Science of the Total Environment 493 (2014) 170–177

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Incorporation of radiometric tracers in peat and implications for estimating accumulation rates

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## HIGHLIGHTS

- $^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^{7}$Be, and tot-Pb and tot Hg were measured in 5 peat cores.
- Two age–depth models were applied resulting in different accumulation rates.
- The CRS-model overestimated peat mass accumulation.
- The new IP-CRS-model improved mass accumulation rates.
- A downwash component gave accumulation rates in better agreement with monitoring.

## ARTICLE INFO

*Article history:*
Received 17 December 2013
Received in revised form 19 May 2014
Accepted 20 May 2014
Available online xxxx

Editor: Mae Sexauer Gustin

*Keywords:*
Beryllium
Downwash
Lead
Mercury
Peat accumulation

## ABSTRACT

Accurate dating of peat accumulation is essential for quantitatively reconstructing past changes in atmospheric metal deposition and carbon burial. By analyzing fallout radionuclides $^{210}$Pb, $^{137}$Cs, $^{241}$Am, and $^{7}$Be, and total Pb and Hg in 5 cores from two Swedish peatlands we addressed the consequence of estimating accumulation rates due to downwashing of atmospherically supplied elements within peat. The detection of $^{7}$Be down to 18–20 cm for some cores, and the broad vertical distribution of $^{241}$Am without a well-defined peak, suggest some downward transport by percolating rainwater and smearing of atmospherically deposited elements in the uppermost peat layers. Application of the CRS age–depth model leads to unrealistic peat mass accumulation rates (400–600 g m$^{-2}$ yr$^{-1}$), and inaccurate estimates of past Pb and Hg deposition rates and trends, based on comparisons to deposition monitoring data (forest moss biomonitoring and wet deposition). After applying a newly proposed IP-CRS model that assumes a potential downward transport of $^{210}$Pb through the uppermost peat layers, recent peat accumulation rates (200–300 g m$^{-2}$ yr$^{-1}$) comparable to published values were obtained. Furthermore, the rates and temporal trends in Pb and Hg accumulation correspond more closely to monitoring data, although some off-set is still evident. We suggest that downwashing can be successfully traced using $^{7}$Be, and if this information is incorporated into age–depth models, better calibration of peat records with monitoring data and better quantitative estimates of peat accumulation and past deposition are possible, although more work is needed to characterize how downwashing may vary between seasons or years.

## 1. Introduction

For more than a century peatlands have been a valuable archive for studying past environmental changes, not only for the history of bog development (von Post, 1913), but also for the changes in landscape vegetation and climate (Granlund, 1931), carbon cycling (Gorham, 1991), and the atmospheric deposition of trace metals and soil dust (Shotyk, 1998; Kylander et al., 2007). Advancements in peatland research require that we continue to develop our understanding of important processes that influence how environmental signals are incorporated and preserved in this natural archive, and those that influence the precise dating of these records, both on long-term (centennial to millennial) and short-term (annual to decadal) scales.

Effort has been put into improving the tools used to date the long-term record; e.g., determining which organic fraction to radiocarbon date (Nilsson et al., 2001), improving radiocarbon age–depth modeling (Blaauw, 2010), and establishing supporting independent chronological markers such as with lead (Pb) pollution (Renberg et al., 2001). For the more recent record (years to decades) radiometric dating using atmospherically deposited radionuclides, i.e., lead-210 ($^{210}$Pb), cesium-137 ($^{137}$Cs), and americium-241 ($^{241}$Am), has been the main technique (Oldfield et al., 1995). While many studies have validated the general temporal patterns of pollutant metal accumulation based on historical

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http://dx.doi.org/10.1016/j.scitotenv.2014.05.088
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usage (Shotyk et al., 1997; Novak et al., 2003) or by the comparability between peat and other archives (Weiss et al., 1999; Farmer et al., 2002), there has been limited critical examination of accumulation records in quantitative terms (Le Roux et al., 2005). To be certain that we extract not only a qualitative record from peat, we must establish a quantitative link between the archive and the few to several decades of data that are now available from contemporary monitoring and research.

Age–depth modeling using $^{210}$Pb has been the main tool since the late 1970s for dating recent stratigraphic deposits such as sediments (Appleby and Oldfield, 1978; Appleby, 2008), peat (Aaby et al., 1979; Oldfield et al., 1995), and soil organic horizons (Kaste et al., 2011). Given its half-life of 22.3 years, $^{210}$Pb age–depth models provide dating on a 100–150 yr time scale, where the Constant Rate of Supply (CRS) model (Appleby and Oldfield, 1978) is the most frequently applied. While the general applicability of $^{210}$Pb dating for peat is well established (Turetsky et al., 2004), refinements in age–depth modeling continue to be developed (Olid et al., 2008; van der Plicht et al., 2013). Critical questions have been raised regarding processes that might affect the accuracy of the modeling such as the mobility of $^{210}$Pb in the peat, especially in the uppermost layers (Urban et al., 1990; Mitchell et al., 1992; Oldfield et al., 1995; Lamborg et al., 2002; Biester et al., 2007; Olid et al., 2008).

The short-lived radioisotope beryllium-7 ($^7$Be, $T_{1/2} = 53.3$ days), which forms high in the atmosphere, is an ideal tracer of rapid downward movement through peat, i.e. downwashing of precipitation, because $^7$Be, like $^{210}$Pb, is delivered to the surface primarily via wet deposition (Wallbrink and Murray, 1996; Whiting et al., 2005). $^7$Be is rapidly bound to soil and organic particles once deposited (You et al., 1989; Taylor et al., 2012), and thus any $^7$Be found at depth in the peat must have been rapidly transported to these underlying levels. In the five peat cores from two peatlands studied here, we found that $^7$Be could be measured to depths of 16 cm in a *Sphagnum* lawn core and 4 cm in an adjacent fen core from an oligotrophic fen, and to depths of 8 to as much as 20 cm in hummock cores ($n = 3$) from an ombrotrophic bog (Hansson et al., 2014). Experimental studies in the laboratory have indicated similar downwashing profiles based on additions of Pb (Vile et al., 1999), Be (Wieder et al., 2010) and Pb, Cu, Ni, and Zn (Hansson et al., under revision). The distributions of added metals and Be with depth in these three experimental studies were similar to our $^7$Be data (Hansson et al., 2014 and here), where only 30% (Pb) and 45% (Be) were retained in the top 2 cm with the remaining additions distributed exponentially down to the approximate height of the water table. Combined, these field and experimental studies provide compelling evidence that the retention of atmospherically deposited elements, which should include $^{210}$Pb, is not always limited to the top-surface layer in the peat, but that a significant fraction can be downwashed to and immobilized in layers below the surface. This is contrary to a main assumption in age–depth models that $^{210}$Pb is immobile.

