holoceno (los últimos ~11600 años). Para conseguir este objetivo general se estudiaron distintos tipos de turberas (ombrotróficas y minerotróficas), ambientes (zonas boreal y templada) e intervalos cronológicos dentro del Holoceno (aunque con especial atención al Holoceno tardío). La investigación se ha centrado en obtener información de cómo diferentes estresores ambientales –como el clima y las actividades humanas– influyeron en los ambientes del pasado. En particular se han abordado los siguientes procesos: 1) la erosión de suelos, tanto natural como antrópicamente inducida, y su posible relación con la evolución de los bosques y con la hidrología de turberas; 2) los cambios del clima en el pasado y su relación con la descomposición de la materia orgánica de la turba, con los cambios en la vegetación así como con otros aspectos ambientales incluyendo la actividad humana, y prestando especial atención a la Pequeña Edad de Hielo, y 3) las variaciones en la contaminación atmosférica metálica pretérita y su posible relación con cambios en la cobertura arbórea. En el campo de la geoquímica se han aplicado el análisis de propiedades tanto físicas (pérdida de peso por ignición y densidad da la turba) como químicas (composición elemental, isótopos estables de carbono y nitrógeno, isótopos de plomo, grado de humificación de la turba y espectroscopía infrarroja); mientras que en el campo de la palinología se han considerado tanto el polen como los palinomorfos no polínicos. Debido a que la complejidad inherente al funcionamiento de los sistemas naturales está detrás de la interacción entre los distintos compartimentos de los ecosistemas (i.e., biosfera, litosfera, hidrosfera y atmósfera), la combinación de geoquímica y palinología ha permitido obtener una visión más integrada de los cambios ambientales ocurridos en el pasado, que difícilmente se habría conseguido mediante la aplicación de estas disciplinas de manera independiente. El conocimiento de la evolución ambiental de los ecosistemas a escalas temporales lo suficientemente amplias es vital para conocer su dinámica y funcionamiento, por lo que habría de ser considerado a la hora de implementar medidas de protección ambiental en el presente.

Palabras clave: geoquímica, palinología, turberas, paleoambiente, erosión de suelos, clima, contaminación por plomo

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SÍNTESE

O principal propósito do traballo de doutoramento que aquí se presenta é explorar como as aproximacións xeoquímicas e palinolóxicas en turbeiras, particularmente cando se consideran conxuntamente, poden axudar a comprender os cambios ambientais do Holoceno (os últimos ~11600 anos). Para conseguir este obxectivo xeral, estudáronse distintos tipos de turbeiras (ombrotróficas e minerotróficas), ambientes (zonas boreal e temperada) e intervalos cronolóxicos dentro do Holoceno (aínda que con especial atención ó Holoceno tardío). A investigación centrouse en obter información de como diferentes estresores ambientais –coma o clima e as actividades humanas– influíron os ambientes do pasado. En particular abordáronse os seguintes procesos: 1) a erosión de solos, tanto natural como antropicamente inducida, e a súa posible relación coa evolución dos bosques ou coa hidroloxía de turbeiras; 2) os cambios do clima no pasado e a súa relación coa descomposición da materia orgánica da turba, cos cambios na vexetación así coma con outros aspectos ambientais incluíndo a actividade humana, e prestando especial atención á Pequena Idade do Xeo, e 3) as variacións na contaminación atmosférica metálica pretérita e á súa posible relación cos cambios na vexetación, especialmente na cobertura arbórea. No campo da xeoquímica, aplicouse a análise de propiedades tanto físicas (perda de peso por ignición e densidade da turba) como químicas (composición elemental, isótopos estables de carbono y nitróxeno, isótopos de chumbo, grao de humificación da turba e espectroscopia infravermella); mentras que no campo da palinoloxía consideráronse tanto o pole coma os palinomorfos non polínicos. Debido a que a complexidade inherente ó funcionamento dos sistemas naturais está detrás da interacción entre os distintos compartimentos dos ecosistemas (i.e., biosfera, litosfera, hidrosfera e atmosfera), a combinación de xeoquímica e palinoloxía permitiu obter unha visión máis integrada dos cambios ambientais ocorridos no pasado, que dificilmente se tería conseguido mediante a aplicación destas disciplinas de xeito independente. O coñecemento da evolución ambiental dos ecosistemas a escalas temporais o suficientemente amplas é vital para coñecer a súa dinámica e funcionamento, polo que debería ser considerado á hora de aplicar medidas de protección ambiental no presente.

Palabras chave: xeoquímica, palinoloxía, turbeiras, paleoambiente, erosión de solos, clima, contaminación por chumbo

Esta síntese foi revisada polo Servizo de Normalización Lingüística da USC

Esta tese de doutoramento está baseada nos seguintes artigos:

Esta tesis de doctorado está basada en los siguientes artículos:

This PhD thesis is based on the following papers:

Artigo I: ***Silva-Sánchez, N.***, Martínez Cortizas, A. and López-Merino, L. (2014) Linking forest cover, soil erosion and mire hydrology to late-Holocene human activity and climate in NW Spain. *The Holocene* 24, 714–725.

Artigo II: ***Silva-Sánchez, N.***, Schofield, J.E., Mighall, T.M., Martínez Cortizas, A., Edwards K.J. and Foster I. (2015) Climate changes, lead pollution and soil erosion in south Greenland over the past 700 years. *Quaternary Research* 84, 159–173.

Artigo III: ***Silva-Sánchez, N.***, Martínez Cortizas, A, Abel-Schaad, D, López-Sáez, J.A. and Mighall, T.M. 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). Accepted by *The Holocene.*

Artigo IV: López-Merino, L., ***Silva Sánchez, N.***, Kaal, J., López-Sáez, J.A. and Martínez Cortizas, A. (2012) Post-disturbance vegetation dynamics during the Late Pleistocene and the Holocene: An example from NW Iberia. *Global and Planetary Change* 92-93, 58–70.

Artigo V: Mighall, T.M., Martínez Cortizas, A., ***Silva Sánchez, N.***, Foster, I.D.L., Singh, S., Bateman, M. and Pickin, J. (2014) Identifying evidence for past mining and metallurgy from a record of metal contamination preserved in an ombrotrophic mire near Leadhills, SW Scotland, UK. *The Holocene* 24, 1719–1730.

Artigo VI: ***Silva-Sánchez, N.*** (2015) Mining and Metallurgical activities in N Iberia and their link to forest evolution using environmental archives (Centuries AD V to XI). *Estudos do Quaternário* 12, 15–26.

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ABBREVIATION LIST

AD	*"anno Dómini"* (*lat:* in the year of the Lord)
cal. yr BP	calibrated years before the present
DPH	degree of peat humification
e.g.,	*"exempli gratia" (lat:* for example)
FTIR	Fourier transform infrared spectroscopy
HdV	Hugo de Vries laboratory
HI-FTIR	humification index obtained by FTIR
i.e.,	*"id est" (lat:* what is)
IUSS	the International Union of Soil Sciences
LIA	Little Ice Age
NA	not applicable
NAO	North Atlantic Oscillation
NPP	non-pollen palynomorphs
PCAR	peat carbon accumulation rate
PCo	principal component analysis of organic variables
Pyrolysis-GC-MS	pyrolysis gas chromatography mass spectrometry
UV-Abs	ultraviolet absorbance
WRB	Word Reference Base for soils

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1. SUMMARY

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1. SUMMARY

The current state of ecosystems is not only related to existing environmental conditions. Today's environments are product of the concatenation of past environmental changes, including the effects of human activity. Therefore, knowledge of the long-term evolution of ecosystems provides useful information to understand present ecosystems and predict their future changes. Palaeoenvironmental research uses indicators (proxies) from environmental archives in order to reconstruct how ecosystems have changed through time. Nowadays, processes such as soil erosion, atmospheric metal pollution and climate change are in the spotlight because of their potential harmful effects for humanity. Soil erosion affects a sizeable proportion of arable and grazing land globally, and may have consequences for soil quality and fertility. It may also reduces cropland productivity and contributes to the pollution of adjacent watercourses. Atmospheric metal pollution has important consequences for public health and depending on the concentrations and the speciation (i.e., forms) of pollutants, adverse/toxic effects are well established. It is generally assumed that these environmental problems are of recent origin and intimately related with recent land management and the start of the Industrial Revolution. However, in order to determine the role of natural and anthropogenic forcings on these processes, as well as to get insights in how climate conditions have affected past societies and environments, a temporal perspective is essential.

Peatlands are wetland ecosystems with a thick water-logged organic soil layer made up of dead and decaying plant material called peat. They are important in regulating climate, the hydrology, the hydrochemistry and soil chemistry in their catchment areas. They are also an important reservoir of biodiversity and have acted as natural carbon sinks during millennia. However, peatlands are not only important because of their ecological function, but also are among the best archives for palaeoenvironmental research. Because of their physicochemical properties and their autochthonous mode of peat production and accumulation, atmospherically deposited particles such as dust, pollutants, or pollen can be trapped in their surface remaining immobilised and being progressively buried as peat grows. This way, a record of past environmental changes is built. Moreover, peat is easily datable material so it is relatively simple to chronologically frame the detected environmental changes. Traditionally, ombrotrophic peatlands (also named bogs), those that are solely atmospherically rain-fed, are considered to be ideal for palaeoenvironmental research. However, minerotrophic peatlands (also named fens), who receive their water inputs both from rain and ground water, can also be good palaeoenvironmental archives.

Considerable progress has been achieved in the application of geochemistry and palynology

in the field of palaeoenvironmental research using peatlands since decades ago, and especially after the popularisation of dating techniques such as radiocarbon dating, which implied a great advance in the accuracy of chronological interpretations and allowed comparison between sites in an unprecedented way. Nevertheless, according to searches on the Web of Science whereas 2422 peat geochemistry papers and 1355 peat palynology papers have been published since 1900, only 247 papers using both geochemical and palynological analyses to peat records were published during the same period of time. Regarding conjoint application of each of these disciplines, a slight upward trend is observed during the last years. Publications approaching geochemistry and palynology on peat records at the 2000s represented 5.6% of papers applying these disciplines in peat, whereas in the 2010-2015 interval they represented a 6.4%. These figures highlight the fact that, although multi-proxy research is becoming more usual, it still represents a little proportion.

The principal aim of the PhD work presented here is to explore how geochemistry and palynological approaches on peatlands, particularly when considered together, can help in the understanding of Holocene (the last ~11600 years) environmental changes. To achieve this general aim, different types of peatlands (ombrotrophic and minerothrophic), environments (boreal and temperate zones) and chronological intervals (although focusing on the Late Holocene) have been studied. Much attention has been given to the study of how different environmental stressors –such as climate and human activities– influenced past environments. A particular focus has been paid on studying the following processes: 1) natural-and human-induced soil erosion and its relation with forest evolution and hydrological changes in wetlands; 2) past climate and its relation with peat organic matter decomposition, vegetation and other environmental aspects, with particular emphasis on the Little Ice Age period, and 3) changes in past atmospheric metal pollution and the possible link of past mining and metallurgy with changes in vegetation, especially in tree cover. Within geochemistry, physical (loss on ignition and density of the peat) and chemical (elemental composition, carbon and nitrogen stable isotope ratios, lead isotope ratios, degree of peat humification and infrared spectroscopy) analyses were applied, whereas within palynology both pollen and non-pollen palynomorphs were considered.

Changes in the concentrations and fluxes of lithogenic elements, loss on ignition and the density of the peat have been used to reconstruct past changes in ***soil erosion***. In this sense confined minerotrophic mires are ideal to reconstruct soil erosion at a basin level. **Papers I and III** include reconstructions of past soil erosion events recorded in fens located at O Bocelo (NW Iberia; representing the last ~3000 years) and El Payo (W Iberia; representing the last ~700 years) respectively. In O Bocelo (Paper I), soil erosion and human activity were highly linked through forest clearance for farming since at least the Iron Age. Their intensity was particularly higher during the Roman Period, but also during Germanic times and the Middle Ages. During these phases, the entire catchment was affected, resulting not only in enhanced soil erosion but also in severe hydrological modifications of the mire. Climate, especially rainfall (reconstructed by the residual variance of Br) may have also accelerated soil erosion during wetter periods. At El Payo (Paper III) the creation of cropland, pastureland and fruit tree plantations, in many cases through the use of fire –reconstructed by carbonicolous fungi and charcoal particles distribution–, promoted soil exposure in the catchment leading to increased dust fluxes to the peatland. Enhanced soil erosion occurred at AD ~1460-1580, AD ~1660-1800, AD ~1830-1920 and AD ~1940-1970. However, despite there is an inverse relationship between forest cover and soil erosion, the large decrease in tree cover at AD ~1550-1650 was not accompanied by any equivalent trend on lithogenic fluxes. What does happen is an associated shift in the sources of lithogenics to the mire, suggesting that the loss of forest stand at AD 1550-1650 and after AD ~1700 affected the origin of the dust arriving to the peatland. Changes in predominant wind direction or wind strength might also explain the detected pattern as they could cause a chemical fractionation of the dust arriving to the peatland, although, according to the previously mentioned evidence this explanation is more speculative. Regarding the chronology of soil erosion events it is noteworthy that at times, e.g., coinciding with Maunder and Spörer minima in solar activity, climatic influence on the soil erosion process at El Payo is probable.

Ombrotrophic peatlands usually have larger dust source areas than fens, although when large increases in lithogenic elements are recorded, local dust sources (i.e., erosion) may be of higher importance. For example, variations in the mineral content of the peat at Sandhavn (**Paper II**; SW Greenland; last ~700 years) were closely linked with soil erosion during phases of human activity in the region. Soil erosion only increased during the Norse period, when European settlers temporally settled southern Greenland due to better climate associated with the Medieval Warm Period, and in the modern era, coinciding with the return of sheep farming to the region. Unfortunately, soil erosion evidence during the Norse period may be compromised because of the proximity of the basal sand/peat interface.

Changes in both organic and inorganic geochemical signals, as well as evidence from palynological analysis, have been used to reconstruct several aspects of ***climate*** and to test how changes in climatic factors affected diverse aspects of ecosystems, including human activity. The records from El Payo (**Paper III**) and Sandhavn (**Paper II**) indicates that between AD ~1300 (AD ~1400 at Sandhavn) and AD ~1800, coinciding with the LIA, peat and carbon accumulation were limited by prevailing cold conditions and, in both cases, they increased after the LIA. This indicate that despite relatively cold conditions being necessary for peat accumulation, as it also reduces primary productivity, excessive cooling may have consequences for peat and carbon accumulation. At El Payo, moreover, after LIA cooling, despite NPP evidence of increased wetter conditions –at least seasonally–, humification (reconstructed by HI-FTIR and UV-Abs) became higher at AD ~1760-1930 evidencing the presence of more decomposed peat. Thus, increased temperature after the 18th century, linked to adequate moisture supply during the favorably reason might have triggered the increase recorded in carbon accumulation, whereas warmer temperatures and seasonal drought might have enhanced peat decomposition. At Sandhavn however, FTIR spectra and UV-Abs lack a general pattern over the LIA but it only have been affected punctually during Spörer and Maunder minima in solar activity as decreased peat decomposition and polysaccharide enrichment (i.e labile fractions) have been detected associated to these periods. However, it is necessary to be circumspect about this surmise given the dating and sample resolution constraints. Br is an halogen of marine origin whose accumulation in peat is dependent on atmospheric wet deposition, enzymatic halogenation of the organic matter and dehalogenation under reducing conditions. At Sandhavn, Br showed low concentrations over the LIA (increasing gradually after AD ~1780) and even lower concentrations were recorded coinciding to LIA solar minima, suggesting that halogenation was limited during cooler periods. At O Bocelo (**Paper I**) however, principal component analysis allowed to build a humidity index based on Br residual variance that matched a pre-existing humidity index for the region constructed by thermal stability of Hg, enabling the extraction of a signal related to wet deposition.

Vegetation communities can also be affected by changes in climatic conditions. Thus, climate, although generally being of minor relevance than human activity, has also acted as a driver of vegetation change during the Holocene. For example, the end of the LIA at Sandhavn led to the replacement of Cyperaceae-dominated steppe communities by *Empetrum nigrum* oceanic heath, which may also have affected the organic composition of the peat, as associated polysaccharide enrichment has been detected. At O Bocelo increases in *Olea* (olive tree) and *Castanea* (sweet chestnut) during the Roman Warm Period, may have been caused by prevailing warmer conditions, although human facilitation may have also played a role. These late-Holocene changes were minor in importance compared to the intense vegetation changes occurred at the Pleistocene-Holocene transition. For example, in the PRD-IV colluvial soil sequence (**Paper IV**; NW Iberia; last ~14000 years), in the framework of this transition, major vegetation changes were detected at both local (*Pleospora* to Cyperaceae –sedge– dominance) and regional (*Betula* –birch– to *Quercus* –oak– dominance) scales, although with a significant delay in the regional signal, indicating that regional vegetation communities was probably more resilient than local communities.

Regarding ***atmospheric metal pollution*** it is noteworthy that a long-term perspective is required in order to establish natural background levels and to contextualise the intensity of modern-day pollution. Previous research from peatlands at different European locations has revealed that atmospheric metal pollution already existed during the Bronze Age, whereas evidence from Greenlandic ice records indicated that humans already polluted the middle troposphere of the Northern Hemisphere two millennia ago. Up to now, and in contrast with the ice records, Greenland peat records failed to reveal significant metal enrichments, but research performed at Sandhavn (**Paper II**) showed a clear pollution signal based on lead enrichment after AD ~1845, and peaking in the 1970s. Based on the chronology of the events, which are in better agreement with the American Industrial Revolution than with the European one, and supported by the detection of the "*Ambrosia*-rise" –a characteristic increase in this nitrophilous taxa happened in Eastern North America after the arrival of European settlers at the end of the 19th century–, an indirect support for a predominantly North American lead source is considered. Lead isotopes analysis in progress will contribute to ascertain more precisely the sources of lead in the Sandhavn record.

Even though an evidence for the deposition of long-range transport of pollutants in bogs is recognised, regional variations in the record of atmospheric metal pollution have been detected from peatlands, reflecting the local development of mining and metallurgical activities. Mining and metallurgy have been the most important sources of anthropogenic emissions until the burning of fossil fuels: one of the main atmospheric sources of Pb from the Industrial Revolution onwards. Research performed in a peat record at Leadhills (Scotland; last ~3600 years; **Paper V**) revealed the history of exploitation of insular ore sources in the Leadhills/Wanlockhed orefield since prehistory. Phases of palaeo-pollution were consistent with documented historical and archaeological records of mining and metallurgy in the region and, as it lacks a discernible Roman lead enrichment –so characteristic of most European records–, provides an example for specific regional variations in past metal atmospheric pollution records.

Regarding possible impacts of mining and metallurgy on vegetation, palaeoenvironmental research has found that, in many locations, intense forest clearance accompanied phases of mining and metallurgy since prehistory. **Paper VI** reviews the research conducted in Northern Spain in relation to the reconstruction of past mining-smelting through the signal of past metal pollution in environmental archives and examines the possible impact of these activities on forest cover. It is apparent that multi-proxy studies combining geochemical and palynological research enabled the evaluation of the influence of minero-metallurgical activities on landscapes. However, sometimes it is difficult to determine the role of mining/metallurgy in forest history independently from other human forcings that may coexist, such as agriculture and grazing.

Essentially, environmental proxy records obtained by geochemical and palynological analyses are indicators for a range of different environmental changes. But, owing to the inherent complexity in the functioning of natural systems, that is behind the interactions among different compartments of ecosystems (i.e., biosphere, lithosphere, hydrosphere and atmosphere), the combined use of geochemistry and palynology provided more accurate interpretations of the environmental changes than those that would be obtained using a single methodology. This, in turn, allowed the obtention of an overview of past environmental changes unachievable by any of these disciplines independently.

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1. RESUMEN

1. RESUMEN

El estado actual de los ecosistemas no es sólo consecuencia de las condiciones ambientales preponderantes en la actualidad, sino que es producto de la concatenación de los cambios ambientales ocurridos en el pasado, incluyendo aquellos debidos a la actividad humana. Por eso, conocer la evolución de los ecosistemas a escalas temporales lo suficientemente largas ofrece una información de gran utilidad a la hora de entender los ecosistemas en el presente y predecir su evolución en el futuro. La investigación paleoambiental está basada en el estudio de indicadores ambientales (*"proxies"*) obtenidos en archivos ambientales para reconstruir cómo el medioambiente ha cambiado a lo largo del tiempo. La erosión de suelos, la contaminación atmosférica por metales y los cambios en el clima son aspectos ambientales que hoy en día están recibiendo atención debido a sus potenciales consecuencias para la humanidad. La erosión de suelos afecta a una gran proporción de la superficie de terreno de pasto y cultivos y, a nivel global, puede tener consecuencias para la calidad y la fertilidad del suelo. También puede reducir la productividad de los cultivos y, además, contribuir a la contaminación de posibles cursos de agua próximos. La contaminación atmosférica por metales puede ocasionar severas consecuencia para la salud pública y, dependiendo de las concentraciones y de la especiación (i.e., las formas) de los contaminantes, sus efectos adversos/tóxicos están bien establecidos. Generalmente se asume que éstos son problemas de reciente aparición que están íntimamente ligados con la explotación territorial del presente y con el inicio de la Revolución Industrial. Sin embargo, para determinar el papel que los distintos forzamientos naturales y antrópicos tuvieron en estos procesos, así como para ampliar el conocimiento acerca de cómo las condiciones climáticas del pasado afectaron a las sociedades y al medio ambiente, la perspectiva temporal es esencial.

Las turberas son ecosistemas húmedos con una capa de suelo orgánico saturado en agua y constituida por material vegetal muerto y en descomposición denominado turba. Las turberas regulan el clima, la hidrología y la química de suelos y aguas en sus cuencas. También son importantes reservorios de biodiversidad y han actuado como sumideros naturales de carbono durante milenios. Sin embargo, las turberas no son solamente importantes por sus funciones ecológicas, sino que están entre los mejores archivos para la reconstrucción paleoambiental. Debido a sus propiedades fisicoquímicas y a su modo de producción y acumulación de turba, partículas atmosféricas de polvo, de contaminantes o de polen pueden depositarse en su superficie, quedando inmovilizadas y enterrándose progresivamente a medida que la turba se acumula. De este modo, se construye un registro de los cambios ambientales del pasado. Además, la turba es un material fácilmente datable por lo que es relativamente sencillo asignar una cronología a los cambios ambientales detectados. Tradicionalmente, las turberas ombrotróficas –que exclusivamente reciben agua de precipitación– son consideradas ideales para la reconstrucción paleoambiental. Sin embargo, las turberas minerotróficas –que reciben agua tanto de precipitación como de escorrentía– también pueden ser buenos archivos ambientales.

En las últimas décadas se ha avanzado considerablemente en la aplicación de geoquímica y palinología al campo de la reconstrucción ambiental a partir de turberas y, especialmente, después de la popularización de técnicas de datación como el radiocarbono, las cuales implicaron un gran avance en la precisión de las interpretaciones cronológicas y la comparación de estudios. No obstante, según búsquedas realizadas en Web of Science, desde el año 1900 se publicaron 2422 artículos de geoquímica y 1355 de palinología en turberas, mientras que, para el mismo período de tiempo, tan sólo fueron 247 los que emplearon ambas disciplinas conjuntamente. Respecto a la aplicación conjunta de geoquímica y palinología, durante los últimos años se observa una ligera tendencia al alza. En el año 2000 las publicaciones en las que se combinaron ambas metodologías representaron el 5.6% del total de publicaciones aplicando geoquímica y palinología a turberas, mientras que en el intervalo 2010-2015 representaron un 6.4%. Estas cifras resaltan el hecho de que, aunque la investigación multi-indicador es cada vez más habitual, todavía representa una pequeña proporción del total.

El objetivo principal de este trabajo de doctorado es el de explorar cómo las aproximaciones geoquímicas y palinológicas, particularmente cuando se consideran conjuntamente, pueden ayudar a comprender los cambios ambientales del Holoceno (los últimos ~11600 años). Para conseguir este objetivo general se estudiaron diferentes tipos de turberas (ombrotróficas y minerotróficas), ambientes (zonas boreal y templadas) y rangos cronológicos (aunque especialmente en el Holoceno tardío). Se dio especial relevancia al estudio de cómo diferentes estresores ambientales –como el clima y las actividades humanas– influenciaron los ambientes del pasado y se prestó especial atención al estudio de los siguientes procesos: 1) la erosión de suelos, tanto natural como inducida por el ser humano, y su relación con la evolución de los bosques y los cambios hidrológicos en turberas; 2) los cambios en el clima en el pasado y su relación con la descomposición de la materia orgánica de la turba, la vegetación y otros aspectos ambientales, con especial atención a los cambios ocurridos durante la Pequeña Edad de Hielo, y 3) las variaciones en la contaminación atmosférica por metales en el pasado y su posible relación con la minería/metalurgia y con los cambios ocurridos en la vegetación, particularmente en la cobertura arbórea.

Dentro de la geoquímica se han aplicado el estudio de las propiedades físicas (pérdida de peso por ignición y densidad de la turba) y químicas (composición elemental, isótopos estables de carbono y nitrógeno, isótopos de plomo, grado de humificación de la turba y espectroscopía infrarroja), mientras que en el campo de la palinología se han considerado tanto los microfósiles polínicos como los no polínicos.

Los cambios en la concentración y en los flujos de elementos litogénicos, la pérdida de peso por ignición o la densidad de la turba, han sido utilizados para reconstruir cambios en la ***erosión de suelos***. En este sentido las turberas minerotróficas confinadas son ideales para la reconstrucción de la erosión de suelos a nivel de cuenca. Los **artículos I y III** incluyen la reconstrucción de eventos de erosión de suelos registrados en turberas minerogénicas localizadas en O Bocelo (NO Ibérico; últimos ~3000 años) y en El Payo (O Ibérico, últimos ~700 años), respectivamente. En O Bocelo (Artículo I) la erosión de suelos y la actividad humana estuvieron íntimamente ligadas a través de la deforestación asociada al desarrollo de prácticas agrícolas y ganaderas desde, al menos, la Edad del Hierro. Su intensidad fue especialmente notable durante el Período Romano, aunque también durante los períodos Germánico y Medieval. Durante estas fases, toda la cuenca se vio afectada, resultando no sólo en un incremento en la erosión sino también en severas modificaciones hidrológicas en la turbera. El clima, especialmente la precipitación (reconstruida mediante la varianza residual del Br), también podría haber acelerado el proceso erosivo durante los períodos húmedos. En el Payo (Artículo III) la creación de tierras de cultivo, pastos y plantaciones de frutales, en muchos casos mediante el uso del fuego, fomentó que el suelo quedase expuesto dando lugar a un incremento en los flujos de polvo a la turbera. La erosión de suelos se incrementa en el AD ~1460-1580, AD ~1660-1800, AD ~1830-1920 y en el AD ~1940-1970. Sin embargo, aunque hay una relación inversa entre la cobertura arbórea y la erosión, el gran descenso que tiene lugar en la cobertura arbórea en el período AD ~1550-1650 no estuvo acompañado por una tendencia equivalente en los flujos de litogénicos. Lo que sí se detecta en cambio es una modificación en las fuentes de elementos litogénicos, lo que sugiere que la pérdida de masa forestal en el período AD ~1550-1650 y a partir del AD ~1700 afectó al origen del polvo que llega a la turbera. Cambios en la dirección predominante del viento, o en su intensidad, también podrían ser la causa de este patrón. Aunque, en base a las evidencias anteriormente mencionadas, esta explicación parece más especulativa. Respecto a la cronología de los eventos de erosión de suelos en El Payo, es destacable el hecho de que, en ocasiones, e.g., coincidiendo con los mínimos de actividad solar Spörer y Maunder, la influencia de factores climáticos en la erosión de suelos es probable.

Las turberas ombrotróficas suelen tener áreas fuente de polvo eólico más amplias que las turberas minerogénicas, aunque cuando el incremento en los elementos litogénicos es suficientemente elevado, las fuentes de polvo local (i.e., erosión) pueden ser las de mayor importancia. Por ejemplo, las variaciones en el contenido mineral de la turba en Sandhavn (SO de Groenlandia; últimos ~700 años; **Artículo II**) han estado íntimamente ligadas con la erosión de suelos durante las fases de ocupación humana en la región. Esta conclusión se extrae del hecho de que el contenido mineral sólo incrementó en dos períodos de fuerte impacto antrópico en la región: durante el período de ocupación Norse, cuando colonos del norte europeo, debido a la mejoría climática asociada al Óptimo Climático Medieval, ocuparon temporalmente el sur de Groenlandia; y en la era moderna, coincidiendo con la reanudación de la cría de ovejas en la región. Sin embargo, la erosión de suelos coincidente con el período de ocupación Norse puede estar comprometida debido a la proximidad de la interfase basal arena/turba.

El estudio en la variación de las evidencias geoquímicas, tanto orgánicas como inorgánicas, y palinológicas se ha utilizado para reconstruir diversos aspectos del ***clima*** y para examinar cómo cambios en factores climáticos afectaron a diversos aspectos de los ecosistemas, incluyendo la actividad humana. Los registros de El Payo (**Artículo III**) y Sandhavn (**Artículo II**) indican que entre el AD ~1300 (AD ~1400 en Sandhavn) y el AD ~1800, coincidiendo con la Pequeña Edad del Hielo, la acumulación de turba y carbono estuvieron muy limitadas por las condiciones de frío dominantes. En ambos casos, tras la Pequeña Edad del Hielo se produce un aumento tanto en la acumulación de turba como en la acumulación de carbono. Esto indica que a pesar del requerimiento de condiciones relativamente frías para que se produzca acumulación de turba, un exceso de frío, dado que reduce la productividad primaria, puede tener consecuencias para la acumulación de turba y carbono. En el Payo, además, tras el enfriamiento de la Pequeña Edad del Hielo, a pesar de las evidencias palinológicas apuntan a un incremento de la humedad –al menos estacionalmente–, la humificación (reconstruida mediante HI-FTIR y UV-Abs) aumentó en el período AD ~1760-1930, poniendo de manifiesto la presencia de turba más descompuesta. Así, el incremento de la temperatura tras el siglo XVIII, unido a un adecuado aporte hídrico en la estación favorable, pudo haber desencadenado el incremento detectado en la acumulación de carbono, mientras que las condiciones más cálidas y la sequía estacional debieron de haber favorecido la descomposición de la turba. En Sandhavn, sin embargo, los espectros de FTIR y la UV-Abs no mostraron una tendencia general durante la Pequeña Edad del Hielo, sino que tan sólo se vieron afectados de manera puntual durante los mínimos de actividad solar Spörer y Maunder ya que, asociados a estos eventos se detectan un descenso en la descomposición de la turba y un enriquecimiento en polisacáridos (i.e., fracciones lábiles). Sin embargo, es necesario ser cautos en esta afirmación ya que existen limitaciones en la resolución a la que se detectan estos cambios. El Br es un halógeno de origen marino cuya acumulación en la turba es dependiente de la deposición húmeda, de la halogenación de la materia orgánica y de la deshalogenación en condiciones reductoras. En Sandhavn, el registro del Br mostró concentraciones bajas durante la Pequeña Edad del Hielo (incrementándose gradualmente a partir del AD ~1780) y concentraciones aún más bajas coincidiendo con los mínimos de actividad solar, sugiriendo que la halogenación estuvo limitada durante los momentos fríos. En O Bocelo (**Artículo I**), sin embargo, un análisis de componentes principales permitió la extracción de un índice de humedad basado en la varianza residual del Br que mostró una gran coincidencia con un índice de humedad preexistente en la región y basado en la estabilidad térmica del Hg, permitiendo de este modo la extracción de una señal relacionada con la deposición húmeda.

Las comunidades vegetales también pueden verse afectadas por los cambios en las condiciones climáticas. Así, el clima, aunque teniendo generalmente un menor impacto que la actividad humana, también ha actuado como una fuerza de cambio en la vegetación a lo largo del Holoceno. Por ejemplo, en Sandhavn el final de la Pequeña Edad de Hielo supuso la sustitución de las comunidades esteparias dominadas por Cyperaceae por el brezal oceánico de *Empetrum nigrum*. Esta sustitución a su vez afectó a la composición de la materia orgánica de la turba, pues simultáneamente se detecta un incremento en los polisacáridos. En O Bocelo, la mayor presencia de *Olea* (olivo) y *Castanea* (castaño) durante el Período Cálido Romano podría haber estado relacionada con la ocurrencia de condiciones más cálidas aunque, la facilitación humana también pudo haber jugado un papel importante. Estos cambios, ocurridos en el Holoceno tardío, fueron de menor intensidad a los ocurridos en la transición Pleistoceno-Holoceno. Por ejemplo, en la secuencia coluvial PRD-IV (**Artículo IV**, NO Ibérico; últimos ~14000 años) en el marco de esta transición se detectan importantes cambios en la vegetación tanto a escala local (de la dominancia de *Pleospora* a la de Cyperaceae) como a escala regional (de la dominancia de *Betula* –abedul– a la de *Quecus* –roble). Sin embargo, el retraso en la respuesta ocurrido a escala regional pone de manifiesto que las comunidades vegetales regionales fueron más resilientes que las comunidades locales.

Respecto a la ***contaminación atmosférica por metales*** cabe destacar que, tanto para establecer los niveles de fondo naturales (pre-antropogénicos) como para contextualizar la intensidad de la polución actual, es esencial tener en cuenta la perspectiva temporal. Investigaciones previas en turberas europeas emplazadas en diferentes localizaciones han demostrado que la contaminación atmosférica por metales existe desde la Edad del Bronce, mientras que análisis de testigos de hielo en Groenlandia evidencian que los seres humanos contaminaron la troposfera media del hemisferio norte hace dos milenios. En contra de las evidencias encontradas en testigos de hielo, los testigos de turba estudiados hasta ahora en Groenlandia no han mostrado enriquecimientos significativos en metales, por lo que los resultados obtenidos en Sandhavn (**Artículo II**), basados en el enriquecimiento por plomo y que muestran una señal de contaminación clara a partir de AD ~1845 y un pico centrado en la década de los 70, son de relevancia. En base a la cronología de los eventos detectados, que está en mayor sintonía con la Revolución Industrial americana que con la europea y, debido a la detección del "aumento de *Ambrosia*" –un característico incremento en este taxa nitrófilo que tuvo lugar en el Este de Norte América debido a la llegada de colonos europeos a finales del siglo XIX–, se puede apoyar de manera indirecta la preponderancia de una fuente de plomo de origen norteamericano. El análisis de isótopos de plomo, que

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se encuentra actualmente en progreso, contribuirá a confirmar cuáles fueron las fuentes de plomo en el registro de Sandhavn.

A pesar de las evidencias de transporte de larga distancia de contaminantes metálicos, en numerosos registros de turba se han detectado variaciones regionales en el registro de la contaminación atmosférica por metales que estarían recogiendo variaciones locales en el desarrollo de las actividades minero-metalúrgicas durante el pasado, ya que, hasta que la quema de combustibles fósiles se convirtió en la mayor fuente de Pb a la atmosfera a partir de la Revolución Industrial, las actividades minero-metalúrgicas fueron las principales fuentes de emisiones antropogénicas. La investigación llevada a cabo en un registro de turba en Leadhills (Escocia; últimos ~3600 años; **Artículo V**) mostró la historia de la explotación de las fuentes minerales de la mena de Leadhills/Wanlockhed desde la prehistoria. Las fases de paleocontaminación detectadas fueron consistentes tanto con las fuentes escritas como con el registro de arqueológico de la región y, ya que carecen del pico de enriquecimiento de Pb de época Romana –tan característico en la mayoría de los registros europeos–, proporcionan un ejemplo de variaciones regionales específicas en los registros temporales de contaminación atmosférica metálica.

Respecto a los posibles impactos de la minería y la metalurgia en la vegetación la acumulación de evidencias paleoambientales en diferentes lugares indica que, desde la prehistoria, de manera simultánea a la detección de fases de contaminación atmosférica metálica, tuvo lugar una intensa reducción del bosque. El **Artículo VI** revisa la investigación llevada a cabo en el norte de la Península Ibérica en relación con la reconstrucción de la minería y la metalurgia en el pasado a partir de la contaminción por metales en archivos ambientales y examina el posible impacto de estas actividades en los bosques. Se deduce que los estudios multi-indicador que combinan geoquímica y palinología permiten la evaluación de la influencia que las actividades minero-metalúrgicas tuvieron en la vegetación. Sin embargo, en ocasiones resulta difícil determinar el papel que la minería/metalurgia tuvo en la evolución del bosque de modo independiente al de otras actividades humanas que pudieron coexistir como la agricultura o la ganadería.

En esencia, los registros de cambio ambiental obtenidos mediante los análisis geoquímicos y palinológicos son indicadores de distintos aspectos ambientales. Sin embargo, debido a que la complejidad inherente a los sistemas naturales está detrás de las interacciones entre los distintos compartimentos de los ecosistemas (i.e., biosfera, litosfera, hidrosfera y atmósfera), el uso combinado de la geoquímica y la palinología permitió interpretaciones mucho más precisas de los cambios ambientales que aquellas que podrían ser obtenidas usando una aproximación única. Lo que, a su vez, permitió obtener una visión de conjunto de los cambios ambientales ocurridos en el pasado que difícilmente se habría obtenido empleando estas disciplinas por separado.

1. RESUMO

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1. RESUMO

O estado actual dos ecosistemas non é so consecuencia das condicións ambientais preponderantes na actualidade, senón que é produto da concatenación dos cambios ambientais ocorridos no pasado, incluíndo aqueles debidos a actividade humana. Por iso, coñecer a evolución dos ecosistemas a escalas temporais o suficientemente longas achega un coñecemento de vital importancia para comprender os sistemas ambientais do presente e dá unha información de gran utilidade á hora de predicir a súa evolución no futuro. A investigación paleoambiental baséase no estudo de indicadores ambientais (*"proxies"*) obtidos en arquivos ambientais para reconstruír como o medio ambiente cambiou ó longo do tempo. A erosión de solos, a contaminación atmosférica por metais ou os cambios no clima son aspectos ambientais que hoxe en día están a recibir atención debido ás súas potenciais consecuencias para a humanidade. A erosión de solos afecta a unha vasta superficie de terra de pastos e cultivos e, a nivel global, pode ter consecuencias para a calidade e a fertilidade do solo. Tamén pode reducir a produtividade de cultivos e, ademais, contribuír á contaminación de cursos de auga próximos. A contaminación atmosférica por metais ten importantes consecuencias para a saúde pública e, dependendo das concentracións e da especiación (das formas) dos contaminantes, os seus efectos adversos/tóxicos están ben establecidos. Xeralmente asúmese que estes son problemas de recente aparición que están intimamente ligados á explotación territorial do presente e ó inicio da Revolución Industrial. Porén, para determinar o rol dos forzamentos naturais e antrópicos nestes procesos, así coma para ampliar o coñecemento acerca de como as condicións climáticas do pasado afectaron ás sociedades e ó medio ambiente, a perspectiva temporal é esencial.

As turbeiras son ecosistemas húmidos cunha capa de solo orgánico saturado en auga e constituída por material vexetal morto e en descomposición denominado turba. As turbeiras regulan o clima, a hidroloxía e a química de solos e augas nas súas concas. Tamén son importantes reservorios de biodiversidade e teñen actuado como sumidoiros naturais de carbono durante milenios. Non obstante, as turbeiras non son só importantes polas súas funcións ecolóxicas, senón que están entre os mellores arquivos para a reconstrución paleoambiental. Debido ás súas propiedades fisicoquímicas e ó seu modo de produción e acumulación de turba, partículas atmosféricas de po, de contaminantes ou de pole poden depositarse na súa superficie, quedando inmobilizadas e enterrándose progresivamente a medida que a turba se acumula. Deste xeito constrúese un rexistro dos cambios ambientais do pasado. Ademais, a turba é un material facilmente datable polo que é relativamente sinxelo asignar unha cronoloxía ós cambios ambientais detectados. Tradicionalmente, as turbeiras ombrotróficas, ás que exclusivamente reciben auga de precipitación, son consideradas ideais para a reconstrución paleoambiental. Porén, as turbeiras minerotróficas, que reciben

auga tanto de precipitación como de escorrenta, tamén poden ser bos arquivos ambientais.

Nas últimas décadas, tense avanzado considerablemente na aplicación da xeoquímica e a palinoloxía no campo de la reconstrución ambiental a partir de turbeiras, e especialmente despois da popularización de técnicas de datación como o radiocarbono, que implicaron un grande avance na precisión das interpretacións cronolóxicas e na comparación de estudos. Non obstante, segundo buscas realizadas na Web of Science, dende o ano 1900 publicáronse 2422 artigos de xeoquímica e 1355 de palinoloxía en turbeiras, mentres que, para o mesmo período de tempo, tan só foron 247 os que empregaron ámbalas disciplinas conxuntamente. Respecto á aplicación conxunta de xeoquímica e palinoloxía, durante os últimos anos obsérvase unha lixeira tendencia á alza. No ano 2000 as publicacións nas que se combinaban ambas metodoloxías representaban o 5.6 % do total de publicacións aplicando xeoquímica e palinoloxía a turbeiras, mentres que no intervalo 2010-2015 representaron un 6.4%. Estas cifras resaltan o feito de que, aínda que a investigación multi-indicador é cada vez máis habitual, aínda representa unha pequena proporción do total.

O obxectivo principal deste traballo de doutoramento é o de explorar como as aproximacións xeoquímicas e palinolóxicas, particularmente cando se consideran xuntas, poden axudar a comprender os cambios ambientais do Holoceno (os últimos ~11600 anos). Para conseguir este obxectivo xeral estudáronse distintos tipos de turbeiras (ombrotróficas e minerotróficas), ambientes (zonas boreal e temperada) e rangos cronolóxicos (aínda que especialmente no Holoceno tardío). Deuse especial relevancia ó estudo de como diferentes estresores ambientais –como o clima e as actividades humanas– influíron os ambientes do pasado e prestouse especial atención ó estudo dos seguintes procesos: 1) a erosión de solos, tanto natural coma inducida polo ser humano, e a súa relación coa evolución dos bosques e os cambios hidrolóxicos nas turbeiras; 2) os cambios no clima no pasado e a súa relación coa descomposición da materia orgánica da turba, a vexetación e outros aspectos ambientais, con especial atención ós cambios ocorridos na Pequena Idade do Xeo, e 3) as variacións na contaminación atmosférica por metais no pasado e a súa posible relación coa minería e metalurxia e os cambios ocorridos na vexetación, particularmente na cobertura arbórea.

Pola banda da xeoquímica aplícanse o estudo de propiedades físicas (perda de peso por ignición e densidade da turba) e químicas (composición elemental, isótopos estables de carbono e nitróxeno, isótopos de chumbo, grao de humificación da turba e espectroscopia infravermella), mentres que no campo da palinoloxía considéranse tanto os restos polínicos coma os palinomorfos non polínicos.

Os cambios na concentración e nos fluxos de elementos litoxénicos, a perda de peso por ignición ou a densidade da turba, usáronse para reconstruír cambios na ***erosión de solos***. Neste sentido as turbeiras minerotróficas confinadas son ideais para reconstruír a erosión de solos a nivel de conca. Os **artigos I e III** inclúen a reconstrución de eventos de erosión de solos rexistrados en turbeiras mineroxénicas localizados no Bocelo (NO Ibérico; últimos ~3000 anos) e no Payo (O Ibérico, últimos ~700 anos) respectivamente. No Bocelo (Artigo I) a erosión de solos e a actividade humana estiveron intimamente ligadas a través da deforestación asociada o desenvolvemento de prácticas agrícolas e gandeiras dende, polo menos, a Idade do Ferro. A súa intensidade foi especialmente alta durante o Período Romano, pero tamén durante o Período Xermánico e o Medievo. Durante estas fases, a conca enteira foi afectada, resultando non só nun incremento da erosión senón tamén en severas modificacións hidrolóxicas da turbeira. O clima, especialmente a precipitación (reconstruída mediante a varianza residual do Br) tamén puido ter tamén acelerado o proceso erosivo nos períodos húmidos. No Payo (Artigo III) a creación de terras de cultivo, pastos e plantacións froiteira, en moitos casos empregando lume, fomentou que o solo quedase exposto dando lugar a un incremento nos fluxos de po á turbeira. Detéctanse incrementos na erosión de solos no AD ~1460-1580, AD ~1660-1800, AD ~1830-1920 e no AD ~1940-1960. Porén, aínda que en xeral hai unha relación inversa entre a cobertura arbórea e a erosión, o gran descenso que tivo lugar na cobertura arbórea no período AD ~1550-1650 non estivo acompañado dunha tendencia equivalente no fluxo de elementos litoxénicos. O que si se detecta en cambio, é unha modificación nas fontes de elementos litoxénicos, o que suxire que a perda de masa forestal no período AD ~1550-1650 e dende o AD ~1700 afectou á orixe do po que chega á turbeira. Cambios nas dirección predominante do vento ou na súa intensidade tamén poderían ser a causa de este patrón aínda que, en base ás evidencias anteriormente mencionadas, esta explicación semella máis especulativa. Respecto á cronoloxía dos eventos de erosión nos solos do Payo, é de destacar o feito de que, en ocasións, e.g., coincidindo cos mínimos de actividade solar Spörer e Maunder, a influencia de factores climáticos na erosión de solos é probable.

As turbeiras ombrotróficas xeralmente teñen maiores áreas fonte de po eólico que as turbeiras mineroxénicas, aínda que cando os incrementos nos elementos litoxénicos son o suficientemente elevados, as fontes de po local (i.e., erosión) poden ser as de maior importancia. Por exemplo, as variacións no contido mineral da turba en Sandhavn (SO de Grenlandia; últimos ~700 anos; **Artigo II**) estiveron intimamente ligadas coa erosión de solos durante as fases de ocupación humana na rexión xa que só se incrementaron durante o período de ocupación Norse, cando colonos do norte europeo debido ó melloramento do clima asociado ó Óptimo Climático Medieval ocupa temporalmente o Sur de Grenladia, e na era moderna, coincidindo coa recuperación da cría de ovellas na rexión. Aínda que, desafortunadamente, a erosión de solos coincidente co período de ocupación Norse pode estar comprometida debido á proximidade da interfase basal area/turba.

O estudo na variación das evidencias xeoquímicas, tanto orgánicas coma inorgánicas, e palinolóxicas foron usadas para reconstruír diversos aspectos do ***clima*** e para examinar coma os cambios en factores climáticos afectaron diversos aspectos dos ecosistemas, incluíndo actividade humana. Os rexistros do Payo (**Artigo III**) e Sandhavn (**Artigo II**) indican que entre o AD ~1300 (AD ~1400 en Sandhavn) e o AD ~1800, coincidindo coa Pequena Idade do Xeo, tanto a acumulación de turba coma a acumulación de carbono estiveron moi limitadas polas condicións de frío dominantes. Isto indica que, a pesar de que a prevaleza de condicións relativamente frías sexa necesaria para que se produza a acumulación de turba, un exceso de frío, dado que reduce a produtividade primaria, pode ter consecuencias importantes para a acumulación de turba e carbono. No Payo, ademais, tralo arrefriamento da Pequena Idade do Xeo, a pesar de que as evidencias palinolóxicas apuntan a un incremento da humidade –polo menos estacionalmente–, a humificación (reconstruída mediante HI-FTIR e UV-Abs) aumentou no período AD ~1760-1930, poñendo de manifesto a presenza de turba máis descomposta. Así, o incremento da temperatura tralo século XVIII, unido a un axeitado aporte hídrico na estación favorable, puido ter desencadeado o incremento detectado na acumulación de carbono, mentres que as condicións máis cálidas e a seca estacional deberon de favorecer a descomposición da turba. En Sandhavn, non obstante, os espectros de FTIR e a UV-Abs non amosaron unha tendencia xeral ó longo do período da Pequena Idade de Xeo, senón que só se viron afectados de xeito puntual durante os mínimos de actividade solar Spörer e Maunder pois, asociados a estes eventos, detectase un descenso da descomposición e un enriquecemento en polisacáridos (i.e fraccións lábiles). Porén, cómpre ser cautos nesta afirmación xa que existen limitacións na resolución á que se detectan estes cambios. O Br é un halóxeno de orixe mariña cuxa acumulación na turba é dependente da deposición húmida, da haloxenación da materia orgánica e da deshaloxenación en condicións redutoras. En Sandhavn, o rexistro do Br amosou concentracións baixas durante a Pequena Idade do Xeo (incrementándose gradualmente a partir do AD ~1780) e concentracións aínda máis baixas coincidindo cos mínimos en actividade solar, suxerindo que a haloxenación estaría limitada durante os momentos fríos. No Bocelo (**Artigo I**), unha análise de compoñentes principais permitiu a extracción dun índice de humidade baseado na varianza residual do Br que amosou unha gran coincidencia cun índice de humidade preexistente na rexión e baseado na estabilidade térmica do Hg, permitindo deste xeito a extracción dunha sinal relacionada coa deposición húmida.

As comunidades vexetais tamén poder verse afectadas polos cambios nas condicións climáticas. Así, o clima, aínda tendo xeralmente un menor impacto que a actividade humana, tamén ten actuado coma unha forza de cambio na vexetación ó longo do Holoceno. Por exemplo, en Sandhavn o final da Pequena Idade do Xeo supuxo a substitución de comunidades esteparias dominadas por Cyperaceae pola uceira oceánica de *Empetrum nigrum*. Isto, á súa vez, afectou a composición da materia orgánica da turba, pois simultaneamente detectouse un incremento nos polisacáridos. No Bocelo, a maior presenza de *Olea* (oliveira) e *Castanea* (castiñeiro) durante o Período Cálido Romano tamén debeu de estar relacionada coa prevaleza de condicións máis cálidas aínda que, a facilitación humana tamén puido ter xogado un papel importante. Estes cambios, ocorridos no Holoceno tardío, foron de menor intensidade ós ocorridos na transición Pleistoceno-Holoceno. Por exemplo, na secuencia coluvial PRD-IV (**Artigo IV**, NO Ibérico; últimos ~14000 anos), no marco desta transición, detéctanse importantes cambios na vexetación tanto na escala local (da dominancia de *Pleospora* á de Cyperaceae) coma na escala rexional (da dominancia de *Betula* –bidueiro– á de *Quecus* –carballo). Aínda que, o retraso ocorrido na resposta a escala rexional indica que as comunidades vexetais rexionais son máis resilientes que as comunidades locais.

No tocante á ***contaminación atmosférica por metais*** cabe destacar que, tanto para establecer os niveis de fondo naturais como para contextualizar a intensidade da polución actual, é esencial ter en conta a perspectiva temporal. Investigacións previas en turbeiras europeas emprazadas en diferentes localizacións ten demostrado que a contaminación atmosférica por metais existe dende a Idade do Bronce, mentres que a análise de testemuñas de Xeo en Grenlandia evidencian que os seres humanos contaminaron a troposfera media do hemisferio norte hai dous milenios atrás. En contra das evidencias atopadas nas testemuñas de xeo, as testemuñas de turba estudadas ata o de agora en Grenlandia non amosaron enriquecementos significativos en metais, polo que os resultado obtidos en Sandhavn (**Artigo II**), baseados no enriquecemento por chumbo e que amosan unha sinal de contaminación clara a partir de AD ~1845 e un pico centrado nos 1970', son de relevancia.

En base á cronoloxía destes eventos, que está en maior sintonía coa revolución industrial americana que coa europea, e debido á detección do "aumento de *Ambrosia*" –un característico incremento neste taxa nitrófilo que tivo lugar no Leste de Norte América debido á chegada de colonos europeos a finais do século XIX– pódese apoiar de maneira indirecta a preponderancia dunha fonte de chumbo de orixe norteamericana. A análise de isótopos de chumbo, que se atópa en progreso na actualidade, contribuirá a confirmar cales foron as fontes de chumbo no rexistro de Sandhavn.

A pesar das evidencias de transporte de longa distancia de contaminantes metálicos, en numerosos rexistros de turba téñense detectado variacións rexionais no rexistro da contaminación atmosférica por metais que estarían recollendo as variacións locais no desenvolvemento de actividades minerometalúrxicas no pasado. Pois, ata que a queima de combustibles fósiles se converteu na maior fonte de Pb á atmosfera a partires da Revolución Industrial, as actividades minero-metalúrxicas foron as principais fontes de emisións antropoxénicas. A investigación levada a cabo nun rexistro de turba en Leadhills (Escocia; últimos ~3600 anos; **Artigo V**) amosou a historia de explotación das fontes minerais da mena de Leadhills/Wanlockhed dende a prehistoria. As fases de paleocontaminación foron consistentes tanto coas fontes escritas coma co rexistro arqueolóxico da rexión e, xa que carecen do pico de enriquecemento de Pb de época Romana –tan característico na maioría dos rexistros europeos–, proporcionan un exemplo de variacións rexionais específicas nos rexistros temporais de contaminación atmosférica metálica.

