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Climate-driven enrichment of pollutants in peatlands

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Abstract. Peatlands play an important role for global carbon dynamics, acting as a sink or source depending on climate. Such changes imply a series of additional effects because peatlands are also an important reservoir of atmospherically derived pollutants. Using a multiproxy approach (non-pollen-palynomorphs, $\delta^{15}\text{N}$, C/N, Se, Br, I, Hg, Ti), we show a relationship between climate (wetter–drier) and peat decomposition, which affected element concentrations in a Spanish bog during the last 5500 years. Changes in superficial wetness played a critical role in the cycling of elements coupled to carbon dynamics. Dry phases caused increased peat mineralisation, resulting in a 2–3 times increase in concentrations of the analysed elements independent from atmospheric fluxes. Under the present trend of climate change large areas of northern peatlands are expected to be severely affected; in this context our findings indicate that the increase in carbon release, which leads to an enrichment of elements, may enhance the export of stored contaminants (Hg, organohalogenes) to the aquatic systems or to the atmosphere.

1 Introduction

Peatlands cover about 5–8% of the earth's continental surface and contain one third of the total soil carbon stock (IPCC, 2000), playing an important role in the carbon cycle. Depending on climatic conditions they may act as sinks or sources of carbon and other elements. A strong connection between climate and the global carbon cycle at the millennial scale was found to be mediated in part by carbon dynamics in peatlands, with carbon sequestration rates being highly sensitive even to minor climatic fluctuations (Yu et al., 2003). It has been estimated that at present the sink component is dominant, but recent modelling studies for boreal areas sug-

gest that about 60% of all peatland area in Canada and a similar proportion in North Eurasia will be severely to extremely severely affected by climate change (Gorham, 1991; Tarnocai and Stolbovoy, 2006), leading to a higher release of carbon dioxide and methane to the atmosphere.

Although the predicted increase in temperature may enhance peat decomposition, the changes in hydrology coupled to changes in precipitation patterns and permafrost thawing are expected to have the highest impact (Tarnocai and Stolbovoy, 2006). In peatlands organic matter turnover is highest in the upper aerated layers, where as much as 80% of the initial plant remains are mineralised and released as CO_2 or dissolved organic matter (DOM) (Worrall et al., 2001; Reynolds and Fenner, 2001; Freeman et al., 2004). In the lower sections the decay rate decreases by two or three orders of magnitude due to the anoxic conditions and usually low pH, as well as by the inhibitory effect of the accumulation of some chemical substances like phenols (Kalviäinen and Karunen, 1984; Freeman et al., 2001). Although a slight release of carbon continues, the peat in the anoxic layers suffers only minor further degradation.

The cycle of biophyle elements (C, N, P and S) in peatlands has been the target of many studies (Ohlson, 1987; Ohlson and Økland, 2002), but not much is known about the cycling of other elements, particularly those of environmental concern such as toxic heavy metals like mercury. Elements are incorporated into peatlands by wet and dry atmospheric deposition (the dominant pathway in ombrotrophic mires, by definition), as well as by groundwater and surface runoff (in minerogenic mires). Once incorporated as solutes or particles, elements can be retained through plant uptake, physical entrainment, complexation by humified organic matter, or through enzymatic microbial mediated formation of organic species. Some elements can also be re-released to the atmosphere through evasion or to the hydrosphere in solution or coupled to DOM release. But the impact of present climate change on the accumulation/release

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of elements from peatlands to the atmosphere and aquatic ecosystems is still largely uncertain.

Heavy metals, particularly Pb and Hg, have been extensively investigated in peat cores to reconstruct long-term variations of their fluxes to the mires and thus to trace atmospheric pollution (Lee and Tallis, 1973; Shotyk, 1998; Martínez Cortizas et al., 2002). These investigations have rarely considered the role played by climate in the control of the deposition fluxes or the modification of element concentrations induced by changes in peat degradation (Biester et al., 2003, 2004, 2007).