Further discussion on the downwash process itself can be found in Hansson et al. (2014), but for clarity a brief description of the definition follows. Downwash is the process that allows atmospherically deposited elements to penetrate the peat surface following percolating rainwater thereby reaching further into the peat column before attaching to the organic substrate and being deposited. It is thus not a question of post-deposition mobility but an extension of the actual deposition itself. Downwash should not, however, be equated with 'smearing' that can be caused by both downwash, or post-deposition mobility and hydrology (fluctuating groundwater, evaporation and capillary activity). The $^7$Be distribution for all cores presented in Hansson et al. (2014), and here, is therefore not a matter of smearing but a direct cause of downwash.

Our main objective here was to test whether downwashing, evidenced previously by $^7$Be, affects the temporal accuracy of the CRS model in our cores, and thus, the quantitative record of trace metal accumulation rates — and more fundamentally also peat accumulation. Specifically, how might downwashing of the radioisotopes used for age–depth modeling influence our quantitative estimates of peat mass accumulation rates and also accumulation rates of metal pollutants? To test the quantitative accuracy of our accumulation records we compare our data to reported peat mass accumulation rates for similar sites and to deposition data available from monitoring programs in Sweden (forest moss biomonitoring and wet deposition; IVL.se). To do so we apply both a conventional CRS model and the newly proposed IP-CRS model (Initial Penetration — CRS; Olid et al., under revision) which considers vertical transport of $^{210}$Pb in the uppermost peat layers.

## 2. Material & methods

The cores collected and analyzed for this study were assessed previously with regard to $^7$Be (Hansson et al., 2014). Below is a brief description of the sites and sampling; more detailed information was published in Hansson et al. (2014) and in our previous studies (Bindler et al., 2004; Rydberg et al., 2010).

### 2.1. Site description and sampling

Store mosse is a large (~8000 ha) ombrotrophic bog in south-central Sweden (57° 15′ N, 13° 55′ E) and Rödmossamyran is a small (~7 ha) oligotrophic fen in northern Sweden (63° 47′ N, 20° 20′ E) close to the city of Umeå. From Store mosse we collected three surface cores (SM1–3) from hummocks in 2008 using a Wardenaar (1987) corer and from Rödmossamyran we collected two monoliths (S1c and F1c) in 2012 using a handsaw sharpened to a knife blade. The Rödmossamyran cores were retrieved from either side of the vegetation boundary separating an open *Sphagnum* lawn (S1c) from the main fen section (F1c). Cores were wrapped in plastic film and aluminum foil, taken back to the laboratory and stored either frozen at −18 °C (SM1–3) or at +4 °C (S1c and F1c) until processing. In a freezer room the outermost 1 cm of the Store mosse cores was removed, the surfaces hand-planed into even dimensions and the cores were cut into 2-cm-thick slices on a band saw with a stainless steel blade. The Rödmossamyran cores were cut into 2-cm slices using the sharpened handsaw the day after sampling. Samples were dried to constant weight at 30 °C (SM1–3 + S1c) or in a freeze drier (F1c), dry masses recorded and bulk density calculated, and finally ground in a ball mill before analysis.

### 2.2. Analytical methods

$^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^7$Be were measured using a Canberra Broad Energy 5030 (high-purity intrinsic Ge detectors with ultra-low background hardware and copper-lined 1000 kg lead shields). Detection limits were in the range of 2–3.5 Bq kg$^{-1}$ for $^{210}$Pb, 1–2 Bq kg$^{-1}$ for $^{137}$Cs, 0.25–1 Bq kg$^{-1}$ for $^{241}$Am and 2–4.5 Bq kg$^{-1}$ for $^7$Be based on mass and time counted. To keep counting errors below 8% (4% for $^{210}$Pb and $^{137}$Cs, and 8% for $^{241}$Am and $^7$Be), samples were counted for 48 h (for near-surface samples) to 100 h (for deeper samples) using 4.5–20 g. All $^{210}$Pb measurements were corrected for self-attenuation using the point-source method (Cutshall et al., 1983). The $^{210}$Pb activities in the deepest layers were considered as supported $^{210}$Pb and subtracted from the total $^{210}$Pb activity to determine the unsupported $^{210}$Pb used for calculating peat ages. Further details can be found in Kaste et al. (2011).

Total Pb concentrations were 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 matrix of the samples (see Supplementary information). The detection limit for Pb is 1 ppm, accuracy ±14% and reproducibility ±1.4 ppm.

Total Hg concentrations were analyzed with a thermal decomposition atomic absorption spectrometer (Perkin-Elmer SMS 100). Calibration of the mercury analyzer was done using different masses (10–200 mg) of NIST 1515, NCS ZC 73002 and NCS DC 73323. Analyses of two standard reference materials (NCS73309 and MESS-3) were within certified ranges and the relative deviation of replicate analyses was ±3%.