Respecto ós posibles impactos da minería e a metalurxia na vexetación, a acumulación de evidencias paleoambientais en diferentes lugares indica que unha redución intensa no bosque ten ocorrido simultaneamente á detección de fases de contaminación atmosférica metálica dende a prehistoria. O **Artigo VI** revisa a investigación levada a cabo no norte da Península Ibérica en relación coa reconstrución da minería e metalurxia no pasado mediante o sinal da contaminación por metais en arquivos ambientais e examina o posible impacto destas actividades nos bosques. Dedúcese que os estudos multi-indicador que combinan xeoquímica e palinoloxía permiten a avaliación da influencia que as actividades minero-metalúrxicas tiveron na vexetación. Porén, ás veces resulta difícil determinar a influencia da minería/metalurxia na evolución do bosque de xeito independente de outras actividades forzamentos humanas que poden coexistir como a agricultura ou a gandería.

En esencia, os rexistros de cambio ambiental obtidos mediante as análises xeoquímicas e palinolóxicas son indicadores de distintos aspectos ambientais. Porén, debido a que a complexidade inherente ós sistemas naturais está detrás das interaccións entre distintos compartimentos dos ecosistemas (i.e., biosfera, litosfera, hidrosfera e atmosfera), o uso combinado de xeoquímica e a palinoloxía de maneira conxunta proporciona interpretacións moito máis precisas dos cambios ambientais que aquelas obtidas usando unha aproximación única. Isto, á súa vez, permitiu obter unha visión de conxunto dos cambios ambientais no pasado que dificilmente se obtería empregando estas disciplinas de xeito independente.

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2. GENERAL INTRODUCTION

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2. GENERAL INTRODUCTION

2.1. Peatlands

2.1.1. Peatlands, definition and development

Peatlands are wetland ecosystems with a thick water-logged organic soil layer made up of dead and decaying plant material (peat) and where the basic soil type is Histosol, which is characterized by the presence of thick organic layers (IUSS Working Group WRB, 2014). Peat forming systems (mires) accumulate peat because waterlogging, and frequently cold conditions within them, impede the decay of the plant material produced by their surface vegetation (Clymo, 1984) by limiting decomposition processes. Thus, relatively cold and humid climatic conditions are ideal for peat development and accumulation.

Peatlands are important in regulating climate, the hydrology, the hydrochemistry and soil chemistry in their catchment areas (Joosten and Clarke, 2002). Globally, they are also important because they have acted as a persistent natural carbon sink during the Holocene so they are a major terrestrial carbon reservoir (Charman et al., 2013). Although species diversity in peatlands may be low, they have a higher proportion of characteristic species than dryland ecosystems in the same biogeographic zone (Parish et al., 2008), which turns them in notable biodiversity reservoirs. All of these reasons, in addition to their role as environmental archives, make peatlands important ecosystems so, today, many of them are regulated by different categories of environmental protection.

Although the exact extent of peatlands is already unknown, it is estimated that they cover around 4 x 10^6 km^2 (i.e., 3%) of the world's continental area. Estimations vary from the most conservative of ~320 million hectares (Pfadenhauer et al., 1993) to the less conservative of ~421 million hectares (Kivinen and Pakarinen, 1981), the latter excluding Africa and parts of South America. Nearly 90% of peatland areas are located in the Northern Hemisphere (Maltby, 1996). Many of them are dispersed in relatively small patches, due to local peculiarities, although extensive areas in the cooler climate areas of Canada, Scandinavia or Russia exist as well. Southern Hemisphere peatlands are more restricted, although remarkable peatland complexes exist in southern Argentina and Chile, the Falkland Islands, New Zealand and the Subantarctic islands. Tropical peatlands, although less extensive, can also be found (Figure 1).

Most modern peatlands were formed in high latitudes after the retreat of the glaciers at the end of the last ice age some 12,000 years ago (Gorham et al., 2007) although, peatlands in the tropics, where environmental conditions have been more constant over time, may have older basal ages (e.g., Weiss et al., 2002; Kylander et al., 2007; Margalef et al., 2014; Horák-Terra, 2014; Pérez-Rodríguez et al., 2015).

Thus, in summary it could be said that peatland formation requires: 1) the continuous annual growth of vegetation; 2) moderate to relatively high levels of rainfall; 3) poor drainage, and 4) the prevalence of anaerobic conditions. According to their formation paths, peatlands can be formed primarily in two ways: by the filling of small lake basins or river flows (i.e., terrestrialisation or lakefill) or by the spreading outward from inorganic soils, with no fully aquatic phase (i.e., paludification or swamping) (Figure 2). First stages of the terrestrialisation process often involve filling in of the former aquatic habitat by sediments as well as grounded mats, floating vegetation or vegetation growing on the margins of the water body. The paludification process, however, includes a shift from forests, grassland or long exposed bare land to peatland.

According to their hydrological sources peatlands are classified in two large types: ombrotrophic (also named bogs) or minerotrophic (also named fens). Ombrotrophic peatlands are those that are just atmospherically rain-fed while minerotrophic ones receive their water inputs both from rain water and ground water. Ground water (i.e., superficial run-off and streams/springs) has flowed over or through rocks, soils or sediments, often acquiring dissolved chemicals which raise the nutrients level and reduce the acidity of the peat. The transition from minerotrophy to ombrotrophy can occur during mire development and involves a physical elevation of the mire surface by peat accretion (Moore, 1995). Ombrotrophic peatlands are said to be diplotelmic (Ingram, 1982), with two layers of peat each having very different physical, hydrological and biological characteristics. The upper, frequently aerated layer, through which water moves freely (and usually laterally), is termed the acrotelm. Beneath this it is the permanently waterlogged, anaerobic peat mass through which water movements are usually slow. This is the catotelm. In fens, in which the deep groundwater that nourished by precipitation are mixed up into a single one, the distinction between acrotelm and catotelm is non-existent.

Peatlands have been in the focus of scientific research for a long time. Gorham (1957) summarizes some of the early works on peatlands since the Renaissance. Apparently, the first attempt to describe and categorise peatlands was that of John Leland, who between 1535 and 1543, during his celebrated tour of Britain, described English and Welsh peatlands. Leland introduced the terms moor, marsh, fen and carr, terms still in use today. In 1652 Gerard Boate classified several types of Irish bogs (Boate, 1652), and in 1685 William King described their development emphasising the changes that happen in plant communities, accompanying peat accumulation (William, 1685). During the mid-18th century, Linnaeus

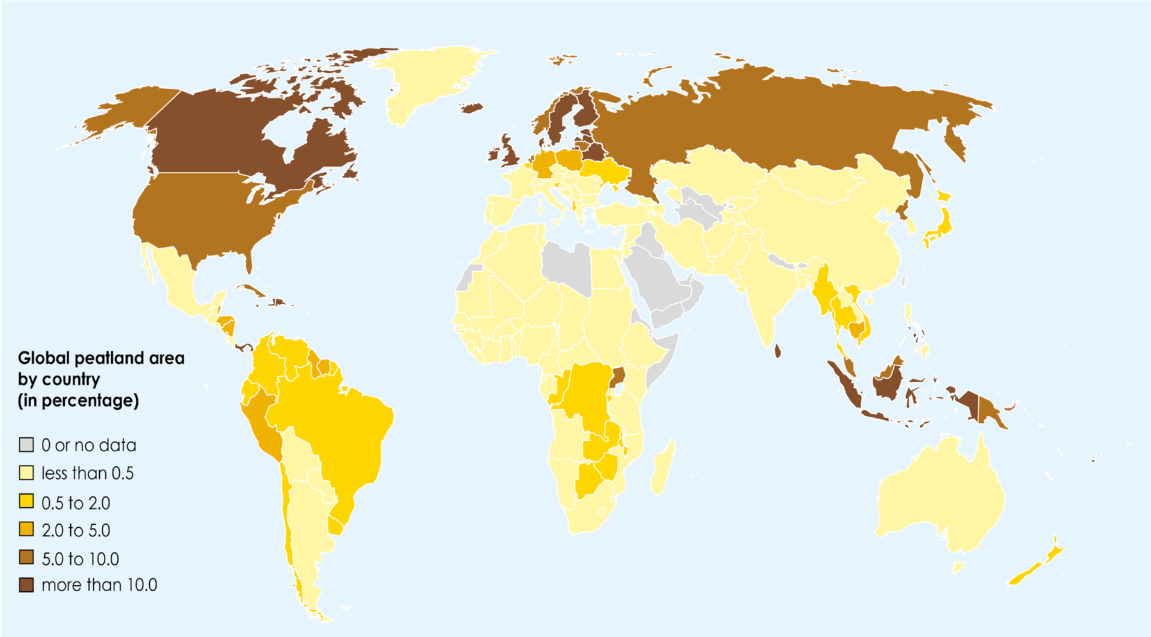

Figure 1. Peat distribution in the world: global peatland area by country. Modified from Parish et al., 2008.

provided information on the flora of bogs, although the first adduction about the plant origin of peat would not happen until the mid-19th, when Léo Lesquereux stated: "*If the vertical section of a peat layer after exploitation is studied from top to bottom, it is seen that living plants that still preserve their shapes gradually lose them by imperceptible degrees and finally reach the peat stage*" (Lesquereux, 1844). During the first part of the 19th century, the study of peatlands increased in response to new demands for agricultural expansion. De Luc in Germany or Aiton and Rennie in Scotland, for example, deserve a special mention. Further advances in the chemical conditions of peatlands (e.g., Malmström, 1952; Gorham, 1953, 1955; Tamm, 1954; Malmer and Sjörs, 1955) and in the factors affecting their formation – i.e., climate, topography, geology, biota and time– (Granlund, 1932; Darlington, 1943; Godwin, 1946; Pearsall, 1950; Sjörs, 1950; Conway, 1954) occur in the early 20th century. Later on, the development, ecology and biogeochemistry of various types of peatlands have received thorough review (e.g., Heinselman, 1963, 1970; Heathwaite et al., 1993; Mitsch and Gosselink, 2003; Wieder and Vitt, 2006).

2.1.2. Peatlands as environmental archives

Many natural and human-induced changes occur over time scales of decades or centuries and these are difficult to comprehend without a historical perspective (Renberg et al., 2009). Palaeoenvironmental research focus on how ecosystems have changed through time, identifies when the triggers of those environmental changes occurred and gets insights about how natural systems have responded to past environmental changes –including those

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related with human activity. This is important to be able to manage today's ecosystems with accuracy and scientific criteria as well as to predict future environmental changes.

The so-called "environmental archives" preserve the evidence of environmental change over long time periods so, past conditions can be inferred from them thousands of years after the event. According to the International Atomic Energy Agency ("Environmental archives," 2015) an ideal environmental archive should:

- be of high temporal resolution,
- be responsive to small environmental changes,
- record a continuous time series of variation,
- be global in distribution, and
- be accurately and precisely datable.

Although meeting all the aforementioned criteria is almost impossible, a variety of archives can be used in palaeoenvironmental reconstruction including, besides peat, ice, sediments, corals, tree rings or speleothems, among others.

Because of their prevailing physicochemical conditions and their dynamics of peat accumulation, peatlands are considered excellent archives of environmental change. On the surface of peatlands, atmospherically deposited particles such as dust, pollutants, or pollen can be trapped. If such particles remain immobilised, they will be progressively buried as peat grows, building a record of past environmental changes. Moreover, the vertical record of abundance of certain identifiable and preserved tissues of once-living organisms (macrofossils and microfossils), with known ecological tolerances for specific environmental variables (e.g., pH or surface moisture), can provide the basis for reconstructing past environments (Wieder et al., 2009). Each of these approximations of past environmental conditions is called "proxy". Palaeoenvironmental proxies have the potential to provide evidence for environmental changes prior to the existence of instrumental or historical documentary records.

In comparison with other environmental archives, peatlands present several advantages for palaeoenvironmental reconstruction (Barber, 1993; Chambers and Charman, 2004):

- The autochthonous mode of peat production and accumulation makes them less susceptible to the redeposition that can bedevil some lake-sediment sequences.
- Their accessible location compared to ice sheets or ocean sediments makes them more readily and economically cored than ice, ocean or lake bottoms.
- They present a great range of proxies, such as pollen, non-pollen microfossils, rhizopods, macrofossils, humification, magnetic properties, tephra layers, elemental

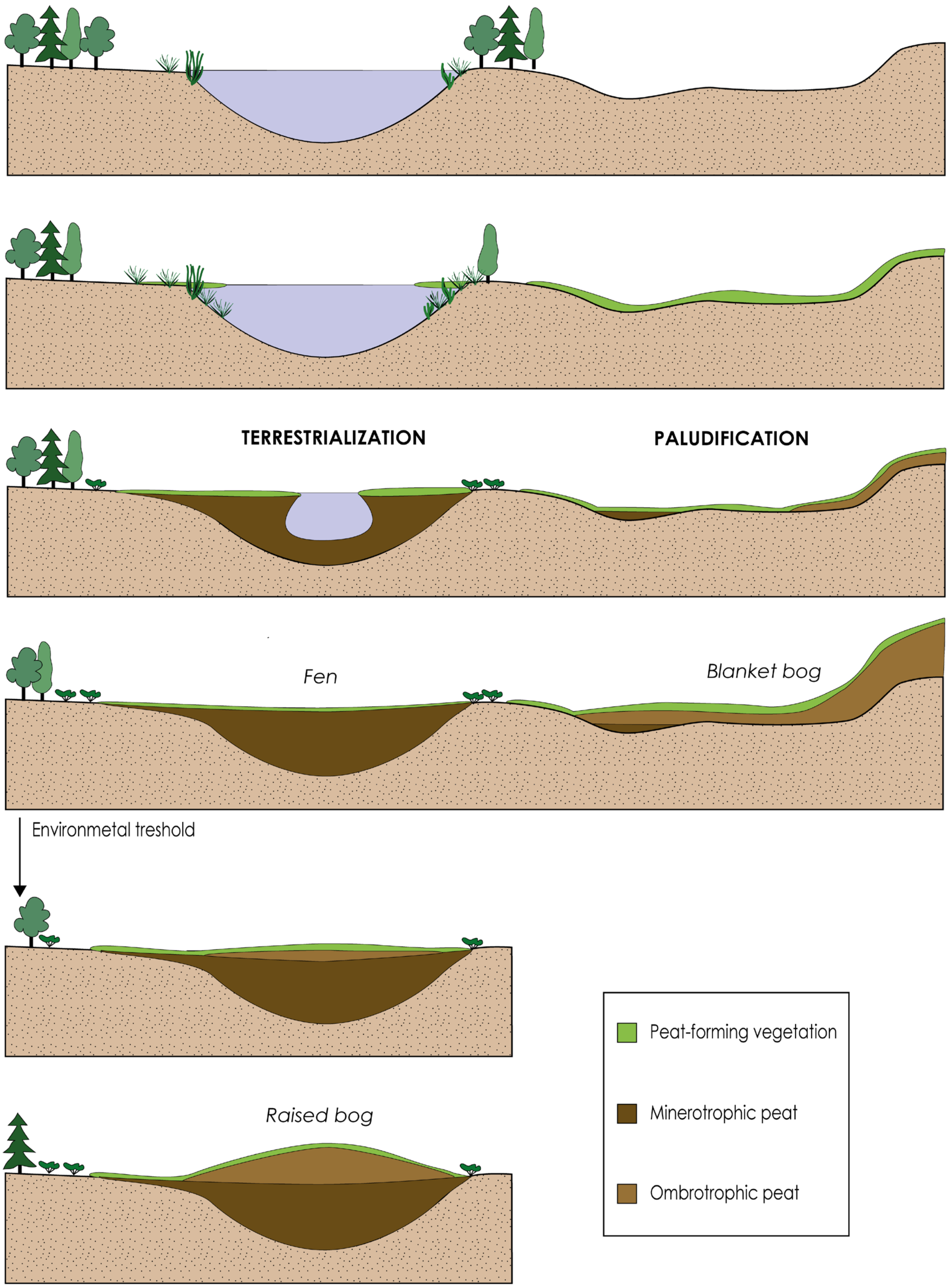

Figure 2. Terrestrialisation and paludification models of peat development and representation of the main resulting types of peatlands.

and isotope geochemistry, etc.

- In most cases the record is continuous. Although, peat cutting or, in very rare cases, certain environmental conditions, may truncate the record.
- There is plenty of easily ^{14}C datable material (high carbon content and very often presence of well-preserved macrofossils).

Thus, it is not surprising that some of the earliest records of global change came from peat archives. Back in the early 19th century, Heinrich Dau (1790-1831) recognised the occurrence of pine stumps and other wood remains buried in Danish mires that were treeless at the time and interpreted them as an evidence that climate conditions in the past were different (Dau, 1829). Dau was also the first scientist to investigate layers in peat. He observed that lighter layers were weakly decomposed while darker layers were highly decomposed. Later on, Japetus Streenstrup (1813–1897) expanded stratigraphical investigations and classified the tree-remain layers on the basis of their species composition (Steenstrup, 1841), while Axel Blytt (1843–1898) hypothesised about the causes behind dark and light layers found by Dau. He argued that the darker layers were deposited in drier periods while the lighter in moister ones (Blytt, 1876). He also analysed the species composition of the plant remains preserved in Norwegian peat and compared the plant macrofossil composition of each layer with the modern floristic assemblages. Thus, Blytt may have been the first palaeoclimatologist using the "assemblage approach" to make palaeoclimate inferences using fossil plant remains from Norway (Birks and Seppä, 2010). Some of the fossil assemblages that he analysed resembled plant communities of the Atlantic shore, so he named the "Atlantic" the climatic period when these communities grew. Other fossil assemblages resembled modern plant communities on continental eastern Norway, so he called the "Boreal" the time period in which these fossil assemblages appeared. Blytt's theory was further extended by the Swede Rutger Sernander (1866-1944), who defined the Subboreal and Subatlantic periods, as well as the glacial periods (Sernander, 1894, 1908). Since then, this classification, which quickly became established all around Europe, is known as the Blytt-Sernander classification. Nowadays, the notion of broad climate periods for the Holocene is considered too simplistic (Chambers and Charman, 2004; Birks and Seppä, 2010) although, despite first signs of disagreement took place in the early 20th century (Andersson, 1909; von Post, 1924; Aario, 1932; Granlund, 1932), its terminology survived in formal chronostratigraphy (Mangerud et al., 1974) until the late 1960s, when advances in radiocarbon dating allowed more reliable correlation of peat-stratigraphical layers over large areas.

First interpretations of peat proxies mainly focused on climate as a force of change. However, palynological evidence from the 1940s started to consider the influence of human activity as a driver of woodlands' compositional changes (e.g., Godwin, 1944, 1948; Mitchell, 1951, 1956; Morrison, 1959; Dimbleby, 1960; Troels-Smith, 1960). Distinguishing cultivated cereal pollen grains from wild Poaceae (Firbas, 1937) established a way of identifying human activities that became key to the study of the origin and development of agriculture.

After the development of macrofossil and pollen analyses to the study of past environmental changes, other proxies started to be studied in peatlands, including charcoal, insects, non-pollen palynomorphs or testate amoebae (e.g., Charman, 2001; van Geel, 2001; Whitlock and Larsen, 2001; Panagiotakopulu, 2004). Thereafter, non-biological proxies such as physical and chemical properties became to be also used to infer past environmental conditions (Shotyk, 1988). They could be obtained by basic procedures such as loss on ignition, peat density or the degree of humification, or they require the use of more sophisticated equipment, such as magnetic susceptibility, elemental and isotopic geochemistry or organic biomolecules characterisation. The methodological approach of this PhD thesis involves both the palynological and geochemical analyses of peat records. Consequently, a brief review on the evolution of palynology and geochemistry as scientific disciplines, with special attention to their development on palaeoenvironmental studies in peatlands, is presented below.

2.2. Brief history of the applied Methodologies

2.2.1. Palynology

The term palynology (gr: palino-dust; logi; study) was proposed by Hyde and Williams (1944) to define the study of the pollen grains and spores produced by fanerogams and cryptogams respectively. At present, the boundaries of palynology are wider as it also comprises the study of other acid-resistant microfossils known as non-pollen palynomorphs (NPP). They are cysts or cyst-like bodies of algae, fungal spores or other microscopic structures of unknown origin preserved with pollen and spores after palynological sample extraction, some of them belonging to the animal kingdom (e.g., acari remains, mandibles of invertebrates, etc.).

Pollen and spores are structures highly adapted to take part in reproduction processes and ensure the continuity of plant species. Spores self-fertilise, whereas pollen grains, which contain the male nucleus, need a female nucleus for fertilization to produce seeds (i.e., a potential new individual). However, it is common that both pollen and spores are produced in excess so most of them do not fulfil any biological function, being instead deposited in soils and sediments by the wind. Pollen grains can also be dispersed by water courses or animals. Animal pollination, in contrast to wind- or water-pollination, is the method

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with the greater specificity and the lower pollen productivity. Especially in the case of wind-dispersed structures, the arrival of pollen grains and spores to possible environmental archives is facilitated, but resistance to environmental damage (i.e., the preservation of the signal) is also required to their use in palaeoenvironmental research. Fortunately, pollination and spore dispersion processes require extremely resistant structures. Pollen grains and spores walls are covered of a polymer called sporopollenin, extremely resistant to most forms of chemical and physical alteration, except oxidation (Brooks and Shaw, 1978). This feature is key for pollen analysis as: 1) palynomorph preservation is assured, particularly in anaerobic environments, such as wetlands, and 2) strong chemicals can be used to remove other components of soil and sediment, thus concentrating microfossils and facilitating their identification and counting (Bennett and Willis, 2001). Moreover, ornamentation and apertures of the external wall of pollen and spores, together with differences in morphology and size, allow their taxonomical identification at the level of family, genera and, less frequently, even species.

Therefore, the composition of the palynological rain (usually called pollen rain) is a function of the composition of the vegetation surrounding the sampled site, i.e., the study of the pollen rain is a snap-shot of vegetation at a particular point in space and time (Birks and Birks, 1980). When pollen spectra are obtained from several samples through a stratigraphical (hence temporal) sequence, they provide a picture of vegetation change through the period of time represented by the sequence. As human activity and climate have modulated vegetation change over time, this can be as well very useful to infer past changes in human activities and climate. Palynological analysis thus enables land use change to be assessed over prehistoric and historic timescales and demonstrates the landscape impacts of woodland clearance, grazing and crop cultivation (Edwards and Whittington, 2001), whereas, through knowledge of species ecological tolerances, it is also a valuable tool for understanding past changes in climate.

In the 20th century several reviews traced back the history of palynology (e.g., Wodehouse, 1935; Manten, 1966; Ducker and Knox, 1985). As the size of most pollen grains is about 5-150 µm, early advances in pollen analysis have been parallel to the developmental stages of the microscopy. Pollen was first observed microscopically in Britain at 1640 by Nehemiah Grew and about the same time, Malpighi noted differences in pollen size and colour. The 19th century, a period of much improvement in microscopy, also led a great advance in the knowledge about the anatomy of pollen and spores. Hugo von Mohl, a German botanist, published the first morphological classification of pollen (von Mohl, 1834) and Heinrich Göppert was the first to describe and illustrate fossil pollen (Göppert, 1836).

Despite these early contributions to the field, it is usually accepted that the beginning of pollen analysis took place with the publication of von Post's dissertation work in 1916, at the

16th Convention of Scandinavian Naturalists in Kristiania (Oslo), where he presented a novel quantitative method for the analysis of vegetation history. He was the first scientist using the so-called "pollen diagram", a graphical representation of palynological information. von Post's doctoral student, Gunnar Erdtman internationalised the subject. He travelled widely and greatly expanded pollen-analytical/statistical studies in many parts of the world in the 1920s, 1930s and 1940s, developing a terminology for pollen morphology that will become dominant. Erdtman's investigations covered a wide range that included pollen morphology, stratification of the pollen wall, use of palynology in stratigraphical geology, palaeoecology, archaeological botany, forensics, etc. He wrote several books including "An Introduction to Pollen Analysis" (Erdtman, 1943) and "Handbook of Palynology" (Erdtman, 1969). Other leaders applying pollen analysis were Firbas in central Europe (Firbas, 1934, 1950), Godwin in Britain (Godwin, 1940, 1956), Jessen in Ireland (Jessen and Farrington, 1937; Jessen et al., 1959), Nejstadt in the Soviet Union (Nejstadt, 1957) and Auer in South America (Auer, 1958) .

After von Post and Erdtman, various researchers deserve a special recognition for publishing the first editions of reference literature: Fægri and Iversen in Scandinavia ("Textbook of Modern Pollen Analysis" (Fægri and Iversen, 1950) and "Textbook of pollen analysis" (Fægri and Iversen, 1964)), Moore and Webb in Britain ("An illustrated guide to pollen analysis" (Moore and Webb, 1978)) and Alfred Traverse in America ("Paleopalynolgy" (Traverse, 1988)) are perhaps the most relevant.

2.2.2. Geochemistry

The term geochemistry was first used by the Swiss-German chemist Christian Friederich Schönbein in 1838 and it refers to the study of the chemical composition and chemical processes of the Earth (Schönbein, 1838). Although, is Victor Goldschmidt, with his early study of the distribution of elements in nature in the early 20th century, who is considered as the father of geochemistry (Goldschmidt, 1923–38). Focusing on peat geochemical research, the variety of peat properties that can be determined are numerous and they include the analysis of physical properties as well as both the organic and the inorganic constituents of peat.

2.2.2.1. Inorganic Geochemistry

Peat is formed largely by organic matter. Mineral matter, in contrast, is mainly allochthonous and represents a little proportion of the total dry weight. Despite its low proportion, the

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amount and composition of mineral matter in peat can give very valuable information about past soil erosion and dust mobilisation processes, variations in atmospheric metal pollution or changes in climate.

Modern studies on the chemical composition of peat can be considered to have started in the early 20th century, being Zailer and Wilk (1907) among the earliest researchers reporting the ash content of various types of peats and peat-forming plants. This early data already pointed to higher ash content in minerotrophic than in ombrotrophic peatlands. In minerotrophic peatlands, particularly in confined ones, local mineral matter sources, both from rain and run-off water, are dominant. The mineral matter found in ombrotrophic bogs, whose only hydrological source is atmospheric precipitation, originates from different sources: pedogenic, resulting from soil erosion; oceanogenic, from sea salt sprays; pyrogenic, from smoke and ash supplied by fires; volcanogenic, from volcanic eruptions; cosmogenic, from meteorites and cosmic dust, and anthropogenic, from industrial sources or vehicle emissions among others (Mattson and Koutler Andersson, 1954). Soil erosion provides the major source of particles via the atmosphere to most bogs, as particles both from local soils and and distal sources are constantly being deposited into the bog (Le Roux and Shotyk, 2006). Anthropogenic forcing on the cycles of lithogenic elements were already reported from early studies in the vertical distribution of mineral matter in peatlands. In Shotyk's review about inorganic geochemistry of peats (Shotyk, 1988), it is recognised that the vertical distribution of ash and lithogenic elements through *Sphagnum* bogs showed a characteristic "C" shape (e.g., Waksman and Stevens, 1928; Gorham, 1949; Mattson and Koutler Andersson, 1954; Walsh and Barry, 1958; Chapman, 1964). The relatively large ash and lithogenic elements contents of the basal peat layers occurred because they are the most minerotrophic, but the upper zone of ash enrichment was considered to be mainly the result of anthropogenic contributions, with the role of plant bioaccumulation of minor importance (Shotyk, 1988). The relation between increased mineral content in superficial peat layers with human activity has also been found in studies performed at geographical scale. Gorham and Tilton (1978) studied ash content of *Sphagnum* mosses from various sites in mid-western North America. They found that the low ash samples were from wilderness areas whereas the high ash samples came from a predominantly agricultural region, concluding that windblown soil was the most important factor affecting the ash content of mosses. Increased soil erosion inputs in peatlands linked to agricultural or grazing activities were also found in the peat record in subsequent studies (e.g., Görres and Frenzel, 1993; Hölzer and Hölzer, 1998; Martínez Cortizas et al., 2005). This has great implications in the field of Environmental Archaeology as palaeoenvironmental reconstruction is the only way of approaching the study of human-landscape relationships in most cases, especially for periods for which archaeological or historical data is absent or scarce.

Mineral inputs to peatlands are not only the result of local scale processes or anthropogenic modifications. Bogs situated in hilltops or in great plains have large source areas, and therefore can record long-distance transported dust. For example, some volcanic eruptions produce large amounts of mineral matter that can be deposited in peatlands forming layers called tephras. These tephras are useful to establish a regional or hemispheric stratigraphy (tephrostratigraphy) and may function as absolute age markers (Lowe, 2011), making possible the construction of accurate chronologies. Under certain atmospheric conditions, Saharan dust may reach northern latitudes so it can also be preserved in ombrotrophic bogs. The identification of its geochemical signature in European peat records is another example of long-distance sources of mineral dust to peatlands (e.g., Kylander et al., 2005; Le Roux et al., 2012) and is useful to infer changes in past atmospheric circulation (e.g., Kylander et al., 2005; De Vleeschouwer et al., 2009; Marx et al., 2011; Vanneste et al., 2015), which is important for modulating climate. Other geochemical imprints in peat can also be used to infer past climatic conditions. For example, variations in halogens or mercury content in peat records have also been successfully used to reconstruct past changes in climate (e.g., Martínez Cortizas et al., 1999, 2007; Biester et al., 2006).

Other "classical" sub-field of peat geochemistry is that related with the detection of past atmospheric metal pollution (e.g., Shotyk, 1996; Martínez Cortizas et al., 1997a, 1997b). Reviews for assessing past and recent atmospheric metal deposition using peat bogs have been presented by Glooschenko et al. (1986), Livett (1988), Shotyk (1996), Kylander et al. (2006) or Hansson et al. (2015). Environmental implications of heavy metal pollution, and particularly that related to lead emissions, became the object of increasing interest during the 1960s (e.g., Cannon and Bowles, 1962). However, peatlands' value for reconstructing past changes in metal atmospheric pollution was not fully exploited until the 1970s. Pioneer work of Rühling and Tyler (1968) using mosses for biomonitoring indicated that they contained small quantities of natural amounts of lead and that Pb concentrations principally reflected an influence of human activity. They measured moss samples across geographical (i.e., samples collected decreasing in distance to large population centres) and historical (i.e., samples collected from 1860 to 1968) grandients. Of relevant importance is also the earlier work of Lee and Tallis (1973) who outlined the possibilities of monitoring past and present concentrations of lead in the atmosphere by the chemical analysis of dated horizons in blanket peat deposits. Other early contributions are those of Aaby and Jacobsen (1978) and Martin et al. (1979). Later on, Oldfield et al. (1978) performed magnetic susceptibility measurements of ombrotrophic peat and found a marked increase in the magnetization of the peat in levels postdating the Industrial Revolution. Peat has a particularly high absorptive capacity for cations, especially heavy metal cations, so it can accurately reflect the extremes of environmental pollution to which it may be exposed (Livett et al., 1979). Although not all heavy metals are bound to peat with the same affinity, the basic premise underlying the method is that certain metals (particularly lead) remain virtually immobile once they are incorporated into peat that a time-sequence of heavy-metal incorporation is represented in the peat profile (Livett et al., 1979). However, vertical distributions of metal concentrations (including lead) in peat have been occasionally interpreted as resulting from at least partial vertical mobility or plant uptake (e.g., Aaby and Jacobsen, 1978; Damman, 1978; Pakarinen and Gorham, 1983; Pakarinen et al., 1983). In contrast, Farmer et al., (1997) found that, although fluxes of Pb for the past few hundred years are generally lower in peat than in lake sediments –pointing towards some post-depositional loss of Pb– in both cases the historical record of Pb pollution was retained. More recent research performed on peat pore waters, although consistent with some degree of mobility for various metals including lead, considered that the usefulness of peat monoliths as archives of past metal pollution will ultimately depend on whether the degree of mobility of the given metal will be small enough to preserve peaks in atmospheric deposition over time (Novak and Pacherova, 2008). In this sense, in a replicated, reciprocal peat 18-month transplant experiment between a heavily polluted and a relatively unpolluted peatland, Pb, Cu and Zn preserved their original vertical patterns at the host site, showing a high degree of immobility and indicating that their concentration profiles in peat are a reliable archive of temporal pollution changes with a wide pH range (2.5-5.8) (Novak et al., 2011). In fact, other works from the 1990s had already reported a very limited downward migration for Pb (e.g., Dumontet et al., 1990; Jones and Hao, 1993; Vile et al., 1999) and had demonstrated that millennial scale peat records from different locations across Europe (e.g., Brännvall et al., 1997; Kempter et al., 1997; Martínez Cortizas et al., 1997b; Weiss et al., 1997; West et al., 1997) showed a general agreement in temporal trends of lead pollution. Moreover, several studies had validated the record of metal accumulation in peat against moss monitoring (e.g., Weiss et al., 1999; Farmer et al., 2002; Steinnes et al., 2005), lake sediments (e.g., Brännvall et al., 1997; Farmer et al., 1997) or ice cores (e.g., Hong et al., 1994; Rosman et al., 2000; Schwikowski et al., 2004). Most research on metal pollution on peat cores has been done on bogs, but minerotrophic peatlands (fens) can also be used to trace atmospheric metal deposition (e.g., Shotyk et al., 1996, 1997; Monna et al., 2004a; Breitenlechner et al., 2010).

2.2.2.2. Organic geochemistry

As peat is mainly formed by partially decomposed plant remains, organic matter represents a large amount of its total dry weight. Organic peat geochemistry thus reflects the composition of the original peat-forming plant assemblage –which is itself dependent on air temperature and hydrology– and the subsequent transformation of the plant remains (McClymont et al., 2010). Decomposition of peat-forming vegetation is greatly affected by prevailing climatic conditions. One of the first approaches to peat organic matter decomposition was through the study of the degree of peat humification (DPH), i.e., humic acid formation during the degradation of plant material, which was interpreted as a proxy of past changes in wetness. Early methods for determining the degree of peat humification relied on visual inspection and squeeze properties such as the von Post's 10-point scale (von Post and Granlund, 1926) or the Troels-Smith's 5-point scale (Troels-Smith, 1955). Nowadays it is measured by colorimetric techniques based on light absorbance of alkali extracts. The colorimetric method was first formulated by Melin and Odén (1916) for characterising humus, and was further developed by and Springer (1938) and Souci (1938). Overbeck and Schneider (1940) first applied the colorimetric method to climate research on peatlands and demonstrated a general correspondence with the von Post´s scale. The colorimetric method was further spread by others (e.g., Bahnson, 1968; Aaby and Tauber, 1975; Aaby, 1976; Chambers, 1984; Blackford and Chambers, 1993; Borgmark, 2005). Total carbon/nitrogen ratios and carbon and nitrogen stable isotopes also reflect changes in peat decomposition so they have also been used as past climate indicators (e.g., Rosswall et al., 1975; Malmer and Nihlgård, 1980; Malmer and Holm, 1984; Kuhry and Vitt, 1996).

More recent techniques approaching peat decomposition, however, study variations in the molecular composition of the organic matter. The premise is that some compounds, such as aromatics or aliphatics, are more recalcitrant than others, like polysaccharides, so they are enriched in more decomposed peat, which is thought to be related to warmer/drier conditions. Pyrolysis gas chromatography mass spectrometry (Pyrolysis-GC-MS) provides semi-quantitatively data on a detailed molecular level whereas FTIR characterises qualitatively the main chemical classes in soil organic matter (carbohydrates, lignins, cellulose, lipids, proteins, etc.), through the vibrational characteristics of their structural chemical bonds. Pyrolysis-GC-MS has been recently used in palaeoclimate research (e.g., Buurman et al., 2006; Schellekens and Buurman, 2011; Schellekens et al., 2011) whereas FTIR has been successfully used on soils to describe, for example, the status of organic matter decomposition in different horizons (e.g., Haberhauer et al., 1998; Haberhauer and Gerzabek, 1999), and recently started to be used to infer peat decomposition (e.g Chapman et al., 2001; Artz et al., 2006; Silamikele et al., 2010; Broder et al., 2012; Biester et al., 2014) although, palaeoclimate interpretations are still limited. Among the major advantages of FTIR are the low cost, the easy sample treatment and the fact that it is non-destructive.

2.3. Studies using palynology and geochemistry: state of the art

The best interpretations of the peat geochemical record in the context of environmental change will likely come when geochemical and biological records are considered simultaneously (Bindler, 2006). Simpler combinations of geochemical and palynological approaches on peat records only used pollen data as a tool to verify or provide chronologies (e.g., Vile et al., 1995; Shotyk et al., 1996, 1997; Appleby et al., 1997), without a real multi-proxy integration. But later on, examples of real integration appear. Thus, by combining palynological and geochemical analysis, it becomes clear that peatlands can function as archives of both climate and human histories, including settlement, farming and land use, as well as ore mining and smelting (Görres and Frenzel, 1997). For example, the combination of lithogenic composition or ash content studies with pollen analysis is very valuable to study the relationship between soil erosion processes and human activities, such as agriculture and grazing (e.g., Bennett et al., 1992; Görres and Frenzel, 1993; Kremenetski, 1995; Hölzer and Hölzer, 1998; Huang and O'Connell, 2000; Vannière et al., 2003; Makohonienko et al., 2004; Hunt and Rushworth, 2005; Lawson et al., 2005; López-Merino et al., 2010; Martínez Cortizas et al., 2005; Zhao et al., 2007; Edwards et al., 2008; Schofield et al., 2010; Schofield and Edwards, 2011), or to infer climate-driven changes in dust deposition (e.g., Anderson and Smith, 1994; Kremenetski, 1995; Tipping, 1995; Mann et al., 2002; Kylander et al., 2007; De Vleeschouwer et al., 2009; Ruiz Pessenda et al., 2009; Yu et al., 2011). Elemental and isotopic analysis of metals linked to palynological research can be used to elucidate how mining and metallurgical activities affected vegetation cover or to deepen in possible synergies among both proxies (e.g., Mighall and Chambers, 1993; Küster and Rehfuess, 1997; Rosen and Dumayne-Peaty, 2001; Mighall et al., 2002b, 2006b; Monna et al., 2004a, 2004b; Martínez Cortizas et al., 2005; Jouffroy-Bapicot et al., 2006; Breitenlechner et al., 2010, 2013; Bindler et al., 2011; Pontevedra-Pombal et al., 2013; López-Merino et al., 2011, 2014) whereas humification or organic geochemistry approaches linked to palynology provide a contrasted information on past changes in climate (e.g., Tipping, 1995; McGlone and Wilmshurst, 1999; Ellis and Tallis, 2000; Magyari et al., 2001; Wilmshurst et al., 2002; Mauquoy et al., 2004; Langdon and Barber, 2005; Anderson, 2008; Lamentowicz et al., 2008).

Despite the above-mentioned multiple examples, the combined application of geochemistry and palynology to palaeoenvironmental research on peatlands still represents a small proportion on the available literature compared to the considerable body of published research in each of these disciplines independently. According to searches on the Web of Science ("Web of Science", 2015), which gives access to multiple databases that reference cross-disciplinary research, 2422 peat geochemistry papers and 1355 peat palynology

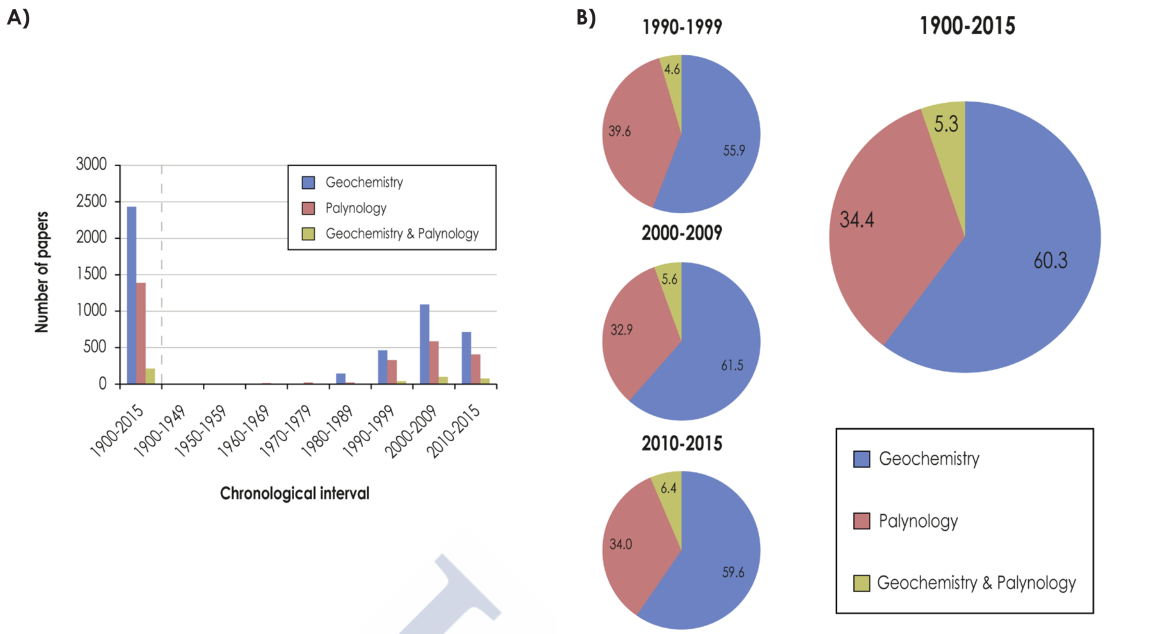

Figure 3. A) Number of papers published in the field of peat palaeoenvironmental research using geochemistry, palynology, or geochemistry and palynology together since 1900 and by decade from 1900. B) Percentage of papers published in the field of peat palaeoenvironmental research using geochemistry, palynology, or geochemistry and palynology together since 1900 and by decade from 1990. Detailed information on the used search fields is provided in *Annex I*.

papers have been published since AD 1900 (Figure 3). However, only 247 papers applying a multi-disciplinary approach using both geochemical and palynological analyses to peat records were published during the same period of time (detailed information on the used search fields is provided in *Annex I* - at the end of the section). Papers applying geochemistry and palynology together increased considerably since the 1990s, but this fact might well be due to a general increase in scientific production (Figure 3). Anyway, a slight upward trend is observed during the last decades. Publications approaching geochemistry and palynology on peat records at the 1990s represented 4.6% of peat geochemistry and peat palynological papers alone, at the 2000s 5.6% whereas in the 2010-2015 interval they represented a 6.4% (Figure 3).

Annex I

Peat geochemistry papers: based on the appearance of the terms "dust" or "soil erosion" or "pollution" or "humification" or "geochemistry" and "peat" or "mire" or "peatland" and the absence of "pollen" and "palynology".

Peat palynological papers: based on the appearance of the terms "pollen" or "palynology" and "peat" or "mire" or "peatland" and the absence of "dust", "soil erosion", "pollution", "humification" and "geochemistry".

Papers applying both geochemistry and palynology: based on the appearance of the terms "dust" or "soil erosion" or "pollution" or "humification" or "geochemistry" and "pollen" or "palynology" and "peat" or "mire" or "peatland".

2.4. Aim and Objectives

The aim of the PhD work presented here is to explore how geochemistry and palynological approaches on peatlands, particularly when considered together, can help in the understanding of past environmental changes. To achieve this general aim, different types of peatlands (ombrotrophic and minerothrophic), environments (boreal and temperate zones) and Holocene chronological intervals (although with special attention to the Late Holocene) have been studied. In particular, the focus has been placed on shedding light on the following specific objectives:

1) how dust transport/soil erosion has been affected by anthropogenic changes in land use versus climate forcings?;

2) how past changes in climate affected organic matter decomposition, vegetation change and other aspects of the environment?, and

3) how past mining and metallurgical activities affected atmospheric metal pollution? Is there any link between mining and metallurgy activities and forest cover decrease?

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3. PUBLICATIONS

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3.1. Paper I

Silva-Sánchez, N., Martínez Cortizas, A. and López-Merino, L. (2014) **Linking forest cover, soil erosion and mire hydrology to late-Holocene human activity and climate in NW Spain**. *The Holocene* 24, 714–725.

JRC IF (2014): 2.283; 55/175, Q2 in Geosciences, Multidisciplinary

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Research paper

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Linking forest cover, soil erosion and mire hydrology to late-Holocene human activity and climate in NW Spain

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Abstract

Forest clearance is one of the main drivers of soil erosion and hydrological changes in mires, although climate may also play a significant role. Because of the wide range of factors involved, understanding these complex links requires long-term multi-proxy approaches and research on the best proxies to focus. A peat core from NW Spain (Cruz do Bocelo mire), spanning the last ~3000 years, has been studied at high resolution by physical (density and loss on ignition (LOI)), geochemical (elemental composition) and palynological (pollen and non-pollen palynomorphs) analyses. Proxies related to mineral matter fluxes from the catchment (lithogenic tracers, *Glomus* and *Entorrhiza*), rainfall (Bromine), mire hydrology (HdV-18), human pressure (*Cerealia*-type, nitrophilous taxa and coprophilous fungi) and forest cover (mesophilous tree taxa) were the most useful to reconstruct the evolution of the mire and its catchment. Forest clearance for farming was one of the main drivers of environmental change from at least the local Iron Age (~2685 cal. yr BP) onwards. The most intense phase of deforestation occurred during Roman and Germanic times and the late Middle Ages. During these phases, the entire catchment was affected, resulting in enhanced soil erosion and severe hydrological modifications of the mire. Climate, especially rainfall, may have also accelerated these processes during wetter periods. However, it is noteworthy that the hydrology of the mire seems to have been insensitive to rainfall variations when mesophilous forest dominated. Abrupt changes were only detected once intense forest clearance commenced during the Iron Age/Roman transition (~2190 cal. yr BP) phase, which represented a tipping point in catchment's ability to buffer impacts. Overall, our findings highlight the importance of studying ecosystems' long-term trajectories and catchment-wide processes when implementing mire habitat protection measures.

Keywords

catchment hydrology, deforestation, geochemistry, HdV-18, non-pollen palynomorphs, pollen, principal components analysis, soil erosion

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Introduction

During the Holocene, and more specifically in the late Holocene, human activities have played, directly or indirectly, an increasing role in the evolution of terrestrial ecosystems. One of the key processes is deforestation (Williams, 2000). Evidence of small-scale human disturbance to woodland cover by hunter–gatherers has been already detected during the Mesolithic (Brown, 1997; Innes and Blackford, 2003; Innes and Simmons, 1988; Schuldenrein, 1986; Siiriäinen, 1980; Smith, 1970; Williams, 2000). More widespread forest clearance for cultivation and grazing has resulted in land degradation from at least the Neolithic onwards (Carrión et al., 2010a; Mazoyer and Roudart, 2006; Starkel, 2005). Late-Holocene climate change, although weaker in amplitude than the dramatic shifts that occurred in the last glacial cycle, has been shown to be larger and more frequent than commonly recognized (Mayewski et al., 2004), and has also influenced environmental change.

Soil erosion is becoming one of the most significant geomorphic processes acting at the Earth's surface (Pimentel, 2006; Wilkinson and McElroy, 2007). Soil erosion is largely caused by human activity and climate. Rain and wind determine climatic erosivity, whereas air temperature controls the occurrence of frost, snowfall, snowmelt and soil moisture, the latter affecting the susceptibility to soil erosion (Boardman and Poesen, 2006). However, today in Europe, the principal causes of soil erosion are agricultural practices, deforestation, overgrazing and construction, all of which are strongly influenced by land use and policy (Boardman and Poesen, 2006; Grimm et al., 2002). Globally, moderate to severe soil degradation affects almost 2000 million hectares of arable and grazing land, an area larger than that of the United States and Mexico combined (FAO, 1995), and has become a serious public health issue (Pimentel, 2006), resulting in increased awareness among scientists and policy-makers. To fully evaluate the importance of soil erosion, a long-term perspective is needed, as it could provide insights on how ecosystems shift in response to soil erosion and the relative contributions of climate and human transformations. Significant soil erosion as a consequence of human activities and climate has been detected in many parts of the world. Examples include the early Neolithic in the Peloponnesus Peninsula, where high sedimentation rates

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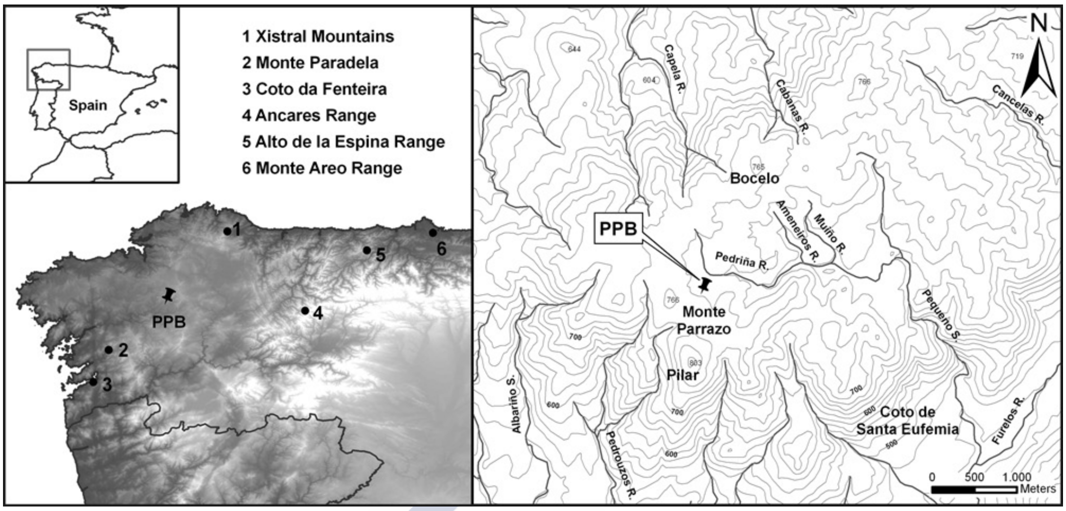

Figure 1. Location of PPB core in Cruz do Bocelo mire (NW Spain) and other places discussed in the text.

suggest that Holocene soil erosion was triggered by human activity and amplified by precipitation (Fuchs, 2007; Fuchs et al., 2004) and from the late Bronze Age in the Drama Basin of Macedonia, where deforestation and agricultural activities made the river system less resilient to natural soil erosion and more sensitive to small changes in climate (Lespez, 2003).

Most of the long-term studies on soil erosion have been undertaken on polycyclic, colluvial or alluvial soils (Benito et al., 1991; Costa Casais et al., 2009; Dreibrodt et al., 2009; Fuchs, 2007; Fuchs et al., 2004; Kaiser et al., 2007; Kirch, 1996; Lespez, 2003; Martínez Cortizas et al., 2000, 2009b; Rochette Cordeiro, 1992; Van Andel et al., 2013; Zádorová et al., 2013). However, peatlands and lakes can also be used to infer erosion as they are good archives of dust/sediment fluxes (Foster et al., 2000; Giguet-Covex et al., 2011; Hölzer, 1998; Le Roux et al., 2012; Lomas-Clarke and Barber, 2004; López-Merino et al., 2010; Martínez Cortizas et al., 2005; Schofield et al., 2010; Shotyk et al., 2001; Simonneau et al., 2013). Moreover, they offer ideal conditions for the preservation of geochemical and palynological proxies to infer environmental changes.

Most palaeoenvironmental reconstructions, especially geochemical studies, use ombrotrophic mires, in which inorganic inputs are derived exclusively from atmospheric deposition (Clymo, 1987). Although less studied, minerotrophic mires can also be used to reconstruct soil erosion at catchment scale since their inorganic inputs are commonly derived from rock–water interactions in the surrounding soils and underlying sediments (Shotyk, 2002). Moreover, they also offer suitable conditions to evaluate variations in water run-off because of disturbances in their catchment. Understanding how disturbances can affect mires, which maintain high levels of biodiversity and are important carbon sinks, could provide additional insights in order to manage such sensitive ecosystems and to prevent further damage.

In this study, we analyse the palaeoenvironmental evolution of a minerotrophic mire located in NW Spain, focusing on the link between climate, human activities, forest evolution, soil erosion and changes in local hydrology. Previous palaeoenvironmental studies in the area performed on peat records mainly focused on vegetation change and peatland inception (Aira Rodríguez et al., 1994; Taboada Castro et al., 1993, 1996). Here, we present a higher resolution multi-proxy study combining physical, geochemical and palynological analyses, as well as a multivariate statistical approach aiming to (1) decipher how late-Holocene anthropogenic transformations and climate change affected both the physical and ecological evolution of the mire's catchment, at both regional and local scales, and (2) get insights into the behaviour of specific palynological and geochemical proxies for soil erosion and peatland moisture.