In this study we compare climate variations since the middle Holocene (~5500 yrs) observed in a Spanish peatland with records of organically bound (e.g., Se, Br, I, Hg) and lithogenic (Ti) elements. We aim to show that the geochemistry of peat is strongly related to climatically controlled carbon dynamics and that the geochemical record in peat was sensitive to Holocene climate changes. Our findings for past climatic changes, contextualized with present scenarios of climate change, may enable a better understanding of the role peatlands play in the global biogeochemical cycles of elements (nutrients and pollutants).

2 Material and methods

We investigated a peat core from Pena da Cadela (PDC), an oceanic ombrotrophic mire located on a mountain summit at 970 m of altitude in the Xistral Mountains (NW Spain), for historical records of trace elements (mercury, bromine, iodine, selenium, and titanium) and peat decomposition (C and N concentrations, C/N ratios and $\delta^{15}\text{N}$). The core is 185 cm deep and has accumulated during the last 5500 cal. years BP. Sampling of the core, sample preparation as well as the records of some elements, such as Pb, are discussed elsewhere (Martínez Cortizas et al., 2002). The ombrotrophic nature of the bog is supported by 1) its location on a blanket mire complex; 2) the smooth microtopography, with hummocks of less than 10 cm in height; 3) low bulk densities (average $0.11 \pm 0.02 \text{ g cm}^{-3}$) and low ash content (average $2.8 \pm 1.4\%$); 4) acidic to strongly acidic peats (pH in water 3.5–4.3, pH in CaCl_2 3.0–3.2); 5) Ca/Mg molar ratios similar to lower than those of the local rainfall water; and 6) very low concentrations of lithogenic elements (Ti average concentration is $172 \pm 59 \mu\text{g g}^{-1}$) (Martínez Cortizas et al., 2002, 2005; Pontevedra Pombal et al., 2006). Present-day vegetation is dominated by sedges (*Carex durieui*, *C. vulgaris*, *C. panicea*, *Eleocharis multicaulis*) and grasses (*Agrostis curtisii*, *A. hesperica*, *Molinia caerulea*, *Deschampsia flexuosa*, *Eriophorum angustifolium*), with presence of some heathers (*Erica mackaiana* and *E. cinerea*) (Fraga Vila, 2001; Fraga et al., 2005; Romero et al., 2005).

Bromine, selenium and titanium were measured using an energy dispersive miniprobe multielement XRF analyzer – its application to peat measurements is discussed in

Cheburkin and Shotyk (1998). Mercury was determined in freeze-dried samples by means of solid-phase thermal combustion atomic absorption spectrometry (LECO-Altec AMA-254); while iodine was determined following the procedure described by Biester et al. (2004). Carbon and nitrogen were analysed by means of a LECO-10000 CNH. $\delta^{15}\text{N}$ was obtained by mass spectrometry.

3 Results and discussion

3.1 A link to climate change

In a study of three bogs from NW Spain Mighall et al. (2006) identified humidity changes (wet and dry phases) in the last 5500 years by correlating biological and geochemical proxies. They found that variations of non-pollen palynomorphs (NPPs T18 and T306) detected in two bogs (Borralleiras – BLL-, and Pena da Cadela -PDC) were related to precipitation variations, based on the ecology of the proxies. A geochemical proxy, based on the proportion of Hg of intermediate thermal stability that was previously related to a humidity component in a third bog (Penido Vello, PVO; Martínez Cortizas et al., 1999), was also synchronous with the variations of the biological proxies. Although changes in peatland surface wetness are not necessarily indicative of changes in climate but to water table-depth (which may be affected by other factors than climate alone, i.e. peat growth), Mighall et al. (2006) attributed the variations in NPPs to precipitation changes because the location of the bogs (in mountain tops) enabled only for atmospheric deposition (wet and dry) and since the three separate bogs responded synchronously they had to be subjected to the same external forcing.

