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Beryllium-7 as a natural tracer for short-term downwash in peat

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Abstract Several factors can affect the integrity of natural archives such as peat records, e.g., decomposition and nutrient cycling, and it has also been hypothesized that some rapid downward transport of atmospherically derived elements may occur. We test this hypothesis by analyzing the short-lived, natural tracer beryllium-7 ($t½ = 53.4$ days) in five cores from two peatlands. In triplicate hummock cores from a raised bog in southern Sweden, ^{7}Be could be measured to 20, 18 and 8 cm depth, and in a nutrient-poor mire in northern Sweden to a depth of 16 cm in a Sphagnum lawn core, but only 4 cm in the dominant, more-decomposed fen peat, indicating some spatial variability both within and between sites. Total ^{7}Be inventories were 320–450 Bq m^{-2} in the bog, and 150 Bq m^{-2} (lawn) and 240 Bq m^{-2} (fen peat) in the mire. 25–79 % of the total inventory of ^{7}Be was located in the upper 2-cm layer. To further test downwashing, in the laboratory we applied a CuBr-solution to two cores and a Cu-solution to one core taken from the mire Sphagnum lawn, all with low water table conditions. About 50 % of the added Cu and ~35 % of the added Br were retained in the surface (2 cm) layer; 1–3 % of the Cu was found at 8–12 cm depth and ~1 % of the Br was measured in the lowest level (20–22 cm). Based on our novel approach using ^{7}Be and experimental work we show that short-term downwashing can occur in peatlands and we suggest the depth of this will depend on the properties of the peat, e.g., bulk density and decomposition, as well as hydrology.

Keywords Beryllium · Downwash · Geochemistry · Peat

Introduction

Because ombrotrophic bogs are strongly coupled with the atmospheric supply of many elements, peat records from such bogs are considered particularly useful as a biogeochemical archive for studying atmospheric deposition of soil dust (Shotyk et al. 2002; Kylander et al. 2013) and pollutant trace metals (Shotyk 1998; Martinez-Cortizas et al. 1999), as well as studying climate change (Chambers et al. 2007; Martinez Cortizas et al. 2012). Given the importance of peatlands as a carbon sink, peat records are valuable for establishing changes in net carbon accumulation over time in response to past

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and especially recent climate changes (Gorham 1991; Fenner et al. 2007; Malmer et al. 2011).

Over longer timescales (decades to millennia) there is a temporal coherence among peat records and between peat and other archives, such as for lead deposition (Weiss et al. 1999; Renberg et al. 2001), which supports the utility of peat records for studying long-term environmental changes. However, a number of studies have identified several factors that can affect the quantitative estimates of past deposition rates based on peat records. These factors include decomposition (Biester et al. 2012), nutrient cycling (Malmer 1962; Malmer 1988), and spatial heterogeneity in accumulation that can occur due to variations in vegetation type and microtopography (Bindler et al. 2004; Le Roux et al. 2005; Coggins et al. 2006; Kempter et al. 2010; Rydberg et al. 2010). Since the 1970's a number of researchers have also hypothesized that downwashing may occur, which could smear the profile of atmospherically supplied elements and pollen in the uppermost layers.

Damman (1978) was among the first to identify the question of downwash in his study of the distribution and movement of elements in cores from bogs in Sweden and Norway. Based on estimates of lead-210 (^{210}Pb, the radioisotope central to age-dating of recent layers, e.g. $\leq$150 years) retention in the annual growth of Sphagnum, Malmer and Holm (1984) concluded that some lead accumulation occurred not only on the upper (growing) parts of the peat-forming plants, but that also some downward transport must occur during deposition. Oldfield and co-workers raised this issue in their review of radiometric dating techniques of recent peat (Oldfield et al. 1995). Specifically they discussed 'Processes displacing Pb-210 in peat', which would affect ^{210}Pb chronologies. They hypothesized that well-aerated hummocks—the coring site of choice in most studies of peat records—could be subject to some rapid downwashing. As an example, in a subsequent study of a peat core from Stor Åmyran in northern Sweden, Oldfield et al. (1997) observed a discrepancy between the age of a tephra layer identified as originating from the AD 1875 eruption of Askja, and the CRS date of 1927 for that level in the peat. A displacement of ^{210}Pb dates relative to carbon-14 (^{14}C) dating was also noted in a review by Biester et al. (2007). A second factor identified by Oldfield et al. (1995) was re-mobilization, which was discussed previously by Urban et al. (1990). In terms of particles, Clymo and Mackay (1987) examined the physical up- and downwash of pollen in a 36 day experimental study conducted on 12 peat cores, where they found a physical displacement of pollen connected to the flow regime.