Material and methods

Study area and sampling

Cruz do Bocelo (42°59′N; 8°01′W; 730 m a.s.l.) is a minerotrophic mire located in the western side of the *O Bocelo* range (Melide, NW Spain; Figure 1), overlying a geological substratum of cataclastic deformed orthogneiss with granitic composition (García Salinas, 1978). The climate is temperate humid, with average annual temperatures of 12–13°C, and annual precipitation of 1600–1800 mm (Martínez Cortizas and Pérez Alberti, 1999). Present land use consists in an association of pasture, horticultural crops, scrubland (*Ulex*, *Erica* and *Cytisus* species) and afforestations of *Pinus pinaster*, *Eucalyptus globulus* and, to a lesser extent, *Betula*, with scattered patches of *Quercus robur* and *Castanea sativa*. The mire is used for grazing cattle and disturbed on one side by the recent construction of a road. Surface vegetation is mainly *Sphagnum*, *Carex, Drosera* and Juncaceae species, with *Calluna vulgaris, Erica tetralix* and *Ulex* spp. in drier and more degraded areas.

A 140-cm-long core (PPB) was collected in 2007 using Waardenar and Russian corers. Below 130 cm, the sediment was a mixture of gravel and sand. The extracted peat sections were protected in plastic guttering and stored under cold conditions (4°C) prior to laboratory analyses. The core was sub-sampled into 2-cm-thick slices, obtaining 70 samples. Sub-samples were taken to measure peat bulk density (BD) and loss on ignition (LOI) and for palynological analysis. The remaining material was dried at 105°C and milled to very fine powder prior to elemental composition analyses.

Physical, geochemical and palynological analyses

BD was determined after drying (105°C) peat plugs to constant weight. The same plugs were then heated at 550°C for 5 h for LOI. Additionally, the concentrations of major and minor (Si, Al, Ti, Ca, K and S), trace lithogenic (Rb, Sr, Zr and Th), redox-sensitive

Table 1. Results of [14]C dating, showing calibrated age ranges (2σ) in cal. yr BP.

Sample	Depth (cm)	Lab code	^{14}C age (BP)	Age (cal. yr BP)	Relative area (%)
B10	18–20	β-259236	110 ± 40	11–150	61.6
B17	32–34	β-259237	340 ± 40	309–487	100
B32	62–64	β-259240	1350 ± 40	1228–1335	81.8
B46	90–92	β-259241	2070 ± 40	1946–2144	94.5
B53	104–106	β-259235	2260 ± 40	2155–2271	60.4
B63	124–126	β-259238	2510 ± 40	2459–2743	94.2
B70	138–140	β-259239	2920 ± 40	2957–3173	87.7

elements (Fe and Mn) and halogens (Cl and Br) were determined using x-ray fluorescence dispersive EMMA-XRF analysers (Cheburkin and Shotyk, 1996). The instruments are hosted at the RIAIDT facility of the University of Santiago de Compostela. The calibration was performed using 26 certified reference materials for organic matrices consisting of tree and vegetable leaves (SRM1515, SRM1547, SRM1575, SRM1570a, SRM1573a, SRM1575a, BCR62), coals (SRM1635, SRM1632b, LECO501020, LECO502433, LECO502435), coke (SRM2718, SRM2719), wheat flour (SRM8436, SRM8437, SRM8438), other plant derivates (SRM8412, SRM8432, SRM8433, BCR129, BCR60), animal derivates (SRM8414, BCR150) and peat (NJV942, NIMT/UOE/FM/001). For the inorganic samples of the base of the core, the calibration included 36 certified reference materials, consisting of rocks and minerals (GSR6, SG1a, SRM1d, SRM278, SRM2780, SRM688, 5365, AGV1, DTS1, SRM607, SRM70a), sands and clays (SRM1413, SRM81a, BCSCRM348, SRM679, SRM97b, SRM98b), ashes (SRM1633a, SRM1633b, SRM2690, SRM2691), soils and sediments (SO2, SO3, SRM2586, BCRCRM277b, LKSD1, LKSD2, MAG1, PACS1, RM8704, SRM1646, SRM1646a, SRM1944, SRM2702, SRM2703) and industrial sludge (SRM2782). Quantification limits were as follows: Si (0.05%), Ti and Fe (0.002%), Al (0.002% for organic; 0.2% for inorganic matrices), Ca (0.002%; 0.01%), K (0.002%; 0.05%), S (0.009%; 0.03%), Zr (0.5 µg/g), Th (2.5 µg/g), Rb (0.5 µg/g; 5 µg/g), Sr (0.5 µg/g; 5 µg/g), Mn (5 µg/g; 30 µg/g), Br (0.5 µg/g; 2 µg/g) and Cl (40 µg/g; 350 µg/g).

The classic methodology (Fægri and Iversen, 1989) with concentration in heavy liquid (Goeury and Beaulieu, 1979) was applied to obtain pollen, spores and non-pollen palynomorphs (NPP). Laboratory work was performed at the Archaeobiology Laboratory of the CCHS (CSIC, Madrid). Pollen counting was conducted at 400× magnification, and at least 500 terrestrial pollen grains (trees, shrubs and herbs) were counted and used for the total land pollen (TLP) sum. Hydro-hygrophytes, fern spores and other NPP counts were excluded from the TLP, although their values are also expressed as percentages of TLP. Identification of pollen types and fern spores was achieved with the aid of keys and atlases (Fægri and Iversen, 1989; Moore et al., 1991; Reille, 1999), while NPP classification follows the nomenclature proposed by the Hugo de Vries (HdV) Laboratory (University of Amsterdam). Microfossil diagrams were drawn using Tilia (Grimm, 1992, 2004). The two basal samples (140–136 cm) were palynologically sterile because of the abundance of mineral matter.

Numerical methods

When dealing with a large set of variables, the use of multivariate statistical approaches help summarize common patterns of variation beyond the raw data and to get insights into the underlying environmental factors.

For geochemical data, principal component analysis (PCA; Hotelling, 1933; Pearson, 1901) was applied using SPSS 15.0, in

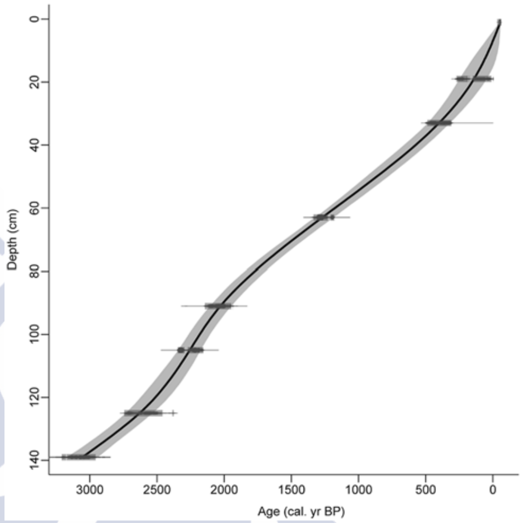

Figure 2. Age–depth model of Cruz do Bocelo mire, fitted with a smooth-spline (smooth = 0.2) using Clam.R (Blaauw, 2010). Blocks in the radiocarbon ages represent the 95% confidence level in radiocarbon dates calibration, and the grey-shaded area the highest density ranges.

correlation mode and by applying a varimax rotation. Prior to analysis, the data were standardized (*Z*-scores) to avoid scaling effects and obtain average-centred distributions (Eriksson et al., 1999). The square of the factor loadings, multiplied by 100, was used as a measure of the explained variance of each variable by each principal component.

For palynological data, constrained incremental sum-of-squares (CONISS) cluster analysis (Grimm, 1987) was performed after applying a square-root transformation and Edwards and Cavalli Sforza's chord-distance dissimilarity measure to all taxa counts in order to delineate pollen assemblage zones.

Radiocarbon dating and chronology

Seven peat samples were sent to Beta Analytic Inc. (Miami, USA) where they were dated by AMS after an acid-wash pretreatment. The obtained ^{14}C dates (Table 1) were calibrated using the IntCaL09.^{14}C curve (Reimer et al., 2009), and an age–depth model was built using Clam.R 1.0 (Blaauw, 2010). The best fit was provided by a smooth-spline solution with a smooth factor of 0.2 (Figure 2). Ages are expressed as calibrated years before present (cal. yr BP) at 2σ level and are set to the year of sampling (2007) by adding the difference from 1950 to all estimated ages. According to this model, the 140-cm sequence represents the last ~3000 cal. yr.

Results

Geochemical record

LOI, BD and elemental composition (Figure 3) variations are summarized in three principal components (Figure 4), which explain 84.3% of the total variance. PC1 explains 48.8% of the variance. Aluminium, Rb, Ti, Sr, K, Si, Zr and Th show high positive loadings, BD has a moderately positive loading, and LOI and S have a high negative and a moderate negative factor loading, respectively. The high positive loadings of the lithogenic elements and LOI are indicative of the amount of mineral matter in the peat. Even variables with moderate loadings support this interpretation. One of the main properties controlling peat BD (positive loading) is mineral matter content, and S (negative loading) is a biophilic and organically bound element. The record of factor scores (Figure 4) indicates that the amount of mineral matter is highest at the bottom part of the core (>130 cm) probably because of its proximity to the inorganic basal sediment. Seven sections with higher inputs of inorganic material (E1–E7; Figure 4) occur in the remainder of the core, and they may reflect soil erosion episodes.

PC2 explains 19.2% of the variance. Cl, Fe and Mn show high positive loadings, and Br shows moderate positive loading. Factor scores are negative from 140 to 118 cm, and then remain around zero up to 8 cm when their values shift sharply to become positive. Fe and Mn are redox-sensitive elements, while Cl and Br are sourced from the oceans (Kabata-Pendias and Pendias, 2001). Although they share some variance, this is unlikely to be related to a unique source/environmental factor, and it seems to be strongly influenced by their high values at the top of the core. The surface enrichment in Fe and Mn is probably related to oxic conditions in the upper sections of the mire which are more favourable conditions for oxidized, less mobile forms of these elements to form (Chesworth et al., 2006). Halogen accumulation in peat and soils is dependent on atmospheric wet deposition (Johanson et al., 2003), enzymatic halogenation of the organic matter (Biester et al., 2006) and dehalogenation under reducing conditions (Van Pée and Unversuch, 2003).

PC3 explains 16.3% of the variance, and it reflects the inverse relationship between biophilic elements such as Ca and S (high positive factor loadings) and Br (moderate negative loading). The record of the scores can be divided in three sections: >90 cm, with positive scores (except from one sample at 129 cm); 90–42 cm, with scores around zero; and <42 cm, with negative scores.

Most of the variation of Br is explained by PC2 and PC3, but a significant part (18%) remains unexplained (Figure 4). We interpret that PC2 and PC3 are related to the processes controlling halogenation and dehalogenation within the peat. The remaining, unexplained, variation is most likely related to atmospheric wet deposition because there is a good chronological match between the residual Br variation (after eliminating the effect of PC2 and PC3) in the PPB core and previous reconstructions of humidity changes in NW Spain (Mighall et al., 2006 and references therein; see Figure 7).

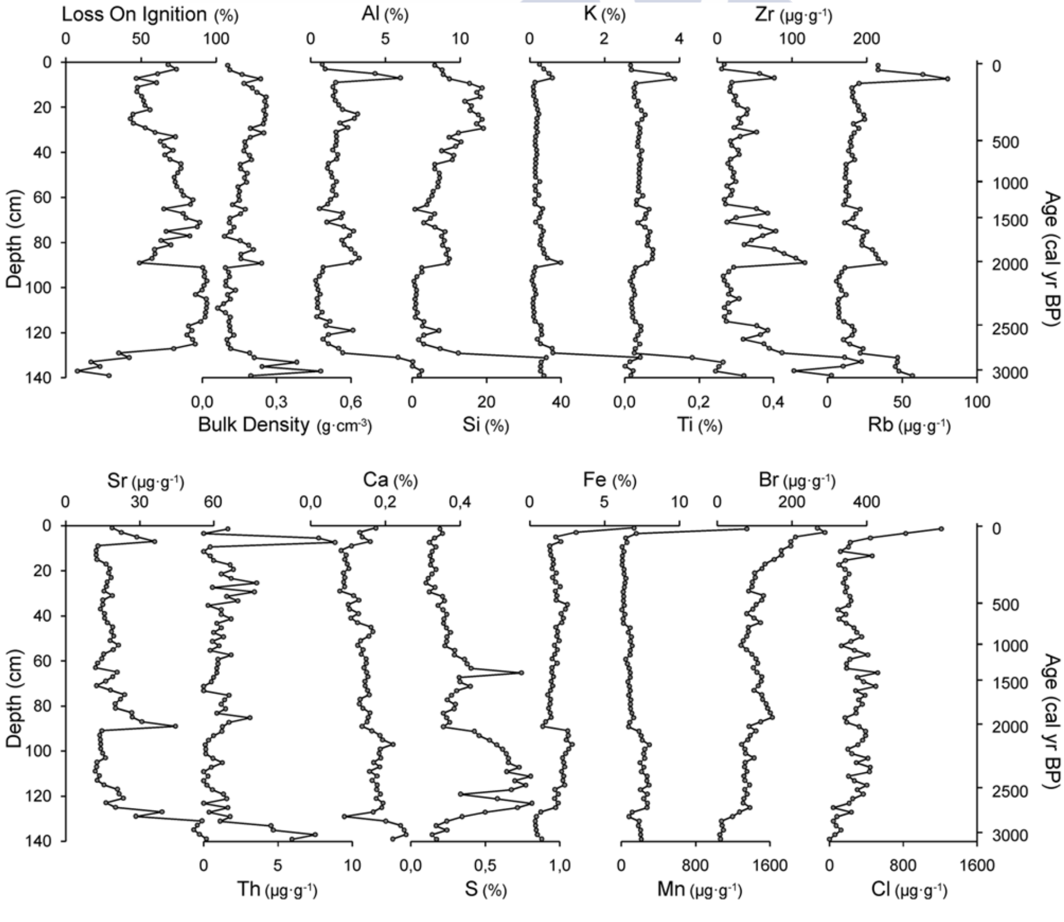

Figure 3. Geochemical results (physical properties and elemental composition) of the PPB core sampled at Cruz do Bocelo mire.

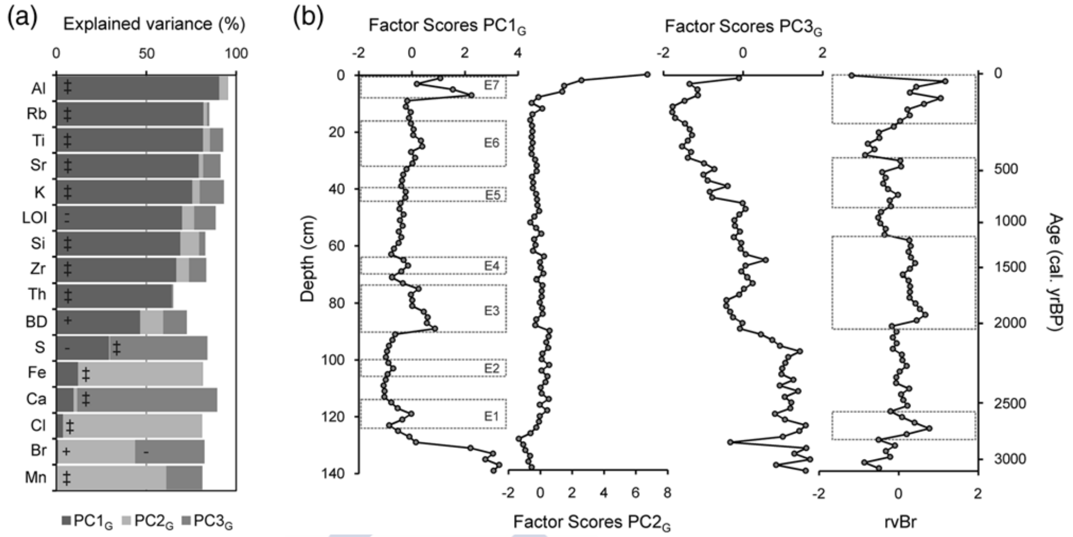

Figure 4. PCA results of geochemical data (physical properties and elemental composition). (a) Percentage of explained variance (square of factor loadings × 100) of the principal components extracted. (b) Records of factor scores of the extracted principal components. '‡': high positive loadings (>0.7); '+': moderate positive loadings (0.5–7); '=': high negative loadings (<−0.7) and '-': moderate negative loadings (>−0.7 and <−0.5).
PCA: principal component analysis; LOI: loss on ignition; BD: bulk density.

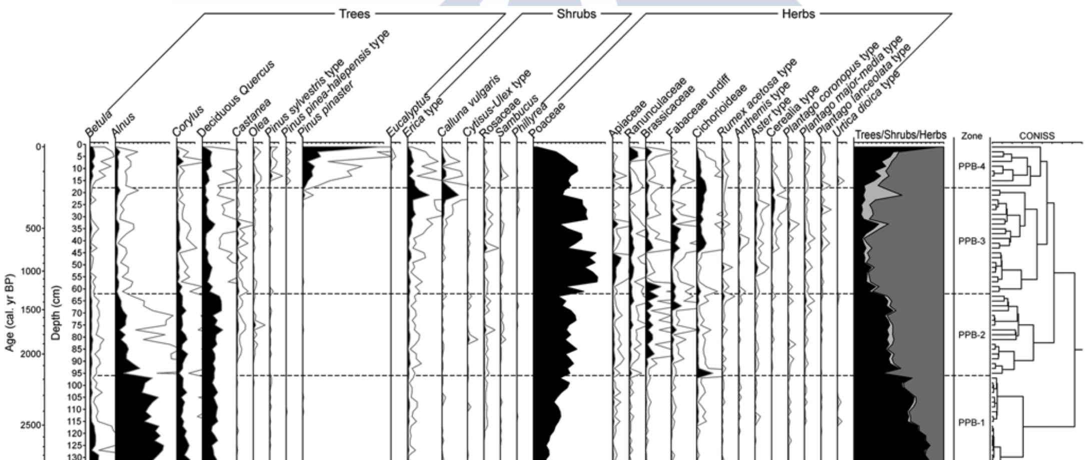

Figure 5. Synthetic palynological diagram of the Cruz do Bocelo mire showing the results for regional types (trees, shrub and herbs). Exaggeration curves have a factor of 5.
CONISS: constrained incremental sum-of-squares.

Palynological record

The regional palynological signal (Figure 5, the complete diagram in supplementary information, Supplementary Figure SI1a, available online) is characterized by the transition from the dominance of arboreal pollen (AP), particularly mesophilous tree taxa, to herbs, indicative of a more open landscape. Shrub percentages remain low throughout the sequence and other trees, like *Pinus*, only become relevant because of recent afforestation. The local palynological signal (Figure 6; Supplementary Figure SI1b, available online) has relatively stable contributors like Cyperaceae and *Filicales monolete* and trilete. The record is also characterized by frequent and intense compositional fluctuations affecting *Pteridium aquilinum*, HdV-18, coprophilous fungi – such as *Sordaria*-type, *Sporormiella*-type and *Cercophora*-type and *Entorrhiza* (HdV-527).

Four palynological zones were identified according to CONISS. *PPB-1* (136–96 cm; 3120–2175 cal. yr BP) is characterized by high percentages of AP (68.9 ± 9.5%), especially *Alnus,*

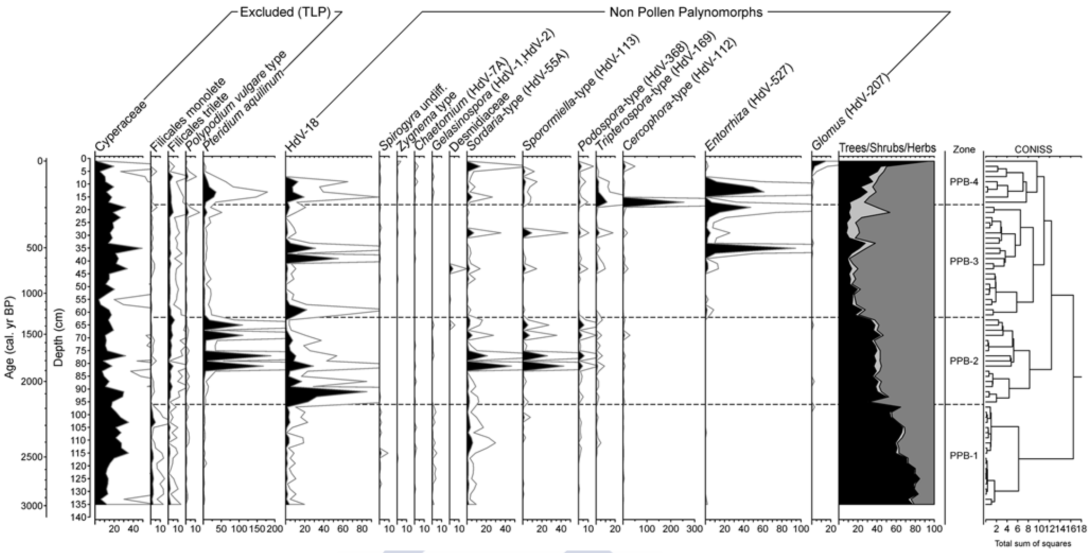

Figure 6. Synthetic palynological diagram of the Cruz do Bocelo mire showing the results for local types (excluded from the total land pollen sum and non-pollen palynomorphs). Exaggeration curves have a factor of 5.
CONISS: constrained incremental sum-of-squares.

Quercus, Corylus and *Betula*. Two phases of forest disturbance were recorded: at 126–110 and 106–98 cm depth. The first one mainly affected *Alnus* and *Betula*, while the second one just *Alnus*. Poaceae is well represented. Trace amounts of *Cerealia*-type is recorded at the bottom of the zone. Cyperaceae is the most abundant hydro-hygrophyte taxa, indicating a well-developed mire vegetation. The coprophilous fungi *Sordaria*-type occurs throughout the zone, increasing its percentages from 114 cm depth upwards. The mycorrhizal fungus *Glomus* is present at 94–96 cm depth. It has been often associated to erosion events (Anderson et al., 1984; Argant et al., 2006; Van Geel, 2001; Van Geel et al., 1989, 2003), since their spores may come from the soils of the catchment. However, peatlands are suitable environments for plants mychorrhized by *Glomus* (Kołaczek et al., 2013), so its presence may also reflect that type of association.

PPB-2 (96–62 cm; 2175–1295 cal. yr BP) is characterized by a major shift from a well-forested environment to a more open one. Mesophilous tree taxa, although still maintaining considerable values (38.1 ± 4.7%), decrease as Poaceae, and other herbaceous taxa such as Apiaceae, Ranunculaceae, Brassicaceae, Fabaceae and Cichorioideae all increase in representation. Percentages of cultivated trees such as *Castanea* and *Olea* increase in this zone. *Cerealia*-type increases its presence within this zone, but it never exceeds 1% TLP, while *P. aquilinum* and *Sordaria*-type, *Sporormiella*-type and *Podospora*-type show several peaks at 81, 77, 69 and 65 cm depth. HdV-18 also increases representation. Mighall et al. (2006) used HdV-18 as a proxy of past rainfall changes in an ombrotrophic peatland in the Xistral Mountains. However, Cruz do Bocelo is minerotrophic, so water supply not only depends on rainfall but also on catchment run-off. *Glomus* is present at 86–88 and at 64–66 cm depth.

In *PPB-3* (62–18 cm; 1295–185 cal. yr BP), Poaceae reaches its maximum percentage for the PPB record. Grassland is the dominant type of vegetation as herbs represent a 77.5 ± 10%, while mesophilous pollen taxa are reduced to 13.6 ± 5.3%. *Cerealia*-type, *Plantago* spp. and nitrophilous taxa such as Cichorioideae, *Anthemis*-type and *Aster*-type increase in values. By the end of the zone, *Erica*-type and *C. vulgaris* increase in representation. Among NPP, coprophilous fungi such as *Sordaria*-type, *Sporormiella*-type, *Podospora*-type and *Tripterospora*-type, as well as *Entorrhiza*, show several peaks. *Entorrhiza* species are parasites on a variety of plants (Vánky, 1994), and their basidiospores have been related to clay sedimentation environments (Van Geel et al., 1983). *Glomus* is present at 36–38 and at 32–34 cm depth. HdV-18 shows an increase at the beginning of the zone, which occurs simultaneously with a decrease in mesophilous pollen taxa, and two peaks centred at 39 and 35 cm depth.

PPB-4 (<16 cm; <185 cal. yr BP) is characterized by a rapid increase in *P. pinaster*, a species that, like *Eucalyptus*, has been regularly planted since the second half of the 19th century in NW Iberia. *Eucalyptus* is entomophilous, and therefore only present in small percentages. *P. aquilinum* and *Sordaria*-type, *Sporormiella*-type, *Podospora*-type, *Tripterospora*-type and *Cercophora*-type abundance are indicative of continued use of grasslands for grazing. Moreover, *Entorrhiza* and *Glomus* show also increase during this zone.

Discussion

Chronology of environmental changes

Bronze and Iron Ages: moderate human pressure. Mesophilous forest was most widespread during this phase (PPB-1). On a local scale, any of the changes in rainfall (humidity indices, Figure 7) has had little observable impact on mire hydrology (HdV-18), probably because the forest acted as a buffer. Nevertheless, the presence of *Cerealia*-type (Figure 7) at the bottom of the sequence reveals that cultivation took place from at least the late Bronze Ages, although late Neolithic and early Bronze Age ceramics, lithic industries and megalithic burials (tumuli and dolmens) from the area attest to an even earlier phase of human occupation (Acuña Castroviejo and Mejide Cameselle, 1991; Criado Boado, 1991; Prieto Martínez, 1995). First evidence of deforestation in the PPB core occurs during the Iron Age (at ~2685–2400 cal. yr BP and ~2310–2220 cal. yr BP), when the increase in coprophilous fungi and/or nitrophilous taxa, indicative of animal husbandry, coincides with a slight decline in mesophilous forest. Contemporary increases in peat mineral matter content (PC1; E1: ~2640–2470 cal. yr BP and E2: ~2310–2250 cal. yr BP) suggest

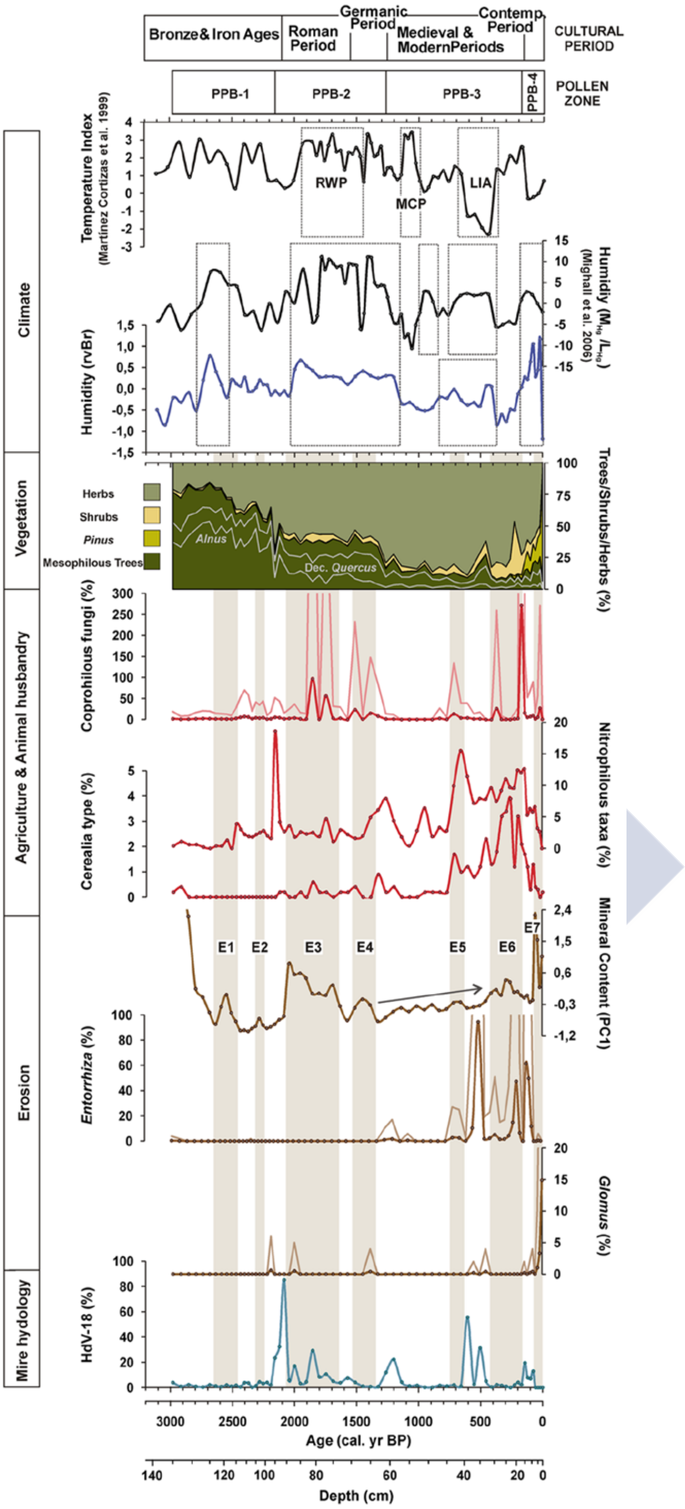

Figure 7. Chronology of the main environmental changes reflected by the Cruz do Bocelo records. Nitrophilous taxa = *Anthemis*-type + *Asphodelus albus*-type + *Aster*-type + Cardueae + Cichorioideae + *Rumex acetosa*-type + *Urtica dioica*-type; Coprophilous fungi = *Cercophora*-type + *Podospora*-type + *Sordaria*-type + *Tripterospora*-type + *Sporormiella*-type; PC1 (mineral content): we have avoided the representation of the most mineral samples near the substrate in order to amplify changes in the peat section of the core.
E1–E7: main erosion phases inferred from the geochemical record; RWP: Roman Warm Period; MCA: Medieval Climate Anomaly; LIA: Little Ice Age.

the inception of soil erosion by human activities during this early disturbance phase. While both forest disturbances have a similar magnitude, it is noteworthy that E2, which occurred during drier conditions (humidity indices; Figure 7), is less pronounced than E1, which happened during a wetter phase. The transition between the local Bronze and Iron Ages is considered to be a critical phase of changes in the exploitation of resources in NW Iberia (Martínez Cortizas et al., 2009a). During this period, evidence of soil erosion and acidification is found in many soil sequences in NW Spain (e.g. Benito et al., 1991; Costa Casais et al., 2009; Martínez Cortizas et al., 2000, 2009b). In some cases, these changes are accompanied by prominent charcoal layers indicating that fire was used to manage the forest. Soil erosion was already of concern for humans from at least the mid-Bronze Age. Although there are issues with regard to the dating of agrarian terraces, the first generation of man-made terraces date to ~3300 cal. yr BP in the Saa Valley (Martínez Cortizas et al., 2009a), and an analogous Iron Age structure was found in Castro de Follente (López-Sáez et al., 2009).

From Roman to late Middle Ages: mesophilous forest falls down. The most dramatic environmental change occurred at the transition from the Iron Age to the Roman Period (PPB-1/PPB-2 boundary). It involved changes at both a regional and local scale. Mesophilous forest suffers another large decline (mesophilous trees sum down to 43%) in a short period of time (~2190–2160 cal. yr BP) in favour of grassland. *Alnus* is the most affected tree. Simultaneous increases in coprophilous fungi and nitrophilous taxa link this decline to grazing. A dramatic increase in HdV-18 points to a higher mire water level. The presence of *Glomus* suggests soil erosion, and a slight increase in mineral matter (PC1) points to a disturbance phase of fairly modest intensity.

A short-lived period of forest recovery is detected (~2120 cal. yr BP). Thereafter, deforestation was more or less continuous from Roman times until the late Middle Ages (~660 cal. yr BP), characterized by two major phases of forest clearance: the first during Roman times (~2120–1750 cal. yr BP) and the second during the Germanic Period (~1510–1260 cal. yr BP). These phases are synchronous with the expansion of grassland and both grazing and cultivation. Despite the overall decrease in mesophilous forest, the percentages of *Olea* and *Castanea* increased. This could be related to warmer temperatures (Figure 7), especially in the case of *Olea*, although the increased presence of the abovementioned anthropogenic indicators does not rule out the possibility that *Olea* and *Castanea* were deliberately managed.

Deforestation during Germanic times represented a tipping point in the history of the mesophilous forest, as its previous importance would never be retained. Analogous responses found in other pollen records of NW Spain indicate that the irreversible decline in mesophilous forest was part of a wider process. Forest declines were found at ~1500 cal. yr BP in a soil sequence in Monte Paradela (Carrión et al., 2010b; Kaal et al., 2011; López-Merino et al., 2012); at ~1400 cal. yr BP in Pena da Cadela and Borralleiras da Cal Grande, two ombrotrophic mires located in the Xistral Mountains (Martínez Cortizas et al., 2005; Mighall et al., 2006); at ~1300 cal. yr BP in Monte Areo, a mire located in the Monte Areo Range (López-Merino et al., 2010); and at ~1200 cal. yr BP in Suárbol bog (Muñoz Sobrino et al., 1997) and at La Molina mire (López-Merino et al., 2011), located in the Ancares and in the Alto de la Espina Ranges, respectively (Figure 1). Thereafter, from ~1260 to ~660 cal. yr BP, pollen of taxa associated with mesophilous forest was at their lowest level (14.6 ± 4.1%). In contrast to other NW Iberian sequences (Allen et al., 1996; López-Merino et al., 2010; Martínez Cortizas et al., 2005; Mighall et al., 2006; Muñoz Sobrino et al., 1997), in the O Bocelo Range, no abrupt reductions in forest cover seem to have occurred. However, a further, slight, deforestation was recorded for the end of the Middle Ages (~710–600 cal. yr BP) at Cruz do Bocelo.

Large increases in the mineral content of the peat (PC1), as well as occasional rises in *Glomus* abundance, indicate severe soil erosion events in the catchment related to forest clearance during both the Roman Period (E3: ~2040–1690 cal. yr BP) and Germanic Period (E4: 1510–1390 cal. yr BP). During Medieval times, mineral inputs (PC1) to the mire gradually increased, culminating in E5 (~710–660 cal. yr BP).

Previous high-resolution studies of soil erosion and its link to forest evolution in NW Iberia (Martínez Cortizas et al., 2005; Xistral Mountains) found that forest clearances during Neolithic, Metal Ages, Roman, Germanic and Medieval times resulted in enhanced fluxes of mineral matter to mountain bogs. These chronologies are quite similar to those found at Cruz do Bocelo mire. However, regional differences are suggested when comparing the relative magnitude of each erosive phase. Erosion during Roman and Germanic times seems to have been more severe in the Bocelo range than in the Xistral Mountains. While medieval soil erosion seems to have been most relevant over the last ~5000 years in the Xistral Mountains, no similar record was observed at O Bocelo, suggesting that human transformation of the landscape varies by region and with altitude across NW Iberia.

Changes in regional vegetation and farming activities between ~2120 and ~600 cal. yr BP also affected the ecological evolution of the Cruz do Bocelo mire. During Roman and German phases of forest decline, high and abrupt increases in HdV-18 and *P. aquilinum* occurred. *P. aquilinum* has been associated with temporary woodland recession as it holds a pivotal role in succession (Marrs et al., 2000) and quickly invades perturbed sites (Ouden, 2000). However, its presence during this period and the good agreement with increases in coprophilous fungi may indicate successional changes on the mire surface because of cattle trampling. Moreover, increases in HdV-18 indicate that the tree cover loss would have decreased water retention in the catchment leading to higher superficial run-off and wetter conditions in the mire; this was probably intensified by the higher rainfall detected during this period (Figure 7).

'Little Ice Age' and contemporary human impact. A change in the trend between accelerated forest reduction and soil erosion occurred between ~605 and ~460 cal. yr BP. Evidence for enhanced soil erosion during this time includes increases in *Glomus* and *Entorrhiza*, the gradual increase in the mineral content of the peat (PC1) and the rise in silicon and LOI (Figure 3; 32–40 cm), which may reflect enhanced inputs to the mire. This appears to be the only soil erosion event which is not associated with a decrease in the mesophilous forest. It is chronologically framed within the cooler and more humid conditions of the 'Little Ice Age' (LIA), and it is probable that climate had a major influence on this episode of erosion. Moreover, increases in HdV-18 indicate wetter conditions in the mire. In NW Iberia, evidence of increased soil erosion and enhanced mineral particle inputs during the LIA have already been documented in Coto da Fenteira Atlantic ranker (Martínez Cortizas et al., 2000) and in Pena da Cadela bog (Martínez Cortizas et al., 2005; Xistral mountains), respectively (Figure 1). Elsewhere in Europe, evidence of higher mineral matter fluxes during the LIA has also been demonstrated by Meurisse et al. (2005) in peat-dune complexes from Northern France, by De Jong et al. (2007) in a raised bog from South Sweden and by De Vleeschouwer et al. (2009) in a bog from Northern Poland.

Although the idea of enhanced erosion during the LIA is commonly discussed, natural forest cover over Europe could have prevented dust deposition in peatlands (De Vleeschouwer et al., 2009). Thus, environments like Cruz do Bocelo where forest clearance occurred over several millennia are key areas for the detection of LIA-induced erosion and provide evidence that this climatic deterioration would have affected the ability of buffering anthropogenic changes. After the cold conditions of the LIA (~410–160 cal. yr BP), anthropogenic indicators (*Cerealia*-type, nitrophilous taxa and coprophilous fungi) show elevated values that, together with the increase of ericaceous shrub, show land degradation. However, as the humidity indices point to drier conditions (Figure 7), climate could have also influenced this shift. The low percentage of mesophilous trees and increases in peat mineral content (PC1) indicate the occurrence of another erosion phase (E6).

The recent afforestation with *Pine* and *Eucalyptus* commenced approximately two centuries ago, although it has intensified in the last decades, having a profound impact in mire catchment. Afforestation is responsible for the highest percentage of total AP in the whole record as the representation of the native mesophilous trees remains very low. Synchronous increases in the mineral content of the peat and *Glomus* indicate that despite increased arboreal cover, erosion was still very intense (E7: last ~80 years). This suggests that *Pine* and *Eucalyptus* afforestation is not as effective as the mesophilous forest in preventing soil erosion. Studies in this field indicate that harvesting practices can increase soil degradation and forest floor disturbance, which may result in soil loss (Beasley and Granillo, 1988; Blackburn et al., 1986; Castillo et al., 1997; Edeso et al., 1999; Rab, 1996). However, wetter climatic conditions (Figure 7) may have also enhanced soil loss and fluxes of mineral matter to the mire. Moreover, during the last decade, the construction of a road on one side of the mire possibly affected the fluxes of mineral matter.

Soil erosion and local moisture proxies responses

The combination of geochemical and palynological approaches allowed us to detect synergic effects and to interpret environmental changes at both regional and local scales at PPB mire. The geochemical principal component reflects the mineral content of the peat (PC1) and has proven to be a highly sensitive erosion index as it was linked to forest reduction during the last ~3000 years. But soil erosion also seems to have been affected by climate, particularly by rainfall. *Glomus*, however, was a less sensitive proxy for soil erosion, as it only increased at specific samples and often only during the episodes of higher erosion intensity, while *Entorrhiza*, which has been related to clay sedimentation (Van Geel et al., 1983), only increased during the LIA and in recent times.

The variable response of each of these erosion indicators is a very good example of how a multi-proxy approach strengthens the interpretation of environmental changes and helps in understanding the response of different proxies to the same environmental stressors. It is also important to know how a given proxy should be interpreted in different environments. In this regard, the fact that HdV-18 may respond to water-table fluctuations in minerotrophic mires (driven by climate or increases in water run-off because of deforestation in the catchment) may be of importance when comparing such patterns reconstructed from ombrotrophic bogs, in which it has been related to changes in rainfall (Mighall et al., 2006). This could be of interest for future reconstructions using peat cores from minerotrophic mires.

Conclusion

The integration of physical, geochemical and palynological data suggests that climate and human activities have been involved in intense landscape changes in the Cruz do Bocelo mire's catchment during the last three millennia.

PCA on geochemical data identified a proxy for the mineral content of the peat (increases in the content of lithogenic elements), which was valuable to infer soil erosion events on a catchment scale, as well as a proxy for changes in humidity (Bromine residual variance), which agrees reasonably well with previous palaeoclimatic records, and was key to climatically contextualize environmental changes and to obtain more accurate interpretations.

The approaches presented in this paper show how human activities and climate have affected both soil erosion and the hydrology of the Cruz de Bocelo's catchment. Although a forested landscape dominated ~3000 years ago, mesophilous forest decline and the development of an open landscape are a more or less continuous feature of the record since ~2685 cal. yr BP (local Iron Age). A link between forest clearance episodes and indicators of farming (*Cerealia*-type, coprophilous fungi, nitrophilous taxa) was clearly established. Deforestation would have triggered a decrease in water retention capacity of the catchment soils that resulted in increased run-off inputs into, and wetter hydrological conditions in, the mire. In this sense, the most prominent feature of the Cruz do Bocelo record is the dramatic change at the Iron Age/Roman period transition. Until then, the mire buffered climate and human impacts, while from this point onwards its hydrology responded abruptly to landscape changes in the catchment. Forest reduction enhanced the physical instability of the soils leading to soil erosion and increased fluxes of mineral matter to the mire. However, the interplay with climatic conditions accelerated these processes.

Differential responses of soil erosion (mineral content vs *Glomus* and *Entorrhiza*) and local moisture (HdV-18) proxies according to their sensitivity or to the type of archive (ombrotrophic vs minerotrophic mire) must be taken into account when reconstructing environmental change. In this sense, the finding that HdV-18 may be a useful proxy of water-table fluctuations in minerotrophic mires is of importance for future research.

Environmental management requires a thorough understanding of long-term environmental processes. In addition, peatlands are key natural ecosystems because of their biodiversity and environmental functions, and although some of them are being protected by different legislation, many are still suffering from degradation, especially minerotrophic mires. Cruz do Bocelo is a good example since the most significant amount of erosion over the last ~3000 years is the one taking place at present. The data presented here indicate that when implementing protection measures in mires, a whole catchment approach should be considered.

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UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

3.2. Paper II

Silva-Sánchez, N., Schofield, J.E., Mighall, T.M., Martínez Cortizas, A., Edwards K.J. and Foster I. (2015) **Climate changes, lead pollution and soil erosion in south Greenland over the past 700 years**. *Quaternary Research* 84, 159–173.

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Climate changes, lead pollution and soil erosion in south Greenland over the past 700 years

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A B S T R A C T

A peat core from southern Greenland provided a rare opportunity to investigate human-environment interactions, climate change and atmospheric pollution over the last ~700 years. X-ray fluorescence, gas chromatography-combustion, isotope ratio mass spectrometry, peat humification and fourier-transform infrared spectroscopy were applied and combined with palynological and archaeological evidence. Variations in peat mineral content seem to be related to soil erosion linked with human activity during the late Norse period (13^{th}–14^{th} centuries AD) and the modern era (20^{th} century). Cooler conditions during the Little Ice Age (LIA) are reflected by both slow rates of peat growth and carbon accumulation, and by low bromine (Br) concentrations. Spörer and Maunder minima in solar activity may be indicated by further declines in Br and enrichment in easily degradable compounds such as polysaccharides. Peat organic matter composition was also influenced by vegetation changes at the end of the LIA when the expansion of oceanic heath was associated with polysaccharide enrichment. Atmospheric lead pollution was recorded in the peat after ~AD 1845, and peak values occurred in the 1970s. There is indirect support for a predominantly North American lead source, but further Pb isotopic analysis would be needed to confirm this hypothesis.
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Introduction

Ombrotrophic peatlands, receiving their inputs (precipitation and dusts) solely from the atmosphere, are widely recognised as important environmental archives. The stratified records of chemical elements and biological proxies contained within raised mires and blanket bogs can be used, for example, to provide information about changes in climate or land use, and levels of atmospheric pollution, during prehistory through to post-industrial times (e.g., Chambers et al., 2012; Meharg et al., 2012; Martínez Cortizas et al., 2013; Pontevedra-Pombal et al., 2013). Peat geochemical studies are available for locations across the major continental land masses and peripheries of North America and Western Europe, yet relatively few Holocene records exist from mid to high latitude North Atlantic islands. Evidence from Greenland, Iceland and the Faroes would enhance spatial data coverage for sites influenced by related atmospheric systems. The North Atlantic islands have relatively short and frequently interrupted histories of human occupation, with continuous recent (European) settlement dating back only to Norse colonisation (*landnám*) during the period ~AD 800–1000 (Fitzhugh and Ward, 2000). Where environmental archives of sufficient continuity and antiquity present themselves, these potentially offer opportunities to establish a geochemical baseline for 'pristine' North Atlantic environments during periods when people were absent from the landscape (cf. Dugmore et al., 2005).

Few peat geochemical investigations have been conducted in Greenland (Fig. 1A). Apart from cost and logistics, this is because peatlands are not extensive and raised bogs are absent (Feilberg, 1984). Some data are available from minerotrophic, groundwater-fed fens which demonstrate that such wetlands may preserve a record of atmospheric deposition, even though the identification of regional atmospheric signals can be complicated by mineral inputs from local sources (e.g. slopewash). Shotyk et al. (2003) used a fen developed between two small lakes near Tasiusaq (Fig. 1B), southern Greenland, to reconstruct fluxes of selected elements, notably mercury (Hg), lead (Pb) and arsenic (As), and related these to atmospheric deposition of anthropogenic origin after ~AD 1950. Their profile extended back ~2500 cal yr BP, but at reduced temporal resolution through the older part of the sequence. Schofield et al. (2010) presented a geochemical record from the nearby site of Qinngua (Fig. 1B), concentrating on the behaviour of lithogenic elements and halogens, and linking this to patterns

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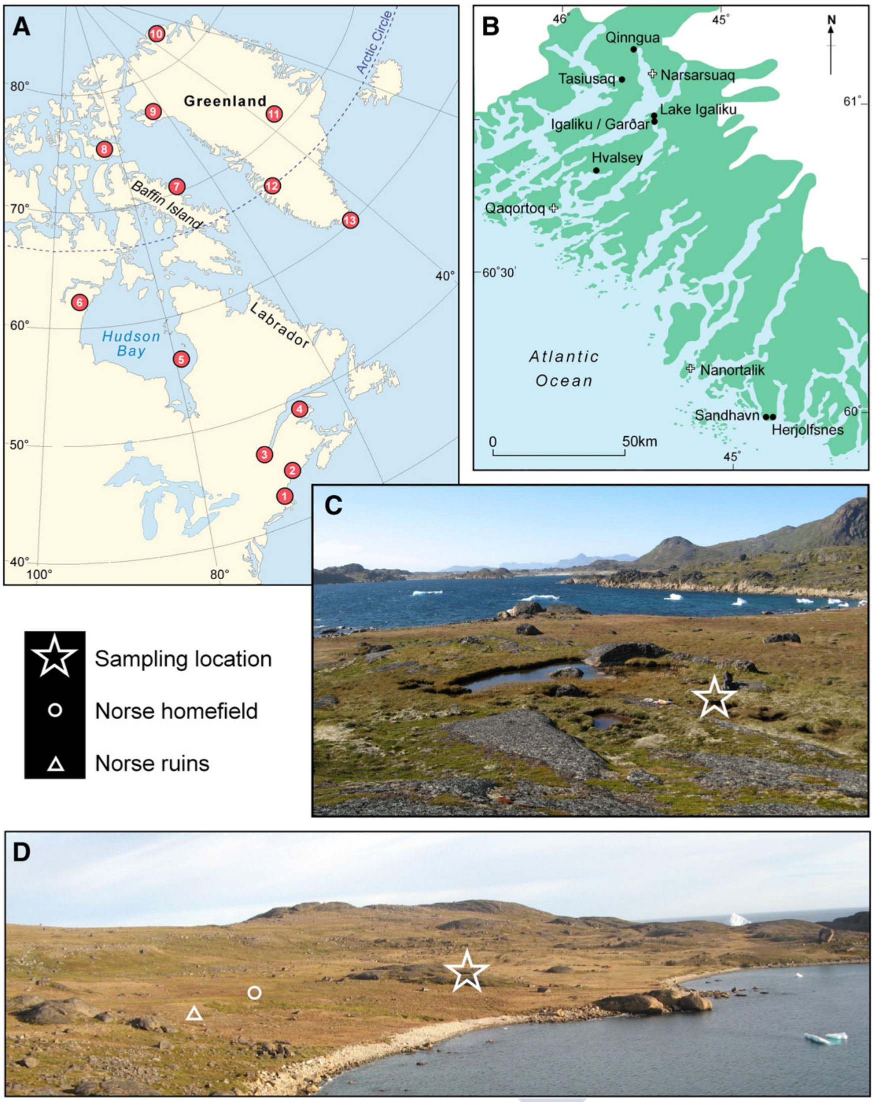

Figure 1. (A) Map of Greenland and northeast North America showing the locations of sites and places mentioned in the text. Key to numbering: (1) Plow Shop and Grove Ponds; (2) Big Heath and Sargent Mountain Pond; (3) Lake Tantaré; (4) Point d'Escuminac; (5) Imitavik Lake; (6) Far Lake; (7) Lake CF8; (8) Devon Island; (9) Camp Century; (10) Lake G07-01; (11) Summit; (12) Kangerlussuaq; (13) Sandhavn and Cape Farewell. (B) The area around Sandhavn, southern Greenland, showing sites and places mentioned in the text. (C) The sampling location at Sandhavn. The white star marks the position from which the peat monolith was taken. (D) The landscape around the sampling location at Sandhavn showing the position of the Norse ruins and former homefields (photographs by J.E.Schofield, August 2008).

of soil erosion and storminess over the last *ca* 1000 yr, albeit noting a significant hiatus in the profile (~AD 1380–1950).

An investigation by Golding et al. (2011) at the Norse farmstead of Sandhavn (Fig. 1B), near the southern tip of Greenland, revealed a small peat-filled depression set within a rock platform (Figs 1C and 1D). The basin appears isolated from the groundwater table and radiometric dating indicates that peat growth has apparently been continuous since the mid-13th century AD. This provided a rare opportunity to characterise the geochemical signal contained within a predominantly rain-fed peat from a Greenlandic setting. The main objectives of the research reported here are: (i) to search for geochemical signatures that are representative of changes in climate and of possible impacts arising from past human activity at the site (e.g. soil erosion); (ii) to study the relationship between climate, vegetation and peat decomposition in a subarctic environment; (iii) to establish high resolution records for atmospheric metal pollution and to discuss likely sources for these. Although the peat profile from Sandhavn spans a relatively short timeframe (~AD 1250–2000) and cannot provide baseline environmental information for the period before the arrival of Norse settlers, the research is important because: (a) it provides data encompassing a significant climatic perturbation – the Little Ice Age (LIA; Grove, 1988); (b) the basin is adjacent to the homefields (i.e. the hay-producing areas) of a Norse farmstead (Fig. 1D) that was in use from ~AD 1000–1400, and the sampling location was anticipated to be particularly sensitive to the environmental impacts arising during the past human occupation and use of the site; and (c) the results presented on peat decomposition may prove informative for studies with a focus on long-term carbon sequestration by peatlands.

Site background and context

Sandhavn (59°59.9′N, 44°46.6′W; Fig. 1) is located on the Ikigait peninsula on the outer coast of Greenland, approximately 50 km northwest of Cape Farewell (the most southerly point in Greenland). The prevailing climate is subarctic, with cold winters and cool summers and a notable feature of the climate regime is frequent strong winds. The seas here are regarded as the windiest in the world's oceans, with speeds exceeding 20 ms^{-1} (equivalent to a strong gale) around 20% of the time (Sampe and Shang-Ping, 2007). Wind direction is bimodal, with a strong probability of observing both westerly and easterly high speed wind events (Moore et al., 2008; Renfrew et al., 2008), which might have implications for the sourcing of atmospheric dusts deposited across the area.

The solid geology of south Greenland comprises granites and gneisses of the Ketilidian mobile belt, with basic and intermediate intrusions (Allaart, 1976). This creates a rugged alpine topography characterised by steep slopes and peaks sometimes exceeding 1000 m a.s.l. The soils can be broadly classified as cryosols, with many showing evidence for podzolization (Golding et al., 2011). *Empetrum nigrum* (crowberry) oceanic heath is the dominant vegetation in the coastal zone. This is replaced by more subcontinental plant communities — primarily *Betula-Salix* (birch-willow) dwarf heath — within the warmer and drier interior (Böcher et al., 1968; Feilberg, 1984). The basin featured in this investigation (Fig. 1C) supports nutrient-poor mire dominated by sedges (*Carex rariflora* and *C. bigelowii*), interspersed with small pools fringed by mare's-tail (*Hippuris vulgaris*). There are no inflowing streams entering the basin, which is set within a rock outcrop that is elevated slightly above the general level of the land around it (Fig. 1D). Consequently any minerogenic inputs reaching the basin via runoff from the surrounding area will have been restricted to an extremely localised radius (~10–20 m) defined by the rocky rim around the basin. Thus, whilst the setting cannot be defined as strictly ombrotrophic, the majority of inputs to the basin must come from the atmosphere. This supposition is further supported by high loss-on-ignition (LOI) values and carbon content, and low concentrations of lithogenic elements in the peat (discussed below).