### 2.3. Age–depth modeling

Because processes such as decomposition and peat compaction alter accumulation rates, the Constant Rate of Supply (CRS) model is the $^{210}$Pb-dating model most widely used to infer age–depth relations in peat records (Appleby and Oldfield, 1978). We applied first the CRS model, and then, the new IP-CRS model (Olid et al., under revision). Unlike the conventional CRS model, the IP-CRS considers that some fraction of the deposited $^{210}$Pb is not retained at the peat surface but could migrate through the uppermost layers. If so, the steady-state distribution of $^{210}$Pb with depth is described by solving the traditional advection–diffusion model (DeMaster and Cochran, 1982), where the amount of $^{210}$Pb in a particular volume is controlled by: the dispersion of the $^{210}$Pb incorporated in the solid matrix; an advection term describing the vertical motion of $^{210}$Pb as a result of the accumulating peat; and the radioactive decay, adding an additional parameter that considers a vertical transport of $^{210}$Pb from the peat surface (which here is informed by the $^{7}$Be data). The inclusion of this new parameter into the conventional advection–diffusion equation was previously used by Soetaert et al. (1996) to study processes of mixing in lake sediments, and more recently applied by Olid et al. (under revision), to estimate the amount of $^{210}$Pb that could be removed from the uppermost peat layers and redistributed at depth.

## 3. Results and discussion

Both bulk density and the $^{7}$Be data for all five cores were previously reported in Hansson et al. (2014), but are summarized here in brief; all other data are novel.

### 3.1. Bulk density, radiometric activities ($^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^{7}$Be) and total concentrations (Pb and Hg)

Bulk density profiles are presented in Fig. 1a and d and are comparable to previous studies (Bindler et al., 2004; Rydberg et al., 2010; Hansson et al., 2013). In brief, the top ~0–2 cm in Store mosse consists of living vegetation, ~2–8 cm of partly decomposed litter and from ~8 cm and onwards all cores generally consist of peat. The bulk density shows an ~2–3 fold increase from the uppermost layers (≤0.05 g cm$^{-3}$) to values of ≥0.09 g cm$^{-3}$ at ~25–30 cm, after which it declines. In Rödmossamyran the top ~0–2 cm consists of living vegetation in

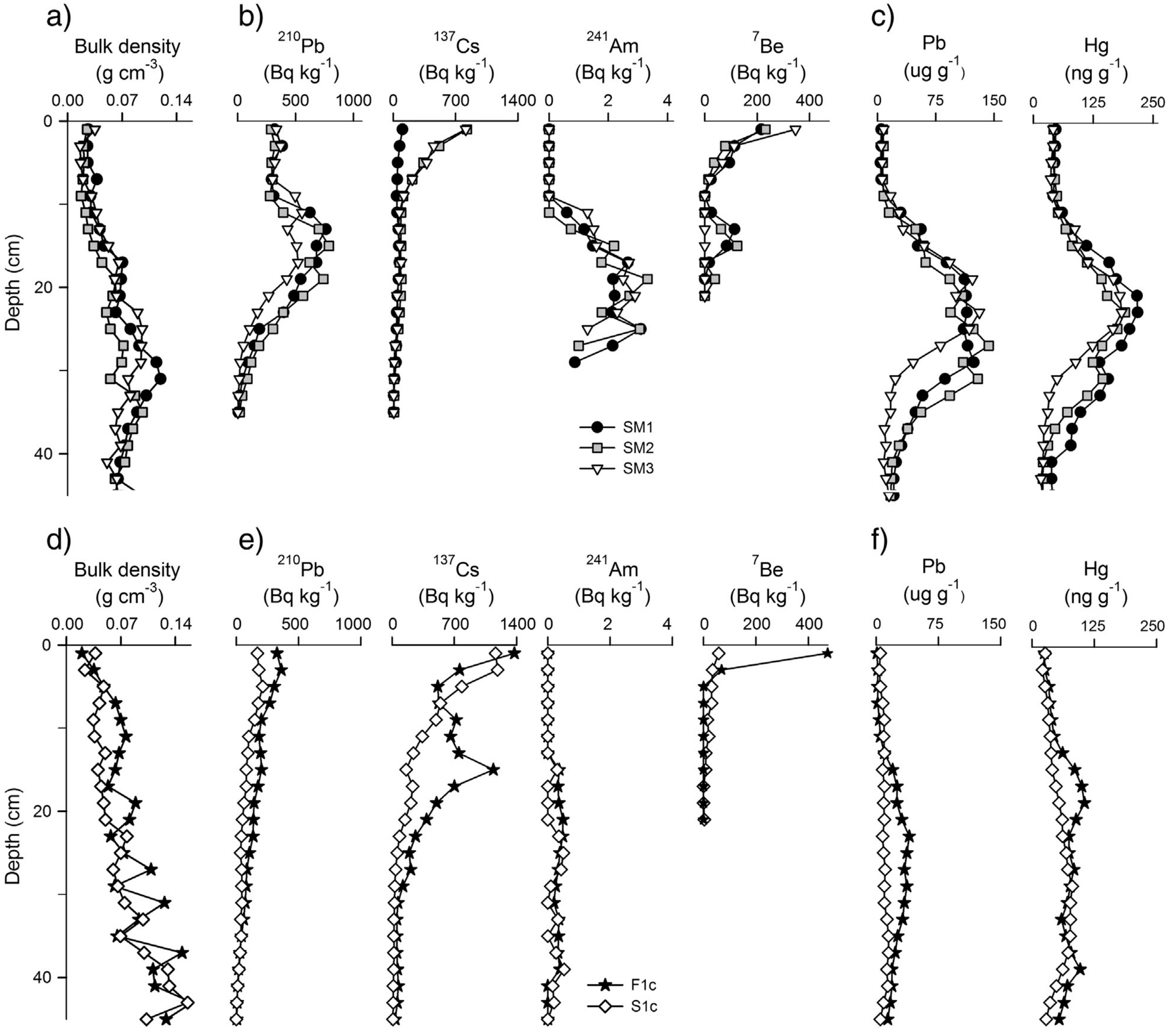

**Fig. 1.** (a) Bulk density (g cm$^{-3}$), (b) activities (Bq kg$^{-1}$) of $^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^{7}$Be, (c) total concentrations of Pb (μg g$^{-1}$) and Hg (ng g$^{-1}$) with depth (cm) in SM1 (filled circles), SM2 (gray squares) and SM3 (open triangles), (d) bulk density (g cm$^{-3}$), (e) activities (Bq kg$^{-1}$) of $^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^{7}$Be, and (f) total concentrations of Pb (μg g$^{-1}$) and Hg (ng g$^{-1}$) with depth (cm) in F1c (filled stars) and S1c (open diamonds).

both cores; however, the transition between litter layer and peat varies between the two cores. In F1c the partly decomposed litter layer transitions into peat already at ~4 cm, whereas in S1c, the litter layer with *Sphagnum* fragments still detectable to the naked eye can be found down to ~16 cm after which the core consists of peat. The bulk density varies between the two cores; in F1c the bulk density varies from ≤0.04 g cm$^{-3}$ near the surface to ≥0.07 g cm$^{-3}$ at ~10 cm, below which it decreases to ~0.05 g cm$^{-3}$ before returning to increasing values (0.08–0.09 g cm$^{-3}$). In S1c bulk density remains fairly stable in the upper section of the core down to ~20 cm depth with values varying from 0.02 to 0.05 g cm$^{-3}$; below this it increases to values of ≥0.7 g cm$^{-3}$.