The measurement of atmospherically supplied radioisotopes is a well-established tool for developing age-depth models in peat (Appleby et al. 1997), which has successfully been applied in numerous studies over the last four decades (Turetsky et al. 2004). However, some studies have reported difficulties in developing age-depth models due to what they speculated was related to mobility. For example, Lamborg et al. (2002) were unable to establish a ^{210}Pb-chronology due to the depths at which unsupported ^{210}Pb was detected and the occurrence of sub-surface peaks at or near the water table. Turunen et al. (2004) encountered similar difficulties in several of their cores sampled in eastern Canada. Although this issue of potential downwash in peat has been hypothesized for decades, there have been few studies that expressly address this question. With these studies in mind, we therefore aim to specifically test the hypothesis of downwash in peat.

With a half-life of only 53.4 days and a continuous production in the atmosphere, beryllium-7 (^{7}Be) is a unique tracer of recently supplied (<6 months) atmospheric elements and environmental processes (Baskaran et al. 1993; Blake et al. 1999; Fitzgerald et al. 2000; Yoshimori 2005; Short et al. 2007; Papastefanou 2009; Walling et al. 2009; Zhu and Olsen 2009; Kaste et al. 2011a, b). This makes ^{7}Be an ideal tool to study short-term downwashing of atmospherically deposited elements in peatlands. In the atmosphere ^{7}Be quickly attaches to aerosols and is delivered to the earth's surface primarily via wet deposition (Wallbrink and Murray 1996; Whiting et al. 2005) and has a similar behavior as ^{210}Pb ($T_{1/2} = 22$ years, Lal and Suess 1968; Short et al. 2007). Once deposited, ^{7}Be is rapidly bound to soil and organic particles due to its high affinity to organic matter leading to strong bonds with oxygen atoms on surfaces of inorganic minerals and organic compounds (Hawley et al. 1986; You et al. 1989; Taylor et al. 2012); experimental studies also indicate that ^{7}Be is not readily remobilized after deposition (Taylor et al. 2012). Thus, any ^{7}Be found at depth in soils, sediments or peat must have been rapidly transported to underlying levels or recently incorporated through physical mixing (such as bioturbation in sediments) or rapid advection. To test the hypothesis of short-term downwashing in peat we measured ^{7}Be-activities in five peat cores from two sites in Sweden: triplicate hummock cores from an ombrotrophic bog (Bindler et al. 2004) and two contrasting peat cores from a nutrient-poor mire (Rydberg et al. 2010). In addition to the ^{7}Be analyses, we also performed a simple replication of core treatments in the laboratory similar to those done by Vile et al. (1999) and Wieder et al. (2010) using cores from the nutrient-poor mire.

Materials and methods

Site description, sampling and experimental set-up

Store mosse is a ~8,000 ha bog complex in south-central Sweden (57°15′N, 13°55′E; 160–170 m a.s.l.). The mean annual temperature is 7 °C (SMHI) and the mean annual precipitation in the region is ~700–1,000 mm. During the 6 months prior to our sampling the average rainfall was 2 mm day^{-1} with peaks up to 32 mm day^{-1} (SMHI). Extensive studies on the development of Store mosse, including peat-forming plant macrofossil stratigraphies, have been previously published (Svensson 1986, 1988; Malmer et al. 1997; Malmer and Wallen 1999; Bindler et al. 2004; Kylander et al. 2013). Surface peat cores (10 cm × 10 cm and ~70 cm in length, labeled SM1, SM2 and SM3) were collected from hummock strings in November 2008 using a Wardenaar (1987) corer within a ~25 m × 25 m area in the southern part of the bog, and within a 100 m distance from earlier work (Bindler et al. 2004). The cores were wrapped in plastic film and aluminum foil, and taken back to the laboratory intact and stored frozen at −18 °C until processing.

Rödmossamyran is a ~7 ha nutrient-poor (oligotrophic) fen located near the present-day coastline of the Gulf of Bothnia in northern Sweden (63°47′N, 20°20′E; 40 m a.s.l.). For a more detailed description of the mire see Rydberg et al. (2010). The mean annual temperature in the region is 3 °C and the mean annual precipitation is 700 mm (SMHI). The average rainfall during the 6 months prior to our sampling was 2 mm day^{-1} (SMHI) with peaks of 37 mm day^{-1} and 12 mm h^{-1} (weather station maintained by Department of Applied Physics and Electronics, Umeå University; www.tfe.umu.se). We collected two cores about 3 m apart on the mire, with one site on the open Sphagnum lawn (dominated by *S. centrale* and *S. subsecundum*), and the other on the opposite side of the vegetation boundary representing the dominant characteristics of the mire with a mixture of Sphagnum (*S. centrale, S. subsecundum* and *S. palústre*), shrubs (e.g., *Calluna vulgaris* and *Ledum palustre* L.) and small, thinly spaced pines (*Pinus sylvestris*). These two coring sites are alongside sites S1 (and S1b) and F1 (and F1b) in Rydberg et al. (2010). The two 50-cm cores, here labeled S1c and F1c, were collected in November 2012 as monoliths by using a handsaw sharpened to a knife blade. The water table at the time of sampling was at the lawn surface for S1c and 14 cm for F1c, but summer water tables can be a few cm below the lawn surface and as low as 35 cm in the F1 site. The cores were wrapped in plastic film, then aluminum foil and taken back to the laboratory intact and stored at +4 °C overnight.