The ruins of a Viking/Norse farmstead and Thule Inuit dwellings can be found at Sandhavn. These, together with landscape, soils and pollen-based evidence from the site (Raahauge et al., 2003; Golding et al., 2011, 2015) attest to a local human presence between ~AD 1000–1400, i.e. throughout most of the period conventionally ascribed to the occupation of the Norse Eastern Settlement of Greenland (Krogh, 1967). The neighbouring farm and port of Herjolfsnes, ~3.5 km east-southeast of Sandhavn, was perhaps in use until slightly later (~AD 1450) before also being abandoned (Arneborg et al., 1999). The Royal Greenlandic Trading Company had a trading station here from AD 1834–1877. Sheep farming occurred briefly on the Ikigait peninsula from 1959–1972 (Arneborg, 2006), although pastoral agriculture has been in continuous operation more widely across southern Greenland since 1924 (Fredskild, 1988). The area immediately around Sandhavn has otherwise been uninhabited, with the possible exception of occasional Thule maritime hunters whose impact on the landscape would probably have been negligible.

Methods

Fieldwork

In August 2008, a short (40 cm) peat monolith was recovered from a small (~30m diameter) basin (59°59.875′N, 44°46.637′W) adjacent to the former homefields and Norse ruins at Sandhavn (Fig. 1C). Samples were collected by inserting a monolith tin into the open face of a pit dug into the mire. The field stratigraphy comprised a base of saturated coarse gray-brown sands overlain by ~36 cm of orange-brown *turfa* (rootlet) peat containing abundant bryophytes. The peat was visibly darker above 17 cm. The top of the profile (5–0 cm) contained the (living) root mat. The monolith was wrapped in polythene and returned to the University of Aberdeen, where it was kept refrigerated (4°C) prior to sub-sampling in the laboratory.

Radiocarbon dating and age-modelling

Four AMS (accelerator mass spectrometry) ^{14}C measurements were taken on bryophytes selected from the peat (Table 1). These were first reported in Golding et al. (2011) where they were used to produce an age–depth model based upon a polynomial fitted through the median probabilities of the calibrated radiocarbon dates. The addition of ^{210}Pb dating to the profile (as outlined below) and developments in software now allow an improved age–depth model to be produced. The revised model uses 'classical' age–depth modelling (*Clam*; Blaauw, 2010) to apply a smoothed spline through the dates. The 'best estimates' from this model have been used to provide calendar dates for events in the geochemical and biological records through the organic (peat) section of the profile.

^{210}Pb-dating

The unsupported $^{210}Pb_{un}$ activity within samples towards the peat surface was ascertained by subtraction of the supported component (measured as ^{214}Pb at 295.22 and 351.93 keV) from the total ^{210}Pb activity measured at 46.54 keV (Wallbrink et al., 2002). ^{210}Pb and ^{214}Pb activities were measured using EG&G ORTEC hyper-pure Germanium detectors in a well configuration (11 mm diameter, 40 mm depth) housed at Coventry University. The method for calculating the age–depth relationship follows procedures described by Appleby and Oldfield (1978), Appleby (2001) and Walling et al. (2002). Accumulation rates varied down core and the CRS dating model was used to calculate ages (Appleby et al., 1988; Appleby, 2001).

Pollen analysis

Full details of the methods are described in Golding et al. (2011). Pollen samples were prepared using NaOH, HF and acetolysis techniques with samples embedded in silicone oil of 12,500 cSt viscosity (Moore et al., 1991). Palynomorphs were counted until a sum in excess of 500 TLP (total land pollen, excluding aquatics and spores) was achieved. Percentage data were calculated using TILIA (Grimm, 1993) and the pollen diagram of selected taxa constructed using TGView. Coprophilous fungal spores (van Geel et al., 2003) were also counted and these are expressed as a percentage of the TLP sum. These spores are given the type numbers assigned by the Hugo de Vries-Laboratory, Amsterdam, and are prefixed *HdV-*.

Table 1
Radiocarbon dates from Sandhavn. All measurements are AMS on bryophytes (*Dicranium*, *Drepanocladus*, *Hypnum*, *Hylocomium* and *Racomitrium* spp.). Calendar ranges are those used by the (*Clam*) age-depth model (Fig. 2) following calibration against the IntCal13 calibration curve (Reimer et al., 2013). See Golding et al. (2011) for a further discussion of the radiocarbon dates.

Depth (cm)	Lab code (SUERC-)	^{14}C age (BP)	AD range (2σ)	$\delta^{13}C$ (‰)
15–14	24657	0 ± 35	1698–1955	−23.6
27–26	24866	230 ± 90	1484–1953	−25.0
33–32	24658	600 ± 35	1297–1408	−25.6
36–35	24659	750 ± 35	1219–1290	−24.8

Loss-on-ignition (LOI) and Dry Bulk Density

The organic content of samples was measured through LOI. This was calculated following the combustion of dried and milled samples in a muffle furnace for 3 hours at 550°C. Dry weights were also used to calculate dry bulk density of the peat which, in turn, allowed the determination of peat carbon accumulation rates (PCAR).

Elemental analysis and isotopic ratio mass spectroscopy

Laboratory sub-sampling for elemental analysis was done at 1cm contiguous intervals. Prior to measurement, samples were dried and milled to a fine powder with an agate mill. Concentrations of major and minor elements (Si, Al, Fe, Ti, Ca, K, P and S), trace lithogenic elements (Rb, Sr, Zr, Nb, Y, Ga), trace metallic elements (Mn, Cr, Ni, Cu, Zn and Pb), halogens (Cl and Br) and selenium (Se) were determined by X-ray fluorescence (XRF) using an EMMA-XRF (Cheburkin and Shotyk, 1996) hosted at the XRD-XRF facility of RIAIDT (Red de Infraestructuras de Apoyo a la Investigación y al Desarrollo Tecnológico) at the University of Santiago de Compostela. Peat and mineral samples were calibrated using a calibration for organic and inorganic matrices respectively. Detection limits (DL) were as follows: Si (0.05%), Ti and Fe (0.002%), Al (0.002% for organic; 0.2% for inorganic matrices), Ca (0.002%; 0.01%), K (0.002%; 0.05%), P (0.009%; 0.03%), S (0.009%; 0.03%), Rb (0.5 μg g^{-1}; 5 μg g^{-1}), Sr (0.5 μg g^{-1}; 5 μg g^{-1}), Mn (5 μg g^{-1}; 30 μg g^{-1}), Pb (0.5 μg g^{-1}), Se (0.5 μg g^{-1}; 2μgg^{-1}),Br (0.5 μgg^{-1}; 2 μgg^{-1}) and Cl (40 μg g^{-1}; 350 μg g^{-1}). Calibrations for Zr were not provided, thus we used normalized intensities with z-score transformation for comparison with other elements.

The elemental analyses of C and N, and the $\delta^{13}C$ and $\delta^{15}N$ isotopic ratio analyses, were carried out using a gas chromatography-combustion elemental analyser (GC/C; EA1108 CarboErba Instruments) coupled by a Conflowll interphase (ThermoFinnigan) with an isotope ratio mass spectrometer (IRMS; MAT253 ThermoFinnigan). Sample isotopic composition is expressed as units of $\delta^{13}C$ and $\delta^{15}N$ using Pee Dee Belemnite (PDB) and air atmosphere as the standards for C and N respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

Spectral characterization of peat samples was made in the IR-RAMAN unit of RIAIDT, and performed by FTIR spectroscopy using a Bruker IFS-66 V FTIR spectrometer. The resolution was set to 4 cm^{-1} and 32 scans per sample were recorded. The operating range was 400–4000 cm^{-1}. One mg of homogenised (milled) sample was mixed thoroughly with 100 mg of KBr (FTIR grade) and a pellet was prepared using a press. To avoid differences in absorbance related to sample preparation and detection, various procedures were applied to transform the baseline corrected spectra (Solomon et al., 2007; Smidt et al., 2008). The main FTIR bands used in this study and their meaning are shown in Table SI1.

Degree of peat humification (DPH)

Peat humification was measured following the method of extracting humic acids from dried and milled peat samples using 8% NaOH and assessing the concentrations of solutions colorimetrically using a spectrophotometer (Blackford and Chambers, 1993). Results are expressed as percentage transmittance.

Statistics

The use of multivariate statistical approaches helps to summarize common patterns of variation within datasets and to gain insights into the underlying environmental factors that control these. For elemental composition data and LOI (collectively PCe), and organic matter properties – FTIR, C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH – (collectively PCo), principal components analyses (PCA) were applied using SPSS 20 in correlation mode and by applying a varimax rotation. Prior to analysis, the dataset was standardized using z-scores (Eriksson et al., 1999).

Results and interpretation

Chronology

Radiocarbon dates are shown in Table 1 and an age–depth model for the profile is presented in Figure 2. This pertains to the organic part of the sequence; the basal sands, which are of unknown age, were not considered. The model shows that the peat accumulation rate has varied considerably over the last ~750 yr. The rate was initially very low, ~0.025–0.033 cm yr^{-1} from ~AD 1250–1400 (equivalent to a deposition time [DT] of ~30–40 yr cm^{-1}). The rate of peat growth reduced further during the period *ca* AD 1400–1800 (~0.020–0.025 cm yr^{-1}; DT ~40–50 yr cm^{-1}). The accumulation of organic matter accelerated rapidly during the last two centuries, especially during the second half of the 20th century when peat accumulation increased to ~0.2 cm yr^{-1} (DT ~5 yr cm^{-1}). This pattern translates into a low temporal resolution for the bottom half of the peat monolith but a highly resolved archive above this.

Pollen analysis

Full details of the pollen analysis have already been presented in Golding et al. (2011). Selected taxa appropriate to the discussion of the new geochemical data are presented in Figure 3.

Elemental composition and LOI

The transition from basal sand to peat (36–35 cm) is the key stratigraphic change in the monolith. This is reflected by sharp differences in LOI and element concentrations across the sediment contact

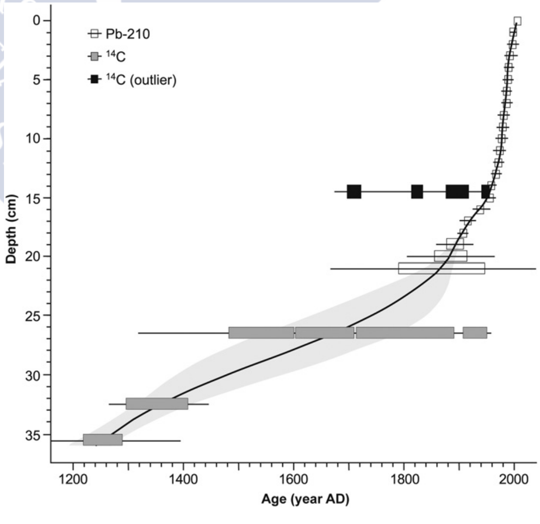

Figure 2. Age–depth model for Sandhavn (after Golding et al., 2011 with minor changes). Shaded (grayscale) boxes represent the 2σ calibrated ranges of radiocarbon dates used in the model; clear boxes are the ^{210}Pb dates (with associated errors). One ^{14}C date – depicted here in black – was considered to be an outlier and has been removed from the model. The solid black line connecting the ^{14}C and ^{210}Pb dates represents the 'best estimate' based on the model, with the gray envelope around this demonstrating the maximum and minimum (95%) confidence limits.

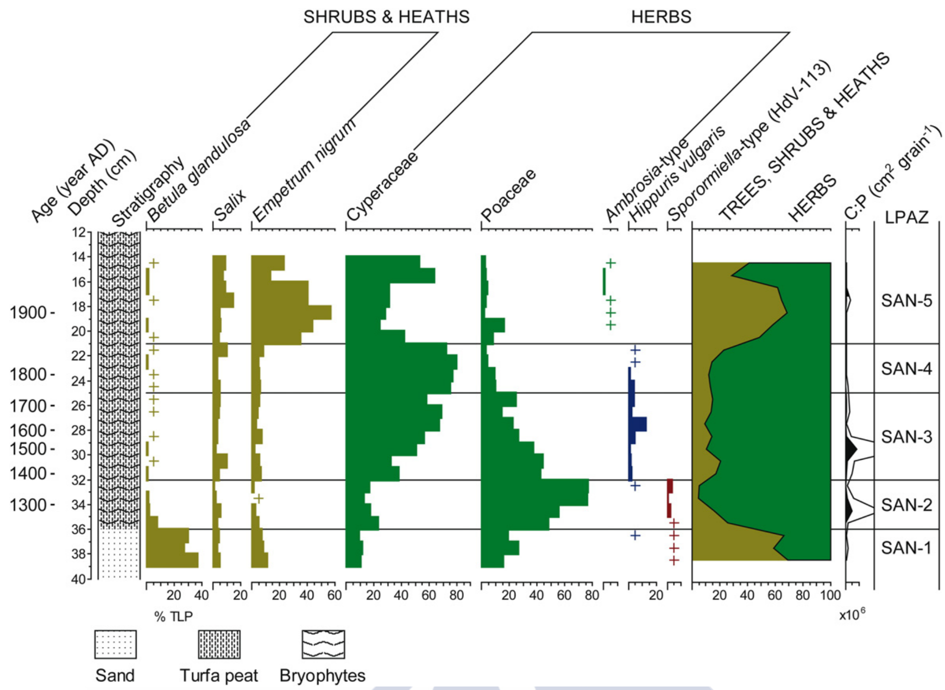

Figure 3. Percentage pollen diagram for Sandhavn displaying selected taxa (after Golding et al., 2011 with minor changes). The SAN-2/3 pollen zone boundary represents the replacement of hayfields and pastures (Poaceae-dominated assemblages) with tundra or steppe vegetation (Cyperaceae-dominated assemblages), and with it the Norse abandonment of the site. This vegetation was to persist until around AD 1850 and the development of *Empetrum nigrum* oceanic heath. *Ambrosia* pollen is recorded in SAN-5. This genus is not native to southern Greenland (Böcher et al., 1968) and must be part of the long-distance component arriving at the site. Curves for *Hippuris vulgaris*, *Sporormiella*-type (coprophilous fungi) and C:P (ratio of charcoal to pollen concentration) act as proxies for the presence of standing water, grazing by animals, and fires/burning, respectively.

(Fig. SI.1). In order to optimise the visibility of changes through the peat section (Fig. 4), PCA was applied only to those samples above the transition (Fig. 5). Three principal components (PCe), which explain 77.1% of the total variance, were extracted (Table SI2).

The first principal component (PC1e) explains 38.9% of the variance. Most lithogenic elements and some trace metals (Ti, Si, Zr, Al and Rb), together with N, P and S, show high positive loadings for PC1e, whilst LOI displays a large negative loading. The record of factor scores can be divided into three main sections. From 35–32 cm the scores are positive but decreasing; from 32–16 cm the scores fluctuate between small negative and positive values; and the scores decrease steadily to large negative values from 16 cm to the surface. The large contribution of lithogenic elements and their opposition with LOI indicate that this component mainly reflects the mineral content of the peat.

The second principal component (PC2e) explains 20.2% of the variance. Iron, Br, Pb and Cl have high positive loadings for PC2e whilst S shows a moderate negative loading. Factor scores for PC2e (Fig. 5) are negative except for a broad peak from 22–9 cm. Iron accumulation in peat is largely controlled by redox conditions (Chesworth et al., 2006), with the concentration of Fe increasing under oxidation (e.g., during water table drawdown). The halogens (Br and Cl) are likely to be of marine origin and are mostly preserved in peat as organohalogenated compounds formed by oxygen-dependent enzymatic processes. Thus, their concentrations in peat, although also dependent on atmospheric fluxes, are mainly controlled by biotic halogenation and dehalogenation (Myneni, 2002; Biester et al., 2004; Leri and Myneni, 2012). Lead may have both geogenic and pollution sources, but its increase here seems to be linked to atmospheric pollution as it does not have a strong association with the major and minor lithogenic elements.

The third principal component (PC3e) explains 18% of the variance and is most strongly related to K, Mn, Ca (high positive loadings), and to a lesser extent Sr (moderate positive loadings) and C (moderate negative loadings). PC3e scores show a similar record to PC1e scores below 16 cm, suggesting that in this peat section, K, Mn and Ca are mainly of geogenic origin. Contrary to PC1e, PC3e scores increase to the surface of the peat, most probably due to biocycling.

Characterization of peat organic matter: FTIR bands, C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH

Trends in organic matter properties (C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH) and selected FTIR bands are shown in Figure 6. Three principal components (PCo), which explain 86% of the total variance, were extracted from these data (Table SI3). The first principal component (PC1o) accounts for 48% of the total variance. Bands representative of recalcitrant compounds such as aliphatics (2852 cm^{-1} and 2922 cm^{-1}), lignins (1514 cm^{-1}), aromatics (3051 cm^{-1}), amides (1660 cm^{-1} and 1550 cm^{-1}), and $\delta^{15}N$ – the enrichment of which has been associated with peat decomposition (Létolle, 1980; Macko et al., 1993; Högber, 1997) – show high positive factor loadings. C/N ratio has a high negative loading, while $\delta^{13}C$ and DPH show moderate negative loadings. Decomposition via residual enrichment of N relative to C (Malmer and Holm, 1984; Kuhry and Vitt, 1996) is associated with a decrease in the C/N ratio. The large contribution of recalcitrant compounds, $\delta^{15}N$ and C/N ratios in this component indicates that the factor is heavily related to the decomposition of peat organic matter. Even variables with moderate loadings support this interpretation, as decreases in $\delta^{13}C$ in peatlands have been associated with enrichment of recalcitrant

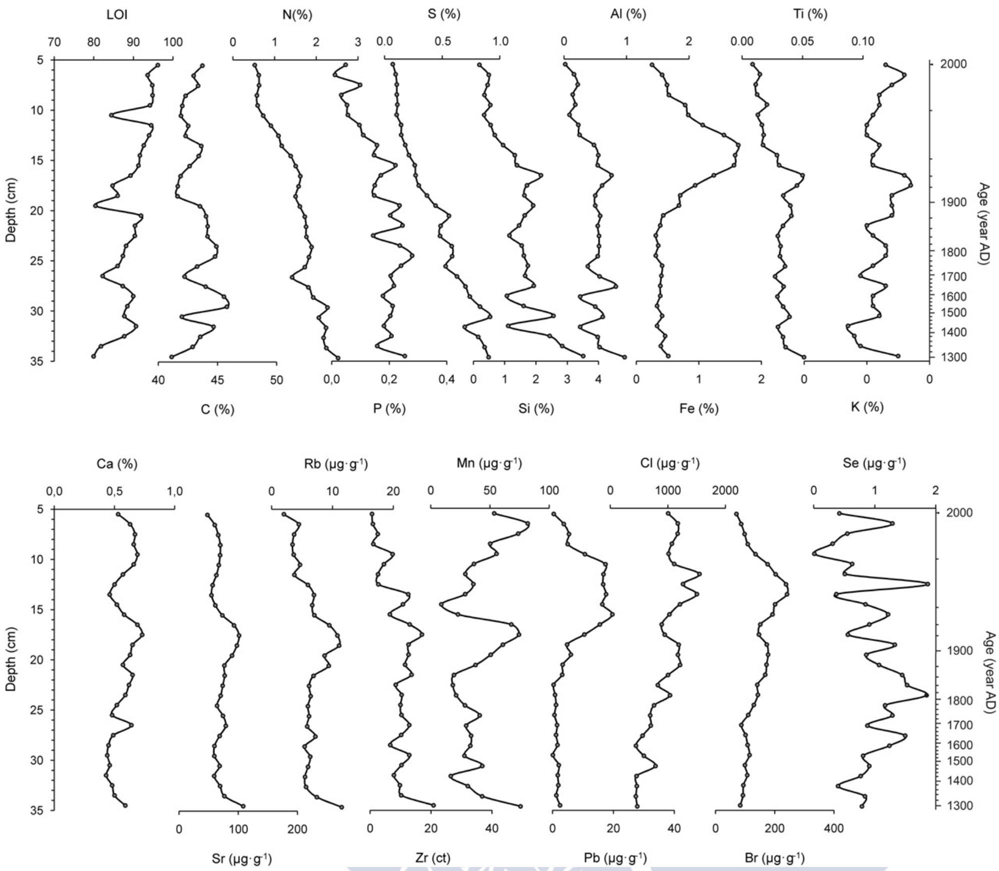

Figure 4. LOI and elemental composition through the peat section of the Sandhavn monolith. Note that x-axes scales and units vary between graphs.

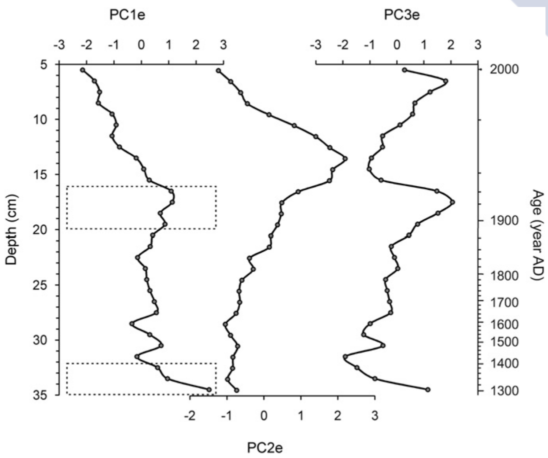

Figure 5. Factor scores for the first three principal components (PC1e, PC2e, and PC3e) extracted from the PCA performed on LOI and elemental composition data from the peat section of the Sandhavn monolith. Boxes with dashed outlines indicate sections with higher PC1e scores (i.e., higher mineral content).

moieties (Alewell et al., 2011; Broder et al., 2012; Biester et al., 2014). Recalcitrant plant fractions appear to be more depleted in ^{13}C compared to the bulk plant material; for example, $\delta^{13}C$ in *Spartina* detritus gradually decreases during biogeochemical processing due to the preservation of substances like lignin which contain less ^{13}C (Benner et al., 1987). Similarly, studies performed on C_4 grasses indicate that lignin-C is up to 4.7‰ lower in ^{13}C compared with the bulk plant material (Schweizer et al., 1999). As decomposition leads to an increase in solubilized humic acids, DPH has been widely used as a measure of the degree of peat decomposition (Blackford and Chambers, 1993, 1995; Borgmark, 2005; Borgmark and Schoning, 2006).

From 35–15 cm, positive factor scores (Fig. 7) indicate a relatively high degree of decomposition compared to the rest of the core, although a generally decreasing pattern of values is detected, reflecting the depth-time dependent nature of decomposition. Lower scores from 29–25 cm and 20–16 cm coincide with smaller amounts of recalcitrant compounds. From 15 cm to the surface, scores become negative, indicating a trend to less decomposed/fresh plant remains.

PC2o accounts for 23% of the total variance. Bands at 1271 cm^{-1}, 1419 cm^{-1}, 1450 $cm^{-1}$and 1720 cm^{-1} show high positive loadings. These bands are indicative of lignin, with the exception of that at 1720 cm^{-1}, which represents carboxylic groups. $\delta^{13}C$ shows a moderate negative loading. The fractionation of commonalities (Table SI3) suggests that lignin and carboxylic acids are related, although with different magnitude, to both PC1o and PC2o. This implies that there are at least

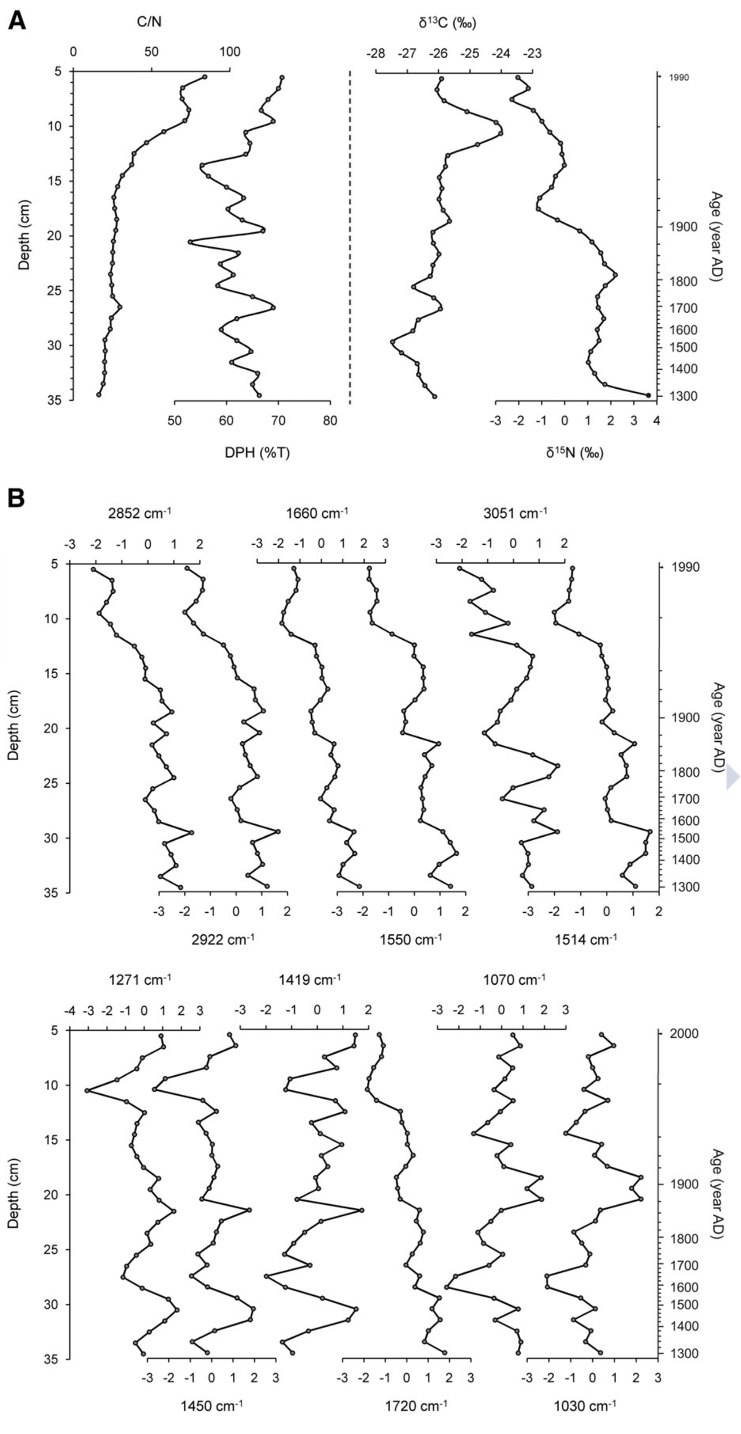

Figure 6. Variations in organic matter indicators through the peat section of the Sandhavn monolith: (A) C/N ratio, degree of peat humification (DPH), and variations in $\delta^{13}C$ and $\delta^{15}N$; (B) Selected FTIR bands (expressed as z-scores).

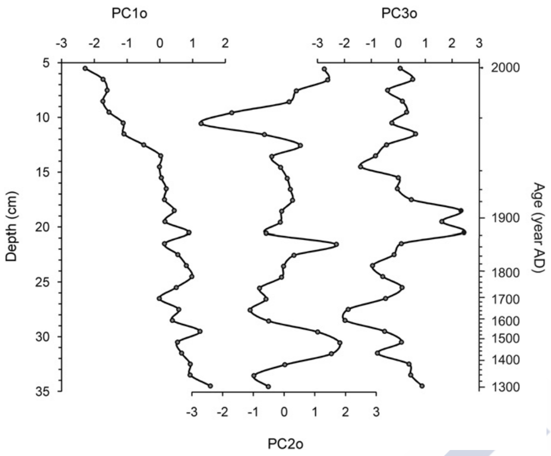

Figure 7. Factor scores for the first three principal components (PC1o, PC2o, and PC3o) extracted from the PCA performed on selected FTIR bands, C/N, $\delta^{13}C$, $\delta^{15}N$ and DPH through the peat section of the Sandhavn monolith.

two factors affecting lignin and carboxylic groups in the peat. Decomposition (as outlined above) is one of the factors affecting the distribution of lignin, but a more complex behaviour (in addition to that of depth enrichment) is indicated by PC2o. Factor scores (Fig. 7) show an alternating distribution between positive and negative values, except for the section between 20–14 cm, where they are around zero. Factor scores are positive (i.e., the lignin content is higher) at 33–29 cm, 22–21 cm and 8–5 cm.

The third principal component (PC3o) accounts for 15% of the total variance. Bands of polysaccharides (1070 cm^{-1} and 1030 cm^{-1}) show high positive loadings (Table SI3) while the band at 3051 cm^{-1} (aromatics) shows moderate negative loadings. Peat decomposition leads to an enrichment in recalcitrant compounds (e.g. aliphatics and aromatics) of the organic matter as reflected by PC1o. PC3o seems to denote reduced decomposition of labile compounds (i.e. polysaccharides). Changes in vegetation type may also have affected the character of organic matter comprising the peat, and consequently the distribution of polysaccharides. PC3o factor scores indicate heavy enrichment in polysaccharides between 21 and18 cm (Fig. 7). Smaller increases are found at 35–32 cm, 30.5 cm, 27–25 cm and 12–5 cm.

Discussion

Mineral content of the peat: a link with induced soil erosion

Although it is possible that some of the lithogenic component might be sourced over long distances, our results suggest that local dusts dominate the signal of major and trace lithogenic elements. The geochemical composition of the peat, and the association of chemical elements in PC1e, is consistent with the character of the local geology (which is composed mostly of granites and gneises). Furthermore, the main chemical ratios (Ti/Zr, K/Rb; Fig. 8), which are commonly applied to determine changes in lithogenic sources, are near-constant through the profile, only increasing after the 1980's, indicating a quite constant composition to the mineral matter over the majority of the period covered by the profile. Increased soil instability linked to human activity may be evidenced at Sandhavn by the enhanced mineral content of the peat and a suite of lithogenic elements (indicated by PC1e; Fig. 8). This would seem to reflect aeolian inputs which are highest (albeit steadily declining in concentration) through a period which is coincident with the end of the Norse settlement at the site. A caveat is required, however, as the peat geochemical record from Sandhavn commences during the settlement phase, which means there are no baseline environmental measurements available prior to the arrival of people. Moreover, this enrichment is registered immediately above the contact with the mineral (sand) base, where sediment mixing might account for a part of the variation. Yet evidence in the form of pollen and coprophilous fungi intimate that land-use induced erosion may have still played a role in the enrichment of mineral matter during the earliest stage of peat development.

The decline in the mineral content of the peat (PC1e; Figs. 4 and 5) to lower values after ~AD 1400 coincides with reduced frequencies of fungal spores and Poaceae pollen (Figs. 3 and 8). This pattern reflects the Norse abandonment at Sandhavn (Golding et al., 2011), occurring at approximately the same time as many other farms across the Eastern Settlement were also falling into disuse (Edwards et al., 2011; Ledger et al., 2014). A number of other studies from the Eastern Settlement of Greenland have produced convincing evidence for an increase in soil erosion following Norse *landnám* on the basis of rising mineral content in peat or lake sediments (e.g., Sandgren and Fredskild, 1991; Fredskild, 1992; Edwards et al., 2008; Massa et al., 2012). At Sandhavn, the

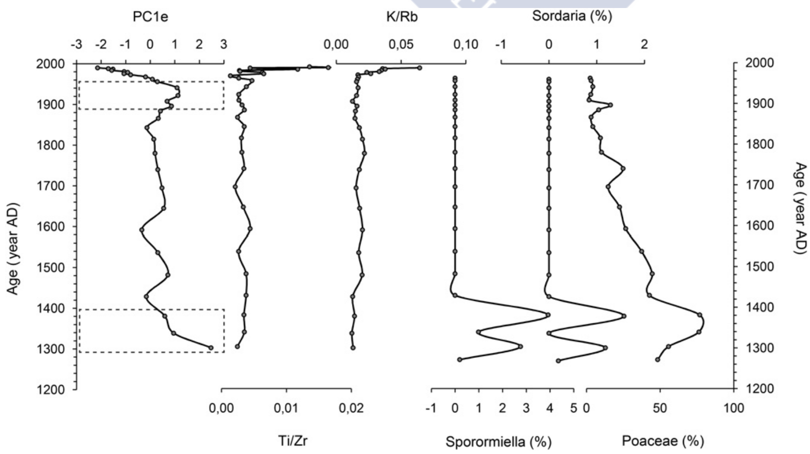

Figure 8. PC1e factor scores (reflecting the mineral content of the peat), Ti/Zr and K/Rb plotted against selected pollen types and spores from the Sandhavn monolith.

concentrations of lithogenic elements remain low throughout the LIA and show little variation until ~AD 1900.

Massa et al. (2012) noted that Ti remained elevated (14% above pre-*landnám* baseline concentrations) at Lake Igaliku for more than four centuries after the farmstead at *Garðar* (modern Igaliku) was abandoned. They suggest that Norse occupation may have altered the physicochemistry of the catchment soils, or that a change in climate at the onset of the LIA led to enhanced aeolian deposition (and hence Ti influx) to the lake because of increased wind speeds and storminess that were characteristic features of the climate after ~AD 1425 (cf. Dugmore et al., 2007). For the period available for examination, this pattern does not seem to be repeated at Sandhavn. The lack of a clear increase in lithogenics during the LIA at Sandhavn suggests that soil disturbance and exposure to wind erosion may have been spatially limited. Changes in vegetation took place immediately after the abandonment of the farm (zone SAN-3; Fig. 3). The increase in Cyperaceae pollen abundance reflects the likely spread of steppe-like vegetation communities (cf. Böcher et al., 1968) across disused home-field areas and the local extension of mire communities in response to cooler and possibly damper conditions. This change in vegetation cover, following the removal of direct human influence from the landscape, may have restricted the availability of erodible material. The next simultaneous increase in most lithogenic elements (PC1e; Fig. 8) is recorded during the early 20th century (~AD 1900–1940) and appears broadly synchronous with the return of sheep farming to southern Greenland (Jacobsen, 1987; Fredskild, 1988).

A number of studies have shown the benefits of integrating chemical data with more traditional proxies such as pollen to reconstruct soil erosion and land use changes (e.g., Hölzer and Hölzer, 1998; Lomas-Clarke and Barber, 2004; Martínez Cortizas et al., 2005; Silva-Sánchez et al., 2014). Most of these studies were conducted in areas of relatively intense human activity and show that both proxies — the pollen and the geochemical record — responded to changing land use and were in good agreement with regional archaeological records. The current study also demonstrates the sensitivity of geochemical proxies to environmental change in a more remote landscape. In such circumstances, human activity was on a relatively reduced scale compared with the significant landscape transformations that have taken place in temperate environments (Western Europe, for example). In spite of this, the data from Sandhavn not only clearly discriminate between periods of human activity and abandonment but also record anthropogenic impacts that appear to closely match the known historical record.

Peat growth, carbon accumulation, organic matter decomposition and bromine: links with climate change

Changes in the rate of peat accumulation at Sandhavn (Fig. 9) apparently reflect broad-scale patterns in the prevailing climate (Barlow, 1994; Dahl-Jensen et al., 1998; Box, 2002), with the cooler temperatures of the LIA coinciding with, and seemingly accounting for, the period of extremely slow peat growth witnessed from ~AD 1400–1800, and generally rising temperatures after this leading to the more rapid build-up of peat over the last ~100–150 yr. Autocompaction of the peat, whereby deeper layers become compressed relative to the surface, is likely to have acted to reinforce this pattern. Although controls over the rate of peat accumulation seem clear, the factors leading to paludification are less obvious.

Organic matter began to accumulate in the basin at Sandhavn from ~AD 1240, suggesting an environmental threshold (climatic or otherwise) had been exceeded. On the basis of the synthesis of various climate proxies, Ogilvie and Jónsson (2001) support the notion of it being slightly colder across the North Atlantic region from ~AD 1250–1900 in comparison to the 20th century. A chironomid record from a lake near Igaliku in southern Greenland also suggests a shift towards cooler conditions from ~AD 1280–1460 (Millet et al., 2014), a time-frame encapsulating the 14th century, the period of lowest temperature in central Greenland during the last 700 years (Barlow, 1994). Further evidence to suggest that the regional climate was beginning to deteriorate from the mid-13th century onwards can perhaps be seen in the archaeological record from the Eastern Settlement. There appears to have been a shift in Norse subsistence away from farming towards a marine-based diet (Arneborg et al., 1999; Dugmore et al., 2012), although the timing for this is not precise and there are many caveats (Arneborg et al., 2012). There are also indications of abandonment at some Norse farms (Ledger et al., 2014) but an intensification at others (Ledger et al., 2013). Yet all the above should be viewed against the baseline offered by Kaufman et al. (2009), in which a synthesis of terrestrial climate proxies (lakes sediments, glacier ice and tree rings) for latitudes above 60° N demonstrates a long-term cooling trend in the Arctic spanning the last two millennia, albeit punctuated by centennial-scale periods of greater relative warmth (e.g. AD 900–1060) and more severe cold (e.g. AD 1600–1860).

The very slow rate of peat growth observed at Sandhavn during the mid-second millennium is mirrored at some other sites across the region. For example, radiocarbon dates from the fen near Tasiusaq (Shotyk et al., 2003), approximately 100 km northwest of Sandhavn, demonstrate very rapid accumulation (~0.3 cm yr^{-1}) for the period after ~AD 1950 but extremely slow peat growth (~0.015 cm yr^{-1}) during the preceding ~950 yr. At the nearby site of Qinngua, a hiatus spanning ~AD 1400–1900 has been recorded in a peat profile (Schofield et al., 2010). This probably represents a period of zero peat growth, although a hiatus resulting from peat cutting should not be discounted. The cutting of peat may have played a part in creating gaps within late Holocene environmental archives drawn from mires across the region (cf. Schofield et al., 2008), although the importance of its role over any climatically-forced slowdown in peat accumulation due to lowered temperatures is difficult to ascertain. It does seem that high-resolution peat archives covering the mid-second millennium AD may be rare in this region, although some exceptions can be found (cf. Ledger et al., 2014).

Associated with extremely slow peat growth at Sandhavn is an increase in *Hippuris vulgaris* pollen (Figs. 3 and 9), which is probably indicative of shallow open water (pools) at the bog surface, at least seasonally. Flooding during milder seasons due to increased ice/snow melt, combined with low spring-summer evaporation rates from lower temperatures between ~AD 1400 and1800, may have increased the habitat suitable for this taxon. Bromine concentrations in the Sandhavn record also seem to be strongly affected by climate as concentrations remain below 150 μg g^{-1} until ~AD 1865, although values do begin to increase gradually after ~AD 1780 (Fig. 9). Research at Qinngua (Schofield et al., 2010) suggested a possible link between variation in the concentrations of halogens and storminess as rising amounts of Br and Cl in the peat appeared to be correlated with increased levels of $Na+$ (sea salt sodium) in the GISP2 ice core (a hiatus in the peat profile at Qinngua, spanning the period ~AD 1380–1950, hindered attempts to directly compare the two records). No such link was found at Sandhavn. The incorporation of bromine into peat is a biological oxygen-dependent enzymatic processes (Myneni, 2002; Biester et al., 2004; Leri and Myneni, 2012) and it is possible that cooling would have slowed down the biological activity of the micro-organisms involved. Flooding of the mire during milder seasons, most favourable for biological activity, could have also limited the incorporation of Br to the peat, a process which in oceanic areas is mostly dependent on oxygen availability rather than atmospheric deposition (Martínez-Cortizas et al., 2007). Organo-bromine compounds can be dehalogenated under reducing conditions (Mohn and Tiedje, 1992; Monserrate and Häggblom, 1997; Bedard and van Dort, 1998), but at Sandhavn anoxic environmental conditions were seemingly unsuitable for halogenation of organic compounds, and so this appears less likely to explain the patterns in Br as depicted in the data presented here.

Some of the variations in the proxies analyzed might have been affected by solar forcing (Fig. 9), a factor that is considered to be a major

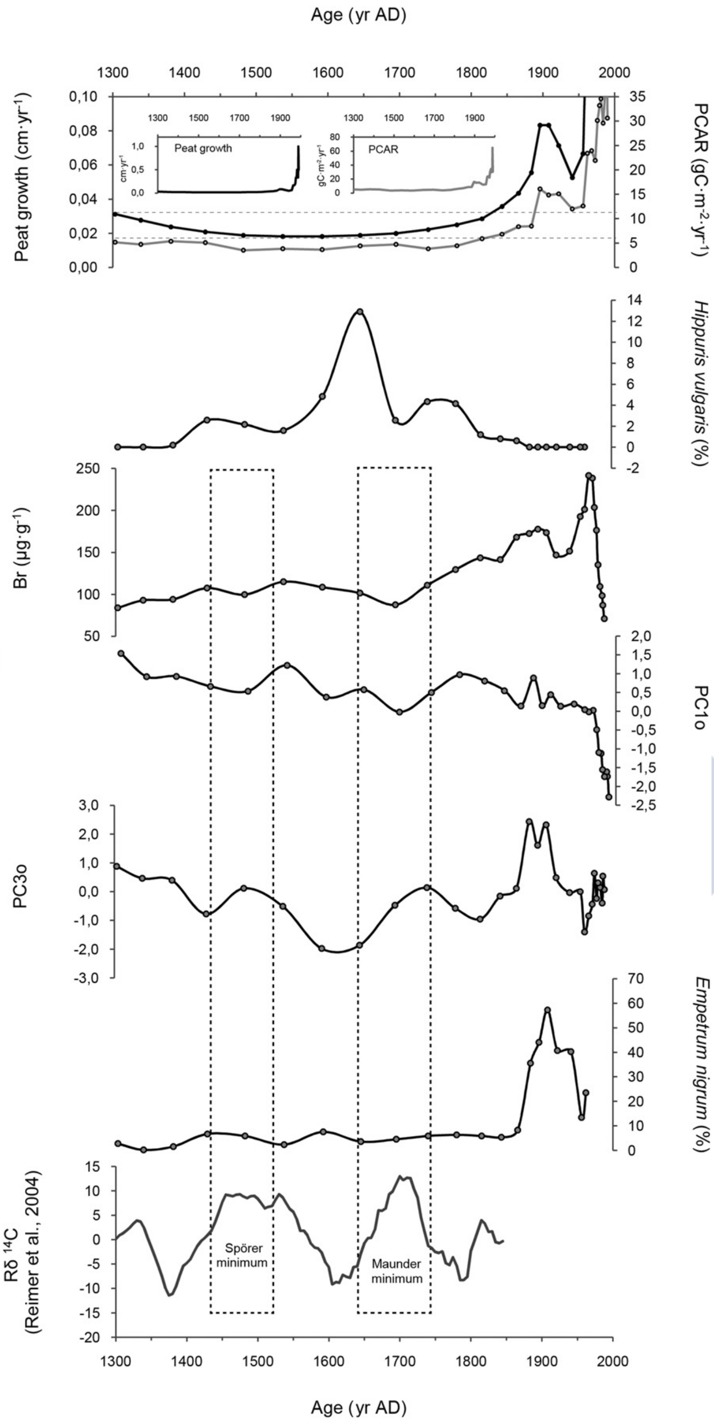

Figure 9. Selected variables through the Sandhavn monolith. From top to bottom: peat growth rate and peat carbon accumulation rate (PCAR: gray line) with y-axis truncated such that very high values recorded after AD 1950 (shown on the embedded graph) are not depicted; percentage of *Hippuris vulgaris* pollen; Br concentration; levels of recalcitrant compounds in the peat (reflected by PC1o factor scores); levels of polysaccharides in the peat (reflected by PC3o factor scores); percentage of *Empetrum nigrum* pollen; variations in Rδ^{14}C (Reimer et al., 2004). Dashed boxes indicate the Spörer and Maunder minima in solar activity.

influence on LIA cooling (Wigley and Kelly, 1990; Lean et al., 1995; Mann et al., 1998; van Geel et al., 1999; Bond et al., 2001). Increased PC3o values at ~AD 1480 and ~AD 1645–1740 broadly coincide with the Spörer and Maunder minima. It is necessary to be circumspect about this surmise given the dating and sample resolution constraints, but if correct, this could indicate that enrichment in polyssacharides (i.e. low degradation of labile organic compounds) might be associated with periods of decreased solar activity. The Br record, which shows systematic low concentrations during the whole LIA, has very low values at ~AD 1480 and ~AD 1645–1740, suggesting that cooler conditions during solar minima may also have strongly limited halogenation in the bog. These patterns indicate a possible link between sunspot minima and reduced microbial activity in the Sandhavn bog. Declines in PC1o also might have occured during solar minima (Fig. 9), indicating that cooling may have limited the decomposition of organic matter during such intervals. Clearly the data coupling proxy records with minima in solar activity during the last millennium at Sandhavn are only tentative, but such associations have been reported from other studies. Mauquoy et al. (2007) identified increases in *Sphagnum tenellum* and *S. cuspidatum* (indicative of cool, moist climatic conditions) in northwestern European bogs that appear linked to LIA solar minima. In their study of Lake Lehmilampi, Finland, Haltia-Hovi et al. (2007) noted a relationship between varve thickness and solar forcing, although the physical mechanism linking these is still to be established. Blackford and Chambers (1995) also found an apparent correspondence between peat humification records and solar oscillations in Irish blanket peat.

Beginning ~AD 1870, a major change in vegetation occurred at Sandhavn with *Empetrum nigrum* oceanic heath replacing Cyperaceae-dominated steppe communities (Figs. 3 and 9). This, plus a more rapid build-up of peat and PCAR over the last ~100–150 cal yr BP, provides evidence of generally rising temperatures following the end of the LIA. At the same time, PC3o variations indicate enrichment of the peat with polysaccharides; this is despite warmer climatic conditions being more conducive to the decay of organic matter (i.e., polysaccharide degradation). The process appears heavily influenced by peat composition, particularly the increased abundance of *Empetrum nigrum* remains which are more resistant to decomposition than the sedge-dominated vegetation that it replaced. The next simultaneous shift in the organic matter indicators (PC1o and Br), peat growth and PCAR, occurred during the last 50 years and seem to reflect the presence of less decomposed peat, typical of the superficial layers of an active mire.

Atmospheric deposition of lead: links with anthropogenic emissions and possible sources

Murozumi et al. (1969) first demonstrated that a record of lead pollution, dating back to the mid-18th century and coinciding with European Pb production, was recorded in Greenland ice (at Camp Century, Fig. 1A). Their findings attest to the long-range transport of pollutants to Greenland from sources in industrialized countries. Subsequent research has extended the onset of Pb pollution, as recorded in Greenland ice, to the early historic period. Studies by Hong et al. (1994) and Rosman et al. (1997) show that Greek and Roman lead and silver mining, and smelting, polluted the middle troposphere of the Northern Hemisphere around two millennia ago. In contrast to the investigations on ice cores, studies of lead contamination using minerotrophic peatlands in southern Greenland (Shotyk et al., 2003; Schofield et al., 2010) have up until this point failed to reveal any significant enrichment in Pb, although Shotyk et al. (2003) suggest that a decrease in the $^{206}Pb/^{207}Pb$ ratio noted in minerotrophic peat from Tasiusaq relates to lead pollution originating from the USA in the 20th century.

The lead record from Sandhavn covers a period of around 700 years, extending back from the present to ~AD 1300 (Fig. 10). Lead concentrations remain below 2.5 µg g^{-1} throughout most of the sequence and then progressively increase after ~AD 1845. Maximum Pb levels (16.4–19.6 µg g^{-1}) were reached in the 1960s and 1970s, while later decades are characterized by a progressive decrease. Low loadings of Pb on PC1e indicate that Pb does not share a significant common variation with the lithogenic component along the sequence, intimating that in the majority of the record, Pb appears to be solely the result of atmospheric pollution. In order to normalise for any possible contribution of geogenic Pb to the bog at Sandhavn, we have calculated the Pb/Ti ratio (Fig. 10). Notwithstanding some minor differences, particularly between ~AD 1900 and 1940 when some of the Pb seems to be linked with increased soil erosion caused by the return of sheep farming to the region in the early 20th century, the pattern for Pb/Ti is almost the same as that of Pb concentrations: values above the baseline occur only after ~AD 1845, and from there they show a progressive increase which is more pronounced after ~AD 1940, peaking at the end of the 1970s, after which values steadily decrease. Recent modelling of atmospheric lead fluxes in southern Greenland has estimated a maximum value during the 1960s of 2400 ± 330 µg m^{-2} yr^{-1} (Massa et al., 2015).

The onset of lead pollution in the Sandhavn monolith occurs later than in records from the Greenland ice core (Murozumi et al., 1969) and lake sediments (Bindler et al., 2001b), where the highest levels of Pb pollution are recorded from ~AD 1750–1800 onwards. The pattern at Sandhavn is thus in closer agreement with the chronology of events from North America (i.e. the onset of the American industrial revolution) rather than that from Europe. Increased Pb deposition just after ~AD 1850 has been found in several North American records including the Great Lakes region (Graney et al., 1995), Maine (Big Heath and Sargent Mountain Pond), and Massachusetts (Plow Shop and Grove ponds), northeast USA (Norton et al., 1997, 2004), Hudson Bay (Imitavik and Far Lakes; Outridge et al., 2002), southern Quebec (Lake Tantaré; Gallon et al., 2005) and Point d'Escuminac, Eastern Canada (Kylander et al., 2009). High levels of Pb pollution at Sandhavn during the 20th century are also in good agreement with the Greenland ice core-based reconstructions made by Murozumi et al. (1969), who ascribed Pb pollution to lead smelting (for the period prior to ~AD 1940) and to the massive use of lead alkyls in gasoline (after ~AD 1940). Given that the dating uncertainty of sediment/peat records is often high for the 19th century, caution obviously needs to be exercised, especially given that some comparable lead records also exist in Europe (e.g. Weiss et al, 1999).

A North American source for the lead is also indirectly supported by the presence of *Ambrosia*-type (ragweed) in the Sandhavn pollen record (Fig. 3). After ~AD 1885, *Ambrosia*-type pollen is consistently present at trace values (typically <1%). *Ambrosia* is a common weed of cultivated land and a prolific pollen producer. The plant is not native to Greenland (Böcher et al., 1968) and, although morphologically-similar pollen is produced by plants present throughout central Europe from the Iron Age forwards, the most likely source for this pollen type is North America. Studies from eastern-central North America (Bassett and Terasmae, 1962; Gordon, 1966; Brugam, 1978; McAndrews, 1988; McAndrews and Boyko-Diakonow, 1989; Baker et al., 1993; Ireland et al., 2014) have demonstrated a rise in *Ambrosia* pollen coinciding with the arrival and expansion of European settlers. It seems that the introduction of intensive agricultural practices linked with forest clearance promoted the increase in *Ambrosia*-type pollen. This pattern has been dated to the 19th century, with only one paper (Brugam, 1978) suggesting an earlier date. The timing of the '*Ambrosia* rise' in North America closely matches the presence of *Ambrosia*-type pollen in the Sandhavn monolith. Bassett and Terasmae (1962) showed that ragweed pollen can be transported through the atmosphere at least 600 km from any known source. Observations of long-distance pollen transport to southern Greenland similarly indicate that northeastern North American source areas are typical (Rousseau, 2003; Rousseau et al.,

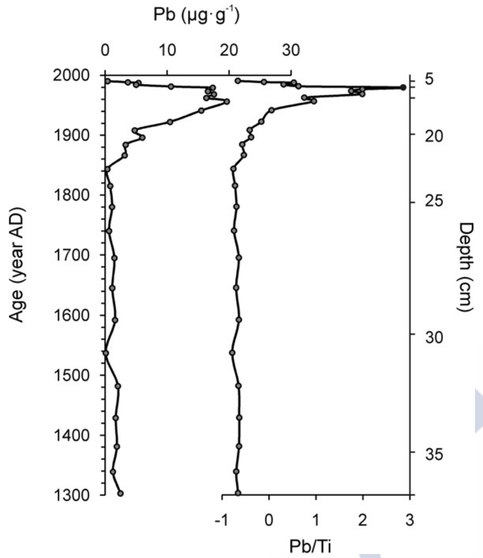

Figure 10. Pb concentration and Pb/Ti ratio (expressed as z-scores) through the peat unit of the Sandhavn monolith.