The vertical distributions of unsupported $^{210}$Pb in SM1–3 are approximately similar. In the Store mosse and Rödmossamyran cores $^{210}$Pb activities range from 288 to 335 Bq kg$^{-1}$ and from 170 to 327 at the surface to maximum values of 763, 788, and 522 Bq kg$^{-1}$ at depths of 13, 15, and 17 cm for SM1, SM2, and SM3, and 361 and 213 Bq kg$^{-1}$ at depths of 3 and 5 cm for F1c and S1c (Fig. 1b and e). From these maxima, $^{210}$Pb activities decrease exponentially with depth to 3–18 Bq kg$^{-1}$ (Store mosse) and 2–4 Bq kg$^{-1}$ (Rödmossamyran) in the deepest measured slice. $^{210}$Pb inventories range from 4430 to 6370 Bq m$^{-2}$ in Store mosse and from 1690 to 3900 Bq m$^{-2}$ in Rödmossamyran (Table 1), where the higher inventory at Store mosse is consistent with the south–north gradient presented by Malmer and Holm (1984).

The maximum $^{137}$Cs activities (Fig. 1b and e) occur in the top samples, i.e., 103, 828, and 815 Bq kg$^{-1}$ for SM1, SM2, and SM3, and 1375 and 1187 Bq kg$^{-1}$ for F1c and S1c, respectively. Activities thereafter decline exponentially with depth to values of 4, 8, and 7 Bq kg$^{-1}$ for SM1, SM2, and SM3, and to 26 and 13 Bq kg$^{-1}$ for F1c and S1c, respectively. $^{137}$Cs inventories vary from 860 to 1700 Bq m$^{-2}$ in Store mosse, and in Rödmossamyran from 4855 Bq m$^{-2}$ in S1c to 11,466 Bq m$^{-2}$ in F1c. The 5–6 fold higher inventories in Rödmossamyran are expected given the higher $^{137}$Cs fallout from the 1986 Chernobyl accident in northern (10–30 kBq m$^{-2}$) than in southern (<3 kBq m$^{-2}$) Sweden (SNA.se).

Detectable activities of $^{241}$Am occur from ~13 cm depth in Store mosse and from 15 cm depth in Rödmossamyran (Fig. 1b). Maximum activities are 2.6, 3.3, and 2.9 Bq kg$^{-1}$ at depths of ~19 cm for Store mosse cores, but only 0.5 Bq kg$^{-1}$ in Rödmossamyran cores but with minor peaks at depths of 21 cm (F1c) and 39 cm (S1c). $^{241}$Am activities can be detected to ~27 cm depth in Store mosse and to 39 and 43 cm in Rödmossamyran. The lack of any clear peaks in $^{241}$Am suggests smearing with depth, which is similar to the diffuse or smeared $^{241}$Am peaks observed by Mitchell et al. (1992) and Biester et al. (2007), who suggested that such distributions and lack of sharp peaks were caused by post-depositional mobility.

The concept of downwash and the distribution of $^{7}$Be in our five peat cores are discussed in detail in Hansson et al. (2014), however a short summary here is still essential. Measurable $^{7}$Be activities occur down to 20, 18, and 8 cm depth in the Store mosse cores (SM1 > SM2 > SM3) and to 16 and 4 cm depths (S1c > F1c) in the Rödmossamyran cores (Fig. 1b, e). For SM1, SM2, SM3, S1c and F1c, respectively, activities are from 216, 232, and 346 Bq kg$^{-1}$, and 58 and 474 Bq kg$^{-1}$ in the surface samples to 17, 39, and 18 Bq kg$^{-1}$, and 8 and 69 Bq kg$^{-1}$ in the deepest levels with measurable activities. Total $^{7}$Be inventories (Table 1) 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). The bi-modal distribution of $^{7}$Be we observe in two hummock cores from Store mosse differs from the expected rapid exponential decline with depth of just a few cm as usually found in soils and sediments (Wallbrink and Murray, 1996; Kaste et al., 2011). Given the strong affinity of Be for organic matter (You et al., 1989; Taylor et al., 2012) downwashing must occur rapidly to transport $^{7}$Be to deeper layers such as during moderate to intense rainfall events, particularly following a prolonged period of dry weather, when rainwater can quickly penetrate into the peat. It should be noted that downwash does not occur evenly within one mire system as it is connected to macropore-structures in the peat and depend upon peat properties such as bulk density, decomposition, and peatland hydrology. We therefore suggest that difference in depth of downwash is connected to preexisting macropores which are not uniformly distributed across the bog, and that relatively intense rainfall events must have occurred prior to our sampling causing a rapid downwash of $^{7}$Be (through macropores) in SM1 and SM2, but not to the same depths in SM3. The fact that significant amounts of $^{7}$Be can be detected below the upper 0–2 and 2–4 cm is evidence on its own that downwash does exist to some extent in all cores.