Four cores (M1, M2 and two controls) were collected in a 2 m × 2 m area from the open Sphagnum lawn on Rödmossamyran, 20 m from site S1c, in mid-September 2012 for treatment in the laboratory. Using the sharpened handsaw, we removed 14 cm × 15 cm monoliths, 24 cm deep, to fit the dimensions of our plexiglass core boxes. The boxes were fitted with a 100 µm mesh on the bottom to allow excess water to flow through the cores. After 2 days in the laboratory, deionized water was applied gently over a 1 h period from a flask until water began to drain from the cores to estimate the cores' water holding capacity, which was >500 ml. After one week, a solution of 0.15 g $CuBr_2$ dissolved in 300 ml deionized water was gradually added to two cores over a 1 h period, which was equivalent to 14 mm of rain; an equal amount of water was added to two controls. This high rate of addition is comparable to some rainfall events; for example, on 27 September 2012 (i.e., during our experimental period), 37 mm of rain fell over a 10 h period, with a peak value of 12 mm h^{-1} (www.tfe.umu.se). Water was not observed draining from the cores during the additions. Two further additions took place at one-week intervals. 0.45 g of $CuBr_2$ was added in total, equaling 0.13 g of Cu and 0.32 g of Br. One week after the third addition the cores were removed from the boxes and cut into 2 cm slices.

Although the added amounts of $CuBr_2$ in the original experiment may be considered very high (yielding a total Cu concentration in peat that occurs near metal smelters; cf. Ukonmaanaho et al. 2004), the resulting concentrations are lower than the maximum adsorption capacity determined experimentally for Sphagnum peat by Gupta et al. (2009). However, to further reduce the potential for exceeding the adsorption binding capacity we re-performed the laboratory addition using an additional peat monolith (M3, 10 cm × 10 cm, 30 cm depth) from the Sphagnum lawn of Rödmossamyran in mid-June 2013 and a lower concentration solution, with a total of 2.523 mg Cu added over a 3-week period. This addition was applied once per week over 3 weeks following the rainfall pattern on 27 September 2012 mentioned above (www.tfe.umu.se, 37 mm 10 h^{-1}), with hourly additions ranging from 0.5 to 12 mm h^{-1} (see supplementary information, Fig. S2, for further details). This final monolith, M3, had a closed bottom and a pre-drilled drain hole to maintain the height of the water table at 15 cm from the sphagnum surface. One week after the final addition the core was subject to a post-conditioning treatment for 2 weeks where 50 mL of deionized water was gently applied every second day to wash away any excess Cu not bound to the organic material. After treatment the core was removed from the box and cut into 2 cm slices.

Sample preparation and analytical methods

For the Store mosse cores (and the last monolith, M3), the outermost part of the frozen cores was removed in a freezer room and the surfaces hand-planed into even dimensions; the cores were first marked and then cut into 2-cm-thick slices on a band saw. The Rödmossamyran cores were cut into 2-cm-thick slices using a hand saw the day following the sampling. All samples were dried to constant weight at either 30 °C (SM1-3 and S1c), 60 °C (lab treatments) or in a freeze drier (F1c), after which the dry masses were recorded and bulk density calculated. All samples were ground in a Retsch ball mill and homogenized before further analysis.

Activities of ^{7}Be were measured using high-purity intrinsic Ge detectors (Canberra Broad Energy 5030) with ultra-low background hardware and copper-lined 1,000 kg lead shields. Detector efficiency for the ^{7}Be region of interest at 477–478 keV for the 25 mL peat sample geometry was determined to be 8.3 % by counting a solution containing certified values (Eckert & Ziegler Isotope Products, Valencia, CA, USA) of over a dozen different nuclides decaying at energies ranging from 46 to 1,836 keV. Detection limits (based on 4.5 g sample counted 48 h) were 4.5 Bq ^{7}Be kg^{-1} peat. Samples were typically counted for 48 h (for near-surface samples) to 100 h (for deeper samples) to keep counting errors below 10 % (see supplementary material, Table S1, for full details). Further details on the radiometric measurements, including calibration set-up, can be found in Kaste et al. (2011a) and references therein. Data are reported in activity per kg (Bq kg^{-1}), and are decay-corrected to the date of collection. The radiometric analyses extended to 36 cm depth in the Store mosse cores and to 22 cm depth in the Rödmossamyran cores.