2006; Jessen et al., 2011). A source outside North America seems improbable; for example, *Ambrosia* is a recent introduction to Europe, first appearing after ~AD 1920 (Comtois, 1998) and spreading after the 1980s (Couturier, 1992; Dechamp and Dechamp, 1992; Thibaudon, 1992).

Cryptotephras have been recorded in peat profiles located adjacent to Norse sites in the Eastern Settlement and further demonstrate the potential for atmospheric particulates to reach southern Greenland from North America. Blockley et al. (2015) have identified tephra shards at three sites in the Eastern Settlement (Herjolfsnes, Hvalsey and Igaliku). These have geochemical signatures that are compatible with volcanic centres in the Aleutian Islands and Cascade Range, with the Augustine and Mount St Helens volcanoes being two of the likely sources.

Although a major North American source for the lead at Sandhavn seems most probable and is consistent with results from other studies, some qualifications remain. Rosman et al. (1993, 1994) analysed the Pb isotopic composition of Greenland snow collected at Summit to derive the relative lead contributions from the USA, Canada, and Eurasia between ~AD 1967 and 1989. They concluded that the United States was a significant source of lead during the 1970s (up to 67% of the measured total) before it declined considerably in relative importance (to 25% in the late 1980s), mirroring reductions in the use of leaded petrol, resulting in the Eurasian and Canadian contribution to the Pb signal becoming predominant. Seasonal investigations on the isotopic composition of Pb on snow collected at Dye 3 in southern Greenland also suggest that most of the Pb pollution signal was primarily sourced from leaded gasoline used in North America, but that the same ice-sheet surface also received lead from elsewhere during certain parts of the year: Pb in autumn and winter snow originated in North America, while that in spring to mid-summer snow was from Eurasia (Rosman et al., 1998). In contrast, a recent isotopic analysis of west Greenland lake sediments near Kangerlussuaq (Bindler et al., 2001a, 2001b) suggests that the lead record at this location was derived from west European and Russian sources. The relative location/latitude of the sites (Fig. 1A) possibly accounts for the differences in lead sourcing. For example, studies have shown that high Arctic sites have largely Russian sources with pollutants transported over the North Pole, whereas lakes in southwest Greenland are considered to have a significant input from west European sources (Bindler et al., 2001b). The lead isotopic signature from aerosol and snowpack samples from Devon Island and from the Canadian High Arctic (Sturges and Barrie, 1989; Shotyk et al., 2005), and from a lake in Pearyland (Lake G07-10), north Greenland, favour a Eurasian source (Michelutti et al., 2009). The origin of lead deposited in Lake CF8 near Nunavut, Baffin Island, could not be determined unequivocally, but investigators suggested an American source to be unlikely (ibid.). In contrast, the evidence from Sandhavn supports atmospheric transfer from North America. Lead isotopic analysis is in progress to ascertain more precisely the sources for lead in the Sandhavn record, and clearly more research is required if a full understanding of the spatial and temporal variation in lead isotopic signatures across Greenland is to be achieved.

Conclusions

The Norse Age section of the Sandhavn peat profile may be compromised in its basal sand/peat interface segment, but variations in the mineral content of the overlying peat may be partly related to local human activity during the later stages of Norse occupation. A subsequent increase in the lithogenic content during the early 20thcentury may reflect soil erosion resulting from the return of (modern) sheep farming to southern Greenland.

Low concentrations of Br are recorded during the LIA — a climatic downturn that is also reflected in extremely low peat accumulation rates at Sandhavn from ~AD 1400–1800. Cold conditions, possibly combined with flooding of the mire surface during milder seasons, which would have created reducing conditions, appear to have caused a slowdown in halogenation that affected Br incorporation into the peat. Low Br concentrations and changes in levels of polysaccharides are possibly in phase with sunspot cycles (Spörer and Maunder minima), though confirmation of a direct link between these parameters and solar activity will require further testing. The local expansion of *Empetrum nigrum* oceanic heath at the end of the 19th century seems to have caused an attendant enrichment in polysaccharides within the peat, suggesting that vegetation type was a major influence over peat organic matter composition at this time.

The site at Sandhavn has proven more useful for reconstructing a record of lead pollution in southern Greenland than the minerotrophic fen peats that have previously been investigated for this purpose. At Sandhavn, atmospheric Pb pollution is recorded after ~AD 1845, with peak concentrations occurring during the AD 1970s. There is indirect evidence of a predominantly North American origin for this signal. Isotopic analyses will be required before the sources for the lead deposited around the southern tip of Greenland can be identified with greater certainty.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.yqres.2015.06.001.

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3.3. Paper III

Silva-Sánchez, N., Martínez Cortizas, A., Abel-Schaad, D, López-Sáez, J.A. and Mighall, T.M. **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)**. Accepted by *The Holocene.*

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Research paper

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)

Accepted by The Holocene
1-13
In press

Noemí Silva-Sánchez[1], Antonio Martínez Cortizas[1], Daniel Abel-Schaad[2], José Antonio López-Sáez[2], Tim Mighall[3]

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. 17th century were likely related to modifications of tree cover and/or variations in wind strength.

Keywords
Geochemistry, Pollen, Non-pollen Palynomorphs, Carbon accumulation, Peat decomposition, Soil erosion, Soil erosion, Dust fluxes, transhumance

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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

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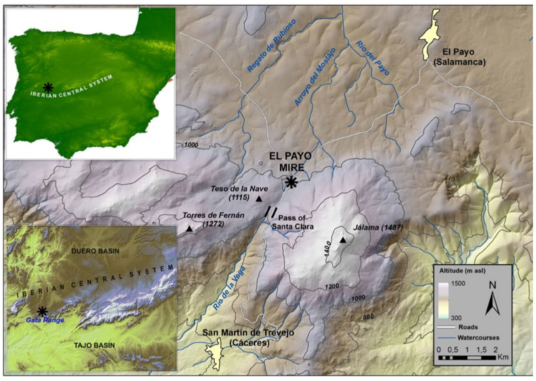

Figure 1. Location map of El Payo mire.

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.

Material & Methods

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.

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).

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.

Table 1. Results of 14C daing, showing calibrated age ranges (2σ).

Sample	Depth (cm)	Lab code	14C age	Age (AD)		Probability
				Min	Max	
PY15	14-15	Ua-38950	107,5 ± 0,3 pM	1956	1955.51	95
PY55	54-55	CNA312	140±80 BP	1652	1953	95
PY71	70-71	Ua-38951	225±30 BP	1641	1683	40.5
				1736	1759	5.2
				1761	1804	36.7
				1936	1954	12.6
PY78	77-78	Ua-38952	320±30 BP	1485	1604	73.1
				1606	1645	21.8
PY100	99-100	Ua-38953	685±30 BP	1269	1313	64.1
				1357	1388	30.7

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).

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).

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.

Results

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 $cm \cdot yr^{-1}$, and very constant between ~AD 1315 to ~1650 (equivalent to a deposition time [DT] of 13.4-11.7 $yr \cdot cm^{-1}$). Then, peat growth increased gradually from ~AD 1650 to 1900 until it reached rates of ~0.33 cm·yr-1 (3.3 $yr \cdot cm^{-1}$), staying stable around this point to the mire surface.

Geochemical record

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.

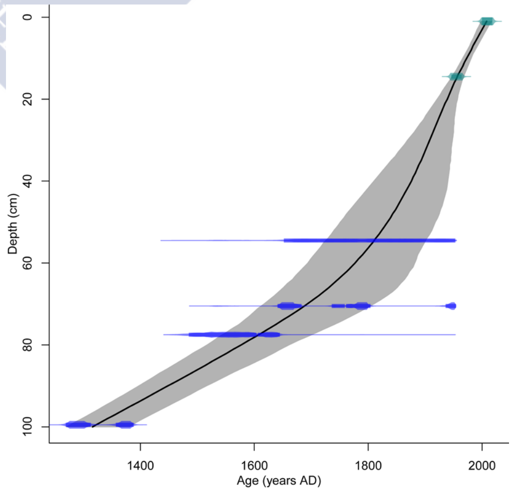

Figure 2. Age depth model of the PY core. Blocks in the radiocarbon ages represent the 95% confidence level in radiocarbon dates calibration, and the grey-shaded area the highest density ranges.

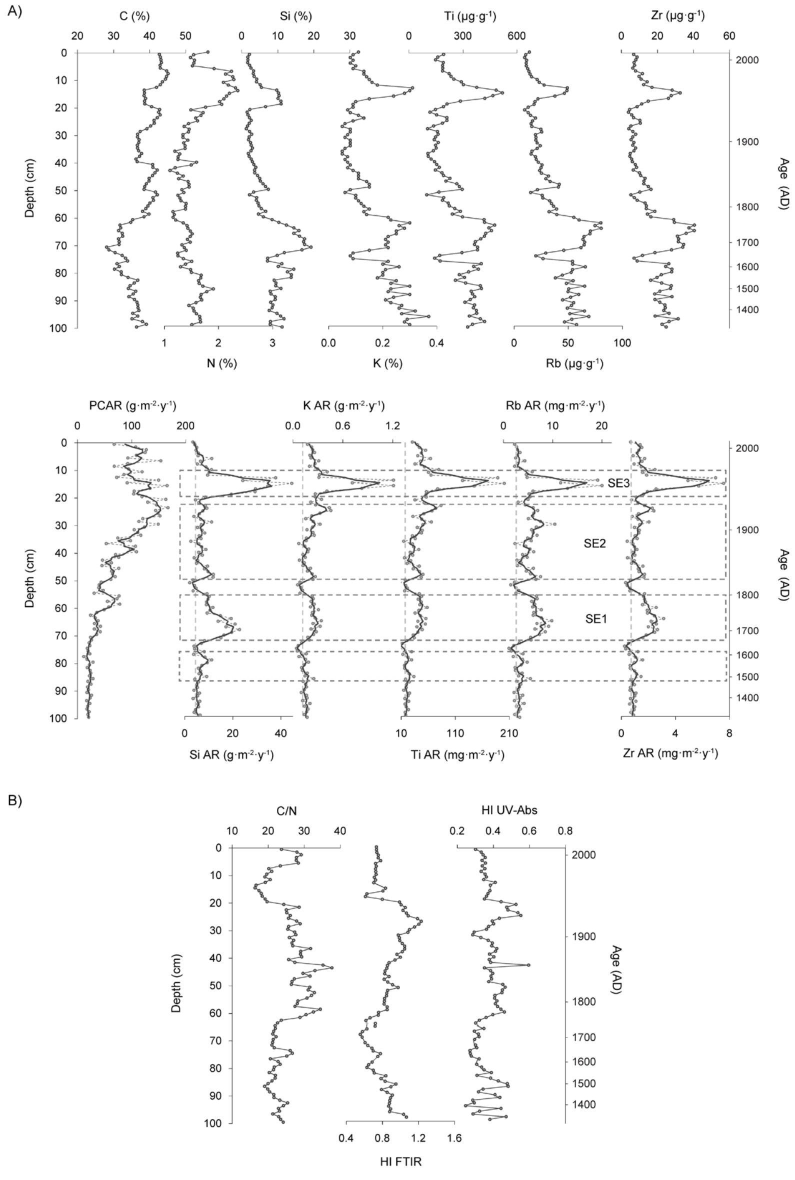

Figure 3. A) Vertical trends in the elemental composition of organic (C, N) and lithogenic elements (Si, K, Ti, Rb, Zr) in the PY core expressed as % and as accumulation rates. For accumulation rates (PCAR, Si AR, K AR, Ti AR, Rb AR and Zr AR) dashed lines connect measured values and solid line represents 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).

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 (Table 2). 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.

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-

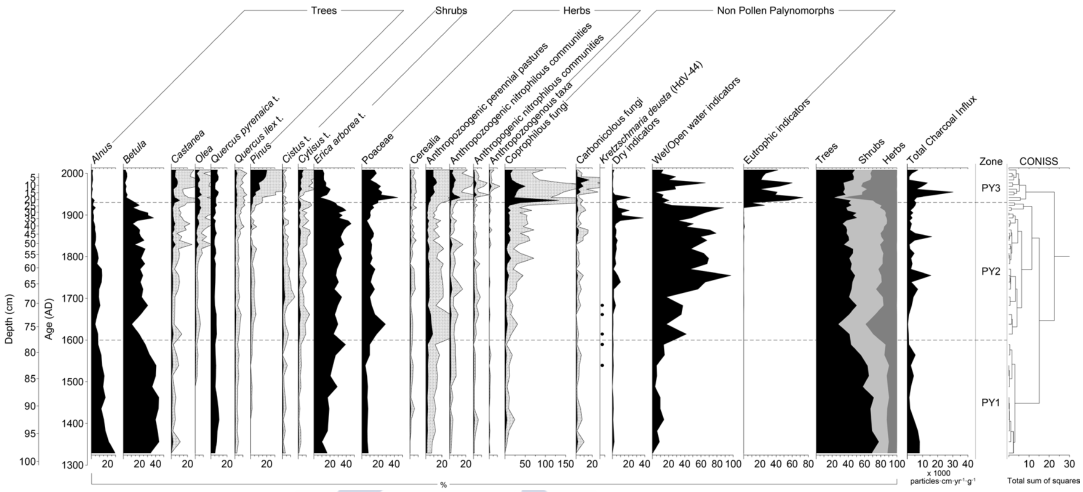

Figure 4. Palynological summary diagram of the PY core. Anthropozoogenic perennial pastures: Apiaceae, Brassicaceae, Campanula, Caryophyllaceae, Fabaceae undiff., Liliaceae undiff., Rosaceae undiff., Scrophulariaceae; Anthropozoogenic nitrophilous communities: Anthemis, Chenopodiaceae, Galium, Plantago, 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.

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).

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.

Discussion

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

Table 2. Bilateral Pearson correlation coefficients (r) (α=0.01) among lithogenic elements

Sample	Si	K	Ti	Rb	Zr
Si	1				
K	0.758	1			
Ti	0.797	0.936	1		
Rb	0.879	0.879	0.871	1	
Zr	0.886	0.905	0.944	0.948	1

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; α = 0.01) whereas with N is -0.77 (r; α = 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.

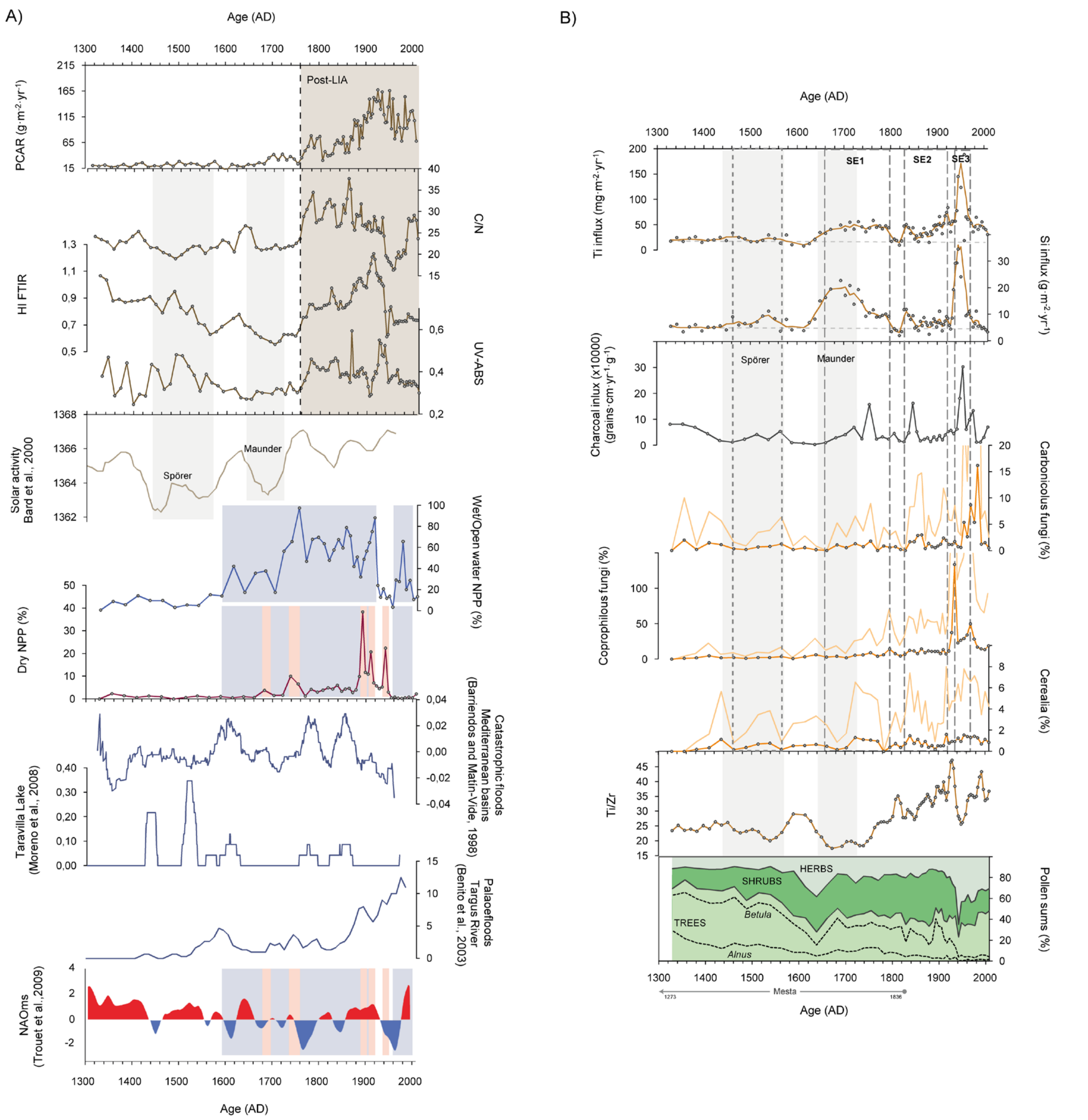

Figure 5. A) variations in indicators of peatland dynamics and climate. PCAR, C/N, HI FTIR, UV-Abs variations and wet/Open water vs. dry non pollen palynomorphs (NPPs) variations the PY core plotted against Solar activity reconstruction by Bard et al., 2000, several paleoflood reconstructions on Mediterranean 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

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).

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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3.4. Paper IV

López-Merino, L., ***Silva Sánchez, N.***, Kaal, J., López-Sáez, J.A. and Martínez Cortizas, A. (2012) **Post-disturbance vegetation dynamics during the Late Pleistocene and the Holocene: An example from NW Iberia**. *Global and Planetary Change* 92-93, 58–70.

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Post-disturbance vegetation dynamics during the Late Pleistocene and the Holocene: An example from NW Iberia

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ABSTRACT

There is a wealth of studies dealing with the reconstruction of past environmental changes and their effects on vegetation composition in NW Iberia, but none of them have focused specifically on the post-disturbance dynamics (i.e. the type of response) of the vegetation at different space and time scales. To fill this gap, we analysed the record of pollen and non-pollen palynomorphs (NPP) of a 235-cm thick colluvial sequence spanning the last ~13,900 years. The aims were to detect the changes in vegetation, identify the responsible drivers and determine the type of responses to disturbance. To extract this information we applied multivariate statistical techniques (constrained cluster analysis and principal components analysis on transposed matrices, PCA_{tr}) to the local (hydro-hygrophytes and NPP) and regional (land pollen) datasets separately. In both cases the cluster analysis resulted in eight local and regional assemblage zones, while five (local types) and four (regional types) principal components were obtained by PCA_{tr} to explain 94.1% and 96.6% of the total variance, respectively. The main drivers identified were climate change, grazing pressure, fire events and cultivation. The vegetation showed gradual, threshold and elastic responses to these drivers, at different space (local vs. regional) and time scales, revealing a complex ecological history. Regional responses to perturbations were sometimes delayed with respect to the local response. The results also showed an ecosystem resilience, such as the persistence of open *Betula*-dominated vegetation community for ~1700 years after the onset of the Holocene, and elastic responses, such as the oak woodland to the 8200 cal yr BP dry/cold event. Our results support the notion that palaeoecological research is a valuable tool to investigate ecosystem history, their responses to perturbations and their ability to buffer them. This knowledge is critical for modelling the impact of future environmental change and to help to manage the landscape more sustainably.
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1. Introduction

Environmental and climatic changes were frequent during the Late Quaternary; some even relatively abrupt (Mayewski et al., 2004). Many of them have been reliably recorded by environmental archives in the form of long-term records, which contain key information that offers a unique opportunity to study the patterns of ecological change (Willis et al., 2010; Williams et al., 2011). Among these records those related to vegetation dynamics are the most investigated. As with any other natural system, vegetation has some resilience to withstand environmental change. However, the capacity to buffer changes, either natural or anthropogenic, varies at different spatial and time scales, and sometimes involves gradual or abrupt modifications/reorganisations of the structure and functioning in response to perturbations (Holling, 1973; Dearing, 2008). Thus, there is an obvious need to understand the post-disturbance responses of vegetation since disturbance is a key factor structuring its composition. As Ritchie (1986: 72) proposed "*The central issue of palaeoecologists is to measure accurately the response of vegetation to environmental change and to express differing patterns of response in quantitative terms*".

Carrión et al. (2010a) outlined the patterns of vegetation change for the Late Quaternary in the Iberian Peninsula, emphasising the strong regional differences, mainly related to the Eurosiberian and Mediterranean biogeographical regions. While in the Mediterranean region a large heterogeneity in vegetation change has been pointed out, in the Eurosiberian one, comprising the north and northwest, as well as in other areas with Atlantic influence, a more homogeneous picture has emerged. Moreover, in the Eurosiberian area the vegetation

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change generally follows the Central European floristic model, where a rapid spread of mesophytic species occurred at the onset of the Holocene. Overall, the last ~14,000 years of palaeoenvironmental and vegetation changes in NW Iberia has been investigated using a variety of proxies, including pollen, non-pollen palynomorphs (NPP), charcoal, plant macroremains, diatoms, geochemistry and molecular markers, in several types of archives such as lacustrine deposits (Allen et al., 1996; Santos et al., 2000; Muñoz Sobrino et al., 2001; Leira and Santos, 2002; Muñoz Sobrino et al., 2004; Jalut et al., 2010; Moreno et al., 2011; López-Merino et al., 2011a), mires (Muñoz Sobrino et al., 1997; Martínez Cortizas et al., 1999, 2005; Mighall et al., 2006; López-Merino et al., 2010a, 2011b; Morales-Molino et al., 2011; Schellekens et al., 2011), colluvial soils (Kaal et al., 2008; Costa Casais et al., 2009; Carrión et al., 2010b; Kaal et al., 2011), coastal sediments (Santos and Sánchez-Goñi, 2003; García-Amorena et al., 2007), marine sediments (Desprat et al., 2003; Muñoz Sobrino et al., 2007a), and archaeological deposits (López-Sáez et al., 2003, 2009; López-Merino et al., 2010b). These studies were mainly undertaken in mountain areas and showed complex histories where climate, fire, vegetation change and human activities, e.g. animal husbandry, agriculture and mining, were ultimately responsible for past and current landscape configuration (Ramil-Rego et al., 1998; Martínez Cortizas et al., 2005; Muñoz Sobrino et al., 2005; Muñoz Sobrino et al., 2007b; Martínez Cortizas et al., 2009). Briefly, from the onset of the Holocene to ~2000 years ago forests expanded and were important in the landscape. Indicators of human impact started to appear around ~7600 years ago, increasing at ~4500 years - cal BP with widespread phases of deforestation since Roman times onwards (Jalut et al., 2010). But despite the many studies focusing upon past vegetation, climate trends and impact of human activities, investigations comparing vegetation composition and post-disturbance dynamics are lacking. The same is true for other parts of the Iberian Peninsula, with notable exceptions for the SE of Iberia. Firstly, the study of the pollen record of Siles Lake by Carrión (2002), which covers the last ~20,300 years, showed gradual, rapid and threshold responses, which involved complete changes in forest composition, as well as abrupt shifts at the local scale, pointing towards hydroclimatic variations. Moreover, lags in vegetation development in comparison with limnological stages were identified at the centennial scale. Secondly, in another study carried out by Carrión et al. (2001) in the Villaverde Lake, timelags in vegetation response to environmental change were detected, especially in response to climate amelioration at the beginning of the Holocene, pointing towards the resilience of established *Pinus* populations during ~2200 years, as well as decadal shifts in the pollen record since the mid-Holocene. Finally, Gil-Romera et al. (2010a) defined ecosystem functioning and resilient behaviour at long-term time scales at two sites. At Zoñar, it seems that disturbance promoted changes in biodiversity and landscape structure, shifting from one state to another; while in Gádor several stable phases linked to arid conditions and the spread of the grassland were detected.

In other parts of Europe a similar picture emerges, as only a few long-term ecological studies have focused upon vegetation response and most of them do not contextualise the type of response to perturbation. Some exceptions include the research done by Tinner et al. (2000) in the Alps, in which they identified several possible responses of plants to fire of medium and high frequency; by Hellberg et al. (2003) in Sweden, where vegetation dynamics and disturbance history has been detected in several deciduous forests; or by Feurdean et al. (2010) in Romania, where they explored the potential driving factors for the vegetation change in eight pollen datasets, but also the response of the vegetation at different spatial and time scales in the sense of differentiation and homogenization, i.e. reduction or increase in similarity, an increasingly important feature for modern-day conservation plans. However, in other parts of the world this approach has been applied more often, i.e. the disturbance history of a *Tsuga*-dominated forest in New England (Massachusetts, Foster and Zebryk, 1993), the threshold responses and differential resilience behaviour of vegetation to environmental perturbation in Madagascar (Virah-Sawmy et al., 2008), and the alternating open and encroaching phases in the Ethiopian savannah that showed a non-linear response to environmental change (Gil-Romera et al., 2010b; also see Willis et al., 2010; Gil-Romera et al., 2010a for more examples). All the examples stress the importance of such knowledge for conservation and management of ecosystems and to better assess the consequences of future changes.

In this paper we present a palynological study of a colluvial soil (PRD-4), spanning the last ~13,900 years, sampled in Campo Lameiro (Pontevedra, NW Iberia). Campo Lameiro is considered a suitable site because, apart from the fact that it is located in an archaeological area with one of the most important collections of pre-historic rock art in Europe, several studies developed there recently (e.g. Kaal et al., 2008; Costa Casais et al., 2009; Carrión et al., 2010b; Kaal, 2011; Kaal et al., 2011) showed that colluvial soils are suitable archives for palaeoenvironmental research. The objectives of this work were to (1) detect changes in the vegetation composition and their drivers; and (2) decipher the post-disturbance dynamics, at regional and local scales. In addition, in order to get statistical information about vegetation composition and response to environmental change, novel multivariate analyses were applied.

2. Materials and methods

2.1. Study area

The PRD-4 sequence is located in the Rock Art Park of Campo Lameiro (42°32′ N 8°31′ W, Pontevedra, NW Spain, Fig. 1), in a local depression on the isolated hill Monte Paradela (260–320 m a.s.l.). The area is located in the Atlantic/Eurosiberian climate region, with mild (mean annual temperature of 15 °C) and humid (mean annual precipitation of 1200 mm) climatic conditions (Martínez Cortizas and Pérez Alberti, 1999). Currently, *Pinus pinaster*, *Quercus robur*, *Pteridium aquilinum* and heathlands with different species of *Erica* and *Calluna vulgaris* are the main components of the vegetation, with remnants of *Eucalyptus globulus* plantations, *Ulex* and *Cytisus*, which are periodically eliminated since 2003 with the setting up of the archaeological park. In the valleys, the riparian vegetation is composed of *inter alia Alnus glutinosa*, *Corylus avellana*, *Fraxinus excelsior*, *Ulmus glabra*, *Populus*, *Betula alba* and *Crataegus monogyna*.

Fig. 1. Location of the study area in NW Spain.

2.2. Sampling and palynological analysis

A soil monolith (PRD-4, 235 cm-thick, Fig. 2) was sampled from a trench and sliced into 5 cm sections. Samples were treated following the classic chemical methodology (Moore et al., 1991) to obtain pollen, spores and other NPP with concentration in heavy liquid (Goeury and de Beaulieu, 1979). Palynological counting was conducted at 400× under the light microscope, and the average total land pollen sum (TLP) was 575 terrestrial pollen grains, excluding hydro-hygrophytes and NPP (expressed as percentages of the TLP). The average sum of hydro-hygrophytes and NPP was 170 palynomorphs. Palynomorphs were well preserved and no taphonomic problems were detected. The identification was aided by the reference collection of the Archaeobiology laboratory (CCHS, CSIC, Madrid), identification keys and atlases (Moore et al., 1991; Reille, 1992). NPP classification follows the nomenclature proposed by the Hugo de Vries (HdV) laboratory of the University of Amsterdam. Pollen diagrams were obtained using TILIA (Grimm, 1992, 2004).

2.3. Radiocarbon dates and chronology

Six samples were selected for ^{14}C dating using the AMS technique. The ^{14}C dates (Table 1) were calibrated using the IntCaL09.14C calibration curve (Reimer et al., 2009). The age–depth model was obtained using the Clam software developed by Blaauw (2010), using a smooth-spline solution. According to this model, the 235 cm represents the last ~13,900 years (Fig. 3).

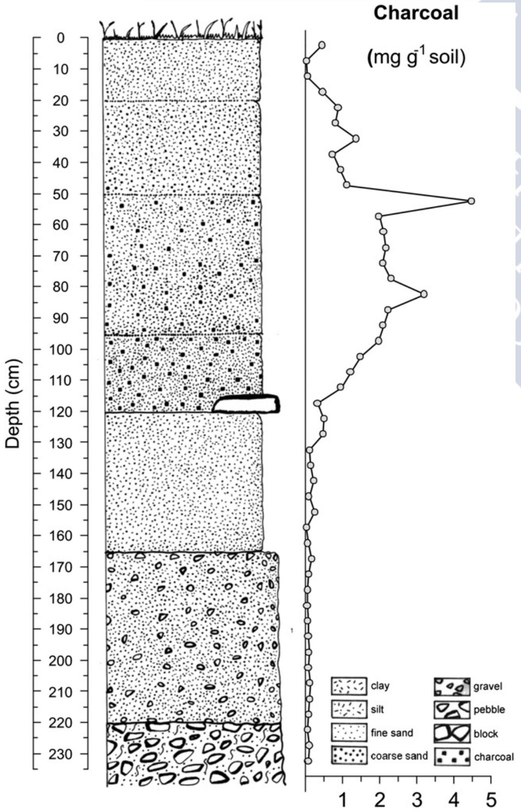

Fig. 2. PRD-4 soil stratigraphy (courtesy of Manuela Costa Casais) and charcoal concentration (Kaal et al., 2011).

Table 1
Results of ^{14}C dating, showing calibrated age ranges (2σ) in cal yr BP.

Sample	Depth (cm)	Lab code	^{14}C age (BP)	Age (cal yr BP)	Probability (%)
PRD-4-02	5–10	Ua-34719	104.3 ± 0.4 pM	Modern	–
PRD-4-06	25–30	Beta-297739	850 ± 30	690–797	89.4
				820–820	0.1
				871–897	5.4
PRD-4-14	65–70	Beta-299229	3080 ± 30	3219–3231	2.9
				3238–3368	92
PRD-4-20	95–100	Beta-299230	4090 ± 30	4448–4466	3.4
				4518–4651	65.6
				4670–4701	6.7
				4759–4808	19.2
PRD-4-25	120–125	Beta-297740	5540 ± 40	6286–6403	100
PRD-4-39	190–195	Beta-240963	9760 ± 50	10,910–10,911	0.1
				11,096–11,258	94.9

2.4. Separating local and regional taxa

In this study we consider the taxa included in the TLP as related to a regional signal, while hydro-hygrophytes and NPP as components of the local signal. When we refer to regional vegetation we mean close regional. Distinguishing local from regional vegetation in a soil sequence, compared to sequences from wetlands such as mires and lakes, is challenging. In the latter, the local vegetation communities can be identified, but in colluvial soils this approach is not as straightforward. However, NPP can be safely considered as local indicators as their dispersal is limited. The case of the hydro-hygrophyte taxa is more complex, as they could also be part of the regional communities. The PRD-4 sequence is located in a small depression, so variations in moisture and water availability could be responsible for differences in local communities. For this reason, we have included the hydro-hygrophytes into the local signal as they follow patterns related to those found for the NPP (Fig. 4), i.e. maximum development of Cyperaceae, Filicales and Ranunculaceae are synchronous with *Spirogyra* and *Mougeotia*, while maximum values of *P. aquilinum* and *Polypodium vulgare* type are coeval

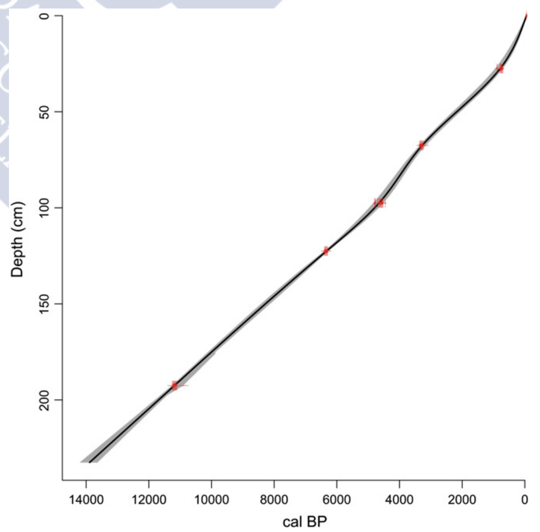

Fig. 3. Age–depth model of the PRD-4 sequence, fitted with a smooth-spline function using Clam (Blaauw, 2010). Red blocks show 95% the highest posterior density ranges. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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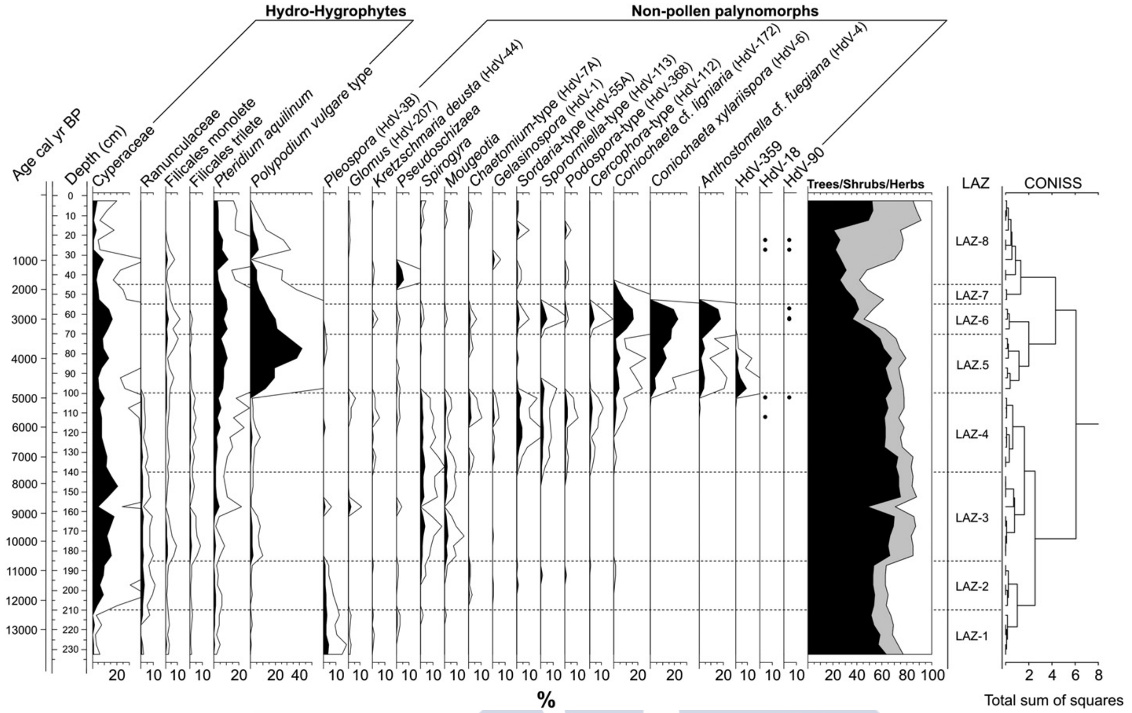

Fig. 4. Local (hydro-hygrophytes and NPP) palynological diagram. The filled silhouettes show the percentage curves of the taxa, while the open silhouettes show the 5× exaggeration curves. CONISS cluster analysis together with the Local Assemblage Zones (LAZ), and the estimated chronology are plotted as well. Values of hydro-hygrophytes and NPP are expressed as percentages of the total land pollen sum (trees, shrubs and herbs).

with the presence of *Coniochaeta* cf. *ligniaria*, *Coniochaeta xylariispora* and *Anthostomella* cf. *fuegiana*. However, it is important to remind that this separation is just an approach, a model to try to understand the changes at different scales. In fact, previous anthracological research (Kaal et al., 2011) demonstrated that woody vegetation was abundant at the margins of the small basin, and that ferns were components of the forest. With the proposed separation into regional and local, we want to extract general trends taking into account the spatial limitations cited here. As an example, in pollen research done in peatlands the general approach is to consider the Ericaceae (*Erica* and *Calluna*) as a component of the regional vegetation, when some species are frequent components of bog communities. The same problem applies to Poaceae, as it is also considered as a regional indicator, or Cyperaceae, considered as local, when both could be part of regional and local communities. But, although with limitations, we believed the established categories enable the assessment of the main general trends and, therefore, the separation of signals proposed could be a valid approach when combined with multivariate statistics.

2.5. Statistical analyses

When working with large datasets of environmental proxies, multivariate methods are helpful to reduce the dimensionality or group/classify samples. With such techniques it is possible to avoid extensive descriptions of results, making the interpretation and explanation of the observed patterns easier in terms of underlying processes operating at relevant spatial and time scales (Birks, 1985). Thus, to extract the information of the local and regional proxies we applied multivariate statistical techniques. Stratigraphically constrained cluster analysis by the method of total sum of squares (Grimm, 1987) was used to define local and regional palynological zones, which are based on changes (in terms of Euclidian distance) in the pollen assemblages between consecutive samples. These zones are usually interpreted as shifts in vegetation composition. Two cluster analyses were performed: one for regional taxa, including the types considered in the TLP; and another for local taxa, including hydro-hygrophytes and NPP. As such, the data comprised 41 and 24 taxa, respectively. Percentage values were used after the palynological data were re-summed to 100% for the taxa not included in the TLP (local signal). Thus the purpose was to perform two independent zonations that enable the comparison between the results of local and regional proxies.

In addition, principal component analysis (PCA) was used to describe the main features of the palynological record and get insights into the representativeness of changes in vegetation composition through time and the type of response to environmental change. Again, separate analyses were performed for regional and local taxa, both on the transposed data matrices (PCA_{tr}); that is, with samples in columns (variables) and taxa in rows (cases). This approach is intuitive to interpret palynological data from an ecological point of view, and it enables summarizing the palynological composition of the samples based on co-variation patterns. Correlation matrices were used, and varimax rotation solutions were applied to constrain the co-variation in the components. PCA analyses were done using SPSS 15.0.

Due to the fact that the number of palynomorphs in the local signal is lower than the number of types in the regional signal, the reliability of the statistical results is of concern. However, the average of the local sum is 170, and the average number of taxa per sample is 10.6, not too low if we consider that the number of counted NPP is often lower in most palynological studies. Nonetheless, some samples have low local sums, mainly at the bottom and the top of the sequence (24–49 palynomorphs), but the taxonomic diversity is not much lower in these samples (6–12 different taxa), so that we believe that the results of the statistical analysis are representative and significant.

The use of a transposed matrix demands a careful interpretation of some key concepts associated to conventional PCA, typically applied to non-transposed datasets (i.e. samples as rows and variables as columns). This is because, contrary to the usual focus of the PCA, i.e. the co-variation of taxa, with PCA_{tr} we detect the co-variation of samples, i.e. the co-variation of the palynological assemblages of the different soil sections/age periods. This allows for the comparison of samples taking into account their palynological composition and the characterization of assemblages of co-existing principal taxa, i.e. ecological groups composing the palynological record, as well as their importance in each sample/age period. For each principal component, the taxa showing large factor scores (i.e. larger abundances) are those explaining most of the variation of the pollen and NPP signal in samples with large factor loadings (Silva Sánchez, 2010). Thus, the PCA_{tr} approach allows the identification of assemblages of palynomorphs with statistically significant contribution to the total variance, and to express quantitatively for each sample the proportion of variance of its composition explained by each principal component (i.e. significant assemblages of palynomorphs). These two aspects are valuable for defining vegetation composition and for assessing the type of response. Regarding the type of responses, we distinguished between gradual, threshold and elastic ones on the basis of the PCA_{tr} results: (1) Threshold, when a complete change from one sample to the next is detected, in terms of the main principal component (i.e. palynological assemblage) explaining most of the variance of the palynological composition of the samples; (2) Gradual, when the change detected in the composition of the vegetation implies the decline of the importance of one principal component and the increase of another. This change could involve a complete or partial replacement of the principal component (i.e. vegetation formation) explaining the variance of the palynological composition of the samples; (3) Elastic, when a complete recovery of the previous palynological composition occurs after a short-term disturbance. Additionally, we have included the term of "sensitivity" for those cases where the cluster analysis identified the boundary of a palynological zone but the PCA_{tr} did not suggest a change in the vegetation composition.

3. Results and interpretation

3.1. Local signal

Eight Local Assemblage Zones (LAZ) were detected by cluster analysis (Fig. 4) while five principal components explained 94.1% of the total variance in the dataset. The percentage of the variance explained by each principal component can be seen in Table 2, and the fractionation of communalities and the factor scores are represented in Figs. 5 and 6.

Table 2
Eigenvalues and variance explained by the principal components obtained by PCA analysis of the transposed data matrix of local taxa (hydro-hygrophytes and NPP).

PCA local taxa						
Component	Initial eigenvalues			Rotation sums of squared loadings		
	Total	% Variance	Cumulative %	Total	% Variance	Cumulative %
$PC1_L$	25.4	54.0	54.0	19.9	42.3	42.3
$PC2_L$	9.8	20.9	74.9	11.0	23.4	65.7
$PC3_L$	4.6	9.8	84.7	6.7	14.3	80.0
$PC4_L$	3.1	6.6	91.3	5.1	10.9	91.0
$PC5_L$	1.3	2.8	94.1	1.5	3.1	94.1

Extraction method: principal component analysis with varimax rotation.

In LAZ-1 (235–210 cm; ~13,900–12,370 cal yr BP) the fourth principal component ($PC4_L$) explains most of the variance (65–96%) of the palynological composition of samples (Fig. 5), with *Pleospora* commanding the largest positive factor score (Fig. 6). *Pleospora* is a fungal ascospore and has been found in relatively dry sections of ombrotrophic peat (van Geel, 1978; Yeloff et al., 2007). PRD-4 is a black, organic-rich, colluvial soil, but the ascospores could still be related to dry conditions.

LAZ-2 (210–185 cm; ~12,370–10,670 cal yr BP) is characterised by the first principal component ($PC1_L$), explaining most of the variance (63–95%) of this zone (Fig. 5). Cyperaceae is the taxon with the largest positive factor score (Fig. 6). The expansion of sedges represented a major change in the palynological composition at local scale (Fig. 5) and it is most likely related to more humid (or wetter?) conditions.

LAZ-3 (185–140 cm; ~10,670–7580 cal yr BP) is also characterised by the dominance of $PC1_L$, reflecting the consolidation of Cyperaceae. It accounts for most of the variance (92–96%), except at a depth of 160–155 cm (32%; Fig. 5). The emergence of *Spirogyra* and *Mougeotia* (van Geel, 1978) and increased percentages of ferns (Fig. 4) seem to reflect a shift towards more humid conditions. At 160–155 cm (~8920–8620 cal yr BP), $PC3_L$ and $PC4_L$ also explain a significant part of the variance (40 and 13%, respectively, Fig. 5). $PC4_L$ indicates dry conditions, while in $PC3_L$ *P. aquilinum* is the taxon with the largest positive factor score and *C. xylariispora* has a moderate negative factor score (Fig. 6). Thus, at this depth, $PC3_L$ reflects an abrupt short-term shift in this zone between sedges and bracken, but also indicates an opposite pattern between *P. aquilinum* and *C. xylariispora*, which may reflect woodland opening and accumulated dead wood, respectively. Moreover, the punctual presence of *Glomus* in this sample could be related to erosion linked to drier conditions.

In LAZ-4 (140–100 cm, ~7580–4800 cal yr BP), $PC1_L$ still explains most of the variance (36–94%), but with increasing proportions accounted by $PC3_L$ (3–56%; Fig. 5), indicating a more or less gradual replacement of Cyperaceae by *P. aquilinum*. The detection of coprophilous fungi, such as *Sordaria*-type, *Sporormiella*-type, *Podospora*-type and *Cercophora*-type (Fig. 4), suggests that this change could be related to grazing activities in the local surroundings. Moreover, the abundance of macroscopic (>2 mm) charcoal particles (from hereon charcoal, Fig. 2) increased simultaneously with the appearance of grazing indicators.

From 100 to 45 cm, corresponding to zones LAZ-5 to LAZ-7, charcoal concentration increased (Fig. 2), most of which originated from deciduous *Quercus* (Kaal et al., 2011). LAZ-5 (100–70 cm; ~4800–3400 cal yr BP) is characterised by the second principal component ($PC2_L$), which explains the vast majority of the variance in the pollen composition of this zone (71–94%; Fig. 5). *P. vulgare* type has a large positive score, while *C. xylariispora* has a moderate positive score (Fig. 6). The increase in charcoal fragments in this zone is not associated to grazing activities, as they are not recorded in tandem with synanthropic pollen and coprophilous fungal spores (Figs. 4 and 7), but could be climate-induced, although human activities with purposes other than animal husbandry could have also been important.

In LAZ-6 (70–55 cm; ~3400–2510 cal yr BP), $PC2_L$ also explains most of the variance (63–85%), although the fifth principal component ($PC5_L$) increases in importance throughout the zone (8–26%; Fig. 5). For $PC5_L$, *Pseudoschizaea* and *P. vulgare* type have large positive factor scores, while *C. xylariispora*, *C.* cf. *ligniaria* and *A.* cf. *fuegiana* have large negative factor scores (Fig. 6). *P. vulgare* type continues to be the main taxon in the local vegetation although soil erosion is inferred from the presence of *Pseudoschizaea*. Soil erosion was probably exacerbated by grazing (renewed appearance of coprophilous fungi) and the lack of arboreal tree cover (low arboreal pollen percentages; Fig. 7).

In LAZ-7 (55–45 cm; ~2510–1830 cal yr BP), $PC2_L$ dominates the record (55–57%), although $PC3_L$ is also important (25–28%; Fig. 5). Thus, *P. vulgare* type and *P. aquilinum* are the best represented local

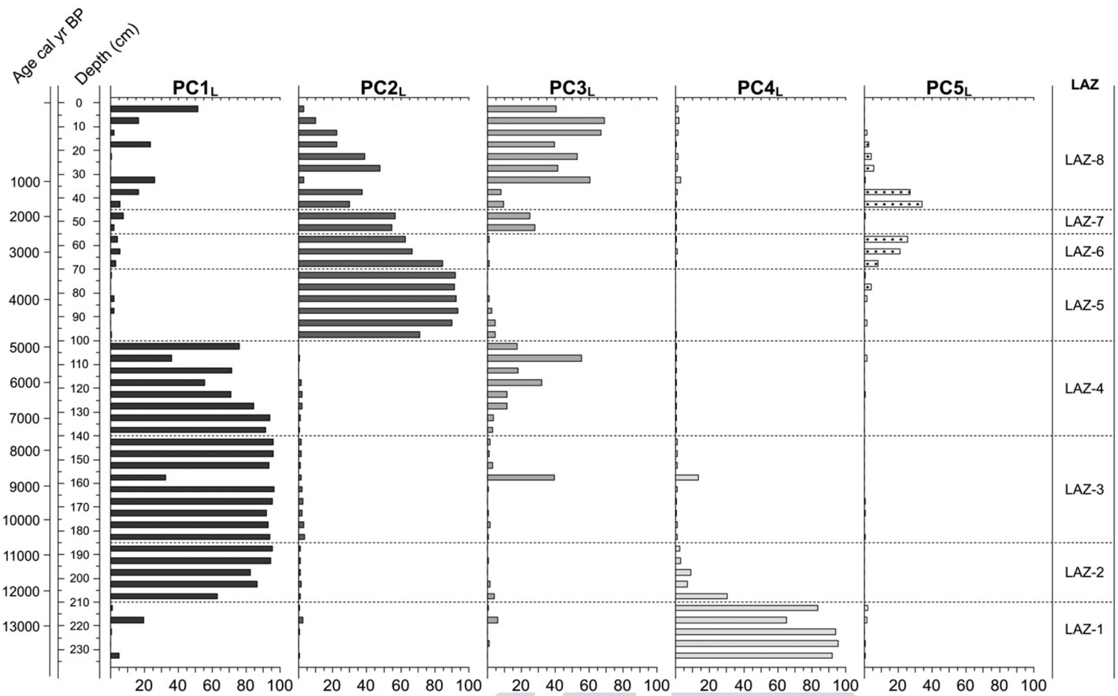

Fig. 5. Squared factor loadings of the five principal components (transposed matrix) explaining the variation of the local signal of PRD-4 soil sequence.

taxa. In this zone, the maximum concentration of charcoal particles was detected (Fig. 2).

Finally, local zone LAZ-8 (45 cm-top; ~1830 cal yr BP-present) is heterogeneous and could reflect a phase of structural reorganisation of the vegetation following long-term fire perturbation, as charcoal concentrations declined. At the beginning of the zone, ~1830–1200 cal yr BP, $PC2_L$ and $PC5_L$ explain most of the variance (30–37% and 27–34%, respectively; Fig. 5), pointing towards an increase in

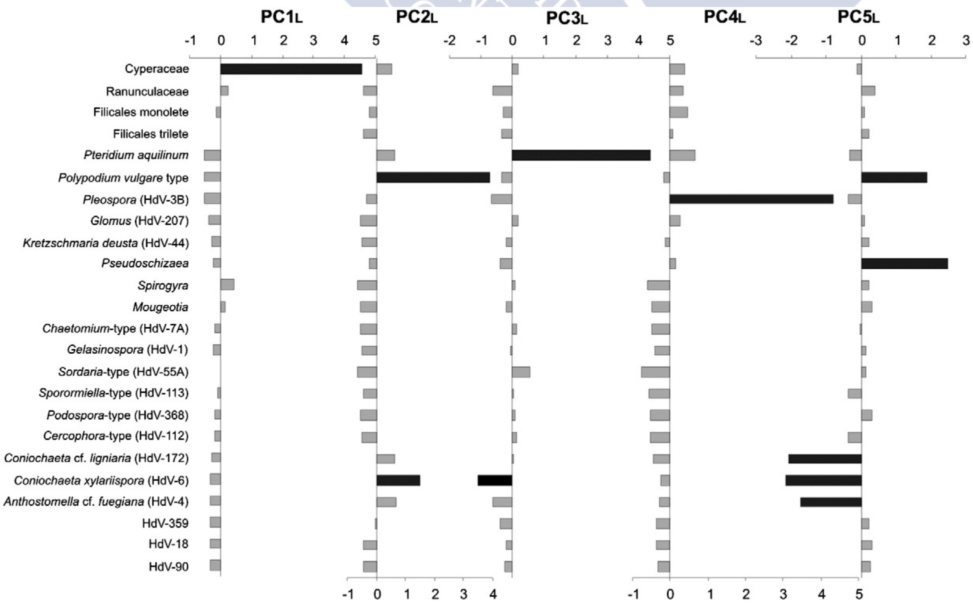

Fig. 6. Factor scores of the five local principal components (transposed matrix) obtained for the local signal of PRD-4 soil sequence.

