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RE-THINKING THE RECORD: ACCUMULATION OF RADIOMETRIC TRACERS AND OTHER ATMOSPHERICALLY SUPPLIED ELEMENTS IN PEATLANDS.

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SUMMARY

The past decade has seen a rapid increase in interest in the biogeochemical record preserved in peat, particularly as it relates to carbon dynamics and environmental changes. However, we still lack a complete understanding of the basic biogeochemical processes and their effect on trace element distributions. Are peat archives an absolute or relative record and what temporal resolution is realistic to interpret by using peat cores? By analyzing radiometric isotopes along with a range of major, minor and trace elements in surface peat cores from a raised bog, we address the question of representativity of single cores and the reliability of dating decadal scale changes within them.

KEYWORDS; Peat, Geochemistry, Beryllium, Lead, Mercury

INTRODUCTION

Because ombrotrophic bogs are strongly coupled with the atmospheric supply of many elements, the peat record from such bogs can be a valuable archive for studying past deposition of, e.g., soil dust as an indicator of past climate conditions and trace metals as indicators of pollution trends. Given their importance as a carbon sink, peat records are also valuable for establishing changes in net carbon accumulation over time in response to past and especially recent climate changes.

Although research was done in the 1970-80's on some of the basic biogeochemical processes and their effect on trace element distributions (Damman 1978), little emphasis has been placed in recent years on improving our understanding of important factors that influence the net retention of atmospherically supplied elements, and questions remain regarding whether this archive is an absolute or relative record and what temporal resolution is realistic to interpret in the archive. A number of studies over the past several years have shown that small-scale spatial variations can occur in the accumulation of trace elements in ombrotrophic peat records. Accumulation rates and cumulative inventories can vary by 2–4-fold over short distances (Bindler et al., 2004; Coggins et al., 2006; Olid et al., 2008). Some studies have also noted issues with variability and smearing of ^{210}Pb (Urban et al., 1990; Oldfield et al., 1995), which introduces some problems for dating the recent record (Lamborg et al., 2002). In this study our objective was to address both of these issues – representativity of single cores and reliability of dating decadal scale changes. To do so we analyzed atmospherically deposited

^{7}Be, ^{241}Am, ^{137}Cs and ^{210}Pb, as well as C, N and a range of major, minor and trace elements in triplicate peat cores from one raised bog. These 75-cm-long hummock cores span the last ca. 500 years. The specific questions we address are: i) How variable is the geochemistry of these cores? ii) Does down-washing of atmospherically supplied elements occur, and if so, how far into the peat does this occur and how does this influence our quantitative estimates of accumulation rates of soil dust, pollutants and even C?

MATERIALS & METHODS

Store Mosse (Fig. 1) is a ~8000 ha bog complex on the South Småland Archaean plain in the boreal-nemoral zone of south-central Sweden (57° 15´ N, 13° 55´ E; 160-170 m a.s.l.). The glacial deposits in the area consist of moraine and fluvial sediments with some occurrences of postglacial sand dunes. Peat formation started about 7000 BP (Svensson, 1988a) when the lake/fen transitioned to a bog. Extensive studies on the development of Store Mosse have been previously published (Malmer and Wallen, 1999; Svensson 1988).

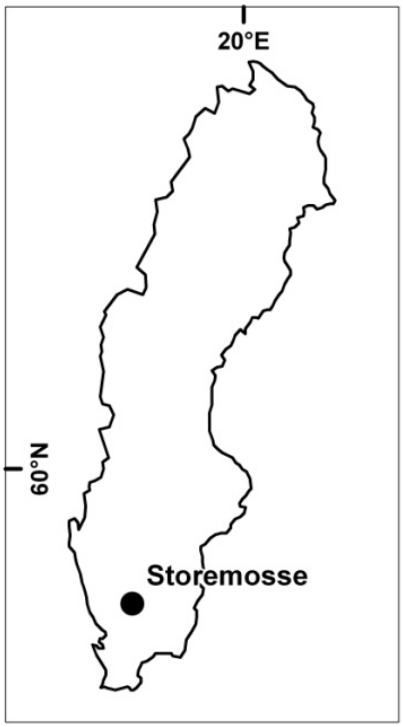

Figure 1. Location of Store mosse in South Central Sweden.