Total Cu and Br concentrations were measured using a Bruker S8 Tiger wavelength-dispersive X-ray fluorescence (WD-XRF) analyzer equipped with a Rh anticathode X-ray tube (modified from De Vleeschouwer et al. 2011 for 0.5 g samples, see supplementary information Tables S2, S3, Fig. S1). The lower limits of instrumental detection estimated by the instrument's software package SpectraPlus are 0.3 ppm for both elements, but the lowest standards in the calibration are 3 ppm for Cu and 1.2 ppm for Br. The Br values in our treatment cores we can only give as reported values, because the Br calibration only spans the interval 1.2–145 ppm and the measured values in our treated cores greatly exceed this range. However, most importantly for our questions in this study, we can trace downwashing of Br to deeper levels given the measurable concentrations in the controls and concentrations within the calibration range for deeper samples from the treated cores. The accuracy of the analyses was checked using certified reference materials: NCS DC73310 ($n = 24$ analyses) with a certified value for Cu of 1,230 ppm versus measured 1,208 ± 17 and for Br 1.7 ppm (certified) versus 1.5 ± 0.4 ppm (measured); and NCS DC73322 ($n = 4$ analyses) with a certified value for Cu of 40 ppm versus measured 42 ± 1, and for Br 4.0 ppm (certified) and 4.3 ± 0.4 ppm (measured). Although intensities measured using WD-XRF are linear with increasing concentration, the Br values reported here in the upper core sections can therefore only be considered as approximate values.

Results

Bulk density (Fig. 1a) in all three Store mosse cores shows a ~2–3 fold increase from the uppermost layers ($\leq$0.05 g cm^{-3}) to values of $\geq$0.09 g cm^{-3} at depths of ~25–30 cm, and in deeper layers declines slightly to values $\leq$0.09 g cm^{-3}. The peak bulk density varies from 0.09 to 0.11 g cm^{-3} in the order SM1 > SM2 > SM3.

In the Rödmossamyran cores the bulk density varies between the lawn (S1c) and the fen (F1c) sites. In S1c the bulk density remains fairly stable in the upper section of

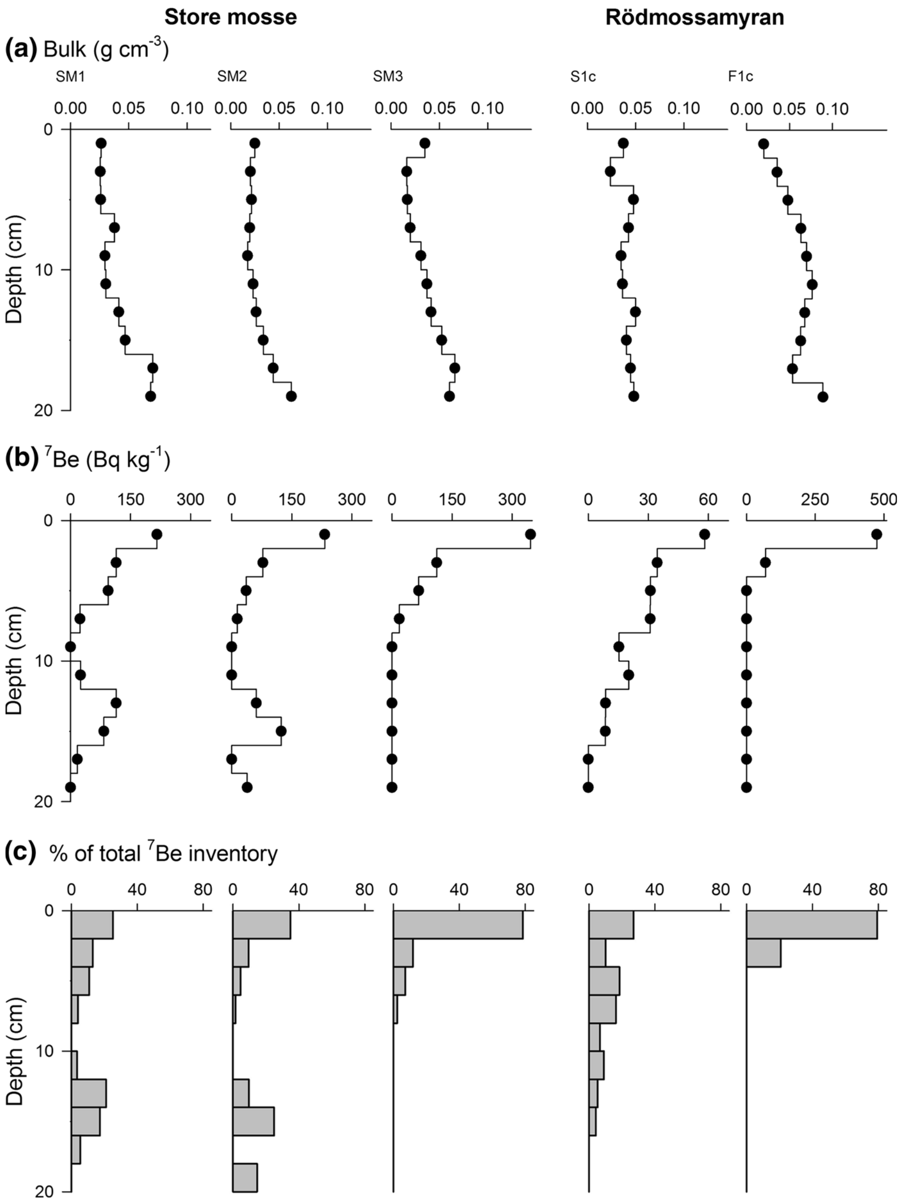

Fig. 1 **a** Bulk density in the triplicate cores (SM1–3) from Store mosse and Rödmossamyran (S1c and F1c); **b** activities of ^{7}Be in the same cores; **c** % of total ^{7}Be inventory