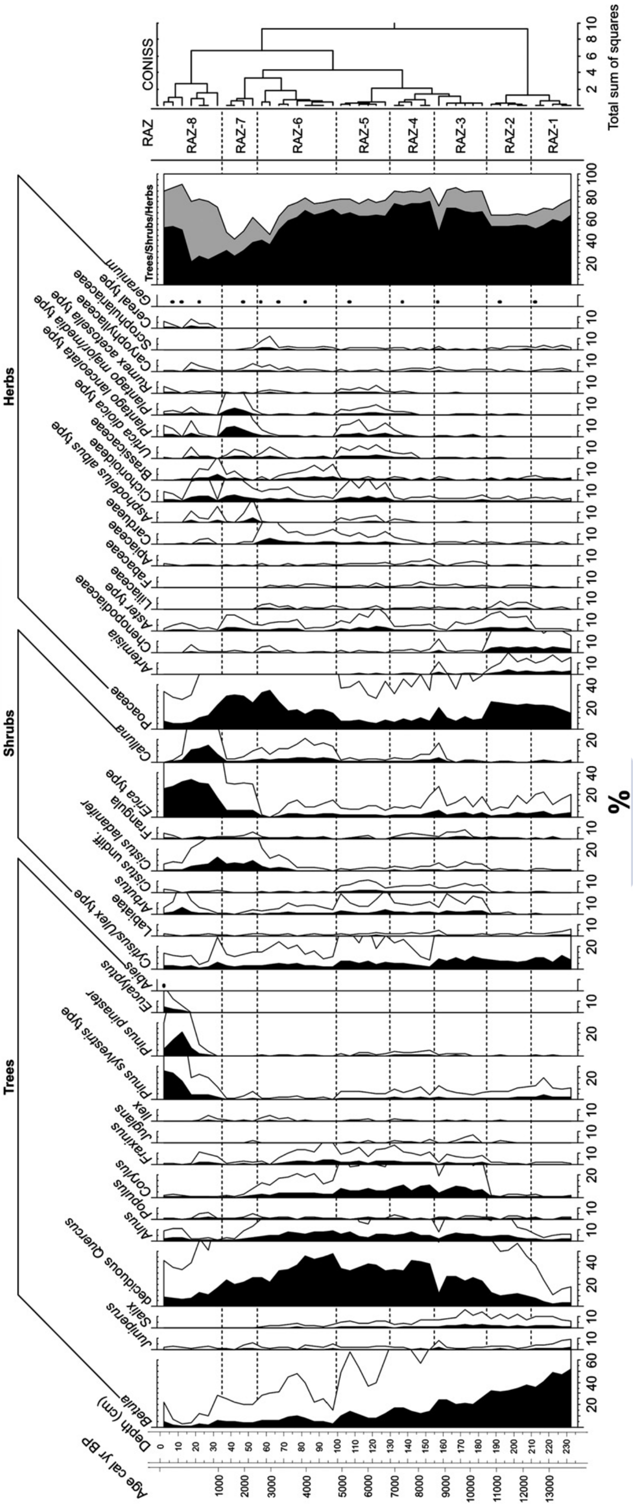

Fig. 7. Regional (total land pollen sum) palynological diagram. The filled silhouettes show the percentage curves of the taxa, while the open silhouettes show the 5 × exaggeration curves. CONISS cluster analysis together with the Regional Assemblage Zones (RAZ), and the estimated chronology are plotted as well. Values of trees, shrubs and herbs are expressed as percentages of the total land pollen sum, meaning the sum of these three groups.

soil erosion (*Pseudoschizaea*) and the persistence of *P. vulgare* type. After this short-term episode, $PC3_L$ explains most of the variance (41–69%), and $PC2_L$ shows decreasing values (3–48%; Fig. 5), reflecting a decline in the abundance in *P. vulgare* type while *P. aquilinum* increased. In the top sample $PC1_L$ (Cyperaceae) is important again, explaining 52% of the variance (Fig. 5).

3.2. Regional signal

Eight Regional Assemblage Zones (RAZ) were detected with the cluster analysis (Fig. 7) while four principal components explained 96.6% of the total variance. The percentage of the variance explained by each principal component can be seen in Table 3, and the fractionation of the communality and the factor scores are given in Figs. 8 and 9, respectively.

In RAZ-1 (235–210 cm, ~13,900–12,370 cal yr BP) the second principal component ($PC2_R$) explains most of the variance (91–98%; Fig. 8). *Betula* has the largest positive factor score, while Poaceae and *Cytisus*/*Ulex* type also have positive scores and deciduous *Quercus* a moderate negative score (Fig. 9). Although these pollen types are the taxa that show the largest statistical association to this zone, *Artemisia*, Chenopodiaceae and *Juniperus* are also present (Fig. 7) and they are indicative of dry, cold conditions.

In RAZ-2 (210–185 cm; ~12,370–10,670 cal yr BP) the $PC2_R$ still explains most of the variance (79–89%), indicating the persistence of the *Betula* open woodland, but with increasing loadings of $PC1_R$ (6–10%) and $PC3_R$ (4.5–10.4%; Fig. 8). In $PC1_R$ deciduous *Quercus* has a large positive factor score, while other mesophytes such as *Corylus*, *Alnus* and *Betula* have moderate ones, while Poaceae has a negative moderate score (Fig. 9). In $PC3_R$, Poaceae shows the largest positive factor score; deciduous *Quercus* and *Cistus ladanifer* have moderate scores, while *Betula*, *Corylus* and *Pinus* show moderate negative scores. Both $PC1_R$ and $PC3_R$ would be indicative of a slight incipient spread of both closed ($PC1_R$) and open oak ($PC3_R$) forests.

In RAZ-3 (185–155 cm; ~10,670–8620 cal yr BP), while $PC2_R$ still explains part of the variance (25–48%), $PC1_R$ becomes more important (49–71% of the variance; Fig. 8). In contrast, in the top sample of the zone (~8920–8620 cal yr BP) $PC1_R$ only explains 13% while the $PC2_R$ explains 73% of the variance. In general, this zone shows a gradual replacement of *Betula* by deciduous *Quercus* forest, but by the end of this zone open *Betula* woodland becomes more important. As found for the local vegetation, the latter could be related to a short-term abrupt shift in environmental conditions.

RAZ-4 and -5 represent the consolidation of the deciduous oak forest. In RAZ-4 (155–130 cm; ~8620–6870 cal yr BP) $PC1_R$ explains most of the variance (81–90%), with $PC2_R$ accounting for only a minor part (3–14%; Fig. 8). This implies that the deciduous *Quercus* forests were extensive and only some remnants of the "cold vegetation", more abundant in previous stages, still persisted. In RAZ-5 (130–100 cm; ~6870–4800 cal yr BP), $PC1_R$ continues to explain most of the variance (86–93%; Fig. 8). It is noteworthy that, although in RAZ-5 the oak forest is well developed, indicators of human pressure such as *Plantago lanceolata* type, *Plantago major*/*media* type, *Urtica dioica* type and *Rumex acetosella* type were also detected (Fig. 7). Additionally, at a local scale, an increase in coprophilous fungi was also detected at 140 cm (~7580 cal yr BP). The local vegetation underwent some changes (see above), but apparently these were minor at the regional scale as they did not affect the overall composition of the regional forest and it seems that only a small reduction of the arboreal cover occurred (Fig. 7).

Table 3
Eigenvalues and variance explained by the principal components obtained by PCA analysis of the transposed data matrix of regional pollen indicators.

PCA regional taxa						
Component	Initial eigenvalues			Rotation sums of squared loadings		
	Total	% Variance	Cumulative %	Total	% Variance	Cumulative %
$PC1_R$	30.3	64.5	64.5	19.9	42.4	42.4
$PC2_R$	7.3	15.5	80.0	12.9	27.5	69.9
$PC3_R$	5.1	10.9	90.9	7.0	14.8	84.7
$PC4_R$	2.7	5.7	96.6	5.6	11.9	96.6

Extraction method: principal component analysis with varimax rotation.

In RAZ-6 (100–55 cm; ~4800–2510 cal yr BP), $PC1_R$ loses significance gradually (18–84% of the variance) while $PC3_R$ shows increasing percentages (12–61%; Fig. 8). This may imply a gradual response of the regional vegetation to the intensification in the fire regime, as suggested by the increase in charcoal concentration (Fig. 2) and the substitution of the mature oak forest by an open oak forest with an increasing expansion of grass- and shrubland. Moreover, palynological indicators of grazing activities (coprophilous fungi, *P. lanceolata* type, *P. major*/*media* type and *U. dioica* type) are detected from 70 cm depth (~3400 cal yr BP), suggesting that there was a phase of fires without simultaneous grazing disturbance beforehand (~4800–3400 cal yr BP).

In RAZ-7 (55–35 cm; ~2510–1200 cal yr BP) the open oak forest is the dominant vegetation community, as $PC3_R$ explains most of the variance (53–70%) of the samples (Fig. 8). A reduction in charcoal concentration was observed for the top 45 cm of the soil sequence (from ~1830 cal yr BP; Fig. 2), although a change in the regional vegetation is not recorded until ~1200 cal yr BP when grazing indicators lose their importance (Fig. 7). At that time a complete change in the vegetation composition defines the onset of RAZ-8 (35 cm-top; ~1200 cal yr BP-present). $PC4_R$ explains most of the variance (29–87%) of the samples (Fig. 8). *Erica* type has a large positive factor score, while *Pinus sylvestris* type, *P. pinaster* and *Calluna* have moderate positive scores. Thus they reflect the spread of heathland and pine occurring during the last few centuries. Additionally, *Eucalyptus* pollen has also been found in this zone (Fig. 7).

4. Vegetation composition and post-disturbance vegetation dynamics

Several features from the results described above are worth emphasising (Fig. 10). First, complex ecological histories reflected by changes in the vegetation composition were detected at both local and regional scales, because multiple drivers were operating across different space and time scales. Second, gradual, threshold and elastic responses occurred during the last millennia. And, third, the regional response to a perturbation was sometimes delayed with respect to the local response.

4.1. Onset of the Holocene, non-equilibrium forests and the 8200 cal yr BP event

In the PRD-4 record, the shift towards warmer conditions during the onset of the Holocene was dated at ~12,370 cal yr BP, which, taking into account the uncertainties of an extrapolated age (no radiocarbon date for the bottom sample of the sequence), matches well with previous studies in NW Iberia (i.e. Allen et al., 1996; Muñoz Sobrino et al., 2001, 2005, 2007b; Carrión et al., 2010a; Moreno et al., 2011). At the local scale a main change in the palynological composition from the pre-Holocene dominance of *Pleospora* ($PC4_L$) to Cyperaceae ($PC1_L$) after the onset of the Holocene is interpreted as a threshold response (Fig. 10). At the regional scale, although the vegetation was sensitive to the change in environmental conditions (the cluster analysis distinguishes a RAZ suggesting a change in the pollen record), an open landscape with *Betula* ($PC2_R$) persisted, with only a minor, incipient, increase of the mesophilous trees ($PC1_R$) (Fig. 10). The regional persistence of an open landscape with *Betula* reflects the resilience of the established Late Pleistocene vegetation to the onset of the Holocene, and indicates that such vegetation could persist in a state of non-equilibrium with climate for ~1700 years.

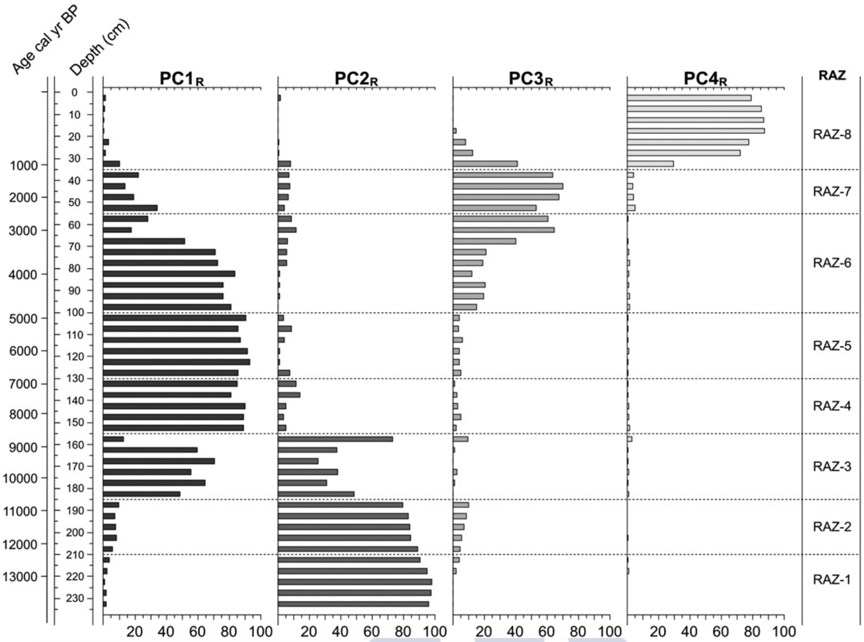

Fig. 8. Squared factor loadings of the four principal components (transposed matrix) explaining the variation of the regional signal of PRD-4 soil sequence.

At ~10,670 cal yr BP a shift towards more humid conditions can be inferred from the presence of *Spirogyra* and *Mougeotia* and virtual disappearance of *Pleospora* (Fig. 4), which are probably related to the onset of the Hypsithermal/Holocene Thermal Maximum. Although the change was recorded, it seems that the increase in humidity did not cause a significant variation in the local palynological assemblage, as $PC1_L$ (Cyperaceae) was still the main principal component. At the regional scale a gradual response is suggested by a shift from the open landscape with *Betula* ($PC2_R$) to a denser oak-dominated forest ($PC1_R$; Fig. 10). The change in vegetation composition points to a gradual spread of the oak forest; however remnants of the Late Pleistocene vegetation were still present. It is likely that the regional vegetation was near its ecological limit and more humid, and probably warmer, conditions prompted a change in the forest.

An abrupt short-lived change in the structure of the vegetation has been detected at ~8920–8620 cal yr BP. At a local scale *P. aquilinum* spread as the main taxon ($PC3_L$), while at regional scale the open landscape with *Betula* ($PC2_R$) became re-established (Fig. 10). Both are considered to be short-term disturbances in which the vegetation showed an elastic response, as its composition (both local and regional) completely recovered thereafter (Fig. 10). This short-term perturbation is likely to be related to the cold 8200 cal yr BP event. Although the chronology in PRD-4 is somewhat older, the difference can be assumed within the uncertainty of the age-model. In fact, in other pollen records of NW Iberia similar short-term forest reductions have been detected and related with this cold event (i.e. Muñoz Sobrino et al., 2004, 2005, 2007b). At the regional scale, the oak forest ($PC1_R$) had expanded after the short-term perturbation and the remnants of the open-landscape with *Betula* ($PC2_R$) almost disappeared.

4.2. Fire events, grazing pressure and the origin of the heathland

Indicators of cattle grazing and fires were detected from approximately ~7580 cal yr BP (Figs. 4, 7 and 10). At the local scale, these perturbations represented the initiation of a gradual response where Cyperaceae ($PC1_L$) decreased in abundance while *P. aquilinum* started to spread ($PC3_L$). Bracken easily colonises disturbed ground, including burnt areas (Salvo, 1990), and the charcoal record provides unequivocal evidence of fires (Fig. 10). However, at the regional scale the well-established oak forest did not show any significant change until ~6870 cal yr BP (Fig. 10), when a sensitive response was detected on the basis of the cluster analysis. Although a decrease in the arboreal pollen (Fig. 7) and an increase in charcoal (Kaal et al., 2011) occurred, this sensitivity did not invoke a major change in the composition of the regionally dominant oak forests ($PC1_R$). This might reflect the upslope reduction in arboreal vegetation but intact downslope vegetation communities (Carrión et al., 2010b). By ~4800 cal yr BP evidence of decreased grazing pressure while the fire regime intensified (higher concentration of charcoal particles, Fig. 10) is detected. Humidity indicators such as *Spirogyra* and *Mougeotia* almost disappeared, indicating local dry conditions, probably related to the end of the Hypsithermal/Holocene Thermal Maximum. The new environmental conditions may have been responsible for the inferred responses at both scales (Fig. 10). At the local scale a threshold response is suggested by the shift to an almost complete dominance of *P. vulgare* type and *C. xylariispora* ($PC2_L$). The fern is likely to grow on dead trunks (in particular after forest fires) while the fungus has been related to the presence of charcoal particles (Blackford et al., 2006; Yeloff et al., 2007) (Fig. 2). At the regional scale the response was gradual with closed oak woodland ($PC1_R$) evolving into an open forest, and the spread of Poaceae and, since ~3400 cal BP, of *C. ladanifer* ($PC3_R$) (Fig. 10). These results for the period between ~4800 and 3400 cal yr BP can be summarized as a regional reduction of forest cover and expansion of ferns and herbaceous species caused by increased fire activity (yet negligible grazing pressure). The shift to locally drier conditions might suggest that the cause of these changes was climatic – this chronology broadly coincides with the Neoglaciation, as found in other records from NW Iberia (Martínez Cortizas et al., 1999; López-Merino et al., 2010a) — but further research, taking into account the

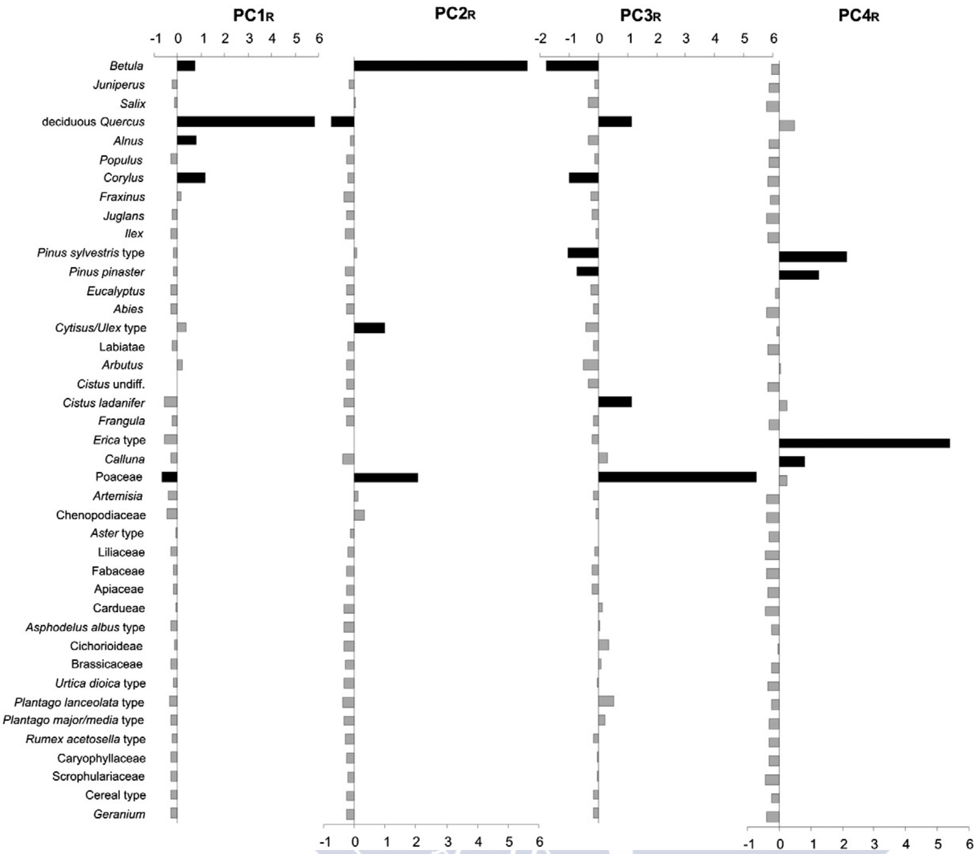

Fig. 9. Factor scores of the four regional principal components (transposed matrix) obtained for the regional signal of PRD-4 soil sequence.

information of nearby environmental records and archaeological findings, is necessary to confirm it. In the nearby PRD-2 soil sequence the overall picture is slightly different, as coprophilous fungi are present in the record since ~5500 cal yr BP, indicating local grazing (Carrión et al., 2010b). But between ~4000 and 3500 cal yr BP a change in the composition occurred, with increased abundance of *Sporormiella*-type, while *Sordaria*-type was more frequently recorded before ~4000 and after 3500 cal BP. From ~4000 to 3500 cal yr BP there was an intensification of the fire regime, probably indicating changes in landscape management.

Multiple responses were identified at PRD-4 after ~3400 cal yr BP. At the regional scale a more open oak forest was dominant between ~2510 cal yr BP and ~1200 cal yr BP ($PC3_R$, Fig. 10), the period with the lowest percentages of arboreal pollen of the whole record (Fig. 7), and for which the maximum concentration of charcoal was found (Fig. 10). In general, a renewed increase in grazing (indicated by coprophilous fungi, *P. lanceolata* type, *P. major/media* type and *U. dioica* type) occurred accompanied by increased soil erosion (*Pseudoschizaea*, $PC5_L$). *P. aquilinum* ($PC3_L$) expanded even though *P. vulgare* type ($PC2_L$) remained the dominant taxon, providing further evidence of local grazing impact. Furthermore, by ~1830 cal yr BP the intensity of the fire regime strongly diminished, although not disappearing, and at the local scale an internal, post-disturbance restructuring of the vegetation took place in three stages: (1) *P. vulgare* type/*Pseudoschizaea* (i.e. erosion); (2) *P. aquilinum*/*P. vulgare* type; and (3) Cyperaceae/*P. aquilinum*. In the last stage (top sample), the palynological composition is dominated by Cyperaceae ($PC1_L$) and *P. aquilinum* ($PC3_L$), which were the main taxa prior to the period characterised by an intense fire regime, indicating an elastic response of the local vegetation. However, at the regional scale there was no such immediate shift in the system, although by ~1200 cal yr BP a threshold response is characterised by the abrupt spread of heathland ($PC4_R$) coeval with the decrease in grazing indicators and greater importance of pine and, somewhat later (~800 cal yr BP), cereal crops (Figs. 4 and 7). This delayed response at the regional scale could be explained by the fires being localised and/or by the oak woodland showing resilience until other drivers amplified the effects of the changing environmental conditions (e.g. lower grazing pressure and perhaps the start of crop cultivation). Heathland is a common feature of the current landscape of NW Iberia, but there are significant differences in the chronology and intensity of the replacement of deciduous woodlands by heathlands. In PRD-2, fire and grazing induced forest regression and Ericaceae/Fabaceae shrubland expansion was significant by around ~5500 cal yr BP, and the complete colonisation of the area by heathland was detected in the pollen record at ~1880–1695 cal yr BP (Carrión et al., 2010b). In other palynological studies in nearby areas the spread of heathlands was found since the initial stages of the Iron Age (~2800 cal yr BP; van Mourik, 1986), while in PRD-4 it was detected during the Medieval Period (~1200 cal yr BP).

5. Conclusions

The palynological study of the PRD-4 sequence allowed us to infer the different environmental factors that have affected the composition of the

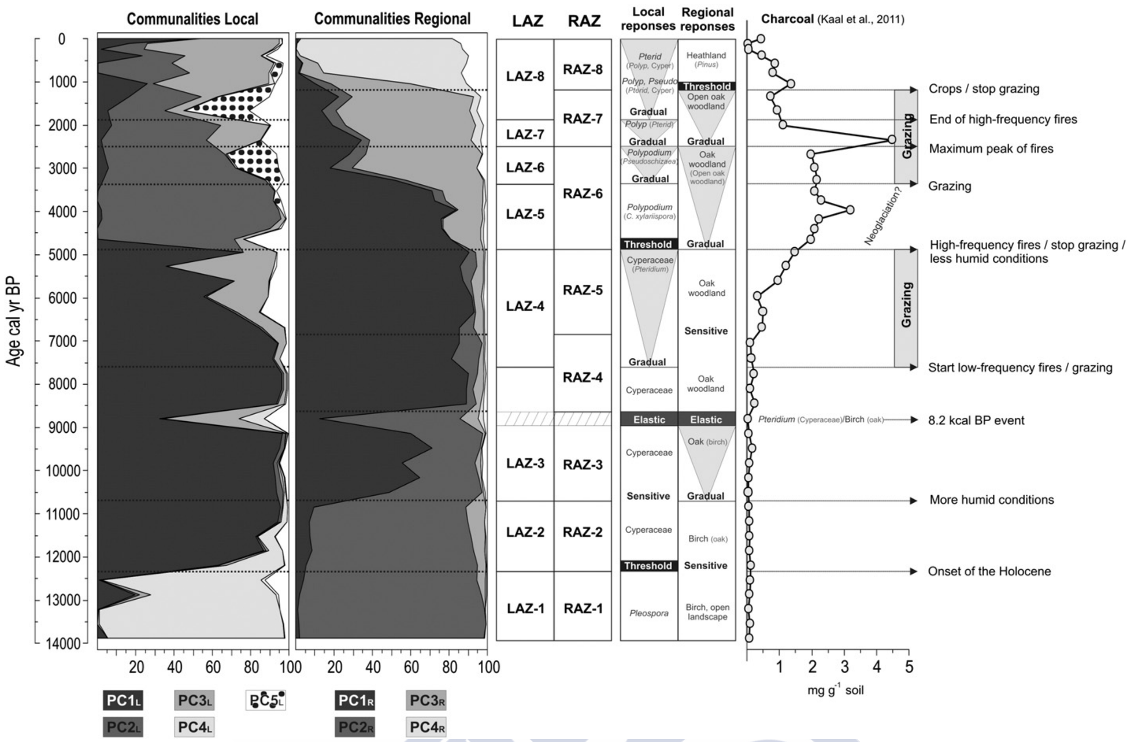

Fig. 10. Synthesis of the palaeoenvironmental history as inferred from the PRD-4 palynological data. The graphs to the left show the proportion of variance of each sample that can be explained by the five extracted local principal components and four regional principal components (communalities) obtained by PCA$_{tr}$. From left to right, the remaining columns present the RAZ and LAZ, the description of local and regional vegetation composition, the type of responses, charcoal concentration and the drivers of environmental change (see text for details).

vegetation, and to understand the variations at local and regional scales. Our results suggest that the vegetation of the studied area showed multiple responses to Late Pleistocene/Holocene palaeoenvironmental changes. One was the resilience of the *Betula* forest in an open landscape for approximately ~1700 years at the beginning of the Holocene, but also other threshold, gradual and elastic responses occurred with centennial delays to the initiation of the perturbations at a regional scale. This variability reflects the complexity of the biotic response to environmental change and the stochastic behaviour that natural systems often show across different spatial and time scales, as well as their resilience and the way systems switch from one state to another.

With regard to the current observed and projected climate change, human-induced perturbations and related vegetation dynamics, we believe that the PRD-4 record offers a good example (Fig. 10) of the complexity and variability of vegetation responses (threshold, gradual, elastic and resilience) to environmental perturbations since the late Pleistocene. The main concern today is the impact of human-induced perturbations, not only on the landscape but also on climate. Therefore a more profound knowledge of the buffering ability of ecosystems is needed to predict to what extent human activities can promote drastic and unforeseen changes, and to help to manage the landscape in a more sustainable way. We have to be aware that the consequences of the increasing human-induced perturbations might be yet to come. In this sense, long-term ecological research is a necessary tool to reconstruct the history of ecosystems and its complexities.

The application of principal component analysis on the transposed data matrices (PCA$_{tr}$) of palynological data seems to be appropriate to obtain information on the structure of the variance of the palynological composition of the samples, resulting in lower dimensions/groupings than the constrained cluster analysis. PCA$_{tr}$ proved to be a valuable tool to identify the type of responses of the vegetation to environmental change. Nonetheless, a systematic comparison with other techniques is necessary to fully understand the advantages and drawbacks of this approach. Moreover, in the studied record the responses usually coincided with the boundaries of the palynological zones, although some of the boundaries did not reflect a real change or reorganisation in the composition of the vegetation.

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3.5. Paper V

Mighall, T.M., Martínez Cortizas, A., ***Silva Sánchez, N***., Foster, I.D.L., Singh, S., Bateman, M. and Pickin, J. (2014) **Identifying evidence for past mining and metallurgy from a record of metal contamination preserved in an ombrotrophic mire near Leadhills, SW Scotland, UK**. *The Holocene* 24, 1719–1730.

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Identifying evidence for past mining and metallurgy from a record of metal contamination preserved in an ombrotrophic mire near Leadhills, SW Scotland, UK

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Abstract

This study presents a new 3600-year record of past metal contamination from a bog located close to the Leadhills and Wanlockhead orefield of southwest Scotland. A peat core, collected from Toddle Moss, was radiocarbon (^{14}C) dated and analysed for trace metal concentrations (by EMMA) and lead isotopes (by ICP-MS) to reconstruct the atmospheric deposition history of trace metal contamination, in particular, lead. The results show good agreement with documented historical and archaeological records of mining and metallurgy in the region: the peak in metal mining during the 18th century, the decline of lead mining during the Anglo-Scottish war and lead smelting during the early medieval period. There may also have been earlier workings during the Late Bronze and Iron Ages indicated by slight increases in lead concentrations, the Pb/Ti ratio and a shift in ^{206}Pb/^{207}Pb ratios, which compare favourably to the signatures of a galena ore from Leadhills and Wanlockhead. In contrast to other records across Europe, no sizeable lead enrichment was recorded during the Roman Iron Age, suggesting that the orefield was not a significant part of the Roman lead extraction industry in Britain. These findings add to the various strands of archaeological evidence that hint at an early lead extraction and metallurgical industry based in southern Scotland. The results also provide further evidence for specific regional variations in the evolution of mining and metallurgy and an associated contamination signal during prehistoric and Roman times across Europe.

Keywords

lead, Leadhills, mining, peat, stable isotope analysis, Wanlockhead

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Introduction

Since its first use approximately seven millennia ago, lead has played an important role in human history, including aspects of art, medicine and technology (Hong et al., 1994; Nriagu, 1998). Lead became particularly important in the 5th millennium BC with the discovery of new smelting and cupellation techniques for lead–silver alloys, and by Roman times, the use of lead was widespread (Nriagu, 1983, 1996). At present, there is a paucity of archaeological evidence for lead mining in prehistoric Britain. It has been proposed that lead deposits in Wales, and by inference elsewhere in Britain, were exploited for lead and silver, since the location of most of the prehistoric mines (where copper was the main target) mostly occur in places with a long tradition of lead and zinc mining (Bick, 1999; Timberlake, 2009). Evidence of limited working of the lead veins and crushing of ores at the Bronze Age mine of Copa Hill in central Wales (Timberlake, 2003) provides some tentative evidence for the extraction of lead ore approximately 300–500 years before its use in metalwork, a phenomenon that might represent a period of metallurgical experimentation rather than actual production (Timberlake, 2003).

Lead in Bronze Age artefacts confirms that it was being used in Britain prior to 1500 BC and hints at the probable early exploitation of insular sources and trade in metal ore (Rohl and Needham, 1998). A smelted lead bead necklace in an Early Bronze Age grave was found in southeast Scotland (Hunter and Davis, 1994), and other early lead finds have been reported from Cornwall (Shell, 1979) and Co. Tipperary (Rafferty, 1961). Lead was also intentionally being alloyed with copper and tin to produce bronze by the Middle–Late Bronze Age (Rohl and Needham, 1998; Tylecote, 1986). Small pieces of lead have also been

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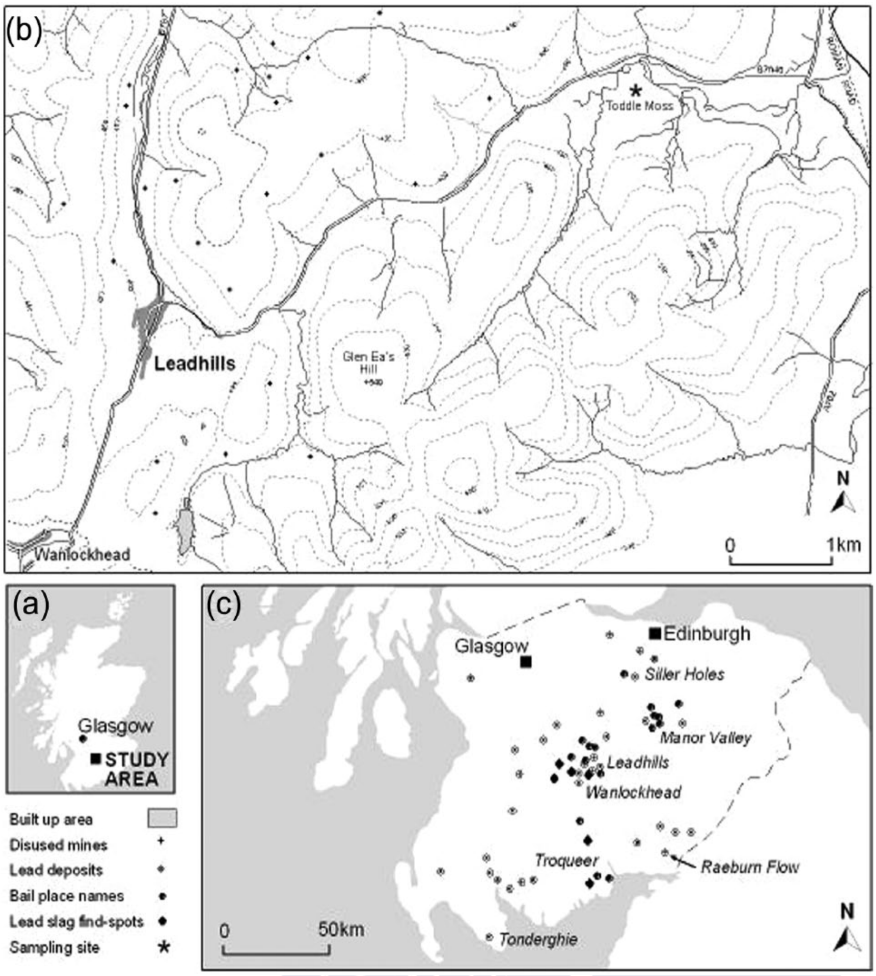

Figure 1. (a) Location of study area in Britain, (b) location of Leadhills, Wanlockhead and Toddle Moss and (c) evidence of early lead working after Pickin (2010). The place name 'bail' is considered to indicate a lead smelting site.

found in Late Bronze Age occupation sites (e.g. Needham and Hook, 1988). The precise sources of this lead remain a matter for speculation (Barber, 2003).

Archaeological evidence for lead extraction, objects and its wider use in later prehistory is also scant. Lead was a rare addition to northern British alloys during the Iron Age (Dungworth, 1996), and only a few examples of lead use in ornaments, or as solder to secure iron objects, exist in Scotland (Toolis, 2007). Roman lead extraction and smelting is more abundant, with known mines and/or smelting sites occurring at Charterhouse in the Mendips, SW Britain, Alderley Edge in Cheshire and sites in Wales (Timberlake et al., in press), but so far, there are no known sites in Scotland. One region that has been not fully investigated is the Leadhills and Wanlockhead orefield in SW Scotland. A study is therefore warranted, especially given the recent discovery of a stone hammer in Wanlockhead, which is indicative of early mining (Pickin, 2008).

The aim of this study was to reconstruct the history of exploitation of insular ore sources in the Leadhills/Wanlockhead orefield from prehistory to the present. To do so, we present an atmospheric metal contamination history from an ombrotrophic mire, Toddle Moss, for the last 3600 years using total concentrations, Pb/Ti ratios and lead isotope ratios ($^{206}Pb/^{207}Pb$) contained in the peat.

Materials and methods

Location, sampling and sub-sampling strategy

The orefield of Leadhills and Wanlockhead, on the border of Dumfriesshire and Lanarkshire, SW Scotland (Figure 1), is rich in metalliferous deposits as a result of two phases of mineralization in Ordovician sediments: a quartz vein mineral phase of Carboniferous age and a possibly metallic one of lead and zinc, both of the Carboniferous era. This was followed by a later phase of secondary enrichment (Pattrick and Polkya, 1993).

Toddle Moss is located approximately 4 km northwest of the village of Leadhills and 0.5 km east of Elvanfoot in the Elvan Water river valley (Figure 1). This area has a rich history of mining. Alluvial sediments have been worked in this valley for gold, and lodes rich in lead and copper have also been exploited, particularly in the AD 1700s (Chapman and Leake, 2005; Rowan et al., 1995). Toddle Moss is an ideal site for studying past records of metal pollution because the bog is ombrotrophic ('rain fed' only) and receives inputs, including pollutants, solely from the atmosphere via precipitation and dry fallout.

A 7.5-m-deep *Sphagnum–Eriophorum*-rich peat core was taken from Toddle Moss using a Russian corer with 30 cm × 10 cm chamber in 2004. The samples were placed in plastic guttering, wrapped in polythene and placed in cold storage. The top 3.5 m was analysed in this study.

Chronology

Radiocarbon dates were determined at Beta Analytic Ltd (Miami) and the Poznań Radiocarbon Laboratory using conventional and accelerator mass spectrometry (AMS) methods, respectively. The total carbon of one sample of fresh peat (Beta-15142) was dated using conventional radiometric dating. For AMS, a 1-cm-thick slice of peat (Poz-19215) and *Sphagnum* macrofossils (Poz-56748) were selected for dating (cf. Nilsson et al., 2001; Piotrowska et al., 2011).

To provide a highly resolved chronology for the last 100–150 years, the unsupported $^{210}Pb_{un}$ activity within samples towards the peat surface was ascertained by subtraction of the supported component (measured as ^{214}Pb at 295.22 and 351.93 keV) from the total ^{210}Pb activity measured at 46.54 keV (Wallbrink et al., 2002). ^{210}Pb and ^{214}Pb activities were measured using EG&G ORTEC hyper-pure Germanium detectors in a well configuration (11 mm diameter, 40 mm depth) housed at Coventry University. The method for calculating the depth–age relationship follows procedures described by Appleby and Oldfield (1978), Appleby (2001) and Walling et al. (2002). The CRS dating model was used to calculate ages as accumulation rates varied down core (Appleby, 2001; Appleby et al., 1988). The CLAM software package (Blaauw, 2010) was used to create an age–depth model, combining the ^{14}C and ^{210}Pb ages, to infer approximate ages for all levels.

Geochemical analyses

The core was cut into contiguous 1-cm-thick slices, oven dried at 40°C and homogenized to improve the efficiency of the chemical digest and to provide better representation of the total metal concentration within the samples. Calcium and magnesium were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES). An estimation of the efficiency of the digestion method and of the accuracy of the analytical measurements was obtained through the use of replicate sub-samples, spiked blanks and certified reference materials (Ebdon et al., 1998; Fifield and Kealey, 2000). Spiked samples of known concentration (10 mg/L) were used to test the efficiency of the acid microwave digestion. Two certified reference materials were also used: *Sphagnum* energy peat (NJV 94-2) and *Carex* energy peat (NJV 94-1). The reference materials were imported from the Swedish University of Agricultural Sciences, Department of Agricultural Research for Northern Sweden, Laboratory for Chemistry and Biomass. Standards of known metal concentrations were used to calibrate the instrument and to ensure it was performing at its optimum efficiency (Holler et al., 1996). Total metal concentrations in each sample are expressed in units of microgram per gram.

Recovery of calcium and magnesium from the CRMs for *Sphagnum* and *Carex* was between 101% and 130%. Three spiked samples yielded recovery of between 101% and 114%. These results suggest that metal recovery using the microwave digestion was very efficient and that the ICP-OES provided reliable data.

The elemental composition of 89 dried, milled and homogenized samples between 0 and 300 cm depth were obtained by EMMA-XRF analyses (Cheburkin and Shotyk, 1996; Weiss and Shotyk, 1998) including concentrations of major and trace lithogenic elements (silicon, aluminium, titanium, gallium, yttrium and zirconium) and trace metals and metalloids (lead, chromium and arsenic). The instruments are hosted at the RIAIDT (Infrastructure Network for the Support of Research and Technological Development) facility of the University of Santiago de Compostela, Spain. Standard reference materials were used for the calibration of the instruments. Quantification limits were 0.001% for Ti, 0.01% for Al, 0.05% for Si, 0.5 µg/g for Pb and 1 µg/g for other trace elements. Replicate measurements were taken for one of every five samples in order to account for reproducibility; all replicates were within 5% agreement.

A total of 28 sub-samples of peat from the same core were selected for lead isotope analysis at the School of Geosciences, University of Edinburgh. Sub-samples (~0.25 g) were air-dried, then washed at 450°C for 4 h and finally digested using a modified US EPA Method 3052 Protocol microwave-assisted HF-HNO_3 digestion method (Yafa and Farmer, 2006; Yafa et al., 2004). Digests were evaporated to 1 mL on a hotplate and then made up to 25 mL with 2% (v/v) HNO_3. All reagents used in sample preparation were of the highest analytical quality available, that is, Aristar nitric acid (69%) and hydrofluoric acid (48%) and high purity water (18.2 MΩ cm) from a Milli-Q water system (Millipore, Watford, UK). Lead isotopic ratios were determined in the prepared 2% v/v HNO_3 solutions using a PlasmaQuad (PQ) 3 ICP-MS instrument (Thermo Electron, Winsford, UK), equipped with a Meinhard nebulizer, nickel sampler and skimmer cones, Gilson autosampler and a Gilson Minipuls 3 peristaltic pump (Anachem, Luton, UK). A solution of the National Institute of Standards and Technology (NIST) common lead isotopic reference standard SRM 981 ($^{206}Pb/^{207}Pb = 1.093$, $^{208}Pb/^{206}Pb = 2.168$, $^{208}Pb/^{207}Pb = 2.370$) was used for calibration and mass bias correction (Farmer et al., 2000). Analytical precision on these ratios was typically <±0.2%.

To ensure the quality of analytical procedures and data, an ombrotrophic peat reference material (NIMT/UOE/FM001) (Yafa et al., 2004) was analysed along with the samples. The mean values ($n = 5$) of 1.177 ± 0.001, 2.093 ± 0.002 and 2.463 ± 0.004 determined for the isotope ratios $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ and $^{208}Pb/^{207}Pb$, respectively, in the reference material were in good agreement with corresponding 'information only' values of 1.176 ± 0.001, 2.092 ± 0.002 and 2.461 ± 0.003 reported in Yafa et al. (2004).

Statistics

Following the procedure described by Martínez Cortizas et al. (2013) and Hermanns and Biester (2013), we used factor analysis by principal component analysis (PCA) to identify sources and processes related to the distribution of the measured elements using the SPSS 20 software package. PCA of compositional data is usually undertaken on transformed variables (Baxter, 1995), particularly when the values cover several orders of magnitude and there are outliers (Baxter, 1999). Transformation also avoids any scaling effects (Eriksson et al., 1999). Thus, the PCA was done on log-transformed and standardized (z-scores) data, using varimax rotation to maximize the variance of the elements in the principal components (Eriksson et al., 1999). Similarly distributed elements will load on to the same principal component and are most likely to be controlled by the same environmental factor(s). Hence, interpretation of the signals with regard to the underlying cause or causes of variation of a group of elements should be more evident.

Results

Age–depth modelling

The results are shown in Table 1 with 2σ calibrated age ranges (in calibrated years BC/AD). A polynomial regression age–depth model is shown in Figure 2. All dates appearing in the following text are cited in calendar years BC/AD, unless otherwise stated, and are given within the 95% confidence intervals derived from the Calib 7.0 model (Reimer et al., 2009; Stuiver and Reimer, 1993), with end-points rounded to the nearest decade.

Geochemistry

The calcium/magnesium ratio (Figure 3) is consistently below 1 and much lower than the measured value for rainwater (approximately 1.9) at Raeburn Flow, which is located approximately

Table 1. Radiocarbon dates from Toddle Moss.

Lab code	Sample	Depth (cm)	Uncalibrated age	Calibrated age range (2σ)
Poz-56748	Sphagnum leaves	102–103	1110 ± 30	Cal. AD 879–1013
Poz-19215	Peat	250–252	2530 ± 35	Cal. 797–539 BC
Beta-15142	Peat	345	3450 ± 50	Cal. 1890–1634 BC

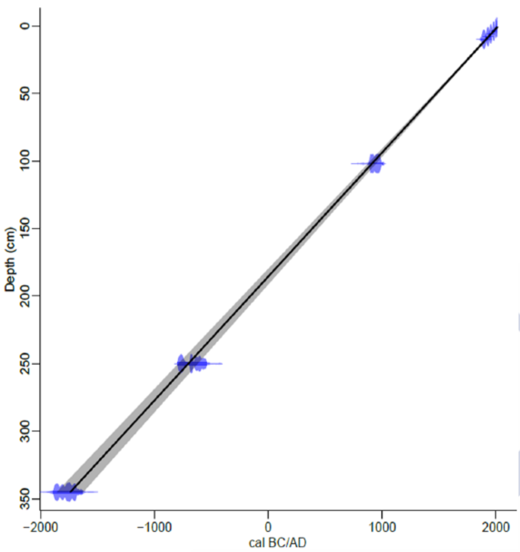

Figure 2. An age–depth model for Toddle Moss using Clam (after Blaauw, 2010).

74 km to the southeast of Toddle Moss (Küttner et al., 2014). These low values are sufficient to infer ombrotrophic conditions for the bog (cf. Shotyk, 1996). Notwithstanding a series of short-lived peaks, titanium concentrations remain relatively constant from the base of the profile to 101 cm. They then rise gradually with a sustained increase from 43 cm to the surface of the bog. Lead concentrations are generally low from the base of the core to 35 cm depth: thereafter, they increase dramatically to peak at 11 cm before decreasing to much lower concentrations at the bog surface. The Pb/Ti ratio follows a similar pattern. The $^{206}Pb/^{207}Pb$ profile shows more radiogenic ratios from 342 to 308 cm (SI Table 1, available online). A shift to less radiogenic values occurs between 308 and 222 cm (Figure 3). Thereafter, the ratios gradually rise from 222 to 24 cm before they become less radiogenic towards the bog surface.

Concentrations of arsenic, chromium, gallium, yttrium, zinc and zirconium, determined using EMMA, are shown in Figure 4. Arsenic, gallium and yttrium have similar trends to lead: low concentrations from the base of the core until 35 cm, a sharp rise to peak in the top 10 cm, followed by a decline to much lower concentrations. Zinc and chromium are characterized by low but highly fluctuating concentrations from the base of the core until approximately 80 cm. They also peak in the uppermost 10 cm with other elements. Chromium concentrations also decline close to the peat surface, but zinc remains relatively high. Zirconium concentrations are more erratic with a series of peaks throughout the profile (e.g. 265, 237, 179, 135, 113, 63, 33 and 17 cm) but show a gradual increase in the upper metre of the profile.

PCA

Two components explain 78% of the total variance (Table 2). The first component (Cp1, 44% of the total variance) is characterized by large-to-moderate positive loadings of metals typically associated with mining/metallurgy (namely, arsenic, zinc, lead and chromium; Table 2). Gallium and yttrium, which are usually considered to be lithogenic elements, show large loadings in Cp1 (Table 2) and thus can also be associated with atmospheric metal pollution, probably derived from dust emissions during mining. This is also supported by the extremely high metal concentrations in the upper section of the peat, which are only comparable with those found close to pollution sources (e.g. in the Harz mountains, Germany, where Pb concentrations exceed 1000 µg/g during medieval times (Kempter and Frenzel, 2000) and equivalent to Pb concentrations determined within several kilometres of a lead smelter (Mihaljevič et al., 2006)). Cp1 scores show a typical record of atmospheric metal pollution, with a large peak in the upper 30 cm of the core and a sharp decrease in the upper 8 cm (Figure 5). It also shows two minor increases in scores during the early medieval period: between 120 and 140 cm (5th–7th centuries AD) and from 90 to 100 cm (9th–11th centuries AD).

The second component (Cp2, 33.7% of the total variance) is characterized by large positive loadings of the lithogenic elements (Ti, Si, Al and Zr; Table 2). This chemical association reflects the mineral content of the peat because of deposition of dust, probably derived from soil erosion. The record of scores shows a ‘see-saw’ pattern, with eight peaks in dust deposition (Figure 5): at 265 cm (*c.* 870 cal. BC), 237 cm (*c.* 560 cal. BC), 179 cm (*c.* 70 cal. BC), 133 cm (*c.* AD 570), 109 cm (*c.* AD 835), 85 cm (*c.* AD 1095), 63 cm (*c.* AD 1335) and 33 cm (*c.* AD 1660). Although most of the variation in the concentrations of the metals is related to the first component (i.e. atmospheric metal pollution), a small proportion of the changes in lead, arsenic, gallium and yttrium are also correlated to Cp2 (Table 2), and therefore, they indicate a geogenic contribution.

Due to the expected large effect on the PCA of the metal concentrations of the peat sections with ages younger than AD 1600, we performed a second PCA using only the data for peat sections with pre-industrial ages (below 38 cm). In this data set, the first component, Cp1-PI, is characterized by the large loadings of the lithogenic elements (silicon, titanium, aluminium, yttrium and zirconium; Table 2). Cp1-PI and Cp2 scores are highly correlated (r = 0.97). Most of the yttrium variance is now in this component, suggesting that in Toddle Moss, its association with the metals associated with pollution occurs only after the start of the Industrial Revolution. This is not the case for gallium, whose variance is still loaded into a metal component (Table 2).

Moreover, in the second analysis, the metal signal is divided into two components: Cp2-PI with zinc, arsenic and chromium which has a record of scores similar to that of Cp2 (r = 0.68) and Cp3-PI with gallium and lead (Table 2). Thus, the metal signature of the peat for pre-industrial times seems to indicate that there were differences in the accumulation of the metals in Toddle Moss. The record of Cp2-PI scores suggests that the history of zinc, arsenic and chromium enrichment is quite similar during late prehistory and early Middle Ages. However, the elevated scores of Cp2-PI between 250 and 236 cm, corresponding to the period *c.* 700–550 cal. BC, are not paralleled by lead.

Interpretation and discussion

Lead is essentially immobile once it becomes incorporated into ombrotrophic peat (MacKenzie et al., 1997; Shotyk et al., 1997),

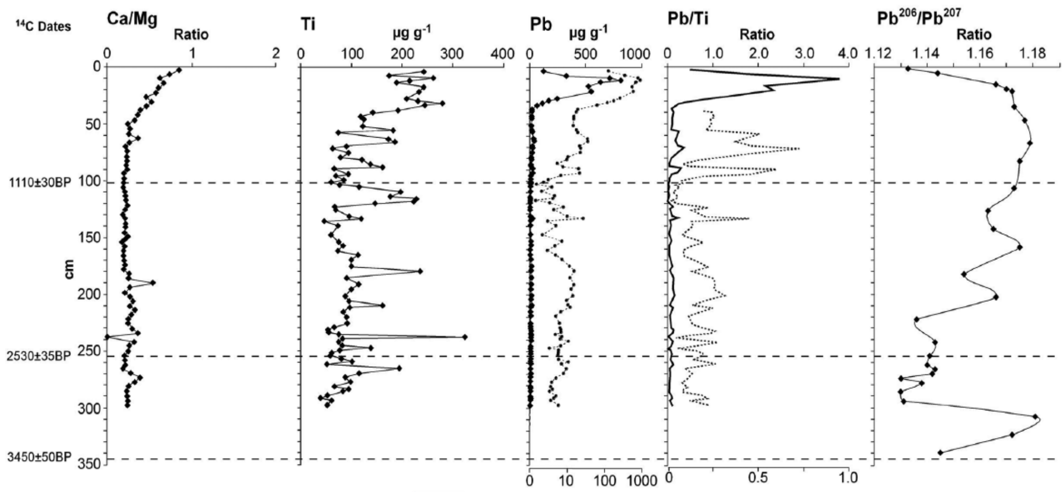

Figure 3. Calcium/magnesium ratio (by ICP-OES), titanium concentrations, lead concentrations (by EMMA; dashed line on a log scale), Pb/Ti ratio and $^{206}Pb/^{207}Pb$ ratios (by ICP-MS) from Toddle Moss.
EMMA: energy-dispersive miniprobe multi-element analyser; ICP-OES: inductively coupled plasma–optical emission spectrometry; ICP-MS: inductively coupled plasma–mass spectrometry.
Dashed line represents exaggerated Pb/Ti ratios from 40 cm down the profile (scale at base of the graph).

and there is a plethora of studies that have demonstrated that the pattern of lead is faithfully preserved in peat bogs which can be reliably matched with other archaeological and historical documentary records (e.g. Mighall et al., 2002b; Shotyk et al., 1997). Lead concentrations, lead–titanium ratios and isotopic ratios are now regularly used to identify evidence of anthropogenic forcing on the lead biogeochemical cycle. Lead–titanium ratios are used to identify non-silicate sources of lead (Görres and Frenzel, 1997; Shotyk, 1996), whereas isotopic ratios are also considered to reflect accurately anthropogenic lead emissions especially when the isotopic signature of potential sources is well known (Martínez Cortizas et al., 2002). The record of lead derived from Toddle Moss presented here should therefore provide a reliable chronological record for past lead deposition onto the bog surface. Notwithstanding the numerous complicating variables that can influence the dispersion of gaseous and particulate pollution from source, bogs located close to industrial sites should provide robust records of emissions from these sites as pollutants are deposited onto the mire surface (Mighall et al., 2002a, 2002b).