**Table 1**
Total inventories of $^{7}$Be, $^{241}$Am, $^{137}$Cs and $^{210}$Pb, total Pb and total Hg (the latter calculated to the depth equivalent to 95 ± 1% of the total inventory of $^{210}$Pb activity measured in each core).

| Site | Total inventories | | | | Inventories to 95% $^{210}$Pb level | | |
|---|---|---|---|---|---|---|---|
| | $^{7}$Be | $^{241}$Am | $^{137}$Cs | $^{210}$Pb | Pb | Hg | Dry mass |
| | Bq m$^{-2}$ | Bq m$^{-2}$ | Bq m$^{-2}$ | Bq m$^{-2}$ | mg m$^{-2}$ | μg m$^{-2}$ | kg m$^{-2}$ |
| SM1 | 450 | 26 | 857 | 6372 | 824 | 1622 | 14 |
| SM2 | 334 | 17 | 1566 | 5193 | 894 | 1465 | 12 |
| SM3 | 309 | 21 | 1697 | 4429 | 728 | 1241 | 12 |
| F1c | 238 | 8 | 11,466 | 3900 | 367 | 1153 | 25 |
| S1c | 161 | 6 | 4855 | 1691 | 192 | 1066 | 24 |

This mechanism of rapid initial transport must logically affect other atmospherically supplied elements such as $^{210}$Pb. This rapid downwashing and post-depositional mobility of atmospherically deposited elements (e.g., Pb, $^{210}$Pb) in the surficial peat layers have been suggested by several authors over the last three decades (Damman, 1978; Malmer and Holm, 1984; Urban et al., 1990; Oldfield et al., 1995; Lamborg et al., 2002), and are supported by these $^{7}$Be data, and by experimental studies (Vile et al., 1999; Wieder et al., 2010; Hansson et al., under revision).

In the Store mosse cores, Pb and Hg concentrations (Fig. 1c) range from surface values of ~7 μg Pb g$^{-1}$ and ~45 ng Hg g$^{-1}$ to maximum values of 124 to 143 μg Pb g$^{-1}$ and 184 to 217 ng Hg g$^{-1}$, but not in the same order of concentrations among cores; SM2 > SM3 > SM1 for Pb and SM1 > SM2 > SM3 for Hg. In Rödmossamyran, Pb and Hg concentrations (Fig. 1f) range from surface values of 1–5 μg Pb g$^{-1}$ and ~25 ng Hg g$^{-1}$ to maximum values of 15 to 40 μg Pb g$^{-1}$ and 105 to 180 ng Hg g$^{-1}$ in the order of F1c > S1c for both Pb and Hg.

Using the depth equivalent to 95 ± 1% of the total inventory of $^{210}$Pb activity as a common level among cores, which reduces the uncertainty associated with estimating the deepest level with unsupported $^{210}$Pb (e.g., Oldfield et al., 1995; Malmer and Wallen, 1999), the inventories of Pb (728–894 mg m$^{-2}$ in Store mosse and 192 and 367 mg m$^{-2}$ in Rödmossamyran) and Hg (1.24–1.62 mg m$^{-2}$ in Store mosse and 1.07 and 1.15 mg m$^{-2}$ in Rödmossamyran) vary by 22–91% and 8–30%, respectively (Table 1), which is in the general range shown for previous studies on Store mosse, Rödmossamyran, and elsewhere (Bindler et al., 2004; Rydberg et al., 2010). Notably for Rödmossamyran the difference in Hg is lower than in previous work (1.9 and 3 mg m$^{-2}$) and the difference in $^{210}$Pb (2200 and 3200 Bq m$^{-2}$) is higher (cf. Rydberg et al., 2010).

Although differences in inventories occur between cores, particularly for Rödmossamyran, the ratios between $^{210}$Pb inventories and those for $^{137}$Cs, and total Pb in F1 and S1 are rather similar: $^{137}$Cs/$^{210}$Pb is 2.94 and 2.87 in F1 and S1, respectively, and Pb/$^{210}$Pb is 0.094 and 0.113 in F1 and S1, respectively. The similarities of these ratios suggest that the composition of deposition to each core site is the same, although inventories indicate that the amount accumulated in each core differs. This is further supported by the $^{206}$Pb/$^{207}$Pb isotope data from three Store mosse peat cores presented in Bindler et al. (2004). Their results suggest that the 3 cores record the same isotopic signal of lead deposition over time, yet the actual Pb concentration varied between cores indicating a within-site variability.

### 3.2. Time trends in metal deposition from biomonitoring (forest mosses) and deposition data

In Figs. 2 and 3 we show the calculated Pb deposition rates since 1970 based on biomonitoring moss data (data host, IVL.se) from sites in south-central Sweden, which are extended back to 1870 based on analyses of herbaria samples (Naturvårdsverket, 1987). Moss Pb concentrations were transformed to deposition rates based on the linear relationship shown in Rühling and Tyler (2001) using the Swedish monitoring program (similar regressions have been shown for Norway; Berg and Steinnes, 1997). The moss data indicate a 3-fold increase in Pb deposition from the 1870s to the peak recorded in 1970 (3.2 to 10.3 mg $m^{-2}$ $yr^{-1}$). Since 1970 Pb deposition has decreased by > 90% to 0.4 mg $m^{-2}$ $yr^{-1}$ in 2005, with the most rapid decline occurring in the late 1970s–1980s and more gradually thereafter. Wet deposition measurements (data host, IVL.se) show a larger decline from 20–50 mg $m^{-2}$ $yr^{-1}$ in the late 1980s (3 active stations in southern Sweden) to about 0.2–0.3 mg $m^{-2}$ $yr^{-1}$ currently (2 active stations).

Mercury was not regularly included in monitoring programs until the mid-1980s, therefore fewer data are available for comparison (Munthe et al., 2001, 2007), and no regression between moss concentrations and deposition is available. A limited forest moss survey ca. 1970 compared to regular monitoring from 1985 indicates that mercury deposition had declined about 50% over this period, from a national average of 186 in 1970 to 78 ng $g^{-1}$ in 1985, and further to 58 ng $g^{-1}$ in 1995 (Rühling and Tyler, 2001). Wet deposition of Hg in the late-1980s in southern Sweden was 10–27 μg $m^{-2}$ $yr^{-1}$ (Iverfeldt et al., 1995) and about 5–10 μg $m^{-2}$ $yr^{-1}$ in the 1990s–early 2000s with only a slight declining trend occurring during this latter period.