Surface peat cores (~75 cm in length, SM1 SM2 and SM3) from closely spaced (~20 m x 20 m area) hummocks were collected in 2008 using a Wardenaar corer (Wardenaar, 1987). The cores were wrapped in plastic film, then aluminum foil and taken back to the laboratory intact and stored frozen at -18 °C until processing.

In a freezer room (-18 °C) the outermost 1 cm of the cores were removed, the surfaces hand-planed into even dimensions, and the cores were then cut into 2-cm-thick slices on a band saw with a stainless steel blade. The samples were dried to constant weight at 30 ^{o}C, after which their dry masses were recorded and bulk density calculated. All samples were then ground in an agate ball mill before further analysis.

The radionuclide, ^{210}Pb, ^{137}Cs, ^{241}Am and ^{7}Be was measured using high-purity intrinsic Ge detectors (Canberra Broad Energy) with ultra-low background hardware and copper-lined lead shields. More detailed description on the radiometric measurements can be found in Kaste et al (2011) and references therein. We specifically included ^{7}Be in our analyses because it is a short-lived atmospherically supplied tracer (half-life = 53.3 d), which can be used to determine how deep into the peat recent deposition can penetrate. The data are reported in activity per area (Bq m^{-2}). The radiometric analyses extended to 36 cm depth in all cores.

Major and trace element geochemistry was measured using a Bruker S8 Tiger wavelength-dispersive X-Ray Fluorescence (WD-XRF) analyzer equipped with a Rh anticathode X-ray tube. A specific calibration was developed in order to optimize the WD-XRF for the matrices of the samples (modified from De Vleeschouwer et al., 2011). The elements included are: P, S, Si, Al, Fe, Ti, Mg, Ca, K, Na, Sr, Rb, Ba, Mn, Ni, Cu, Zn, Pb, Cl and Br. The detection limits for trace elements were in the range of 1-7 ppm; accuracy was within ±9% for all elements except for Pb (14%), P (20%), S (25%) and Br (27%).

Total mercury was analyzed with a thermal decomposition atomic absorption spectrometer (Perkin-Elmer SMS 100). Analytical quality for Hg was controlled using additional certified reference materials (CRMs) and replicates, which were included with every five samples (NCS73309 and MESS-3). All CRMs were within certified ranges and the relative deviation of replicates was within ±0.5%.

RESULTS

Total inventories in three cores of atmospherically supplied ^{210}Pb range from 4430 to 6370 Bq m^{-2} in the order SM1>SM2>SM3. Activities in the deepest measured slice (34-36 cm) in the cores range from only 3 to 18 Bq kg^{-1}, and represent <0.6% of the total inventory and thus the 34-cm depth interval analyzed captures essentially the complete 150-year inventory. ^{137}Cs inventories vary from 860 to 1700 Bq m^{-2}, but not in the same order amongst cores (SM3>SM2>SM1). Using the depth equivalent to 95±1% of the total inventory of ^{210}Pb activity as a common level among cores (Malmer and Wallen, 1999), the inventories of atmospherically supplied metals such as Pb and Hg vary by 12% and 43%, respectively (SM1>SM3≥SM2). Ti, a soil dust proxy, also varies by 50% and in the same order amongst cores as for Pb and Hg. Importantly, these apparent differences in the accumulation of ^{210}Pb, Pb, Hg and Ti follow the same trend among the cores as the overall trend for total mass accumulation (SM1>SM3≥SM2). Activities of ^{7}Be (Fig. 3) were detected to 20, 18 and 8 cm depth in the three cores (SM1>SM2>SM3); total inventories in the cores followed the same pattern. Given the short half-life of ^{7}Be, this indicates that down-washing to these depths occured over the previous approximately half year. Based on CRS modeling of the ^{210}Pb activities, these depths for the deepest measurable ^{7}Be correspond to peat dating to ca. 2004 for SM3, but ca. 1980 for both SM1 and SM2.