the core (corresponding to the samples measured for radiometric activity) with values varying from 0.02 to 0.05 g cm^{-3}. Below this point the bulk density increases to values of $\geq$0.7 g cm^{-3} and a peak value of 0.12 g cm^{-3} occurs at 43 cm. In F1c the bulk density varies from $\leq$0.04 g cm^{-3} in the uppermost slices to $\geq$0.07 g cm^{-3} at depths of ~10 cm after which it decreases to ~0.05 g cm^{-3} before returning to increasing values (0.08–0.09 g cm^{-3}) down core in samples corresponding to the depths of samples measured for radiometric activity. The overall peak bulk density is measured at 43 cm depth with a value of 0.6 g cm^{-3}. Visually, S1c shows much lower levels of decomposition with easily recognizable Sphagnum fragments throughout the core in contrast to F1c. This visual evidence of lower decomposition in the S1 versus F1 site is also supported by analyses of C/N ratios and light transmission in the original transect by Rydberg et al. (2010).

Measurable activities of ^{7}Be (Fig. 1b) in the three Store mosse cores occur down to depths of 20, 18 and 8 cm (SM1 > SM2 > SM3), with values from 216, 232 and 346 Bq kg^{-1} in the surface samples to 17, 39 and 18 Bq kg^{-1} for SM1, SM2 and SM3, respectively, in the deepest levels with measurable activities. For

Rödmossamyran the measurable activities of ^{7}Be occur down to depths of 16 and 4 cm (S1c > F1c) with activities of 58 and 474 Bq kg^{-1} in the surface samples and 8.6 and 69 Bq kg^{-1} for S1c and F1c, respectively, in the deepest levels with measurable activities. The total inventories of ^{7}Be for the two sites are 320, 335 and 450 Bq m^{-2} in Store mosse (SM3 ≈ SM2 < SM1) and 150 and 240 Bq m^{-2} in Rödmossamyran (S1c < F1c). 25–80 % of the total inventory is retained in the 0–2 cm sample. The ^{7}Be inventories at specific depths and the corresponding % of total ^{7}Be inventory are shown in Fig. 1c.

For both our high and low Cu-treatments to the three Rödmossamyran monoliths (Fig. 2a, b) the distribution of Cu is quite similar, with 49 ± 1 % of the added Cu retained in the top 2 cm slice (10100 μg g^{-1} and 450 μg g^{-1} respectively, Fig. 2a, b). Overall, the inventories of Cu per 2-cm slice display an approximately exponential decline with depth ($R^2 = 0.88$ and 0.96), with only 1–3 % of the added Cu detected in the 8–10 (M1 and M2) and 10–12 (M3) cm slice of each core. Only trace quantities (≤31 μg g^{-1}) of added Cu were detected in the interval 10–16 cm and below that only background values (≤3 μg g^{-1}) equal to those in the two control cores were measured. Our calculated Cu inventories were 0.128 and 0.136 g, i.e., 98 and 105 % recovery of the 0.13 g added (High Cu-treatment) and 0.0022 g, i.e., 88 % recovery of the 0.0025 g added (low Cu-treatment). For the high Br addition (M1 and M2) a smaller estimated fraction was retained in the top 2 cm slice, 35 ± 2 % of the added inventory; thereafter Br showed a greater degree of downwashing than for Cu. Elevated Br concentrations occurred to the base of the open-bottomed cores with >100 μg g^{-1} in the lowest levels of the treated cores in comparison to only 5–11 μg g^{-1} in the controls. Our estimated inventories for Br were 0.268 and 0.271 g, which represents 84–85 % of the 0.32 g added—note, however, that the high Br concentrations in the upper layers exceed our calibration and thus entail an unknown analytical uncertainty.