### 3.3. CRS accumulation rates

Based on CRS modeling (Appleby, 2008), the maximum mass peat accumulation rate in the uppermost layers of the 5 cores is calculated as 415–630 g $m^{-2}$ $yr^{-1}$ for Store mosse, and 415 and 427 g $m^{-2}$ $yr^{-1}$ for F1c and S1c, respectively (Figs. 2a and 3a). These values are more than twice those typically reported for such mires; e.g., typical recent mass accumulation rates range from 30 to 300 g $m^{-2}$ $yr^{-1}$ for sites in Sweden including Store mosse (Malmer and Wallen, 1999), the UK (Clymo, 1970), and Germany (Kempter and Frenzel, 2007). Based on the evidence from $^{7}$Be, i.e., that a significant fraction of the $^{7}$Be activities could be detected below the surface, we suggest that our two-fold higher mass accumulation rates are caused by downwashing of $^{210}$Pb, which results in an underestimate of the ages of the upper layers in the conventional CRS age–depth model (Biester et al., 2007). This problem of underestimating ages was observed, for example, in a peat core from Stor Åmyran, which is only ~10 km from Rödmossamyran, by Oldfield et al. (1997), who identified a tephra layer originating from the AD 1875 eruption of Askja at depth with a CRS date of 1927.

Underestimation of peat ages would result in overestimates of peat accumulation rates but also to problems establishing Pb and Hg accumulation rates. Comparing monitoring to the CRS-modeled record there are two main differences. First, as seen in our calculated accumulation rates based on the CRS-model (Figs. 2 and 3), there is an increasing trend in

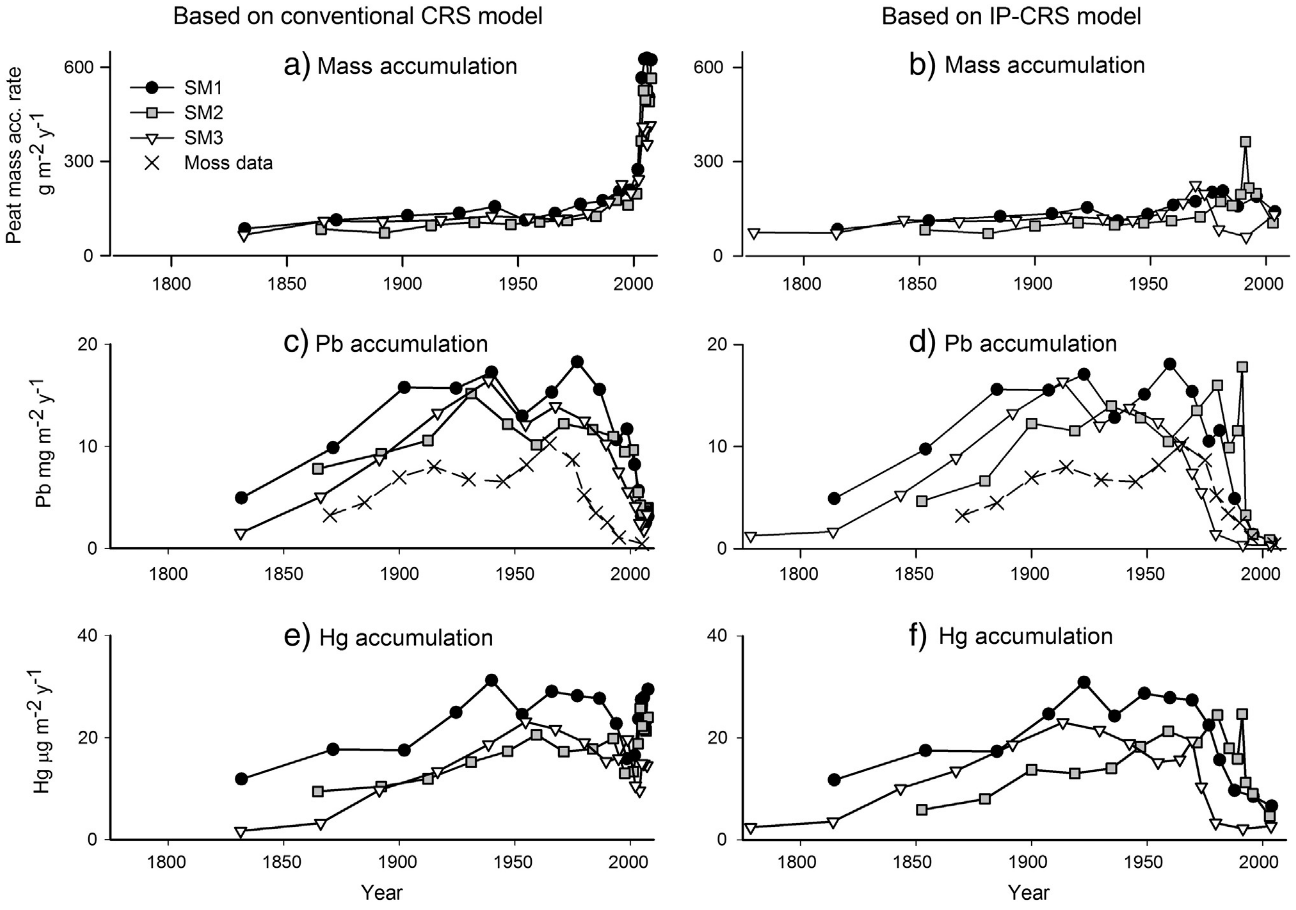

**Fig. 2.** (a) Store mosse: peat mass accumulation (g $m^{-2}$ $yr^{-1}$) vs. year based on CRS model. (b) Peat mass accumulation (g $m^{-2}$ $yr^{-1}$) vs. year based on IP-CRS model. (c) Pb accumulation (mg $m^{-2}$ $yr^{-1}$) vs. year based on conventional CRS model + modeled Pb deposition (mg $m^{-2}$ $yr^{-1}$) from biomonitoring moss data (IVL.se, Naturvårdsverket, 1987). (d) Pb accumulation (mg $m^{-2}$ $yr^{-1}$) vs. year based on IP-CRS model and modeled Pb deposition. (e) Hg accumulation (μg $m^{-2}$ $yr^{-1}$) vs. year based on CRS model. (f) Hg accumulation (μg $m^{-2}$ $yr^{-1}$) vs. year based on IP-CRS model. SM1 (filled circles), SM2 (gray squares), SM3 (open triangles) and for panels c and d biomonitoring moss data (crosses).