Slightly elevated lead concentrations (Figure 3) might well be attributed to Middle–Late Bronze Age metallurgical activities: centring on 272 and 247 cm (*c*. 940 to 670 cal. BC) and higher Pb/Ti ratios between 270 and 247 cm (Figure 3). Although the concentrations recorded in the core are low, they are elevated above those recorded below 280 cm, and so, the trends described here may hint at the possibility of early lead working in the area. The discovery of a stone hammer at Wanlockhead (Pickin, 2008) is indicative of prehistoric mining. This particular stone hammer is very similar typologically to the grooved hammerstones found at the prehistoric copper mine at Alderley Edge (Timberlake and Prag, 2005), which are thought to have been used as crushing and pounding implements. There is no contextual evidence for the stone hammer found at Wanlockhead as it was discovered by a mine manager and the exact location is unknown. Perhaps, the strongest evidence for an early insular mining/metallurgical industry in Scotland is provided by the isotopic analysis of Early Bronze Age lead beads from Peeblesshire and West Water Reservoir in the Borders. The data indicate that a Scottish Southern uplands source – possibly Leadhills – was exploited (Hunter in Toolis, 2007; Hunter et al., 2006). Taken together, these separate strands of archaeological evidence are suggestive of activities possibly ranging from experimental exploitation on a small scale to more significant activity, which could have produced sufficient amounts of pollution to be recorded in the bog more widely, and such activity would have taken place during the Middle–Late Bronze Age when lead is found in bronze alloys. However, the introduction of lead into bronzes or other copper alloys is rare in northern Britain (Dungworth, 1996), and while it points towards a demand for lead, it does not provide convincing evidence of an early insular lead industry in southern Scotland. Indeed, lead is found in the St Andrews Hoard, but an analysis of the impurities in the artefacts suggests that some of the metals may have been re-worked or produced from different metal sources that might originate from outside Scotland (Cowie et al., 1998).

For purposes of comparison, the lead isotope ratios of the Toddle Moss peat samples are plotted in Figure 6 besides selected lead ores from other locations in the British Isles and the major Spanish mines of Rio Tinto and Murcia (Rohl, 1996; Stos-Gale et al., 1995). Lead isotopic signatures from Flanders Moss and Lindow Moss (cf. Cloy et al., 2005; Le Roux et al., 2004) fall within the cluster of British ores from the Mendips, Alderley Edge, NE Wales and the mines at Leadhills and Wanlockhead. Because of the overlap of the isotopic ratios, it is not possible to attribute the origin of this lead to a particular British ore source (cf. Cloy et al., 2005; Le Roux et al., 2004). Nevertheless, the results clearly show that the lead is likely to be of British origin, as the isotopic values for the British ores are clearly separable from those of the heavily exploited Spanish sources (Shotyk et al., 1998).

The peat samples from Toddle Moss of the section between 296 and 224 cm clearly fall outside all of the clusters shown in Figure 6. An analysis of galena samples from Wanlockhead has established the isotopic signature for lead ore at this location. Cloy et al. (2005) reported a $^{206}Pb/^{207}Pb$ ratio of 1.172 ± 0.003, which is in close agreement with a value of 1.170 ± 0.003 for the Leadhills and Wanlockhead lead ore reported by Sugden et al. (1993). Rohl (1996) calculated the mean $^{206}Pb/^{207}Pb$ ratio from five ore samples from Wanlockhead plus six from Leadhills as 1.171 ± 0.001. All these values plot within the 'British ore' cluster (Figure 6). This suggests that the source of lead determined within the Toddle Moss peat samples between 296 and 224 cm does not originate from the main galena bearing lodes from the Leadhills

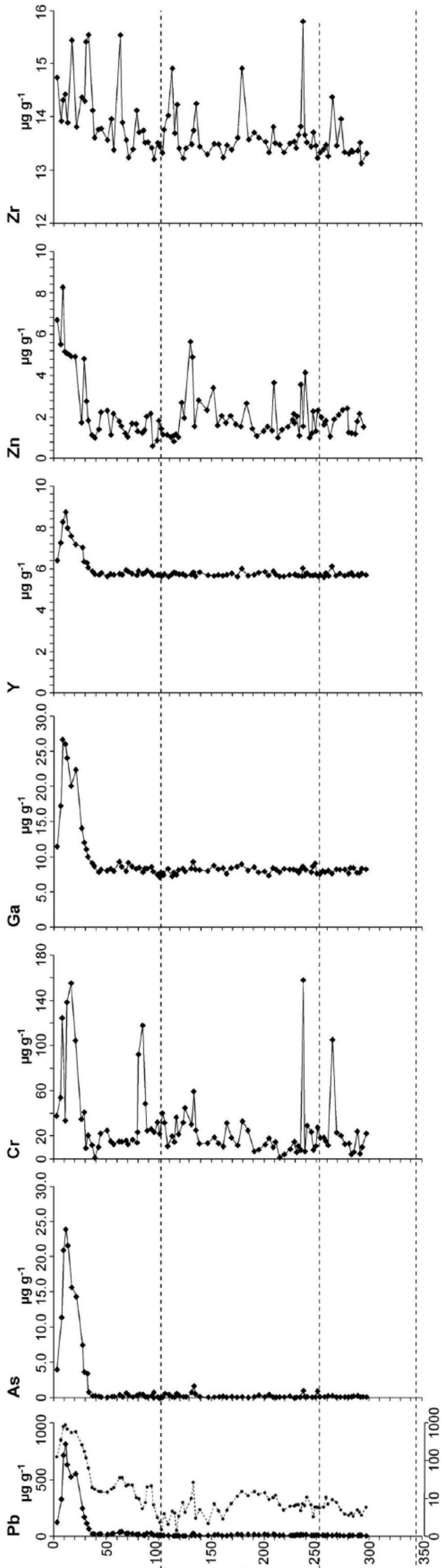

Figure 4. Concentrations of lead, arsenic, gallium, yttrium, zinc and chromium as determined by EMMA. Dashed line represents lead plotted on a logarithmic scale (scale at base of the graph).

or Wanlockhead orefield. However, one sample of galena from Wanlockhead has a $^{206}Pb/^{207}Pb$ ratio of 1.142, and it is plotted in Figure 6 as the 'Wanlockhead outlier'. This ratio is in much better agreement with the Toddle Moss samples between 296 and 224 cm. If early miners and metallurgists did exploit lead at Wanlockhead, then they appear to have targeted lodes bearing a similar lead isotopic signature.

A more extensive analysis of the isotopic signatures of the mineralized zones in the orefield could resolve the apparent signature discrepancies between the peat samples, the Wanlockhead 'outlier' and the other Leadhills ore samples. Whether the two distinct phases of lead formation at Leadhills resulted in the different isotopic signatures is unknown. The natural lead isotope composition of rocks depends upon the age of the lithogenic system, the U/Pb and Th/Pb ratios of the system and mixing during remobilization and metamorphism (Keinonen, 1992). During the formation of lead ore deposits, lead is separated from the parent uranium and thorium isotopes, with the lead isotopic composition of hydrothermal fluids being 'frozen' into lead-bearing minerals (Church et al., 1993). Thus, the isotopic composition of a given ore deposit is a function of four parameters: (1) the decay rate of parent isotopes, (2) the initial ratio of the abundance of the parent to the abundance of Pb ($^{238}Pb/^{204}Pb$, $^{232}Th/^{204}Pb$) in the source reservoir (e.g. mantle or continental crust), (3) the initial isotopic composition of reservoir Pb and (4) the duration of reservoir evolution prior to separation of Pb by geological processes (Sangster et al., 2000).

A second phase of increasing lead enrichment and relatively higher Pb/Ti ratios at Toddle Moss occurs during the late Iron Age *c.* cal. 365 BC–AD 70 (between 219 and 179 cm; Figures 3, 4 and 7). Whether this represents pollution generated from local lead extraction or metallurgy is still contestable as there is a lack of local archaeological evidence. However, the shift in the $^{206}Pb/^{207}Pb$ ratio towards values close to those determined from Leadhills and the average value for atmospheric lead in Scotland in the 19th century AD provides evidence of industrial activity within the region at this time. While the initial rise of lead concentrations does correlate quite closely with the suggested age of the Carghidown promontory fort lead beads dated *c.* cal 360 BC–AD 60 (Toolis, 2007), these finds are exceptional. Hunter et al. (2006) suggest that circumstantial evidence, such as described earlier including at West Water Reservoir (see above), points to the use of lead sources in prehistory at Leadhills and Tonderghie in Dumfries and Galloway, but in general, there is very little evidence of native lead use in the Iron Age.

Shifts in the $^{206}Pb/^{207}Pb$ ratios and/or increased lead have been regularly recorded in peat profiles dated to the Late Iron and Roman times (De Vleeschouwer et al., 2010; Martínez Cortizas et al., 1997; Renberg et al., 2001). This includes sites in the British Isles: northwest and southwest England (Le Roux et al., 2004; Meharg et al., 2012), central Wales (Mighall et al., 2002b, 2009), at Flanders Moss in central Scotland (Cloy et al., 2005, 2008) and Raeburn Flow in southern Scotland (Küttner et al., 2014). The results suggest that British ores were exploited at least two centuries before the Roman occupation (Cloy et al., 2005) and that Roman exploitation always followed an earlier indigenous (British) lead extraction industry. The equivalent time frame at Toddle Moss is contained between approximately 182 and 148 cm (AD 40–410; Figure 3). Across this part of the core lead concentrations and Pb/Ti ratios remain low: this is rather unusual. Lead concentrations initially fall and then rise slightly between 150 and 160 cm before declining once again. This small peak may represent small scale, episodic mining/metallurgical activity towards the end of the Roman occupation of Britain, but a clear phase of enrichment is not observed in contrast to the one recorded during across the Iron Age and Roman transition in peat bog records elsewhere in Scotland and further afield (e.g. Küttner et al., 2014, and

Table 2. Loadings of the variables in the components extracted by PCA on the chemical composition of the peat.

	Cp1	Cp2	Com		Cp1-PI	Cp2-PI	Cp3-PI	Com
As	0.93	0.27	0.95	Si	0.83	0.08	0.15	0.71
Ga	0.93	0.26	0.93	Ti	0.83	−0.18	0.03	0.72
Y	0.90	0.33	0.91	Al	0.79	0.04	0.21	0.67
Zn	0.82	0.05	0.67	Y	0.71	0.15	0.06	0.53
Pb	0.82	0.43	0.85	Zr	0.69	−0.16	0.06	0.51
Cr	0.51	0.35	0.38	Zn	−0.27	0.75	0.25	0.69
Ti	0.29	0.86	0.83	As	0.04	0.74	0.13	0.56
Si	0.35	0.85	0.83	Cr	0.44	0.59	−0.54	0.83
Al	0.15	0.84	0.73	Ga	0.16	0.18	0.83	0.74
Zr	0.21	0.80	0.69	Pb	0.43	0.23	0.67	0.69
Eigv	4.40	3.37		Eigv	3.45	1.63	1.58	
Var	44.0	33.7		Var	34.5	16.3	15.8	

Cp1 and Cp2: components extracted using the whole data set; Cp1-PI to Cp3-PI: components extracted using data for pre-industrial peat sections; Eigv: eigenvalues; Var: percentage of total variance; Com: communality (proportion of variance of each element explained by the two principal components); PCA: principal component analysis.

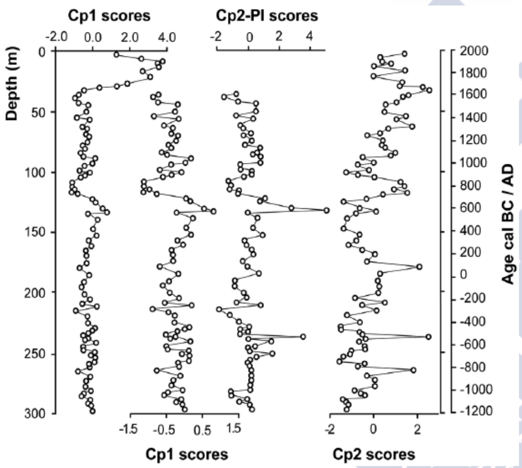

Figure 5. Records of scores of the extracted principal components.
Cp1 and Cp2 are the components extracted using the whole data set; Cp2-PI corresponds to a component characterized by high Zn, As and Cr loadings extracted using data for pre-industrial peat sections. The second panel from the left shows the Cp1 scores without the superficial samples (note that, as indicated in the text, these scores are essentially the same as those of Cp1-P1, $r = 0.97$).

references previously cited; Figure 7b). Notwithstanding the coarse resolution of the isotope data, there is an increase in $^{206}Pb/^{207}Pb$ ratio from 1.154 ± 0.0006 at 182–184 cm (*c*. AD 25) to 1.175 ± 0.0021 at 158–160 cm (*c*. AD 280) (Figure 3), which is consistent with the mean ratio derived by Rohl (1996) from six galena samples from Leadhills and five from Wanlockhead. However, the low concentrations recorded in the Toddle Moss peat core also imply that local lead ores remained unexploited or that any such activity was small in scale and may have only generated a pollution signal that is below the level of detection using current methods. Moreover, there is a lack of any definitive local archaeological evidence for lead mining and metallurgy for this period.

The Roman occupation of Scotland was short and intermittent, spanning approximately 150 years between the late 1st century and early 3rd century AD, with actual occupation by the Roman army occurring over as few as 40 years (Breeze and Dobson, 1987). There is evidence that the Romans were present in the area around Toddle Moss as a Roman road – with associated forts and temporary camps – extended northwards from Carlisle up to Crawford (Fairhurst, 1955; Figure 1). The road passes the Elvanfoot valley which runs westwards to Leadhills and Wanlockhead. There was also a fortlet at Sanquhar to the southwest of Leadhills and Wanlockhead. Such a transient occupation may not have allowed or encouraged the development of any large scale mining operation although both Wilson and Flett (1921) and MacDonald et al. (2005) have suggested that lead extraction may have occurred during Roman times. If the gradual rise in lead concentrations between 219 and 176 cm at Toddle Moss does indicate the existence of a local Iron Age lead extraction industry at Leadhills or Wanlockhead, another unknown factor possibly acted as a disincentive to further, more expansive Roman exploitation. The rarity of silver in Scotland and northern Britain lead ores may have depreciated its importance. This is in contrast with the record from Raeburn Flow, approximately 74 km to the southeast, and at Flanders Moss to the north, where small but more discernible lead contamination occurred during the pre-Roman and early part of the Roman period (Cloy et al., 2005; Küttner et al., 2014) (Figure 7b and c). However, Raeburn Flow is much closer to the Northern Pennine orefield, the lead and zinc mines in the Caldbeck fells and Carlisle, where there is evidence for lead smelting: all of which could have been pollution sources (Murphy, 2011). While lead artefacts have been found in both native and Roman contexts during the Roman Iron Age in Scotland, and although the finds suggest some interaction between the Romans and natives, it is still unclear where the objects originated from and who manufactured them (e.g. Hunter, 1996).

Martínez Cortizas et al. (2013) note that records from mires, lakes and lagoons do not always show metal enrichment during the Late Iron Age and Roman period. For example, some studies, such as those from southern France (Labonne et al., 1998), the Eifel area and Ireland (Schettler and Romer, 2006) do not show any evidence of contamination during the Iron Age while mires from Bavaria (Küster and Rehfuess, 1997), central and southeastern France (Baron et al., 2005; Monna et al., 2004) also show no metal enrichment during the Roman period. The Toddle Moss record provides additional evidence for specific regional variations in the evolution of mining and metallurgy during prehistoric and Roman times across Europe (cf. Martínez Cortizas et al., 2013).

The results suggest that phases of enhanced chromium accumulation occurred between 191 and 161 cm (*c*. 60 cal. BC–AD 225) and from 135 to 79 cm (*c*. AD 550–1150) Chromium was first discovered in the 18th century, so it is unlikely to have been intentionally exploited until then (Jacobs and Testa, 2005). Its occurrence in the Toddle Moss record is possibly as a by-product of mining, although lead concentrations were low at this time,

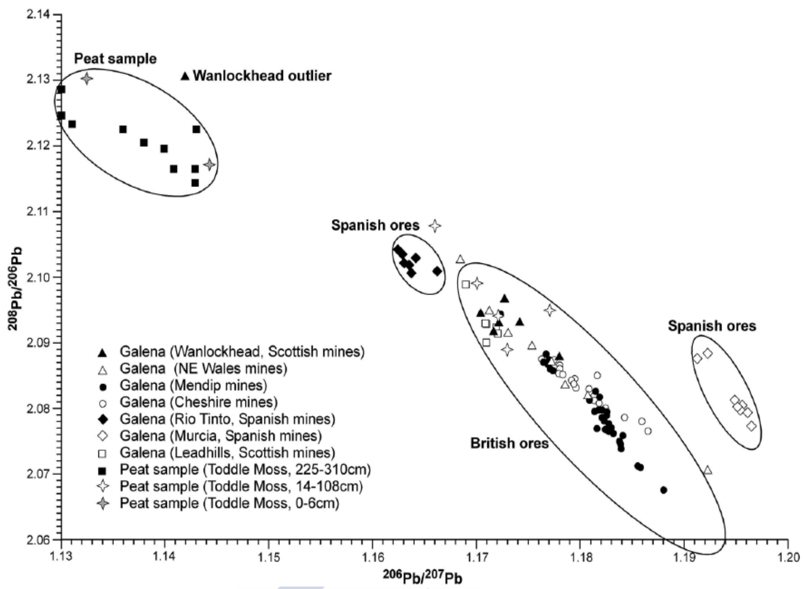

Figure 6. Plot of $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ ratios from samples from the Toddle Moss core and galena from various British and Spanish ores. Data from Rohl (1996) and Stos-Gale et al. (1995).

suggesting that little or no mining took place locally, or it is deposited as dust produced from wider land-use changes as a proportion of the changes in chromium is also correlated to Cp2 indicating a geogenic contribution. Chromium is relatively enriched in bedrock regionally (MacDonald et al., 2005).

Despite the low concentrations, the lead record between AD 400 and 1610 appears to document the rise of the extraction and metalworking industry. The $^{206}Pb/^{207}Pb$ ratios initially drop to 1.163 ± 0.0010 at 126–128 cm (*c.* AD 655) but then return to more radiogenic values thereafter: values of 1.17 and 1.18 from 112 (*c.* AD 800) to 25 cm (*c.* AD 1750) (Figure 5) are consistent with the isotopic values determined for galena at both Leadhills and Wanlockhead. The pollution component identified by PCA (Cp1) shows three peaks in the period AD 400–1610, supported by increased lead concentrations and Pb/Ti ratios, pointing to small-scale mining/metallurgical activity at Leadhills/Wanlockhead during the 5th–7th and 9th–11th centuries AD (Figures 3, 4 and 6). The first peak occurs at 133 cm (*c.* AD 572), with a short-lived peak in Cp1 and Cp1-PI cores, lead concentrations and Pb/Ti ratio. Lead shows a sustained rise after *c.* AD 900 (103 cm) as the $^{206}Pb/^{207}Pb$ ratio increases to 1.173 ± 0.0010 (106–108 cm, *c.* AD 855). Lead peaks at 93 cm (*c.* AD 1010) along with a peak in the Pb/Ti ratio subsequently fall (to 85 cm) before increasing again to 65 cm (*c.* AD 1310). Charcoal, taken from a lead slag scatter at Glennkip in the Leadhills, has been radiocarbon dated to the early 11th century AD, while smelting sites date to the late 10th and 11th centuries at Manor Valley (Pickin, 2010). While the first record for lead mining in the Leadhills district is provided by the Monks of Newbattle dated to AD 1239 (Wilson and Flett, 1921), the series of small but discernible peaks occur throughout the early medieval period.

After AD 1310, there is a gradual decrease in the Toddle Moss lead concentrations. This trend continues up the core to 50 cm (*c.* AD 1475). This coincides with the timing of the Anglo-Scottish war, a period for which there are no documentary accounts of lead mining in Leadhills/Wanlockhead. Written records recommence from AD 1466. After this date, the lead concentrations in the peat slowly begin to rise, possibly in response to the establishment of post-medieval smelting mills in the upper reaches of Glengonnar and Wanlockhead Water (Pickin, 2010).

Lead, arsenic, chromium and zinc concentrations all increase above 38 cm (*c.* AD 1610) (Figures 3 and 4). The expansion in lead mines at Leadhills and Wanlockhead is well documented for the 17th century, with peak activity occurring between AD 1850 and 1920. Through this part of the peat record (24 cm and above), the $^{206}Pb/^{207}Pb$ ratio generally falls within the range 1.17–1.18. This range is consistent with the isotopic signature of indigenous lead ore smelting from Leadhills and Wanlockhead (Figure 6) and coal combustion ($^{206}Pb/^{207}Pb$ ratio of 1.181) as recorded elsewhere in Scotland (e.g. Cloy et al., 2005; Farmer et al., 2005). A double peak in lead concentrations, dated to the latter part of the 18th and late 19th/early 20th centuries, respectively, is shown. The date of the uppermost peak is consistent with total lead concentrations measured in a channel bank in Glengonnar Water and average production figures from Leadhills (Rowan et al., 1995).

Increased concentrations of zinc, arsenic and, to a lesser extent, gallium are most likely to be associated with lead mining, coal combustion (Oremland and Stolz, 2003; Rothwell et al., 2009; Shotyk et al., 1996) and/or plant uptake (Zaccone et al., 2008). Coal was used as fuel for lead smelting from AD 1727, and small amounts of copper and zinc were also extracted locally (Wilson and Flett, 1921). Chromium is also used as an alloy in steel making (Jacobs and Testa, 2005).

The marked reduction of lead, arsenic, chromium and gallium concentrations in the top 10 cm reflects the demise of the Leadhills and Wanlockhead mines in the 1930s and the subsequent phasing out of leaded gasoline. Less radiogenic $^{206}Pb/^{207}Pb$ ratios once again fall close to the isotopic ratio of the Wanlockhead outlier (Figure 6).

These values reflect a change in the source of the lead deposited onto the bog, with the final closure of the mines and the loss of the main Leadhills isotopic signature, the increasing influence of imported Australian lead ($^{206}Pb/^{207}Pb$ ratio = 1.04) and other alkyl lead additives in petrol which are also phased out in the recent past. These sources would dilute any remnant lead deposition from the Leadhills galena ores. These trends are commonly recorded in bogs across the British Isles (e.g. Cloy et al., 2008; Farmer et al., 1997; Le Roux et al., 2004; Mighall et al., 2002b, 2004, 2009; West et al., 1997). The acrotelm is also affected by

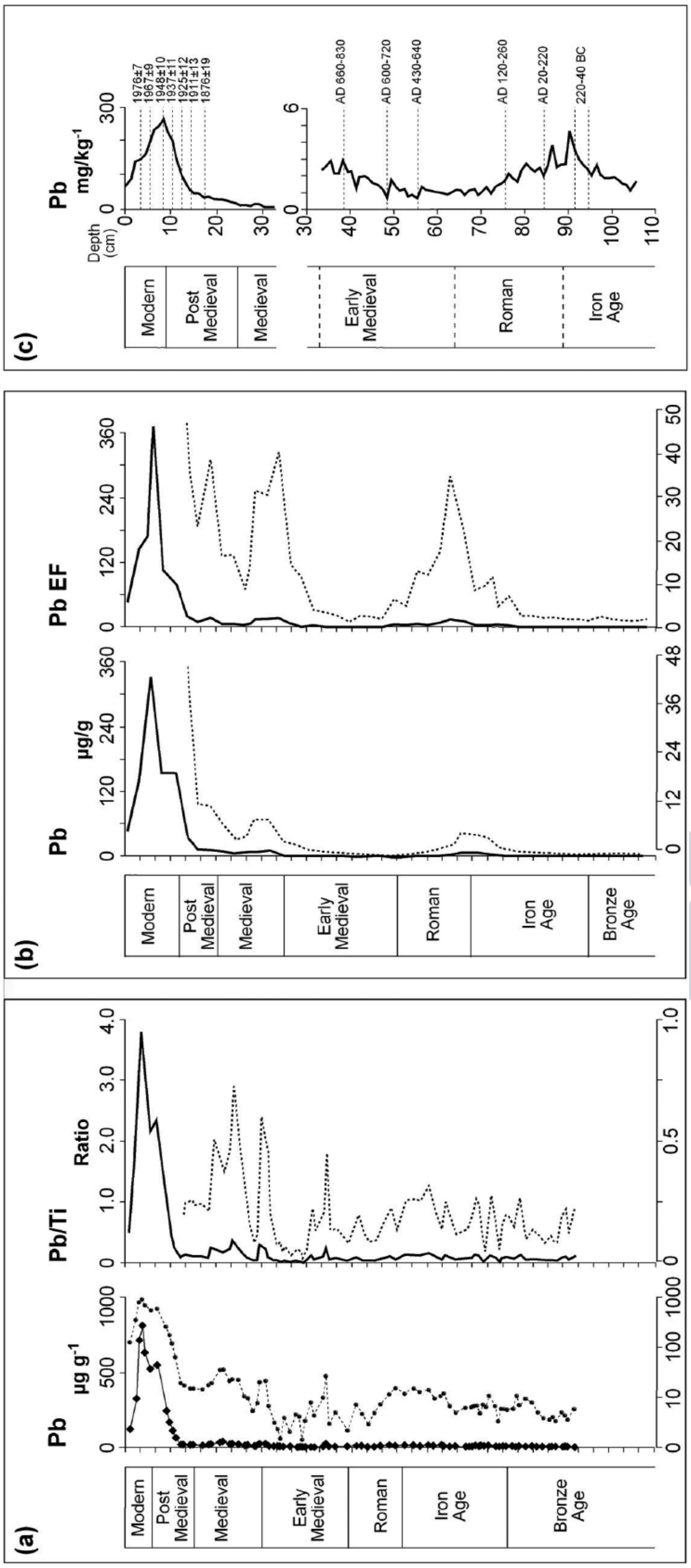

Figure 7. Comparison of lead records from selected peat bogs in Scotland. (a) Leadhills lead concentrations and Pb/Ti ratio; dashed line represents exaggerated values down the profile (scale at base of the graph). (b) Raeburn Flow lead concentrations and lead enrichment factor. Enrichment factor is calculated using the equation proposed by Shotyk (1996). Titanium was used as the reference lithogenic element (from, and full details in, Küttner et al., 2014). Dashed lines represent exaggerated values down the profiles (scale at base of the graph). (c) Flanders Moss lead concentrations (from, and full details in, Cloy et al., 2005).

ongoing peat forming processes such as decomposition, plant uptake/recycling, element mobility and fluctuations at the acrotelm/catotelm transition (e.g. Martínez Cortizas et al., 2007). These processes may also have played a role in influencing the distribution of elements through the peat such as zinc (Biester et al., 2012; Espi et al., 1997; Jones, 1987; Shotyk, 1988).

Conclusion

The Toddle Moss record provides evidence of three major phases of atmospheric metal contamination which accord well with historical and archaeological records of mining and metallurgy from medieval times to present: 5th–7th centuries AD, 9th–11th centuries AD and the latter part of the 18th and late 19th/early 20th centuries, respectively. No evidence of major Roman activity was discovered, which provides further evidence for specific regional variations in the evolution of mining and metallurgy and an associated contamination signal in Roman times across Europe.

Patterns of lead might reflect earlier activity during the Bronze and Iron Ages, but further analysis will be required to confirm whether the Leadhills/Wanlockhead was an early source of metals as part of an insular metal mining industry.

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3.6. Paper VI

Silva-Sánchez, N. (2015) **Mining and Metallurgical activities in N Iberia and their link to forest evolution using environmental archives (Centuries AD V to XI)**. *Estudos do Quaternário* 12, 15–26.

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MINING AND METALLURGICAL ACTIVITIES IN N IBERIA AND THEIR LINK TO FOREST EVOLUTION USING ENVIRONMENTAL ARCHIVES (CENTURIES AD V TO XI)

NOEMÍ SILVA-SÁNCHEZ [(1)]

Abstract: Research on palaeoenvironmental archives has challenged the widely accepted view that atmospheric metal pollution started with the Industrial Revolution, by demonstrating that it dates back to the Bronze Age when mining and metallurgical activities spread. These activities and the exploitation of natural resources for metal extraction and smelting involved intense transformation of the landscape from the Iron Age onwards, with forest decline, among others, one of the most common. This paper examines the methodology used for the detection of past atmospheric metal pollution and other environmental impacts associated with mining and metallurgy and reviews the research performed in this field in North Iberia, with special attention to centuries AD V-XI.

Keywords: mining, metallurgy, atmospheric metal pollution, North Iberia, impacts on vegetation

Resumen: **Minería y metalurgia en el Norte de la Península Ibérica y su relación con la evolución del bosque a partir de archivos ambientales (Siglos V-XI)**
La investigación paleoambiental realizada en las últimas décadas en archivos ambientales ha demostrado que, a pesar de hasta hace poco se creía que la contaminación atmosférica metálica habría comenzado con la revolución industrial, las evidencias más antiguas se remontan ya a las primeras sociedades metalúrgicas. Las actividades mineras y metalúrgicas así como la explotación de los recursos naturales para la extracción y procesado de los metales supuso intensas modificaciones del paisaje, siendo la tala de bosques, entre otras, una de las más habituales. En este trabajo se examina la metodología empleada para el estudio de la evolución de la contaminación atmosférica metálica y otros impactos asociados con la minería y la metalurgia y se revisa la investigación realizada en este campo en el Norte de la Península Ibérica, con especial atención al periodo comprendido entre los siglos V-XI AD.

Palabras clave: minería, metalurgia, contaminación atmosférica metálica, Norte ibérico, impactos en la vegetación

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1. INTRODUCTION: THE STUDY OF PAST ATMOSPHERIC METAL POLLUTION AND ITS IMPACTS

For a long time atmospheric metal pollution was considered to have started with the onset of the Industrial Revolution, forced by increased population and an unprecedented technological and economic development. This has been commonly accepted despite archaeological evidence that human activities, like mining and metallurgy, already caused atmospheric pollution several millennia ago. Some of the first studies of palaeopollution were published in the 1980s (NRIAGU 1980; 1983). Later research on palaeoenvironmental archives demonstrated that the evidence of atmospheric metal pollution dates back indeed to metal culture age (e.g. MARTÍNEZ CORTIZAS *et al*. 1997; LEBLANC 2000; MIGHALL *et al*. 2002a; PONTEVEDRA-POMBAL *et al*. 2013). Minero-metallurgical activities produced intense environmental changes since ancient times. Some of the most well studied European prehistorical mining centres are found in mid Wales, UK, where the Early Mines Research Group did an exhaustive study of the environmental impact associated with Early Bronze Age copper mining (e.g. CREW & CREW 1990; MIGHALL *et al*. 1993; CRADDOCK 1995; TIMBERLAKE 2001). While the first evidence of environmental impact associated to mining goes back to the Bronze Age, the Roman period can be considered a key point when evaluating the environmental impact associated with mining (e.g. LEWIS & JONES 1970; DURALI-MUELLER *et al*. 2007; MARTÍNEZ CORTIZAS *et al*. 2013; LÓPEZ-MERINO *et al*. 2014; PY *et al*. 2014).

One of the most emblematic examples of the changes that happened during this period can be found in Las Médulas (León, Spain), where, interestingly, landscape forms created by mining operations are now protected by different legal

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figures: Spanish Heritage Cultural Interest Site (1996), UNESCO World Heritage Site (1997) and Spanish Heritage Natural Monument (2002). Unfortunately, despite the existence of such remarkable examples, the interpretation of mining landscapes is, frequently, complex. Based solely on the evidence from archaeological excavation it is difficult to ascertain when metallurgical activity actually commenced, its duration and whether it took place continuously or in phases. A furnace, for example, can be archeomagnetically or radiocarbon dated, but this date only provides an indication of its construction age and/or when it was last used (Mighall *et al*. 2006b). The great majority of old metal mines are multi-period. Some of them have been exploited repeatedly over hundreds/thousands of years. Moreover, later activity and a lack of dateable artefacts can make it difficult to build an accurate chronological sequence of events using archaeological material alone (Orejas 1996; Mighall *et al*. 2006b). Palaeoenvironmental studies on natural archives can produce indirect evidence that may provide a solution for some of these issues. The study of certain indicators -both abiotic: elemental composition, physical-chemical properties, etc., and biotic: pollen, spores, etc- that are deposited in environmental archives through time, combined with absolute dating methods, may be of help to reconstruct the intensity and the chronology of the environmental transformations that took place in a given landscape. Ice cores (e.g. Murozumi *et al*. 1969; Hong *et al*. 1994; Rosman *et al*. 1994, 1998), lake sediments (e.g. Farmer *et al*. 1996, 1997; Renberg *et al*. 2000, 2002; Bindler *et al*. 2001; Brännvall *et al*. 2001; Outridge *et al*. 2002; Yang & Rose 2005; Michelutti *et al*. 2009) and peatlands (e.g. Shotyk 1998, 2002; Weiss *et al*. 1999; Shotyk *et al*. 2001; Martínez Cortizas *et al*. 2002b; Mighall *et al*. 2002b, 2006b, 2009, 2014; De Vleeschouwer *et al*. 2010; Küttner *et al*. 2014) constitute the environmental archives more often used for atmospheric metal pollution. However, in North Iberia, the scarcity of permanent ice sheets makes of peatlands (e.g. Martínez Cortizas *et al*. 1997, 2002a, 2002b, 2013; Kylander *et al*. 2005; Pontevedra-Pombal *et al*. 2013) and to a lesser extent lakes (e.g. Camarero *et al*. 1998; Leblanc, 2000; García-Alix *et al*. 2013) the most used environmental archives. With the study of these archives at an appropriate sampling resolution, phases of mining and metallurgy can be identified and dated, thus providing valuable information about the duration and chronology of these activities, specially when archaeological information is scarce or confused (Mighall *et al*. 2006b). In fact, one of the main advantages of the application of palaeoenvironmental research to the detection and quantification of mining and metallurgical activities is that, contrary to other disciplines, it offers a nearly continuous record of environmental change. Multiproxy approaches have been widely used to detect the impacts linked to the development of minero-metallurgical activities (e.g. Monna *et al*., 2004b; Martínez Cortizas *et al*. 2005; Jouffroy-Bapicot *et al*. 2006; Mighall *et al*. 1997; 2006b, 2013; Breitenlechner *et al*. 2010; López-Merino *et al*. 2011; Pontevedra-Pombal *et al*. 2013).

This paper reviews the methodology that has been developed for the detection of past atmospheric metal pollution and the impacts associated with past mining and metallurgy. I also review the research conducted in this field in North Iberia, a key region for studying past metal pollution due the wealth of mineral deposits, the multi-period history of the industry and the variation in the intensity of mining exploitation through time. Although focused on the period from AD V to XI, the information on previous periods also warrants comment in order to contextualize this phase in a wider framework. The geographic location of relevant zones in the study of palaeopollution in the North of the Iberian Peninsula is shown in Figure 1.

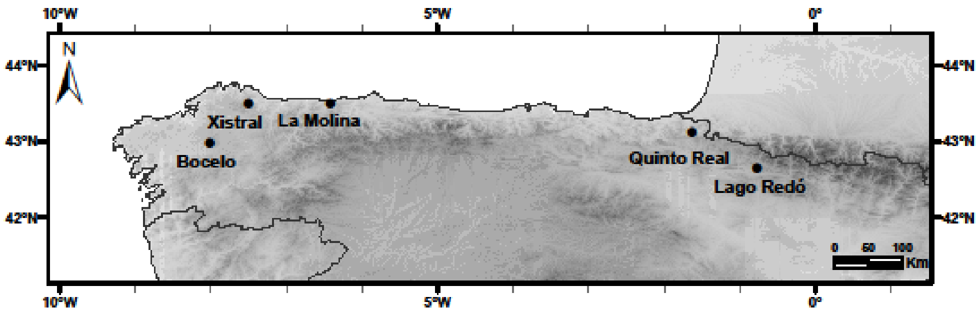

Fig. 1. Location of the studied areas most cited in the text
Fig. 1. Localización de las áreas de estudio más citadas en el texto

2. RECONSTRUCTION OF ATMOSPHERIC METAL POLLUTION: GEOCHEMICAL PROXIES

Until the exploitation of fossil fuels as a main source of metals to the atmosphere, anthropogenic metal emissions were mainly related to mining and metallurgical activities. In fact, the reconstruction of the intensity of this type of activity is based on the application of geochemical methods for the quantification of palaeopollution. Despite numerous factors can affect the dispersion of gaseous and particulate pollutants from their emission sources (e.g. DAVIES 1983; MACKLIN 1992), peatlands near minero-metallurgical production centres, capture pollutants on to their surface, thereby giving an accurate chronological record of its activity (MIGHALL *et al.* 2006b).

Among metals, lead is the most widely used for the reconstruction of atmospheric pollution history, as it has been one of the first metals for which the lack of postdepositional remobilization was demonstrated (e.g. SHOTYK *et al.* 1996; MACKENZIE *et al.* 1997) as well as one of the most common pollutants from ancient times to recent periods (KYLANDER *et al.* 2005). More recently, the utility of Hg, Cu, Ni or Cd has been also demonstrated (e.g. MIGHALL *et al.* 2002a; YANG & ROSE, 2005; PONTEVEDRA-POMBAL *et al.* 2013; KÜTTNER *et al.* 2014).

Metals content in peat, as well as its concentration in the atmosphere (from which they are deposited), also depends on matrix properties (like the type of minerals present or the proportion of mineral matter). Thus, the metals can have both anthropogenic and natural sources. Because of that, metal concentrations are not reliable enough to reconstruct anthropogenic vs. natural sources of the metals in the atmosphere. Other approaches are needed. One solution proposed to solve this problem is the calculation of enrichment factors (EF) (e.g. SHOTYK, 1996). An enrichment factor is a normalized ratio between a metal concentration and the concentration of a conservative element in a sample with regard the same ratio in a reference material usually either the Earth crust, a given rock type, soils or, as desirable and if possible, pre-pollution samples of the environmental archive studied. Thus, an EF provides a way to evaluate the magnitude of the atmospheric fluxes exceeding the natural background in an area. The higher the pollution levels the higher the EF will be. EF can be very useful for the reconstruction of relative variations through time but they also present some limitations. For example, Reimann & De Caritat (2000) strongly criticized the use of Earth crust values in EFs calculations and they suggest the need to use statistically significant environmental data. One problem is that the concentration of conservative elements used for the normalisation of EF can show regional variations due to differences in mineralogical composition (WEISS *et al.* 2002) limiting the comparison of pollution levels in different environments. Even at a local scale, differences due to physical fractionation during wind transport (MARTÍNEZ CORTIZAS *et al.* 2002a) can affect the EF. Because of these limitations, some authors suggest that multivariate statistic solutions are desirable to separate natural and pollution signals (e.g. MARTÍNEZ CORTIZAS *et al.* 2013).

The increase in research on lead isotopes in natural archives in recent years (e.g. KOMÁREK *et al.* 2008 and references there in) indicates that they have also become important for the evaluation of the enrichment and the sources of atmospheric metal pollution (e.g. BINDLER *et al.* 2001; SHOTYK *et al.* 2003; KYLANDER *et al.* 2005, 2010). Lead isotopic signatures are commonly expressed as ratios between two isotopes. The most widely used is the $^{206}Pb/^{207}Pb$ ratio, which tends towards lower values with increasing pollution. When lead sources are known and the isotopic signatures of materials are properly characterised, it is possible to calculate the relative contribution of each source applying simple mixing models (RENBERG *et al.* 2002). Despite their limitations, EF are still used and often compared with other pollution indicators such as lead isotopes (e.g. WEISS *et al.* 1999). Thus, metal concentrations, enrichment factors and isotopic ratios, with few local peculiarities, should reflect very similar patterns.

3. RECONSTRUCTION OF FOREST EVOLUTION: PALYNOLOGICAL PROXIES

Atmospheric metal pollution is not the only detectable environmental impact of mining and metallurgy. Besides the large transformations of the landscape linked to the construction of extraction facilities, that in some cases even resulted in creation of new habitats that still exist today (like lakes or wetlands) (e.g. LÓPEZ-MERINO *et al.* 2011), the exploitation of natural resources for the extraction and further processing of metals, also in many cases led to intense environmental modifications. For example, the use of wood as raw material in the construction of extractive facilities and as fuel for smelting may have caused intense reductions in forest cover (e.g. MONNA *et al.* 2004b; JOUFFROY-BAPICOT *et al.* 2006; MIGHALL *et al.* 2006b, 2013; BREITENLECHNER *et al.* 2010; PONTEVEDRA-POMBAL *et al.* 2013). Although there is also plenty of evidence of woodland management (vs. clearance) to produce firewood or in order to ensure charcoal supply (e.g. MCKEOWN 1994; MIGHALL *et al.* 2000; SZABÓ *et al.* 2015), since charcoal was needed by metalworkers as fuel to ore smelting.

Pollen and spores preserved in environmental archives are among the earliest environmental proxies studied (e.g. IVERSEN 1941). The reconstruction of past vegetation is a useful tool for studying the use past human populations made of its environment in general and of vegetation in particular. Pollen analysis is based in the fact that pollen and spores preserved in environmental archives can be taxonomically identified and quantified. This, combined with an accurate chronological control, allows the reconstruction of past changes in vegetation. Initially, palaeopalynological studies mainly focused on pollen and moss and ferns spores, thus regional signals prevailing over local signals. In the last decades however, palaeopalynology has broaden its range of application as many other "non pollen palynomorphs" (NPP), mainly produced by fungi and algae, have been included in pollen studies. NPP, due to their limited dispersal, give valuable information at a local scale (e.g. VAN GEEL *et al.* 1989; VAN GEEL 2001). Among them there are proxies for anthropogenic pressure on landscapes -grazing, fire incidence or soil erosion- (e.g. ANDERSON *et al.* 1984; RIERA *et al.* 2006; LÓPEZ-MERINO *et al.* 2009; CUGNY *et al.* 2010; EJARQUE *et al.* 2011; ABEL-SCHAAD & LÓPEZ-SÁEZ 2012; GILL *et al.* 2013) and proxies for environmental conditions such as hydrological changes or the erosion of catchment soils (e.g. MIGHALL *et al.* 2006a; MEDEANIC & SILVA 2010).

Despite timber being of great importance for the development of mining and metallurgical activities, until recent times, the role of mining and metallurgy in forest evolution has been an aspect almost neglected, at the expense of other forcings in cultural landscapes such as agriculture and grazing (CHAMBERS 1993). One of the reasons of this bias is possibly related with methodological reasons. Palynological proxies provide information about both forest evolution and agriculture (cereal presence) and grazing activities (anthropozoogenous and nitrophilous taxa as well as coprophilous fungi), whilst the detection of mining and metallurgical activities needs geochemical approaches and/or the presence of well studied and contextualised archaeological sites. Thus, multiproxy approaches are needed for detecting this type of synergies. Something that, even nowadays, is relatively uncommon. Another aspect behind this bias could be the fact that agriculture and mining/metallurgy coexist making very difficult to disentangle the effects caused by each activity.

Forest clearance linked to timber extraction for minero-metallurgy development would have occurred since prehistory (e.g. MIGHALL & CHAMBERS 1993, 1997; MONNA *et al.* 2004a, 2004b). It is usually reflected in palynological diagrams by a decrease in total arboreal pollen, although sometimes selective clearance of one or two taxa might not affect the total arboreal signal.

Thus multiproxy approaches combining palaeopollution reconstruction and other geochemical methods with palaeopalynology allow for the evaluation of possible synchronicities between minero-metallurgical activities and other aspects of environmental change such as forest clearance, soil erosion or hydrological changes at a basin scale (e.g. MIGHALL & CHAMBERS 1993; MARTÍNEZ CORTIZAS *et al.* 2005; MIGHALL *et al.* 2006b, 2013; LÓPEZ-MERINO *et al.* 2011, 2014; PONTEVEDRA-POMBAL *et al.* 2013).

4. EVOLUTION OF ATMOSPHERIC METAL POLLUTION IN NORTH IBERIA

4.1. First evidence of atmospheric metal pollution

Until recently, the oldest evidence of metal pollution in Iberia dates back to about 4500 years ago. It was detected in estuarine sediments from the Tinto River, where a sharp increase in Pb, As and Cu concentrations was recorded (LEBLANC, 2000). This was attested by the presence of small slags in the sediment that proved the development of metallurgical activities at a local scale dating to 2530 BC. More recently, Galop *et al.* (2001) found a geochemical anomaly (enrichment in Pb and decrease in the ratio $^{206}Pb/^{207}Pb$ ratio) in a section with an age earlier than 2600 BC of peat core from the Basque country. Moreover, ongoing research in La Molina mire (Asturias) suggests that the first evidence of atmospheric metal pollution in North Iberia may even be traced back to the Early Bronze Age, around 5000 years ago (Martínez Cortizas, 2014: personal communication). This diversity of ages in the onset of atmospheric metal pollution suggests that the timing of mining and metallurgy was locally variable and the impact was spatially restricted. In Galicia, the oldest evidence of palaeopollution dates back to about 3000-3500 years and has been found in peatlands from the Xistral Mountains. Martínez Cortizas *et al.* (1997), based on the study of enrichment factors in a peat core, detected the first evidence of atmospheric pollution in layers with an age of 930 BC. Subsequently, the study of the Pb isotopic composition revealed that Pb atmospheric pollution would have indeed begun by 1260 BC, although it was not until 1000 BC when it dominated (> 50%) Pb deposition (KYLANDER *et al.* 2005). More recent studies in other metals in peatlands of the Xistral mountains pushed back the onset of atmospheric metal pollution to 1400 BC, when the first Ni enrichments were recorded (PONTEVEDRA-POMBAL *et al.* 2013). Although Garcia-Alíx *et al.* (2013) recommend to take the date of this proposed anthropogenic "nickel event" with caution due to Ni being a redox -sensitive element.

4.2. Atmospheric metal pollution during the Roman Period: pre-industrial climax

North Iberia becomes one of the most important mining centres during the Roman Period. Iberian mines generated 60% of the European lead production (NRIAGU 1983) and in Northwest Iberia around 500 mines were exploited. Mining activity mainly focused on gold, but also on lead, zinc, cooper, silver, iron and tin. The timing of this exploitation comprises the first two centuries AD and its start and end are connected to the operation of the Roman monetary system based on gold-silver bimetallism (CAAMAÑO 2007). During this period, both at a European and Iberian level, atmospheric metal pollution produced by minero-metallurgical activities was widespread and increased in intensity. In peat cores records from North Iberia an increase in atmospheric metal pollution is detected both in Galicia – Xistral mountains (Figure 2A; MARTÍNEZ CORTIZAS *et al.* 1997, 2002a; KYLANDER *et al.* 2005) and Bocelo mountains (Figure 2B; SILVA – SÁNCHEZ 2010) –, in the Basque country – Quinto Real (GALOP *et al.* 2001, 2002; MONNA *et al.* 2004a) – and in Asturias – Alto de la Espina range (Figure 2C; MARTÍNEZ CORTIZAS *et al.* 2013). Polymetallic studies in the Xistral mountains also show increases in the enrichment factors of nickel, arsenic and cadmium (MARTÍNEZ CORTIZAS *et al.* 1997; PONTEVEDRA-POMBAL *et al.* 2013). While most of the records show increased pollution from 200 BC to AD 400, maximum values, especially in the northwest, occurred in centuries AD I-II. A good example is the Alto de la Espina record, which has an extraordinary chronological resolution for the Roman period and in which pollution lead increases from 20 to 88% over these two centuries (MARTÍNEZ CORTIZAS *et al.* 2013). The close proximity of "Alto de la Espina" to well known gold mining centres may account for this intense pollution. The collapse of the Roman Empire signalled a general decline in atmospheric metal pollution, though timing of the decline is slightly different in western and eastern North Iberia, indicating local differences in the processes of abandonment of mining activities.

4.3. Atmospheric metal pollution in V-XI centuries AD

After the fall of the Roman Empire metal pollution levels in the atmosphere drastically decreased, occurring earlier in Galician (~450 AD) than in Asturian and the Basque records (~550 AD; Figure 2). Disarticulation of Roman power structures greatly affected mining intensity, representing a sharp break with the precedent model of exploitation of natural resources. However, the intensity of the process was not the same throughout North Iberia. For example, in Quinto Real (Basque country) (GALOP *et al.* 2001, 2002; MONNA *et al.* 2004a) the collapse in minero-metallurgical production happened more gradually than in the other North Iberian sites. This is probably because Romanization was also less intense in this region than at other sites in North Iberia (MONNA *et al.* 2004a).

With the onset of the Germanic Period, around AD 550-600, atmospheric pollution signals become again relevant, indicating a recovery of minero-metallurgical activities, at least in Galicia, while in Asturias and in the Basque Country there is still no sign of a resumption (Figure 2). In Xistral (Galicia; Figure 2A), despite lead concentrations in the peat abruptly decrease from Roman times and slightly increase around AD 1050, with the isotopic composition more sensitive to low intensity pollution (MUNKSGAARD & PARRY, 1998). Both signals indicate a gradual increase in anthropogenic emissions to the atmosphere between AD 500 and 1200, with brief occasional increases centred at AD 675 and 1050. In Bocelo (Galicia; Figure 2B) however, pollution lead increased as early as AD 620 and more intensely between AD 900 and 1240, peaking around AD 1060. This trend suggests that in Medieval Galicia mining and metallurgy would have peaked in the transition between AD VI-VII and X-XI centuries. Although lead enrichment factors show a trend to decreasing values from AD 400, the isotopic signal indicates a continuous increase in metal pollution from AD 550 to 1110 in Quinto Real peatland (Basque Country) (GALOP *et al.* 2001, 2002; MONNA *et al.* 2004a); while in La Molina mire (Asturias; Figure 2C) the recovery of minero-metallurgical activities did not take place until AD 610. Here the isotopic composition points to an increase in metal pollution between AD 610 and 980 (with a maximum at AD 750) and between AD 1110 and 1270 (with a maximum at AD 1190). Comparing Medieval and Roman times, it is noteworthy that in Bocelo the intensity of medieval minero-metallurgical activities in some phases would have been similar, or even higher (towards AD 1000), to that of Roman times. In La Molina, Xistral and Quinto Real however, medieval atmospheric pollution signals seem to have been of lower intensity than the Roman ones. According to this, minero-metallurgical activities during the Middle Ages were probably less intense than in Roman times. Although it cannot be ruled out that the new mining and metallurgy production centres would have been further away from the mires or that technical improvements in extraction resulted in lower metal emissions to the atmosphere, causing lower metal deposition.

Atmospheric pollution levels in North Iberia indicate that despite archaeological evidence of medieval mining being much lower than in Roman times, mining/metallurgy could have been, at least in some areas, such as Bocelo, an important economic activity. Differences in the signal recorded by the environmental archives considered here indicate that the local history may have played a very important role in the evolution of metal pollution. In fact, and far from the norm, in some isolated places the first evidence of exploitation of local mines occurred in Middle Ages. This is suggested, for example, by a research performed on lake sediments from Redó Lake (Pirineos; CAMARERO *et al.* 1998). Here, lead concentrations and lead isotopic composition showed little variation in sediments layers of Roman age. Changes in these indicators from AD 470 point towards the initiation of extractive activities at a local scale that would have been in operation until AD 1100, with a maximum around AD 660.