Discussion

The potential for some rapid downward transport of atmospherically derived elements in peat has been hypothesized for decades (Damman 1978; Urban et al. 1990; Oldfield et al. 1995, 1997; Lamborg et al. 2002), but with the exception of Clymo and Mackay (1987) in their study of post-depositional relocation of pollen grains, this question has not been directly addressed—particularly from a geochemical perspective. Based on our novel approach using the natural short-lived tracer ^{7}Be, we have unambiguous support for our hypothesis that a rapid downwash occurred both in the well-aerated hummock peat (SM1-2) and in the Sphagnum lawn (S1c), but also that a more limited downwash occurred in one of the hummock cores (SM3) and especially in the fen core (F1c). Given the short half-life of ^{7}Be and its origin solely from recent atmospheric deposition, the fact that ^{7}Be can be measured in layers below the surface (0–2 cm) samples and, more importantly, measured down to depths ≥16 cm in three of our five cores (Fig. 1b, c) provides compelling evidence that a rapid downwashing of ^{7}Be occurred during the ≤6 month period prior to our sampling dates.

The differences between the two Rödmossamyran cores are notable with two regards. As observed previously for ^{210}Pb and Hg for adjacent core sites to ours, F1c has a higher total inventory of ^{7}Be as compared to S1c—60 % higher in F1c than S1c. Rydberg et al. (2010) attributed the higher ^{210}Pb and Hg inventories to both microtopography (F1 being higher) and to field-layer vegetation that increase interception and scavenging (and for Hg also the potential for increased evasion from S1 given the higher water table). The ^{7}Be results are consistent with these earlier findings. The second aspect is that the extent of downwashing is much less in F1c than in S1c. We suggest that downwashing is more extensive in S1c because of its open, less-decomposed structure; we can trace continuous Sphagnum stems down to at least 10 cm depth, and below that the peat is still composed of recognizable Sphagnum fragments (Fig. 3). In contrast F1c has a higher turnover rate of organic matter and a more decomposed, fragmented and compact structure. The top slice includes fresh Sphagnum, litter and then decomposed peat. CN ratios and light transmission analyses (data from Rydberg et al. 2010) both indicate higher decomposition for the F1 site (CN ratios 54–76 and light transmission 31–89 % in the top 20 cm) as compared to the S1 site (CN ratios 87–150 and light transmission 74–84 % in the top 20 cm).

Interestingly, in two of the Store mosse hummock cores (SM1 and SM2) the vertical distribution of ^{7}Be does not show a coherent exponential decline with depth. In all three cores activities are highest directly

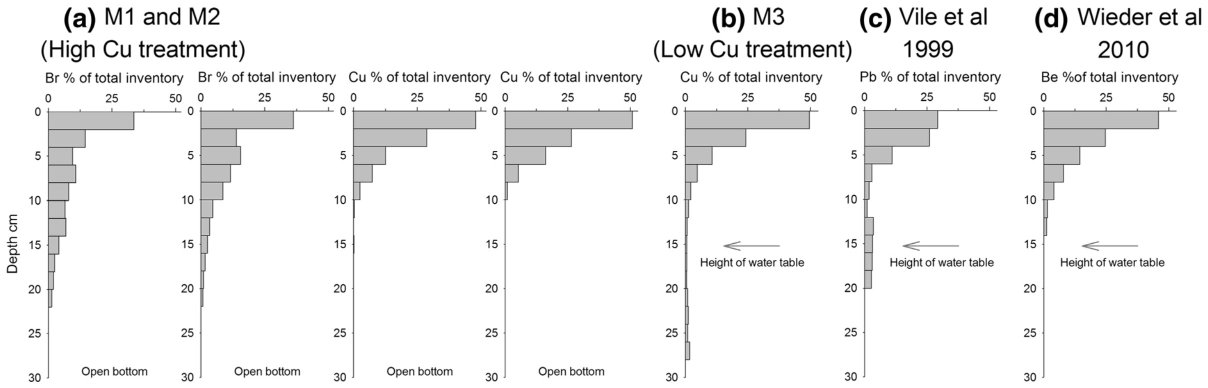

Fig. 2 **a** Distribution of Cu and Br with depth in two High Cu-treatment cores from the open Sphagnum lawn from Rödmossamyran, and **b** The distribution of Cu in the low Cu-treatment core in comparison to: **c** the Pb additions in low water table treatment from Vile et al. (1999), and **d** the Be additions in low water table treatment from Wieder et al. (2010). (**c**, **d** Redrawn from data in Vile et al. 1999 and Wieder et al. 2010)