Figure 1a shows the records of the non-pollen palynomorphs (NPPs) T18 and T306, and $\delta^{15}\text{N}$ and C/N ratios in a core sampled at PDC, the bog located at higher altitude (970 m a.s.l.) and which seems to have been the most sensitive in recording the changes in rainfall of those sites previously studied. The NPPs show intense changes during the last 5500 years, which indicate alternating wet (high T18 and low T306 abundances) and dry (low T18 and high T306 abundances) climate periods. There are five main wet phases in this peat record at 150–160 cm, 130–138 cm, 114–126 cm, 84–100 cm and 32–64 cm, which correspond to ca. 3950–3590, ca. 3090–2790, ca. 2580–2260, ca. 1760–1430 and ca. 1030–530 yr cal BP, respectively. The duration of each of these wet phases was about 300–360 years except for the most recent one that may have lasted 500 years. The wet and dry phases are coeval with increased fluvial activity in Spain (Gutiérrez-Elorza and Peña-Monné, 1998; Thorndyraft and Benito, 2006), but opposite to those found for central and western Europe based on lake-level reconstructions (Magny, 1999, 2004; Arnaud, et al., 2005; Holzhauser et al., 2005) or plant macrofossil remains in peat records (Hughes et al., 2000). This supports the hypothesis proposed by