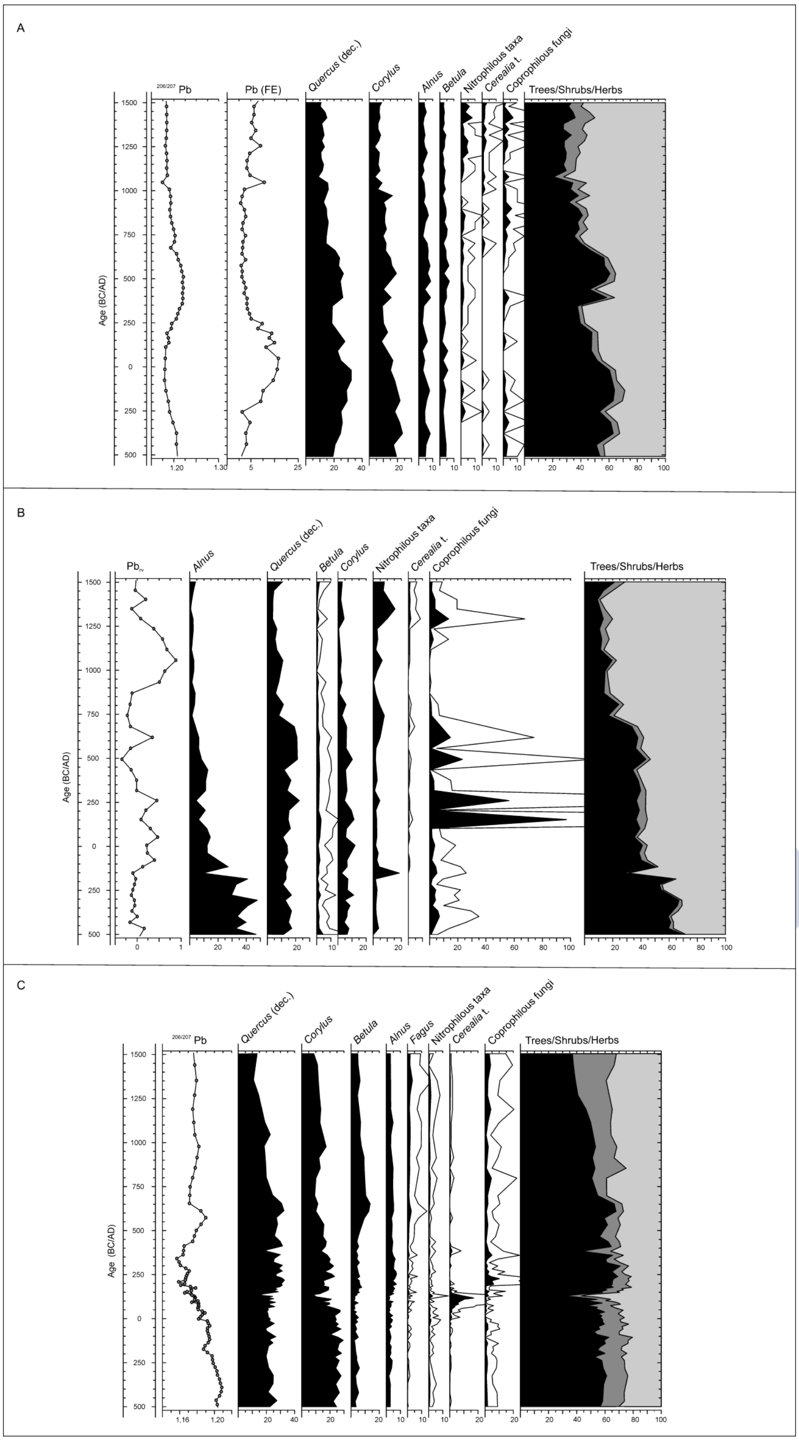

Fig. 2. Atmospheric metal pollution indicators and selected palynological taxa (in percentage) from: A) Penido Vello bog (PVO core), Xistral mountains, Galicia (MARTÍNEZ CORTIZAS *et al.* 1997, 2002a; KYLANDER *et al.* 2005; MIGHALL *et al.* 2006a); B) Cruz do Bocelo mire (PPB core), Bocelo mountains, Galicia (SILVA-SÁNCHEZ 2010; SILVA-SÁNCHEZ *et al.* 2014) and C) La Molina mire (TAE core), Alto de la Espina Range, Asturias (LÓPEZ-MERINO *et al.* 2011, 2014; MARTÍNEZ CORTIZAS *et al.* 2013). Quercus (dec.): oak; Corylus: hazel; Betula: birch; Alnus: alder; Fagus: beech.

Fig. 2. Indicadores de contaminación metálica atmosférica y porcentajes de indicadores palinológicos seleccionados de: A) turbera e Penido Vello (testigo PVO), Montañas del Xistral, Galicia (MARTÍNEZ CORTIZAS *et al.* 1997, 2002a; KYLANDER *et al.* 2005; MIGHALL *et al.* 2006a); B) turbera de Cruz do Bocelo (testigo PPB), Montes del Bocelo, Galicia (SILVA-SÁNCHEZ 2010; SILVA-SÁNCHEZ *et al.* 2014) y C) turbera de La Molina mire (testigo TAE), Sierra del Alto de la Espina, Asturias (LÓPEZ-MERINO *et al.*, 2011, 2014; MARTÍNEZ CORTIZAS *et al.* 2013).

5. COUPLING FOREST EVOLUTION AND OTHER IMPACTS OF MINERO-METALLURGICAL ACTIVITIES IN NORTH IBERIA

5.1. Changes in forest evolution linked to the first evidence of atmospheric metal pollution

In North Iberia, several studies have reported a reduction in forest cover associated with prehistoric mining and metallurgy. Decreases in several tree taxa characteristic of the mixed deciduous forest occurred at the same time that the first evidence of metal working was being recorded in natural archives. As reported by PONTEVEDRA-POMBAL *et al.* (2013), after the Neolithic period and the subsequent recovery of the forest, a new deforestation phase, beginning at ca. 3500 cal BP (Bronze Age), was synchronous with the first evidence of metal pollution in the region, which was recorded locally by an increase in nickel. In the palynological diagram (MIGHALL *et al.* 2006a) it can be seen that this corresponds to a decrease in alder, oak and hazel. In Quinto Real (GALOP *et al.* 2001, 2002; MONNA *et al.* 2004a) Middle Bronze Age to Iron Age phases of atmospheric metal pollution occur simultaneously with the loss of oak and hazel. Since indicators of agropastoral and slash-and-burn activities also decrease or are simply absent, forest decline was possibly linked to mining/metallurgical activities.

5.2. Changes in forest evolution linked to atmospheric metal pollution during the Roman Period

Scale and duration of minero-metallurgical activities largely influenced the magnitude of the environmental impact that these activities had on vegetation and other landscape features (MIGHALL *et al.* 2006b). The aggressive methods of mining extraction during Roman times caused a diversification of environmental impacts. The most evident and persistent over time and, thus, the most well known is the geomorphologic transformations derived from the large amounts of material removed by hydraulic extraction methods (*ruina montium*). Examples of this type of transformation can be found in Las Médulas (León) and in Monte Furado (Lugo) (LEWIS & JONES 1970; SÁNCHEZ-PALENCIA *et al.* 2009).

But mining production in Roman times also caused perturbations that either have left no tangible mark on the present day landscapes or are not so obvious to the naked eye. This is the case of environmental changes that took place in La Molina mire in Asturias. A place that has been declared as Site of Community Interest (Natura 2000) and that would not appear to have had anything to do with mining. Nearby La Molina, in the Narcea-Pigüeña area, a complex hydraulic system to funnel water from the mountains (FERNÁNDEZ MIER 1999) was found. Hydraulic systems consisting in canals (*corrugi*) and water reservoirs (*piscinae o stagna*) were common in Roman mines for carrying out mining extraction. From the geochemical and palynological study of La Molina mire, López-Merino *et al.* (2011) concluded that between the AD 20 and 140 the peatland would have been used as a *piscinae*. Taxa indicative of riparian habitats were detected and the content of organic matter increased. The use of the peatland as a water deposit caused a no-return point in the hydrological conditions of the wetland, leading to a change from minerotropic to ombrotropic status. Curiously, this characteristic, ultimately proved to have had an anthropogenic origin, and survives until today, has been one of the key properties taken into consideration to declare the mire as Site of Community Interest in the Natura 2000 network. The use of La Molina mire as *piscinae* also produced other changes in the landscape. Although metal extraction and processing is normally linked with forest decline, in the case of La Molina arboreal pollen percentages increased (Figure 2C; LÓPEZ-MERINO *et al.* 2014). Analyzing the pollen record in detail it turned out that this was due to relative increases in oak, birch, alder, ash, elm and maple. Damper conditions linked to the presence of shallow open water would have led to the spread of these taxa. Other trees, such as hazel and, in some particular phases, even oak decreased in abundance coinciding with minero-metallurgical production peaks. However, as an increase in agriculture and grazing indicators is recorded at the same time, it is difficult to attribute the observed changes to a single cause. So, a combination of factors seems to be the most probable scenario.

In other areas of North Iberia, Roman mining may have caused a decrease in most arboreal taxa. In Bocelo (Galicia; Figure 2B), the increase in atmospheric metal pollution was accompanied by a sharp decrease in total arboreal pollen, mainly due to the decrease of alder and to a lesser extent hazel and oak. But, synchronous increases in cereal pollen suggest agriculture could also account for the forest decline. Anyway, the abrupt and intense deforestation that took place in these mountains during the Roman Period triggered a series of cascading environmental changes (SILVA-SÁNCHEZ *et al.* 2014). Increased mineral matter inputs into the mire and the presence of the NPP *Glomus* (HdV-207) indicate intense soil erosion due to forest clearance. At the same time, larger abundance in NPP HdV-18 points to an increase in the water-table level of the mire, which was probably related with a loss of water retention capacity of the soils of the catchment as a result of forest loss. In the Xistral mountains (Galicia; Figure 2A) and in Quinto Real peatland (Basque country; GALOP *et al.* 2001, 2002; MONNA *et al.* 2004a) the increase in metal pollution is coeval with decreases in total arboreal pollen characterised by a decline in oak, hazel and alder in the first instance and subsequently oak and hazel. No substantial increases in farming indicators occurred, suggesting a much more clear relationship between forest changes and minero-metallurgical activities. Moreover, anthracological research performed in Quinto Real area indicates that oak was used for coal production during the Roman Period (GALOP *et al.* 2002).

5.3. Changes in forest evolution linked to atmospheric metal pollution between centuries AD V-XI

Collapse of minero-metallurgical activities after the Roman Period generally led to a decrease in the anthropogenic pressure on the forests of North Iberia and in some cases their recovery to a nearly pre-Roman situation.

In Galicia, forest clearance associated with minero-metallurgical and farming activities between centuries AD V and IX led to a permanent decrease of mixed woodland. In Xistral (Fig. 2A) the lead isotopic signal showed a relative maximum in atmospheric metal pollution towards AD 675. At this moment, coinciding with the rise of the mining and metallurgical activities, and evidence of the intensification of farming, the percentage of total arboreal pollen decreases sharply due to declining oak, alder and hazel. Although alder partially recovered after that, the decrease in oak and hazel was permanent and the pre-Germanic level of forest cover was never reached again. Forest retreat in the Xistral Mountains led to a much more open landscape dominated by heath scrub. This landscape that is still dominant nowadays and declared as Site of Community Importance in Natura 2000 (due to the presence of habitats 4020 “Temperate Atlantic wet heaths of *Erica ciliaris* and *Erica tetralix*” and 4030 “European dry heaths”, among other). In view of the evidence, this landscape could have been consolidated phytosociologically in the Germanic period due to the action of human activity. In Bocelo (Fig. 2B), the decrease of alder and hazel began by AD 450-500, probably due to an expansion of agricultural land and grazing at a local scale. Although, towards AD 620, Germanic lead pollution was at its highest level, so the influence of mining and metallurgy on the demise of the forest cannot be totally ruled out. Between AD 680 and 805, in a moment when metal atmospheric pollution was minimal, both cereal and nitrophilous taxa increased while oak, which until that moment was the most abundant tree taxa due to the selective pressure exerted over alder and hazel, sharply decreased. In Bocelo, forest clearance also promoted more open landscapes, but in this case dominated by herbaceous formations instead of heather shrubs.

Between the centuries AD X and XIII AD a new regressive event in the history of the Galician forest took place. In Xistral, the geochemical studies indicate an increase in atmospheric metal pollution towards AD 1050 in association with considerable decrease of oak, hazel and to a lesser extent alder. But, again, the presence of cereal pollen grains and coprophilous fungi does not enable to rule out other agricultural causes. In Bocelo, maximum medieval pollution levels had a longer chronological distribution (AD 900-1240) and magnitude. However, the decrease in the mixed deciduous forest seems to have been more related with variations in cereal pollen and coprophilous NPP than with mining and metallurgy.

At La Molina mire (Fig. 2C), mining and metallurgy expansion between AD 610 and 980 and AD 1110 and 1270 coincided with both decreases in oak and hazel. During these periods cereal percentages are maintained, and although grazing indicators increased punctually, the good agreement between the trend in atmospheric metal pollution and those tree taxa, allows the attribution of most of the woodland change to mining and metallurgical activities. Like elsewhere in North Iberia, the permanent decline in deciduous forest, dated to the late AD VII century, allowed heathland to form. In Quinto Real (GALOP *et al.* 2001, 2002; MONNA *et al.* 2004a) however, there is no a clear link between oak, hazel and beech decreases and metal pollution during AD 550-1100, as *Cerealia* showed a large expansion over the period. Pollen records of La Molina and Quinto Real show a peculiarity not seen at their Galician counterparts. Since the change of era, beech became increasingly important in mixed deciduous forest. In La Molina mire beech presence did not prevent the collapse of the forest during the Germanic Period, but in Quinto Real the larger abundance of beech allowed the deciduous forest to endure into the AD XVI century - despite that after AD VII most of the other tree taxa showed very low values.

6. CONCLUSIONS

The study of metal accumulation in peatlands allows insights into the development of mining and metallurgy activities over time, at local and regional scales. The Roman period led to an unprecedented increase in the development of mining and metallurgy in North Iberia, especially in AD I-II centuries. These activities were closely related with the power structures of the Roman Empire so that its fall, although with different chronologies for East and West North Iberia, led to a collapse in mining and metallurgy. In Galicia, the decline in atmospheric metal pollution indicators occurred around AD 450, while in Asturias and in the Basque country it was delayed by a century. Between AD V and XI centuries, in the Middle Ages, atmospheric metal pollution rose again in North Iberia. In the Galician records maxima were detected between AD VI-VII and X-XI centuries, becoming in some areas (i.e Bocelo) of greater magnitude than that occurred during the Roman Period. While in Asturias, medieval phases of pollution would have been more extensive (AD VII-X and XII-XIII), but smaller in magnitude when compared to the Roman Period. In Quinto Real, the medieval phase of metal pollution was the longest (VI-XII), but also the one of lowest intensity. Despite the intense mining activity that occurred in Roman times in North Iberia, some new mines only became active in Middle Ages. For example, in sediments from lake Redó evidence of metal pollution started by AD 470 (CAMARERO *et al.* 1998).

Multiproxy studies combining geochemical and palynological research enable us to evaluate of the influence minero-metallurgical activities on vegetation. In regions located far away from where the minero-metallurgical activities took place, the decrease in forest cover was only recorded when metallurgical activities were at its maximum. However, it is sometimes difficult to determine the role of mining/metallurgy in forest evolution independently of other human activities (as agriculture and grazing). Although the taxa affected and the magnitude of changes differed between sites, in general the seventh century AD marked the time of permanent forest clearance in the North Iberia.

Despite the great advances made in the understanding of mining and metallurgy and its impacts in North Iberia, future multiproxy research at both palaeoenvironmental and at archaeological levels would be welcome. Special attention would be required on the identification of possible medieval mining centres.

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4. GENERAL DISCUSSION

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4.1. Soil erosion: land use and climate forcings

Soil erosion is a natural phenomenon that implies the movement of soil matter from a source to a certain destination. Nowadays, erosion of topsoils is considered a worldwide-scale problem and one of the most severe degradation processes affecting soil quality (Pimentel, 2006; Wilkinson and McElroy, 2007). To properly understand the main drivers of soil erosion, however, not only current levels have to be taken into account, but also a long-term perspective is needed. In this sense, multi-proxy research on peatlands offers a great opportunity to trace soil erosion back through time, as peatlands have acted as a sink for soil particles and pollen from their catchment. In regions with long histories of human activity, deforestation and the establishment and expansion of agriculture or grazing have triggered soil erosion (e.g., Bennett et al., 1992; Hölzer and Hölzer, 1998; Martínez Cortizas et al., 2005). On the other hand, certain weather conditions –i.e., torrential rains, strong winds, etc.– may also enhance soil erosion, as it has been found for certain periods i.e., the Little Ice (e.g., de Jong et al., 2007; De Vleeschouwer et al., 2009).

One of the objectives of this PhD work is to shed light on how the intensity of dust transport/soil erosion has been affected by anthropogenic and climate changes. For this purpose three different peatlands, one located in the boreal region (Sandhavn, southern Greenland, Paper II) and two in the temperate one (O Bocelo, in the Atlantic area of North-western Spain, Paper I; and El Payo, in the Mediterranean area of Central Spain, Paper III) have been studied.

At O Bocelo (Paper I), where palaeoenvironmental information over the last ~3000 years is available, seven periods with higher inputs of inorganic material reflecting increased soil erosion (E1 to E7; Paper I: Figure 7) were identified. First evidences of soil erosion were detected in the Iron Age (E1: ~2640-2470 cal. yr BP, and E2: ~2310-2250 cal. yr BP), synchronous to periods of forest depletion. This deforestation is likely to be related to the creation of pastureland for livestock feeding, as indicated by the rise in palynological indicators such as coprophilous fungi and/or nitrophilous taxa (Paper I: Figure 7). Other soil erosion events associated to forest clearance due to grazing and agriculture have been identified during Roman (E3: ~2040-1690 cal. yr BP), Germanic (E5: ~1510-1390 cal. yr BP), Medieval (E6: ~710-660 cal. yr BP) and more recent times (E7: last ~80 years). The highest intensity of soil erosion occurred during the Roman period, and it was associated with the largest forest clearance. Important changes specific to the local mire conditions also took place. Until the largest soil erosion phase at Roman times, the mire had buffered climate and human impacts but, from this point onwards, the hydrological status of the mire –inferred by HdV-18 trends–, responded abruptly to the changes in precipitation reconstructed by rvBr (see point 3.2 in this discussion; Paper I: Figure 7). Therefore, changes in precipitation prior to Roman times do not seem to have affected the hydrology of the O Bocelo mire. However, a comparison of the two Iron Age soil erosion episodes (E1 and E2) reveals that, despite both events experienced similar levels of forest clearance, mineral inputs to the mire were higher during E1 –which was wetter than E2–, suggesting a climatic amplification of induced soil erosion. Similarly, rainfall amplification of soil erosion during wetter periods may have also occurred during Roman and Germanic times. Soil erosion as a consequence of human-climate coupling has also been detected at the early Neolithic in the Peloponnese Peninsula, where high sedimentation rates evidenced increased soil erosion due to human activities, but enhanced by precipitation (Fuchs et al., 2004; Fuchs, 2007), and at the late Bronze Age in Macedonia, where deforestation and agriculture made the river system less resilient to natural soil erosion and more sensitive to small changes in climate (Lespez, 2003). During the Little Ice Age, which has been reconstructed as humid in O Bocelo, mineral inputs to the mire showed an increasing trend despite a lack of forest clearance. Elsewhere in Europe, evidence of higher mineral matter fluxes during the LIA are also found in peat-dune complexes from Northern France (Meurisse et al., 2005), in a raised bog from Southern Sweden (de Jong et al., 2007) and in a bog from Northern Poland (De Vleeschouwer et al., 2009).

Glomus (HdV-207) and *Entorrhiza* (HdV-527) are NPP that are interpreted as soil erosion proxies in peatlands (Ejarque et al., 2010; López-Merino et al., 2010, 2011; Wieckowska et al., 2012). The former is an endomycorrhizal fungus whose spores may come from soils of the catchment (van Geel et al., 1989) although, as some plants growing in peatlands may be also mycorrized by *Glomus*, they can also be of local origin (Kołaczek et al., 2013), compromising its value as soil erosion indicator in peatlands. *Entorrhiza*, however, has granulometric specificity and it has been related to clay sedimentation (van Geel et al., 1983). In O Bocelo, *Glomus* values just increased at specific samples and often only during the episodes of higher erosion intensity, while *Entorrhiza* percentages only increased during the LIA and in recent times (Paper I: Figure 7). The comparison between trends in the mineral content of the peat inferred by geochemical analysis, *Glomus* and *Entorrhiza* reminds us the risk of just relying on palynological evidence to infer past changes in soil erosion, particularly in peatlands.

At El Payo mire (Central Western Spain; Paper III) the creation of cropland, pastureland and fruit tree plantations evenly promoted soil exposure in the catchment leading to increased dust fluxes to the peatland (Paper III: Figure 7). Three major periods of enhanced soil erosion (SE1: AD ~1660-1800, SE2: AD ~1830-1920, and SE3: AD ~1940-1970) occurred associated with increases in the use of fire to create agriculture and pastureland although, at times, a climatic influence seems probable. For example, during SE1 fluxes of many lithogenic elements peak at the Maunder minimum, but Cerealia-type and coprophilous fungi only increased thereafter. Moreover, by AD ~1460-1580 a first slight increase in the fluxes of most lithogenic elements coincides with the Spörer minimum, without any noticeable shift of local indicators of human interference. Thus, at El Payo, human activity plus atmospheric changes associated to minima in solar activity are behind the detected phases in soil erosion. Although the exact mechanism that connects solar activity and soil erosion has not been yet established, previous research already suggested a link between minima in solar activity during the LIA and increased dust fluxes (de Jong et al., 2007; De Vleeschouwer et al., 2009). In relation to the role of forest in modulating mineral inputs to confined mires, the taxa dominating the arboreal pollen signal at El Payo –i.e., *Betula* and *Alnus*–, are more related with the sourcing of dust than with the total amount of inorganic material reaching the mire. At El Payo, despite there is a negative relationship between forest cover and soil erosion, large decreases in *Betula* and *Alnus* percentages between AD ~1550 and 1650 do not seem to have caused an associated soil erosion event. What does happen is a coeval increase in the Ti/Zr ratio (Paper III: Figure 7). Titanium is enriched in fine soil fractions compared to Zr (Schuetz, 1989; Taboada et al., 2006) so an increase in Ti/Zr ratios indicates that smaller grain size material reached the mire. Changes in wind strength might also explain this pattern (e.g., Martínez Cortizas et al., 2002; Fábregas Valcarce et al., 2003) but, given the large decreases in *Betula* and *Alnus* percentages, the most probable explanation is that the detected changes in tree cover modified the potential source areas of inorganic material (e.g., Kempter and Frenzel, 1999).

While in both mires studied at the temperate zone (O Bocelo and El Payo), both human and climate seem to have had a role in soil erosion, the peatland studied at the boreal zone provides a different picture. At Sandhavn (southern Greenland; Paper II), the geochemical composition of the peat failed to reveal any clear climatic influence of the LIA in the lithogenic element record over the last ~700 years and, phases of increased mineral content of the peat closely matched the known historical record of human occupation. The sampling site at Sandhavn is located adjacent to a homefield (i.e., hay-producing areas) of a Norse farmstead that was in use from AD ~1000-1400 and, although caution is required when interpreting the lowermost peat layers because of the proximity of the mineral (sand) base, increases in lithogenics are detected from the peat accumulation onset (AD ~1300) to AD ~1400. These increases are coeval to higher Poaceae and coprophilous fungi values providing evidence of Norse activity in the area (Golding et al., 2011) and suggest that enhanced mineral inputs to the mire may be due to human impact (Paper II, Figure 8). The finding at Sandhavn is in agreement with other studies performed on the Eastern Settlement of southern Greenland, which also provided convincing evidence for an increase in soil erosion following Norse landnám (e.g., Sandgren and Fredskild, 1991; Fredskild, 1992; Edwards et al., 2008; Massa et al., 2012). As well as the anthropogenic impact on soil erosion during the Norse period, increased Ti concentrations in Greenlandic lake sediments corresponding to the LIA have been detected by Massa et al., (2012). The authors suggested that Norse occupation may have altered the physicochemistry of the catchment soils, or that a change in climate at the onset of the LIA led to enhanced eolian Ti deposition. The core at Sandhavn, in contrast, lacks clear increases in mineral content of the peat during this climatic event. On the contrary, the next soil erosion event is recorded in more recent times, during the early 20th century (AD ~1900-1940), and occurs broadly synchronous with the return of sheep farming to southern Greenland (Jacobsen, 1987; Fredskild, 1988), providing further evidence of the strong link between soil erosion and human activity at this location. Present-day soil erosion events in O Bocelo (Paper I) and in El Payo (Paper III) are synchronous with maximum arboreal pollen values linked to *Pinus* afforestation (Paper I: Figure 7 and Paper III: Figure 5, Figure 7), highlighting that it is not only arboreal presence what is important for the control of soil erosion and that *Pinus* and *Eucalyptus* monoculture is not preventing soil erosion in the catchment as native mesophilous forest once did. Other factors, however, such as the recent construction of small roads nearby the peatlands or the type of harvesting practices applied to the afforested woodlands, also has to be considered as they may also have influenced the soil erosion processes.

From the methodological point of view it is noteworthy that the best aproximations to the soil erosion process in the case of O Bocelo and Sandhavn were based on lithogenics concentrations, whereas in the case of El Payo, as the density of the peat and trends in lithogenics were not correlated, the calculation of accumulation rates offered a better picture of past changes in mineral content of the peat than concentrations considered alone.

4.2. Changes in climate: effects on geochemical and palynological proxies

Although weaker in amplitude than the glacial cycles of the Pleistocene, Holocene climate variations have been of larger amplitude and more frequent than was commonly recognised (Mayewski et al., 2004). For the Late-Holocene in particular, although spatial patterns remain poorly defined, global temperatures are also known to have varied (Mann et al., 2009). For example, the Medieval Climatic Optimum (AD ~900–1300) was a period during which the reconstructed temperatures in Europe and neighbouring regions of the North Atlantic are comparable of those of the late 20th century (Mann, 2002a). The LIA, a cold period following the Medieval Climate Optimum, is though to have impacted Europe during the 16th–mid 19th centuries AD (Mann, 2002b). However, the timing and global character of the

LIA are still a matter of debate (e.g., Mann et al., 1998, 2009; Bertler et al., 2011). Even though much more research is needed regarding regional manifestations of these events and the causal factors behind them, considerable progress has been done over the past decade in using climate "proxy" data to reconstruct large-scale trends in past centuries (Delworth and Mann, 2000). For example, changes in peat accumulation dynamics (e.g., Ovenden, 1990; Tolonen and Turunen, 1996; Yu et al., 2003; Page et al., 2004), in the organic and inorganic composition of the peat (e.g., Létolle, 1980; Blackford and Chambers, 1993; Högber, 1997; Martínez Cortizas et al., 1999; Krull et al., 2004; Kylander et al., 2007; Ise et al., 2008; Charman et al., 2009; Marx et al., 2011) or in NPP archived in peatlands (e.g., Huntley, 1990; Desprat et al., 2003; Barnekow et al., 2007; Bjune et al., 2009) have proved to be sensitive to past climate change. In the present PhD thesis, all of these proxies have been analysed in different types of peatlands and taken together in order to get insights in how past changes in climate affected organic matter decomposition, vegetation change as well as other aspects of the environment.

Peat and carbon accumulation are function of the balance between primary production of living plants and decomposition of organic remains. Although they are dependant of complex and non-linear relationships with temperature and moisture conditions (Yu et al., 2001) and temperature and hydrology can be shaped by local factors (Klein et al., 2013), climate is thought to be one of the main drivers affecting them. Therefore, they are employed as proxies to infer changes in climate (e.g., Charman et al., 2013; Garneau et al., 2014). At El Payo (Central Western Spain; Paper III) and Sandhavn (Greenland; Paper II), peat accumulation and peat carbon accumulation rates (PCAR) were largely affected by cooler conditions during the more rigorous times of the LIA. From AD ~1300-1400 to 1800 –coinciding with an increase in solar activity after the Maunder minimum–, peat accumulation and PCAR values are lower than in following periods (Paper III: Figure 6; Paper II: Figure 9), suggesting a clear climate control on the rate of peat and carbon accumulation at those sites. Thus, despite relatively cooling conditions being necessary for peat accumulation, as they also reduce primary productivity, an excessive cooling may reduce peat and carbon accumulation.

Greenland was settled by Norse people during the relatively warm Middle Ages (Ogilvie et al., 2000; Mikkelsen et al., 2008) but the onset of the LIA meant a change in their lifestyle, likely because of the effect of lower temperatures on hay-crop yields and on their ability to over-winter livestock successfully (Barlow et al., 1997; Panagiotakopulu, 2004; Dugmore et al., 2007), leading to the Norse abandonment of Greenland. The latest documented evidence for Norse activity in the Eastern Settlement is a reference to a marriage at Hvalsey church in AD 1408 (Krogh, 1967; Seaver, 1996), although it is generally accepted that the Norse may have remained in Greenland beyond this date and probably into the mid-

15th century AD (Berglund, 1986; McGhee, 2003). At Sandhavn, Norse abandonment was recorded through reduced frequencies of fungal spores and Poaceae pollen after AD ~1400 (Golding et al., 2011; Paper II: Figure 3). Demographic impacts of the LIA in Europe might have been weaker than those in boreal latitudes. Even so, in the mountainous sector where El Payo is located, Cerealia-type is recorded during the LIA but after the Maunder minimum its values are systematically higher (Paper III: Figure 7), probably due to climatic amelioration.

Warmer/drier climates enhance peat decomposition, increasing the accumulation of recalcitrant moieties and humic acids, whilst under colder/wetter conditions labile fractions are dominant. FTIR spectra (informing about recalcitrant vs. labile fractions) and the degree of peat humification (DPH; informing about humic acid content) can also be used to infer past climate through its relation with the degree of decomposition of organic matter. DPH has been used in peat research for a long time (e.g., Bahnson, 1968; Aaby and Tauber, 1975; Borgmark, 2005). FTIR analysis applied to palaeoenvironmental studies on peatlands is, on the contrary, more novel and restricted to a few examples (e.g., Krull et al., 2004). At El Payo, FTIR humification index (HI-FTIR; higher values mean more recalcitrant moieties) and DPH (UV-Abs; higher values mean more humified peat) become higher at AD ~1760-1930 (Paper III: Figure 6), indicating that warming at late 18th century led not only to an increase in carbon accumulation, as suggested by PCAR, but also to a rise in peat decomposition. Roughly at the same time, although they had already started to rise at AD ~1550, NPP indicative of wetter conditions showed a sharp increase (Paper III: Figure 6). However, NPP indicative of drier mire conditions are also present pointing towards high intra-annual hydrological fluctuations (Paper III: Figure 6). Particularly higher levels of dry indicators occur at AD ~1740-1760 and AD ~1870-1940. According to this data, warming and adequate moisture supply favored the carbon accumulation increase after the 18th century, whereas warming and the existence of intense drought, although only seasonally, may have stimulated peat decomposition and thus recalcitrant moieties accumulation and the formation of humic acids. The chronology of the hydrological changes is coherent with other studies showing wetter conditions with intermittent droughts after the 16th century in Mediterranean Spain (e.g., Barriendos Vallve and Martin-Vide, 1998; Benito et al., 2003a, 2003b; Moreno et al., 2008; Valero-Garcés et al., 2008; López-Sáez et al., 2009; Morellón et al., 2012) as well as with changes in the North Atlantic Oscillation (NAO) reconstructed by Trouet et al. (2009) (Paper III: Figure 6), as the wetter conditions of the LIA occurred synchronously with the weakest NAO –i.e., weak subtropical high and weak Icelandic low.

At Sandhavn, FTIR and UV-Abs (whose variation is summarized by PCo, Paper II) failed to reveal a systematic climate signal over the period of the LIA (Paper II: Figure 9), but instead they might be punctually affected coinciding with Spörer and Maunder minima in solar activity. It is essential to be cautious about this interpretation given the dating and sample resolution constraints, but if correct, decreased peat decomposition and enrichment in polysaccharides (i.e., low degradation of labile organic compounds) might be associated with periods of decreased solar activity.

Bromine concentrations in Sandhavn remained low until AD ~1865 (Paper II: Figure 9), although values begun to increase gradually after AD ~1780, coinciding with the exit of the Maunder minimum. It is possible that at Sandhavn cooling associated with LIA or high water table, at least during milder seasons as indicated by the increase in *Hippuris vulgaris* pollen (Paper II: Figure 9), could have limited the incorporation of Br into peat. Bromine is a halogen of marine origin whose incorporation into peat is a biological oxygen-dependent enzymatic process (Myneni, 2002; Biester et al., 2004; Leri and Myneni, 2012) which, in oceanic areas, is mostly controlled by oxygen availability rather than atmospheric deposition (Martínez-Cortizas et al., 2007). It might be possible that further decreases in Br were associated with minima in solar activity although caution is required because of the resolution constraints. At O Bocelo, the good pre-existing information on dry-wet phases reconstructed by thermal stability of Hg (Martínez Cortizas et al., 1999; Mighall et al., 2006a) allowed the validation of a humidity index (Paper I: Figure 7) constructed based on the residual variance of Br (i.e., the remaining variance after detrending the Br from the effect of halogenation/dehalogenation), which is likely to be related to the source of Br to the peatland, that in this continental location would be wet deposition. Four wetter periods were inferred to occur at O Bocelo area within the last ~3000 years during: the Iron Age (~2800-2500 cal. yr BP), the Roman and Germanic times (~1200-2000 cal. yr BP), the LIA (~800-400 cal. yr BP) and the present (last ~200 yr).

Vegetation change, reconstructed by pollen analysis, can also be used to infer past changes in climate although, as human pressure also plays an important role as a driver of Holocene vegetation change, isolating the climate signal is more complex for intra-Holocene shifts than for the Pleistocene-Holocene transition (e.g., Seddon et al., 2015). At the PRD-IV colluvial soil sequence (North-western Spain; Paper IV), a threshold response at a local level occurred at the Pleistocene/Holocene transition with the dominance of *Pleospora* replaced by Cyperaceae, indicating a shift towards warmer conditions (Paper IV: Figure 10). At a regional level, although with ~1700 years delay, a change from a *Betula* open woodland to a mesophilous oak forest took place. The persistence of the open landscape with *Betula* reflects the resilience of the established Late Pleistocene vegetation to the onset of the Holocene, indicating that caution has to be taken when interpreting biological proxies, as organisms can withstand unfavourable environmental changes depending on their resilience. Contrary to the generally weaker intra-Holocene climatic shifts, intense vegetation changes at the Late Glacial-Holocene transition have been recorded in many pollen records around the world (e.g., Davis, 1961; Muñoz Sobrino et al., 2004; Peyron et al., 2005; Fernández et al., 2007; Tarasov et al., 2009; González-Sampériz et al., 2010; Bamonte and Mancini, 2011). Other times, vegetation can respond to short-term climatic pulses with an elastic clear response, as it is seen at PRD-IV during the 8200 cal. yr BP event (Paper IV: Figure 10), in which both local and regional vegetation suffered a shift at the onset of the cold event but recovered when the event finished. For the Late Holocene, although human impact on the environment is usually strong, it is also possible to detect some changes with a clear climate-driven control. For example, increases in *Olea* and *Castanea* during the Roman Period at O Bocelo (Paper I: Figure 5), although probably mediated through human management, may have also been connected with the prevailing warmer temperatures (Martínez Cortizas et al., 1999) at that time. Similarly, at AD ~1870 at Sandhavn, a major change in vegetation occurred with *Empetrum nigrum* oceanic heath replacing Cyperaceae-dominated steppe communities (Paper II: Figure 3). This change, according to the associated increase in peat accumulation and PCAR, may have occurred linked to generally rising temperatures following the end of the LIA. At the same time, and contrary to what would be expected for an increased temperature favouring peat decomposition, an enrichment in polysaccharides is detected (Paper II: Figure 9). This appears to be strongly related to changes in peat vegetation composition, as *Empetrum nigrum* remains are more resistant to decomposition than the sedge-dominated vegetation that it replaced. This, linked to previous evidence found in other decomposition proxies (e.g., van Smeerdijk, 1989; Kuhry and Vitt, 1996; Caseldine et al., 2000; Yeloff and Mauquoy, 2006; Schellekens et al., 2011), highlights the importance of considering the effect of potential changes in vegetation when interpreting proxies related to organic matter characterisation.

4.3. Atmospheric metal pollution: minero-metallurgy and forest evolution

Lead and other metals are found naturally in the Earth crust. However, their multiple applications resulted in increased anthropogenic fluxes to the atmosphere as well as their availability in the environment. The consciousness about metal dispersion in the atmosphere and the awareness about potential health issues associated to the large increase in metal emissions greatly expanded in the 1960s due to the increase in atmospheric lead pollution levels consequent with the introduction of alkyl lead additives to gasoline. For example, Cannon and Bowles (1962) have demonstrated how fodder and food crops that grew close to much travelled highways in some parts of the United States contained from 4 to 20 times their normal complement of lead and Patterson (1965) alerts about the increase of lead blood levels in United States population. But, when did metal pollution in the atmosphere actually started?

For establishing natural background levels and contextualising today's pollution, a long-term perspective on lead pollution is essential. Before palaeoenvironmental research started to study metal fluxes in the past, it was generally assumed that atmospheric metal pollution began with the Industrial Revolution. However, Lee and Tallis (1973)'s pioneer work on peat records from Britain revealed a small peak in lead at AD ~500, which may represent Roman lead mining activities in the region. In fact, studies by Hong et al. (1994) and Rosman et al. (1997) in Greenland ice cores showed indeed that Greek and Roman lead and silver mining and smelting polluted the middle troposphere of the Northern Hemisphere around two millennia ago. The first evidence of lead pollution from peatlands in Europe, probably indicating the development of local/regional mining or smelting activities, has been dated back to ~5000 years ago in North Spain (Martínez Cortizas et al., 2016) and Wales (Mighall et al., 2009). Evidence of early pollution have been also found at ~4600, ~3400, ~3260 and ~2930 cal. yr BP in other records of Northern Spain (Martínez Cortizas et al., 1997b; Galop et al., 2001; Kylander et al., 2005; Pontevedra-Pombal et al., 2013) or at ~3350 cal. yr BP in Switzerland (Shotyk et al., 1998).

The last objective of this PhD endeavours to delve into the knowledge of the links between past mining and metallurgical activities and atmospheric metal pollution, and to approach the existing knowledge on their consequences on forest evolution. A ~700 years and a ~3600 years old peat cores from southern Greenland (Paper II) and Scotland (Paper V) respectively, were analysed in order to get insights on past changes in atmospheric metal pollution and its possible sources. Moreover, to explore potential links between forest cover and past mining and metallurgy activities the related literature available for Northern Iberia was reviewed (Paper VI).

In contrast to the investigations performed on ice cores, research on lead pollution using peatlands in southern Greenland have up until this point failed to reveal any significant enrichment (e.g., Shotyk et al., 2003; Schofield et al., 2010). Although, Shotyk et al., (2003) suggested that a decrease in the $^{206}Pb/^{207}Pb$ ratio noted in minerotrophic peat from Tasiusaq related to lead pollution originating grom the USA in the 20th century. The lead record from Sandhavn peat (Paper II) revealed a robust pollution record of the past ~1300 years (Paper II: Figure 10). Above baseline Pb enrichment occurred only after AD ~1845. Since then, they show a progressive increase, which is more pronounced after AD ~1940, peaking at the end of the 1970s. After this maximum, values steadily decrease, probably due to a reduction in the use of leaded antiknock agents in gasoline as it has been already pointed in previous investigations (Rosman et al., 1993). The start of lead pollution at Sandhavn (AD ~1845) is in closer agreement with the onset of the American Industrial Revolution rather than with the European one, suggesting a predominant American source of lead. Moreover, the lead pollution chronology is consistent with that found in many records in North America (e.g., Graney et al., 1995; Norton et al., 1997, 2004; Outridge et al., 2002; Gallon et al., 2005; Kylander et al., 2009). However, given the dating uncertainty of sediment/peat records at recent times, caution is needed. Additional evidence supporting dominant American lead sources at Sandhavn is provided by the presence of *Ambrosia*-type (ragweed) pollen after AD ~1885 (Paper II: Figure 3). The plant is not native to Greenland (Böcher et al., 1968) and studies from Eastern-central North America demonstrated a rise in *Ambrosia* pollen in the 19th century linked to the arrival and expansion of European settlers (e.g., Bassett and Terasmae, 1962; Ogden, 1966; Brugam, 1978; McAndrews and Boyko-Diakonow, 1989; Ireland et al., 2014). A European source of *Ambrosia*-type pollen is unlikely given that *Ambrosia* first appeared in Europe after AD ~1920 (Comtois, 1998) and spread after the 1980s (Couturier, 1992; Dechamp and Dechamp, 1992; Thibaudon, 1992). Observations of long-distance pollen transport to southern Greenland similarly indicate that North-eastern American source areas are typical (e.g., Rousseau, 2003; Rousseau et al., 2006; Jessen et al., 2011). Moreover, a recent study (Blockley et al., 2015) have identified tephra shards at three sites in southern Greenland with geochemical signatures compatible with volcanic centre in the Aleuntian Islands and Cascade Range. All of these examples support the hypothesis that the most likely source of *Ambrosia*-type, is North America.

Previous work regarding possible sources of lead in Greenland found evidence both from predominant US and predominant Eurasian/Canadian sources (Rosman et al., 1993, 1994, 1998; Bindler et al., 2001a, 2001b; Michelutti et al., 2009) at different locations/times. It is possible that the relative location/latitude of the different sites accounts for the differences in lead sourcing, and even that may have changed through time. Up to now, indirect evidence from Sandhavn supports predominant North American sources at South-western Greenland, although lead isotopes analyses (in progress) will contribute to ascertain more precisely the sources of lead in the Sandhavn record.

Studies on the geographical variation of atmospheric metal deposition from point-sources (such as smelters) suggest that significant correlations existed between the distance from smelting operations and the concentrations of metals in the peat (e.g., Gignac and Beckett, 1986; Glooschenko et al., 1986; Zoltai, 1988). Thus, despite evidence of long-range pollution arriving to Greenland, for peat records from the more densely populated and polluted areas, local/regional changes in metal emissions to the atmosphere may account for most of the pollution signal recorded in the peat. Until the burning of fossil fuels became one of the main sources of Pb to the atmosphere from the Industrial Revolution onwards, mining and metallurgical activities had been the most important sources of anthropogenic emissions. This has implications for palaeo-reconstruction of mining and metallurgical activities, especially given the fact that, many times, the archaeological record is absent or scarce (Mighall et al., 2006b).

Research performed in a peat record at Leadhills (Toddle Moss, Scotland; Paper V) revealed the history of exploitation of insular ore sources in the Leadhills/Wanlockhead orefield from prehistory (~3600 years ago) to the present. The discovery of a stone hammer at Wanlockhead (Pickin, 2008), despite lacking any contextual evidence, attests for prehistoric mining in the region. It was found by a mine manager and the exact location of its finding is unknown, but typologically it is very similar to the grooved hammerstones found at the prehistoric copper mine at Alderley Edge (Timberlake and Prag, 2005), which are thought to have been used as crushing and pounding implements. Patterns of lead at Toddle Moss might reflect earlier activity during the Bronze and Iron Ages, but further analysis will be required to confirm whether the Leadhills/Wanlockhead orefield was and early source of metals as part of an insular metal mining industry. Three major phases of atmospheric metal pollution were found: 5th-7th centuries AD, 9th-11th centuries AD, and at the later part of the 18th and the late 19th/early 20th centuries (Paper V: Figure 3). These phases are consistent with documented historical and archaeological records of mining and metallurgy in the region (Wilson and Flett, 1921; Pickin, 2008, 2010). The decrease in lead concentrations by AD ~1310-1475 is framed at the time of the Anglo-Scottish war, a period for which there is no documentary accounts of lead mining in Leadhills/Wanlockhead.

Shifts in the isotopic ratios and lead enrichment have been regularly recorded in European peat profiles during the Late Iron and Roman times (e.g., Martínez Cortizas et al., 1997b, 2013; Shotyk et al., 1998; Renberg et al., 2001; De Vleeschouwer et al., 2010), including the British Isles (e.g., Mighall et al., 2002, 2009; Le Roux et al., 2004; Cloy et al., 2005, 2008; Meharg et al., 2012; Küttner et al., 2014). Contrary, at Toddle Moss no evidence for metal pollution was recorded in Roman times, providing evidence for specific regional variations in mining and metallurgy. Although there is a common narrative of historical lead and metal pollution across much of Europe, there are, nevertheless, local pictures showing important differences, which are of particular interest for local historical and archaeological narratives (Martínez Cortizas et al., 2013, 2016). Other examples in which metal enrichment during the Late Iron Age and Roman period is not discernible were also found in central and Southern France (e.g., Labonne et al., 1998; Monna et al., 2004b; Baron et al., 2005), Western Germany and Ireland (e.g., Schettler and Romer, 2006) as well as in South-eastern Germany (e.g., Küster and Rehfuess, 1997).

The development of mining and metallurgical activities involved intense transformations of the landscape from the Iron Age onwards. Besides the large landscape modifications linked to the construction of extraction facilities, and the associated atmospheric metal pollution, mining and smelting also led to a severe affection of forests in many cases. The use of wood for mining operations or as fuel for smelting may have caused intense reductions in forest cover. Although there is plenty of evidence of woodland management to produce firewood or in order to ensure charcoal supply for ore smelting (e.g., McKeown, 1994; Mighall et al., 2000; Szabó et al., 2015), many papers have also reported decreases in arboreal pollen percentages linked to increases in pollution proxies (e.g., Mighall and Chambers, 1993; Monna et al., 2004b; Martínez Cortizas et al., 2005, 2013; Jouffroy-Bapicot et al., 2006; Mighall et al., 2006b, 2013; Pontevedra-Pombal et al., 2013; López-Merino et al., 2014). Paper VI examines the research conducted in Northern Spain in relation to past mining and metallurgy and its possible associated impacts on forest. In North Iberia several studies have reported a reduction in forest cover associated with metallurgy since prehistory (e.g., Galop et al., 2001, 2002; Monna et al., 2004a; Pontevedra-Pombal et al., 2013). Later on, during the Roman period plenty of written, archaeological and palaeoenvironmental evidences show an unprecedented development of mining in Iberia, and of its associated environmental impacts too. To get an idea of the magnitude of this change, it is estimated that 60% of the European lead production came only from North Iberia (Nriagu, 1983). The fall of the Empire, although with different chronologies for East and West North Iberia posed a collapse in mining, which generally resumed, from 6th century AD. Multi-proxy studies combining geochemical and palynological research enabled the evaluation of the influence of minero-metallurgical activities on vegetation. In most cases, and associated to the detection of mining/metallurgy phases, a decrease in mesophilous forest is detected. However, it has to be said that sometimes it is difficult to disentangle the role of mining/metallurgy in forest cover independently of other synchronous human forcings such as agriculture and grazing.

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5. CONCLUSIONS

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The combined application of geochemical and palynological analyses led to more accurate interpretations of environmental changes than those that would be obtained using a single-proxy approach. Essentially, variables obtained by each of these disciplines are proxies of different environmental aspects, i.e., lithogenic elements account for the content of mineral matter in the peat and in confined mires can be used to infer soil erosion at catchment scale, whereas tree pollen indicate how important the forest is in relation to other plant communities. Cerealia-type, nitrophilous taxa, coprophilous fungi or carbonicolous fungi provide indirect evidence of human activities such as agriculture or animal husbandry. Changes in the recalcitrant vs. labile moieties of organic matter, the degree of peat humification, variations of some elements constituting peat or variations in some palynological taxa give indication of prevailing climate conditions at local or hemispherical scales, whereas metal enrichments can be used to trace the development of mining and metallurgy. In a strict sense, duplicity is not common in geochemical vs. palynological proxies. However, because complexity in the functioning of environments is behind interactions among different compartments of ecosystems (i.e., biosphere, lithosphere, hydrosphere and atmosphere), the use of geochemistry and palynology allowed us to obtain an overview of past environmental changes hardly assessable by each of these disciplines independently.

Concentrations of lithogenic elements usually are enough to infer past changes in soil erosion (Papers I and II). However, when the density of the peat and trends in lithogenics are not correlated (Paper III) the calculation of accumulation rates offers a better picture of past changes in mineral content of the peat than concentrations considered alone. This may happen when changes in mineral matter arriving to the peatland are not restricted to its quantity but also to its quality (i.e., changes in the mineral composition).

Phases of increased soil erosion during the Holocene generally agree with known periods of cultural activity, which often are associated with an agriculture and livestock intensification (Papers I, II and III), at times associated with an intensification in the use of fire (Paper II).

Human-induced deforestation for the creation of pastureland and agriculture generally led to exposure of soil cover and a decrease in the water retention capacity of the soils of the catchment which makes the land more susceptible to soil erosion. However, forest cover, besides affecting the intensity of soil erosion, can provoke shifts in the sources of lithogenics arriving to peatlands (Paper II) as well, changing the chemical signal of peat inorganics.

Climate conditions may also have played a role on soil erosion. Wetter periods, specially

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when forest cover is reduced, may enhance the amounts of inorganics reaching confined mires (Paper I) while adverse climate conditions during Spörer and Maunder minima in solar activity may also have enhanced soil erosion at certain locations (Paper II, but no Paper III). Cooler conditions during the LIA (particularly at ~1300-1800 AD) decreased peat and carbon accumulation in locations at both boreal and temperate zones (Papers II and III).

The LIA also affected the organic matter composition of the peat. At El Payo (Paper II), coinciding with higher temperatures after the late 18th century, peat decomposition increased. Seasonal drought may also be behind this pattern. At Sandhavn (Paper III), although the low chronological resolution of the record means that caution needs to be exercised, changes in recalcitrant vs. labile fractions might be related with changes in solar irradiance as small and punctual increases in polysaccharides and decreases in recalcitrant compounds occur associated to Spörer and Maunder minima in solar activity.

Because halogenation is a biological enzymatic process, variations in Br in peatlands are dependent on both Br atmospheric fluxes and the environmental factors affecting halogenation. At O Bocelo (Paper I), a humidity index based on Br matched a previous humidity index based on thermal stability of Hg. At Sandhavn (Paper II) the effect of lower temperatures during the LIA linked to higher water table levels, detected through a *Hippuris vulgaris* pollen increase, may have limited Br incorporation into peat.

Interpreting changes in organic matter functional groups without considering possible changes in vegetation may be dangerous. For example, at Sandhavn, an increase in *Empetrum nigrum* oceanic heath associated with the exit of the LIA caused polysaccharide enrichment.

Despite the above-mentioned *Empetrum nigrum* increase, and other examples mentioned in the text, overall, climate-induced changes in vegetation are much weaker during the Holocene, where human activities play an increasing role, than at the Pleistocene-Holocene transition (Papers I, II, III, IV).

When long enough sequences are considered and the local and the regional vegetation signals distinguished, it is apparent that responses in regional vegetation (i.e., trees, shrubs, herbs) to perturbations may be delayed with respect to those in the local palynological signal (i.e., fern spores, fungi spores, etc.) (Paper IV).

Long- and short-distance sources of metals operate in peat archives at different locations/times. Patterns of lead enrichment at Sandhavn (Paper II) reflect broad-scale patterns in recent atmospheric enrichment, whereas evidence from Leadhills (Paper V) accounted for regional changes in the exploitation of insular ore sources in the Leadhills/Wanlockhead orefield from prehistory to the present. In this sense, the lack of a pollution phase during Roman times at Leadhills is of special relevance as it gives further evidence of regional variations in past metal pollution records.

In the absence of more accurate evidence, and under certain circumstances, palynological data may provide useful information of metal pollution sources. At Sandhavn, although lead isotope analysis in progress will allow verification, the detection of the "*Ambrosia*-rise" provided an indirect evidence of North American sources of lead.

In North Iberia several studies account for forest cover decreases associated to metallurgy since prehistory. Multi-proxy studies combining geochemical and palynological research enabled the evaluation of the influence of minero-metallurgical activities on vegetation. However, sometimes it is difficult to determine the role of mining/metallurgy in forest evolution independently from other human forcings such as agriculture and grazing.

The research presented here provides evidence that the study of the evolution of past environments gives crucial information about the functioning of ecosystems that should be considered when implementing environmental policies.

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6. RECOMMENDATIONS FOR FUTURE RESEARCH

6. RECOMMENDATIONS FOR FUTURE RESEARCH

- Based on the obtained results in this PhD research, it is strongly recommended to continue combining palynological and geochemical evidence in the field of palaeoenvironmental research. Particularly when focusing on past changes in soil erosion, when approaching palaeoclimate history or when reconstructing past mining and metallurgy and their associated environmental impacts.

- To better understand soil erosion at local scales in different environments a multi-proxy palaeoenvironmental research approach combining geochemistry and palynology is required, particularly in confined fens where sources are closer and more easily related with processes happening at a catchment scale.

- FTIR has proved to be a useful tool to infer past changes in climate. Moreover, it is a non destructive, fast and cheap technique. Although up to now it has been sparsely used in palaeoclimate studies on peatlands, it would be desirable to turn it into a reference method.

- Peat records hardly (if) ever show intra-annual resolution. However, evidence from this PhD suggests that the combination of NPP with methods of organic peat geochemistry may inform on seasonal changes in humidity and their consequences for peat organic matter decomposition. As this has important consequences to understand the role of peatlands as carbon sinks, this research line should be further explored.

- As changes in peat-forming vegetation may affect the organic matter signal of the peat, even though pollen analysis may sometimes account for local changes in vegetation, when technically possible, the study of plant macrofossil remains is recommended.

- A considerable progress has been made during the last decades on the reconstruction of past changes in atmospheric metal pollution. But even so, more local studies on palaeo-pollution would be required to construct a global picture on metal pollution and the possible link between past mining/metallurgy and forest history.

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7. ACKNOWLEDGEMENTS

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8. REFERENCES

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Knowing the past evolution of ecosystems at large enough temporal scales is crucial to understand their dynamic and functioning. The research presented here explores how combined geochemistry and palynological approaches on peatlands can help in the understanding of Holocene environmental changes (those happened in the last ~11600 years). Different types of peatlands (ombrotrophic and minerotrophic), environments (temperate and boreal zones) and Holocene chronological intervals (with special attention to the Late-Holocene) have been studied. The focus has been on gaining insights into the trends of the following processes: 1) soil erosion, 2) climate and 3) atmospheric metal pollution.

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