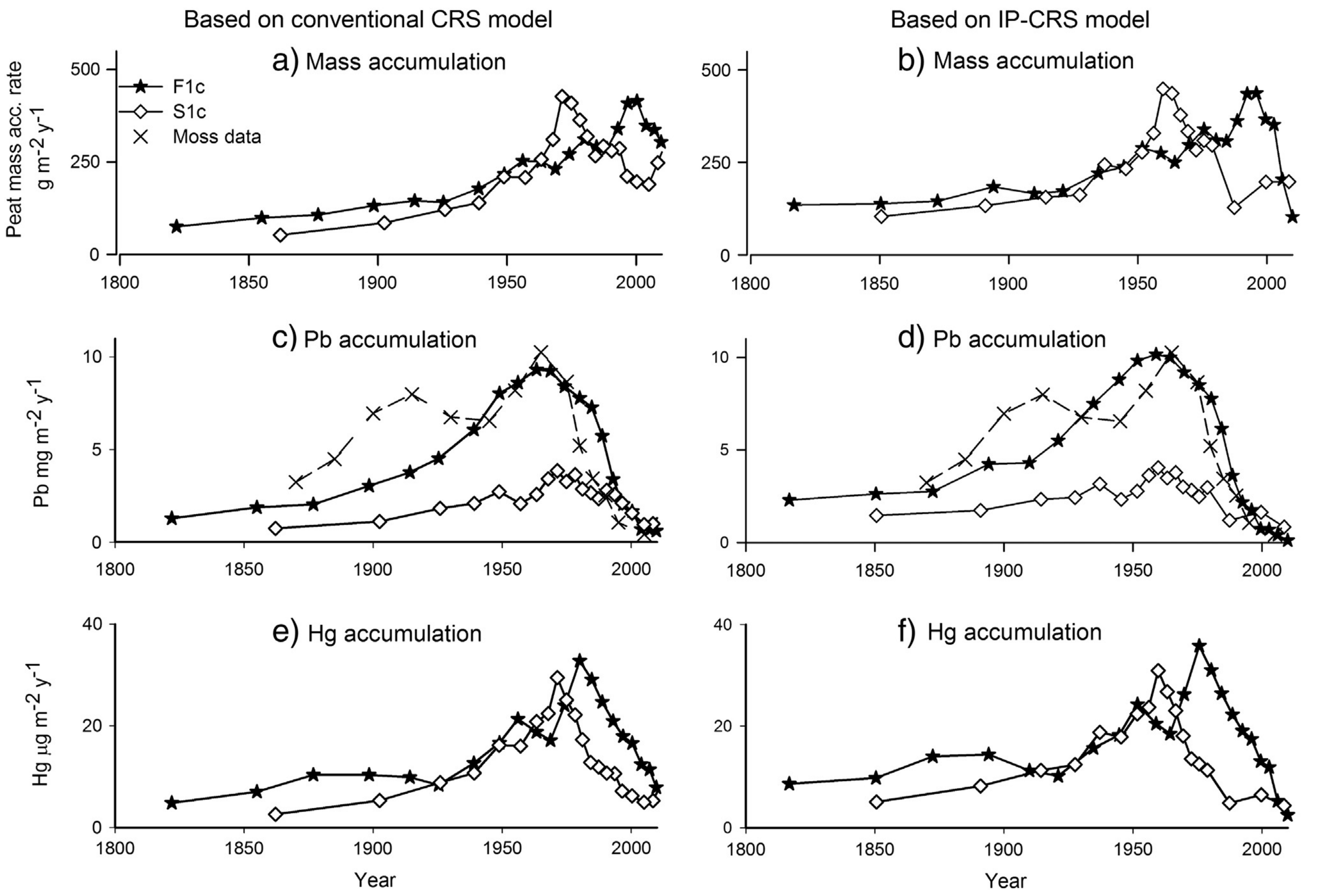

**Fig. 3.** (a) Rödmossamyran: peat mass accumulation (g $m^{-2}$ $yr^{-1}$) vs. year based on CRS model. (b) Peat mass accumulation (g $m^{-2}$ $yr^{-1}$) vs. year based on IP-CRS model. (c) Pb accumulation (mg $m^{-2}$ $yr^{-1}$) vs. year based on conventional CRS model + modeled Pb deposition (mg $m^{-2}$ $yr^{-1}$) from biomonitoring moss data (IVL.se, Naturvårdsverket, 1987). (d) Pb accumulation (mg $m^{-2}$ $yr^{-1}$) vs. year based on IP-CRS model and modeled Pb deposition. (e) Hg accumulation (μg $m^{-2}$ $yr^{-1}$) vs. year based on conventional CRS model. (f) Hg accumulation (μg $m^{-2}$ $yr^{-1}$) vs. year based on IP-CRS model. F1c (filled stars), S1c (open diamonds) and for panels c and d biomonitoring moss data (crosses).

both Pb accumulation and Hg accumulation in recent years, which contradicts the clear declining trend observed in monitoring, and the accumulation rates are substantially higher than recent deposition rates. The calculated Hg accumulation rates based on the CRS model (Fig. 2e) are unrealistic with recent accumulation rates of 15–30 μg $m^{-2}$ $yr^{-1}$, which are analogous to measured wet deposition rates in the 1980s. Second, based on monitoring, as well as lake-sediment records including annually laminated sediments (Renberg et al., 2001), Pb deposition has declined ~90% since 1970. Whereas this decline occurred most rapidly earlier in this period and has been slower in the past decade in monitoring, the output of the CRS model for our peat cores (Fig. 2c) would suggest that the decline in Pb accumulation has unrealistically occurred mostly in the past several years, and more critically that there is an increasing accumulation in recent peat.