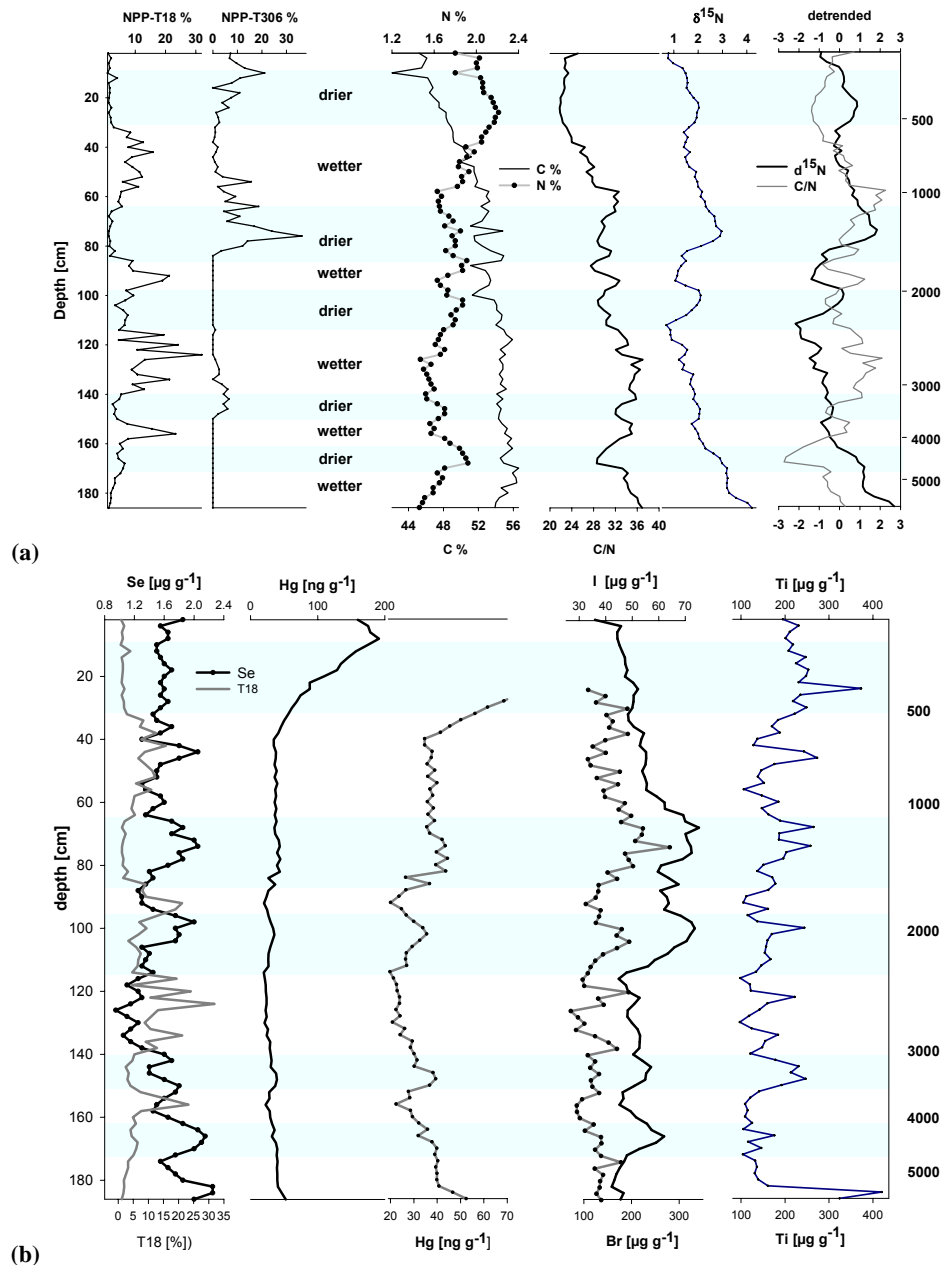


Fig. 1. (a) Records of NPPs T18 and T306 (after Mighall et al., 2006), and $\delta^{15}\text{N}$ and C/N ratios in the PDC core. The detrended C/N ratios were calculated by subtracting the C/N ratio of individual peat slices to the long-term trend modelled by a linear regression equation and are expressed as standardized residuals. (b) Concentrations records of organically-bound (Br, I, Se and Hg) and lithogenic (Ti) elements in the PDC core (all in $\mu\text{g g}^{-1}$ except for Hg in ng g^{-1}). The bottom axis of the mercury record was cut in 70 ng g^{-1} so the variations in the deeper sections of the core are observable.

Magny et al. (2003) that Holocene cooling in the North Atlantic Ocean coincided with drier conditions in southern (and northern) Europe.

In order to extract information on climatic effects on peat decomposition it is necessary to remove the secondary changes imposed by the gradual, long-term diagenetic effects

that occur in the buried peat. For example, there is a general increase in the C/N ratio from around 20 in the surface peat to 37 at the base of the PDC core that is caused by the preferential mineralization of N relative to C during organic matter diagenesis, which has been shown in other ombrotrophic bogs from the same area (Pontevedra Pombal, 2004) and

documented in other studies for a number of sedimentary environments including ombrotrophic bogs (Herczeg, 1988; Updegraff et al., 1995; Khury and De Vitt, 1996). In Figure 1a we have detrended both the C/N ratio and $\delta^{15}\text{N}$ records and expressed them as standardized residuals ($\delta^{15}\text{N}_{\text{detrend}}$ and $\text{C/N}_{\text{detrend}}$, respectively). $\delta^{15}\text{N}_{\text{detrend}}$ and $\text{C/N}_{\text{detrend}}$ have a generally inverse behaviour with higher $\delta^{15}\text{N}_{\text{detrend}}$ values corresponding to relatively lower $\text{C/N}_{\text{detrend}}$. Low $\text{C/N}_{\text{detrend}}$ values are indicative of more decomposed and humified peat, while higher $\delta^{15}\text{N}$ values are indicative of higher N fractionation. The decomposition of the organic matter preferentially mineralizes ^{14}N , causing an enrichment in ^{15}N and thus in $\delta^{15}\text{N}$ (Létolle, 1980; Macko et al., 1993).