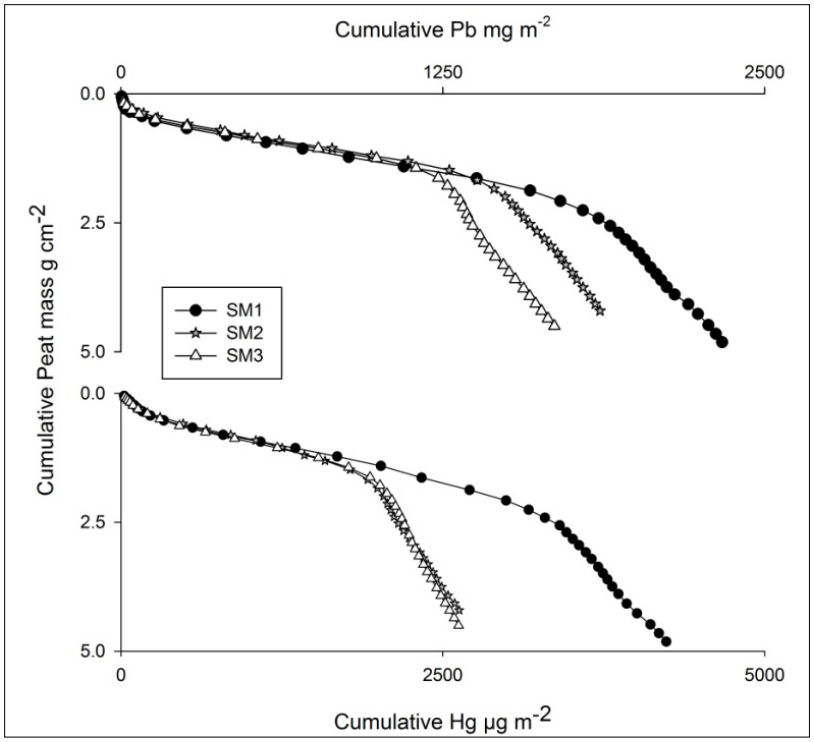

Figure 2. Top: Cumulative Pb inventories (mg m^{-2}) with depth (cumulative peat mass g cm^{-2}) in SM1, SM2 and SM3. Bottom: Cumulative Hg inventories (µg m^{-2}) with depth in SM1, SM2 and SM3.