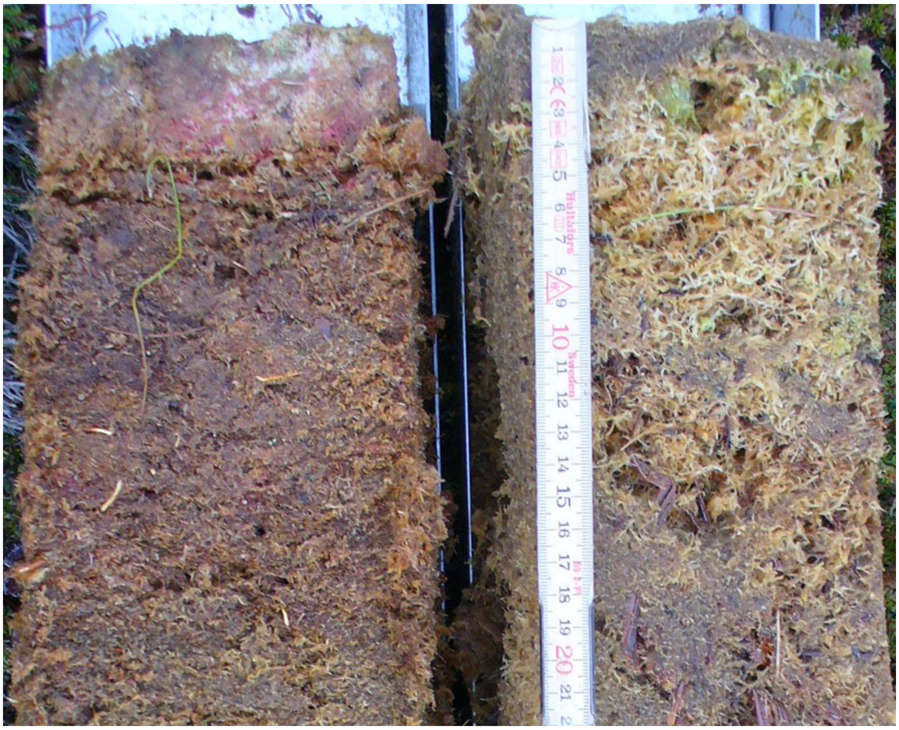

Fig. 3 Core F1c and S1c from Rödmossamyran representing fen peat (*left*) and sphagnum lawn (*right*). Note the visible difference in the fragmentation and degree of decomposition between the two cores

in the surface layer and decline rapidly a few cm below the surface, but in SM1 and SM2 there is also a subsurface maximum at discrete depths of 18 and 16 cm, respectively (Fig. 1b), which is proximate to the water table at the time of sampling. This 'bi-modal distribution' of ^{7}Be in the peat that we document here is rather unique in that ^{7}Be profiles in soils and sediments almost always show a very simple exponential-like decline with depth on scales of just a few cm (Wallbrink and Murray 1996; Kaste et al. 2007, 2011a), as is the case for the other three cores here. The distribution of ^{7}Be in the upper 8 cm can be explained by a simple downwashing front, but the re-occurrence of ^{7}Be activities further down suggest that the downwash process is more complex than can be fully addressed within the scope of this study. One possible explanation of the secondary peaks found in SM1 and SM2 is that relatively intense rains caused rapid downwash of ^{7}Be to the water table along pre-existing macropores prior to our core collection. The fact that SM3 has no secondary ^{7}Be peak indicates that macropore structures in the upper 20 cm of peat are not spatially homogenous, such that downwash is not uniform at the meter scale. A second factor that cannot be excluded is the influence of peatland hydrology and particularly lateral flow. A lateral flow could in part explain the secondary peak found at depth in SM1 and SM2, but it would not explain the overall downward distribution of ^{7}Be because this vertical distribution still requires that recently deposited ^{7}Be was transported downward to the location of the upper water table. Lateral flow would likely cause a smearing of the ^{7}Be, not a spatial variation in enrichment at depth.

Beryllium-7 forms strong bonds with oxygen atoms on surfaces of organic matter and inorganic minerals, and is highly competitive for adsorption sites (Hawley et al. 1986; You et al. 1989; Taylor et al. 2012), thus it is unlikely that the surfaces of the peat are saturated with respect to Be. Rather, the process of rapid downwashing is more likely driven by the movement of rainwater and the structure of the organic matter, which in some cases facilitates elemental transport without the appropriate solid–solution contact time for adsorption to occur. Most equilibration studies show that metals, including Pb and Be, typically require more than 12 h to reach equilibrium with respect to surface adsorption (Bloom and Crecelius 1983; Nyffeler et al. 1984). Thus, downwashing must occur rapidly during moderate to intense rainfall events where rainwater can quickly penetrate into the peat before adsorption to the top layer can occur. Downwashing of ^{7}Be by infiltrating rainwater was also shown in unsaturated marsh-soils by Olsen et al. (1985), who found that ^{7}Be was able to penetrate deeper into the soil through small cracks in the soil surface that were formed during times of drought. Because peat and particularly hummocks are naturally less compacted than soils, and have a high porosity regardless of surface moisture, some downwashing of ^{7}Be and other atmospherically deposited elements by percolating rainwater is even more likely to occur.

That downwashing may occur is further supported by our experimental data (Fig. 2a, b) as well as previous results of Vile et al. (1999) and Wieder et al. (2010; Fig. 2c, d). The $CuBr_2$ was selected for the treatment because it completely dissolves in water and gave us two separate tracers: Cu^{+2}, a metal cation that binds rapidly and more strongly than Pb (Villaverde et al. 2009), and Br^-, an anion that is bound to organic matter through interaction with humic substances (Yamada 1968; Yuita 1994; Zaccone et al. 2008) and in peat exists mostly in organic form (Maw and Kempton 1982; Biester et al. 2004). The large amounts of Cu (0.13 g in total) and Br (0.32 g in total) added in the high Cu-treatment were excessive relative to their natural abundances in the peat ($\leq$3–20 μg Cu g^{-1} and (5–60 μg Br g^{-1}), but allowed us to more easily assess the maximum depth to which downwashing might occur in the cores.