The variations in $\delta^{15}\text{N}_{\text{detrend}}$ and $\text{C/N}_{\text{detrend}}$ coincide with the changes in climate (wetter-drier) as indicated by the biological climate proxies (NPPs). Wetter phases are characterized by positive $\text{C/N}_{\text{detrend}}$ values and low $\delta^{15}\text{N}_{\text{detrend}}$ values, whereas drier phases show the opposite – the decline in C/N ratios and increase in N fractionation are indicative of peat decomposition/mineralisation. In fact, the degree of humification of the peat was found to be a proxy for wet/dry cycles (Blackford and Chambers, 1993; Caseldine et al., 2000; Roos-Barraclough et al., 2004). Under saturated conditions oxygen availability in the peat is reduced, which inhibits the phenoloxidase enzyme activity controlling phenol accumulation (Freeman et al., 2001). Increased phenol accumulation under saturated conditions restricts the biological degradation of the organic matter; specifically, the elevated phenol concentrations restrain the activity of hydrolitic enzymes responsible for peat decomposition. In contrast, during dry periods when the water table is lower and formerly saturated peat levels are aerated, enzyme activity increases and promotes peat degradation. In ombrotrophic mires oxygen availability is connected to water table depth, which in turn depends on effective precipitation and thus on changes to wetter or cooler climates (Aaby, 1976; Barber, 1981; Chambers and Charman, 2004; Mauquoy et al., 2002).

3.2 Variations in element concentrations

The concentration records of the organically bound (Br, I, Se and Hg) and lithogenic (Ti) elements are quite similar (Fig. 1b), with the only exception of Hg in the upper peat sections. The concentrations of bromine, selenium and titanium in the PDC core vary by 2.5–3 times (Br: 120–350 $\mu\text{g g}^{-1}$; Se: 0.9–2.2 $\mu\text{g g}^{-1}$; Ti: 100–250 $\mu\text{g g}^{-1}$), while mercury and iodine concentrations vary by 12–17 times (Hg: 19–230 ng g^{-1} ; I: 3–50 $\mu\text{g g}^{-1}$). Below 36 cm the variation in mercury concentration is only 3.5-fold, which is comparable to those of bromine and selenium, suggesting that mercury must be influenced by anthropogenic emissions in the upper section of the peat core as found in other peat records in the area (Martínez Cortizas et al., 1999). Notwithstanding this exception, the records of the analyzed elements show a remarkable similarity. The ocean is the main source of atmo-

spheric selenium, bromine and iodine (Kabata-Pendias and Pendias, 1992; Görres and Frenzel, 1993), which are mostly incorporated into the bog through wet deposition. For example, concentrations of bromine in peat and pore waters have been used to trace differences in sea spray inputs (Shotyk, 1997), thus assuming a direct relationship with atmospheric fluxes – mainly wet deposition. Mercury deposition is also dominated by the wet component, and the oceans contribute to mercury emissions to the atmosphere, although there is an additional strong terrestrial source (weathering and degassing of the Earth's crust) (Schroeder and Munthe, 1998; Scholtz et al., 2003). Hg^0 , the predominant form in the atmosphere, has a mean residence time of about one year and it is subject to long-range transport (Mason et al., 1994; Nriagu and Pacyna, 1988; Schroeder and Munthe, 1998; Scholtz et al., 2003).

The similarity between the records of the organically-bound elements suggests a common source or deposition mechanism. However, titanium, a conservative lithogenic element whose source is atmospheric dust deposition, also shows remarkably synchronous changes in concentration. Because the deposition of atmospheric aerosols increases in dry periods and decreases during wet periods (Mouline et al., 1997; Prospero and Lamb, 2003), the simultaneous increase in the concentration of organically bound and lithogenic elements is counterintuitive and has to be influenced by another factor than atmospheric deposition alone.

The comparison of the concentration records of selenium, bromine, iodine, mercury and titanium (Fig. 1b) with the climatic reconstruction reveals that, in the PDC core, elevated concentrations of these elements are found in sections corresponding to drier climate periods with greater humification (more positive $\delta^{15}\text{N}_{\text{detrend}}$ values and lower $\text{C/N}_{\text{detrend}}$ values), whereas lower concentrations correspond to wetter periods with less-degraded peat (low $\delta^{15}\text{N}$ values and high C/N ratios). The elevated element concentrations are not the result of increased wet deposition, but instead indicate a relationship between the degree of peat transformation, i.e., decomposition, and the variations in the concentration of the elements. We do find a strong correlation between carbon accumulation and the accumulation of organically bound elements. The correlations between the net accumulation of carbon and selenium, bromine, iodine and mercury (excluding the top 30 cm impacted by pollution) are highly significant ($r^2=0.9$; data not shown). For the organically bound elements this is a consistent result, because selenium, bromine, iodine and mercury all have a high affinity for binding to organic matter and are therefore usually enriched in organic-rich soils (Kabata-Pendias and Pendias, 1992; Görres et al., 1993; Biester et al., 2003). Selenium and mercury can form complexes with organic matter by abiotic mechanisms (Zhang and Moore, 1996; Xia et al., 1999), particularly when specific functional groups are available (e.g. S-groups for Hg). Bromine and iodine are retained in organic matter through formation of organohalogen by