### 3.4. IP-CRS accumulation rates

To compensate for the effect of downwashing indicated by our $^{7}$Be results we applied the newly proposed IP-CRS model by Olid et al. (under revision). This model corrects for downwashing of $^{210}$Pb in the uppermost peat layers and represents a first approximation to incorporate downwashing. Based on the depth of the initial exponential decline of $^{7}$Be in each core, the IP-CRS model assumes that downward transport occurred in the uppermost 4 cm and 8 cm as measured in F1c and SM3, and the upper 12 cm of SM1, SM2, and S1c. The model output reduces the estimated peat mass accumulation rates in the uppermost layers in Store mosse to 105–140 g $m^{-2}$ $yr^{-1}$, and in Rödmossamyran to 105 and 200 g $m^{-2}$ $yr^{-1}$ for F1c and S1c, respectively (Figs. 2b and 3b), which are in closer agreement with published values for peat in these mire types. The IP-CRS model also yields accumulation rates of Pb and Hg that are in better agreement with the temporal trends and deposition rates from the biomonitoring data, than those estimated from the conventional CRS-model.

Using the IP-CRS model for both sites the calculated Pb accumulation rates follow the temporal trends indicated by the biomonitoring data to a greater extent. In Store mosse the model shifts the decline in Pb accumulation back to the 1980s–1990s, which is still somewhat later than indicated by monitoring, but in Rödmossamyran the decline in accumulation follows the established trend more closely. The most recent Pb accumulation rates (0.3–0.8 mg $m^{-2}$ $yr^{-1}$) are in close agreement with biomonitoring data (0.4 mg $m^{-2}$ $yr^{-1}$). Pb accumulation rates for Store mosse for the entire period are higher than those indicated by monitoring, which may be due to a number of factors we cannot address, such as the specific deposition on Store mosse relative to the average value from the regional biomonitoring. For Rödmossamyran the apparent difference in Pb accumulation between cores is likely due to the greater surface unevenness on the main fen section, which has field-layer vegetation including vascular plants, than the more even surface of the *Sphagnum* lawn (Rydberg et al., 2010). A second critical factor is that we show that downwashing affects $^{7}$Be, and in laboratory studies also Pb and other pollutant metals; thus, would not metal deposition need also to be corrected for downwashing? This contradiction must therefore be resolved in future studies and possibly justify the discrepancies seen between the model output and monitoring data.

The calculated Hg accumulation rates for both sites also show better agreement with monitoring data; notably the lack of an increasing trend in recent times as given by the CRS-model. Instead, Hg accumulation (Figs. 2f and 3f) shows a decreasing trend during the last decade or more from peak values of 23–31 μg $m^{-2}$ $yr^{-1}$ to ~3–7 μg $m^{-2}$ $yr^{-1}$ in Store mosse, and from 31–36 μg $m^{-2}$ $yr^{-1}$ to 3–5 μg $m^{-2}$ $yr^{-1}$ in Rödmossamyran, which is closer to measured deposition trends, although the fact that accumulation is equally high at the northern site as at the southern site was unexpected. However, Hg inventories are also only about 25% lower at the northern than the southern site and given the history of pulp and paper industries in and around Umeå, there is support for the high peak fluxes in the northern mire. As is the case for Pb, the IP-CRS model still indicates a lag relative to monitoring. With either model, the peak in Hg accumulation in the two Rödmossamyran cores is still not synchronous, with the S1c peak occurring in the 1960s, which is similar to an annually laminated sediment record 140 km to the SW (Rydberg et al., 2008), whereas the F1c peak occurs in the mid-1970s.

## 4. Conclusion

Beryllium-7 data from 5 peat cores provides compelling evidence that downwashing of atmospherically supplied elements occurs. Downwashing is also evident when we make quantitative comparisons of the peat accumulation rates and metal accumulation rates calculated from application of the CRS-model to data on peat accumulation for similar mire types and to data from monitoring programs for trace metal deposition (wet deposition and moss biomonitoring). Peat accumulation rates from the CRS-model yield unusually high mass accumulation rates for our cores, while the CRS-model generates a chronology of atmospheric metal deposition substantially different from monitoring; namely a decline in Pb only over the last decade as opposed to since 1970 and for Hg a slight or significant increase in recent accumulation although monitoring indicates declines since at least the late 1980s. Ongoing development of a (IP-)CRS-model by Olid et al. (under revision) that includes an advection term that can accommodate the effect of downwashing, which in the case of our cores is informed by the initial exponential decline in $^{7}$Be in each core, into $^{210}$Pb age–depth modeling is a step forward. Application of that model yields accumulation rates and trends for Pb and Hg that are closer to monitoring than is the case with a conventional CRS model, yet some differences between cores and between the peat records and monitoring occur. One factor is that the $^{7}$Be measurements represent the distribution of downwashing at one occasion, but it likely varies over time, for example in years with exceptional rain events. In addition, the complexity of downwash in peat as shown for $^{7}$Be in 2 of the 3 Store mosse cores, with higher activities at depth, is not fully accounted for in either model.

Most importantly for our objective here, i.e. to test how downwashing of the radioisotopes used for age–depth modeling might influence our quantitative estimates of accumulation rates, we find that uncritical application of the CRS model to our cores yielded unrealistic quantitative estimates for metal deposition in comparison to monitoring data and sediment records. $^{7}$Be data here, and experimental studies, provide evidence that rapid downwashing can explain this uncertainty in the CRS output. Improving age–depth models by allowing for such mobility, such as the proposed IP-CRS, is a step forward to correct for this effect.

## Acknowledgments

The authors wish to thank Gaël Le Roux and Jonatan Klaminder for valuable discussions during different stages of the project regarding the data and modeling; the County Administrative Board of Jönköping for granting permission for fieldwork within Store mosse National Park. This research was supported by grants from the Swedish Research Council, the Kempe Foundation, and Stiftelsen Anna och Gunnar Vidfelts fond för biologisk forskning. We also thank David Diego, Albert Benseny and Jordi Garcia-Orellana for the support in running the IP-CRS calculations.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.05.088.

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