Despite the extreme concentration in our high Cu-treatment (1,000-fold greater than the ambient concentration, but similar to concentrations in the vicinity of metal smelters) the observed distribution is comparable to both our lower Cu-treatment and the distribution shown for Be in low and variable water table treatments by Wieder et al. (2010). Similar to our Cu additions, nearly half of their added Be ($\leq$45 % after 40 days of treatment) was retained in the top 2-cm slice of their cores, and declined exponentially with depth with about 1 % of the total inventory measured in the 12–14 cm slice, just above the lowest water table level at 15 cm depth. For their high water table (3 cm) treatment about 55 % of the Be was retained in the top 2-cm slice, but about 15 % had migrated below the 3-cm water table to the 4–6 cm slice, which is less migration than we observe in our Sphagnum lawn core where the water table at the time of sampling was at the surface, but similar to our more decomposed fen peat. In an earlier study on Pb retention in peat cores, Vile et al. (1999) found a somewhat lower inventory of the added Pb (30 %) was retained in the top 2-cm slice, and a small fraction of the Pb was detectable at or even below the 15 cm water table (3 % in the 18–20 cm slice).

Despite the artificial nature of the lab treatments, the amount and rate of water added to the cores (3.2 mm per addition every other day for Vile et al. and Wieder et al.; 14 mm per addition one time per week or 0.5–12 mm per hourly addition once a week for our cores) can be considered as equivalent to episodic rainfall events. For example, as noted in the methods, our low-Cu addition replicated a natural rain event where a total of 32 mm of rain fell within a 10 h period (with a 1-h peak of 12 mm in the 8th hour of the event). Shorter and more intense rainfall events such as this are common and would allow for a rapid downwash of atmospheric elements to depths below the surface layers in the peat—most notably those we observe in two of the well-aerated hummock cores from Store mosse.

As previously concluded by Vile et al. (1999) and Wieder et al. (2010), these addition experiments with Pb, Be and here also Cu show that these cations are effectively retained in peat cores. Even our high addition of Cu is effectively bound, and shows the same decline with depth as our lower Cu addition and the Pb and Be additions. Although the largest fraction is retained in the top 0–2 cm slice in all additions (30–50 %) as well as in the measurements of natural ^{7}Be in our field study (25–80 %), all of these data are indicative of a downwashing component, which might attenuate an atmospheric signal.

On the basis of our ^{7}Be data (Fig. 1b, c) as well as the experimental work here and by others (Clymo and Mackay 1987; Vile et al. 1999; Wieder et al. 2010, Fig. 2a–d), there is good evidence to support our hypothesis—posed previously by Oldfield et al. (1995)—that downwashing does occur at some sites. The depth of this downwashing will depend on the properties of the individual peat profile, such as degree of compaction and decomposition, as well as peatland hydrology. Hummock cores (SM 1–3), which can have low bulk densities (Fig. 1a) and a very open structure in the well-aerated, living vegetation and less-decomposed peat in the top several cm or more, would be most susceptible to downwashing. Our data suggest this can occur downwards to the water table as observed at the time of our sampling (Fig. 1b, c). With a higher water table (surface level), such as our S1c (Fig. 1b, c) site on Rödmossamyran, the downwashing of ^{7}Be can still occur, and in the case of this core to at least 16 cm depth. In the more decomposed peat of our F1c core (Fig. 1a), where the high water table in the fall is only up to 14 cm depth but may be as low as 35 cm in the summer, the depth of downwashing is restricted—only to the 2–4 cm slice (Fig. 1b, c). Based on the empirical evidence from ^{7}Be here, there is good reason to go further with mechanistic studies that specifically consider, for example, the variability in downwashing over time, the properties of the peat (e.g., decomposition, fragmentation) and peatland hydrology.

From our data it is reasonable to speculate that this mechanism of rapid initial transport must affect other atmospherically supplied elements. Given the similar atmospheric and depositional patterns and processes for ^{7}Be and ^{210}Pb (Short et al. 2007), and the discussion regarding ^{210}Pb-mobility discussed in previous work (Damman 1978; Malmer and Holm 1984; Oldfield et al. 1995; Biester et al. 2007), we hypothesize that downwashing would also influence ^{210}Pb, which is the fundamental tool for age dating the most recent 150 years of peat accumulation. Because ^{7}Be can be measured simultaneously with ^{210}Pb via gamma spectrometry we propose that ^{7}Be would be an ideal tool to estimate the extent of downwashing at any specific site.

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