oxygen-dependent enzymatic processes involving haloperoxidases (Gribble, 2003; Keppler and Biester, 2003) and are enriched during the decomposition of the organic matter (Myneni, 2002; van Pée and Unversucht, 2003). Some authors have suggested that halogens in peat are fixed by organic matter, and recent studies have demonstrated that they exist mostly as halogenated organic compounds (Biester et al., 2004).

The coincidence of increased peat decomposition and higher titanium concentrations may also be indicative of wet/dry cycles, but for completely different reasons. Higher peat decomposition is typical of dry periods during which enhanced soil erosion and dust deposition on the bog surface are likely, which would result in higher titanium concentrations. However, a residual enrichment of titanium could also result from the degradation of the organic matter, i.e., a loss of substrate.

We suggest that changes in climate, here expressed as variations in wetness or dryness, exerted a fundamental control on the evolution of the decomposition of the peat at the surface of the bog and consequently on the concentrations of many elements. The lowering of the water table during dry periods increased the oxygenation of the superficial peat layer and triggered/enhanced microbial decomposition. This not only resulted in an increase in mineralisation but also in humification, enhancing the potential for metal and halogen retention (Meili, 1991; Mierle and Ingram, 1991; Yin et al., 1996). Thus, the increase in decomposition and humification and the enrichment of metals and halogens are concurrent processes.

Contrary to what is commonly assumed changes in concentrations, at least for organically bound elements, seem to depend to a larger extent on internal transformations of the peat matrix and related mass loss, and not on variations of atmospheric fluxes alone as some have suggested (Shotyk, 1997). This result is also consistent to that found at greater spatial scales for soil organic horizons and supports the hypothesis that the enrichment of organically bound elements is also biologically mediated and climate dependent and would change with factors such as temperature and rainfall (Reimann and de Caritat, 2005). Other factors such as plant cover and composition, and bog microtopography have been reported to affect the accumulation of elements in peat (Olfield et al., 1979; Norton et al., 1997), although we think these factors didn't played a significant role in the PDC bog.

4 Conclusions

Here, we have shown that there has been a clear relationship between climate (wetter-drier) and peat decomposition and its effect on element concentrations in a Spanish bog during the last 5,500 years. Our findings have important implications for present day wetland environments. Projected changes in climate, particularly in areas of increased summer

dryness, will increase rates of peat decomposition and thus loss of carbon as both CO₂ and DOC. During subsequent wetter periods dissolved organic matter, which is enriched in pollutants, may be exported to surface waters. An increased export of dissolved organic matter related to droughts has in fact already been observed in some rivers draining peatlands (Worrall and Burt, 2007). The relationship between the release of DOC and that of organically bound elements from peat has been shown to occur for iodine and bromine (Biester et al., 2006). The surface layers of many bogs are artificially enriched in many metals, such as mercury, because of historical pollutant deposition and increased decomposition will magnify these already elevated concentrations. We speculate that Hg, due to its affinity to bind to organic complexes might be increasingly released from peatlands as Hg-DOC complexes. The changes we report here are from a mid-latitude bog, but the changes in carbon loss are expected to be much greater in the vast peatlands found at higher latitudes, particularly in permafrost areas that are or will be affected by severe thawing. Current climate research is focused largely on carbon dynamics, but these changes imply a series of additional effects. For example, a release of contaminants presently stored in high-latitude peatlands would exacerbate the current concern for high-latitude pollution.

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