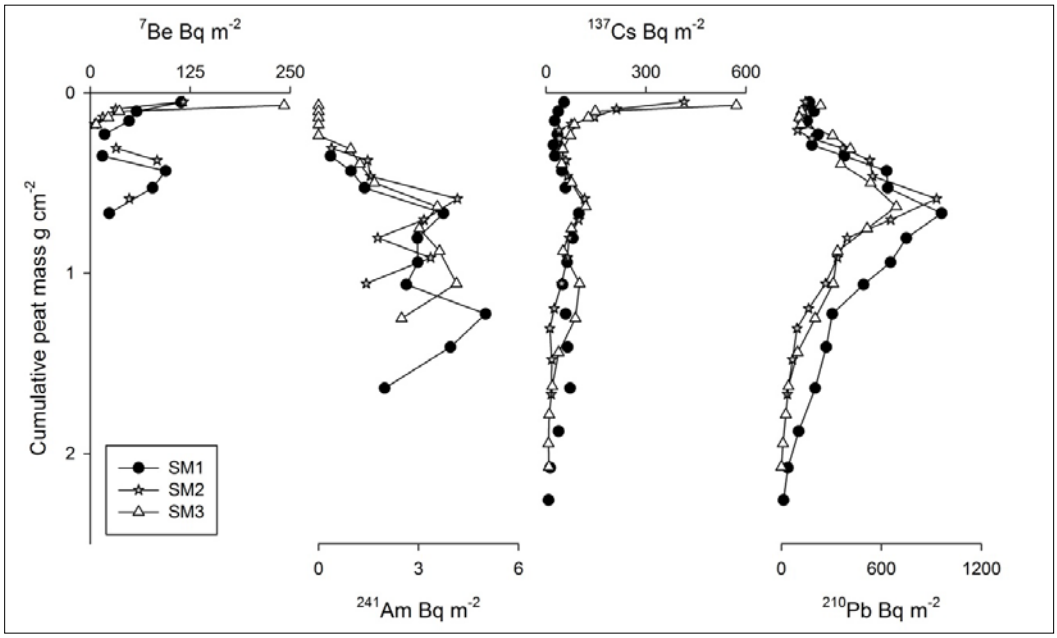

Figure 3. From Left to right: Activities of ^{7}Be (Bq m^{-2}), ^{241}Am (Bq m^{-2}), ^{137}Cs (Bq m^{-2}) and ^{210}Pb (Bq m^{-2}) with depth (cumulative peat mass g cm^{-2}) in SM1, SM2 and SM3.

Although the inventories of different elements varies amongst the three cores, the general pattern with depth for each element is consistent among cores. This indicates that they are recording the same relative changes over time.

DISCUSSION

Atmospheric radioactive fallout from both natural and anthropogenic sources are often used to date surficial peat deposits and are very useful tools when dating recent records on short timescales 1-100 years (Appleby, 2008; Kaste et al., 2011). Here we used ^{210}Pb, ^{137}Cs, ^{241}Am and ^{7}Be in order to chart the accumulation and potential mobilization of trace elements, e.g. Pb and Hg, in a peat bog in south-central Sweden. Two important patterns appear from the analyses. First SM1 shows the highest accumulation of ^{210}Pb, ^{241}Am ^{7}Be, Hg, Pb and also Ti with the overall trend in the order SM1>SM3≈SM2. For example ^{210}Pb and ^{241}Am inventories, respectively, are 6370/26 Bq m^{-2} in SM1, 5220/17 in SM2 and 4430/18 in SM3. Using the depth equivalent of 95±1% of the total ^{210}Pb inventory (ca. AD 1915) as a comparative level among cores, peat mass accumulation also follows this same general pattern. This indicates that the spatial variability for the accumulation of atmospherically supplied elements on the bog surface, which has been shown in several recent studies of trace metals and ^{210}Pb (Bindler et al., 2004; Coggins et al., 2006; Olid et al., 2008), is in part reinforced by peat accumulation rates themselves (Oldfield et al., 1995).

The second important result is that activities of ^{7}Be (Fig. 3) were detected to 20, 18 and 8 cm depth in the three cores (SM1>SM2>SM3). This supports our hypothesis that down-washing of recently supplied elements does occur. The depth to which ^{7}Be can be detected is related to the depth of the water table, where smearing of ^{241}Am also occurs. ^{241}Am can be measured in peat layers dated by ^{210}Pb CRS modeling to 1900-1940, well prior to bomb testing. Only ^{137}Cs differs from the general accumulation pattern with inventories in the order SM3>SM2>SM1, which is likely connected to its greater mobility. More critically for research focused on C and metal accumulation rates, the short-term, downward mobility of ^{7}Be raises a number of questions for estimating accumulation rates for the past 150 years. Whether this down-washing of ^{7}Be is an important analogue for the short-term mobility of ^{210}Pb, Pb or Hg remains to be established. In well-aerated hummocks such as those found on Store Mosse, mobility of atmospherically supplied elements clearly occurs, but we speculate that in more compact peat mobility should be less important.

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