Incorporation and preservation of geochemical fingerprints in peat archives

Sophia V. Hansson
Till minne av

Patrick, Magnus och MickE
-
Som också borde vara här...
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Abstract

The present status of the environment, including environmental problems such as heavy metal accumulation in aquatic and terrestrial ecosystems, is in part the consequence of long-term changes. Cores from peatlands and other natural archives provide us with the potential to study aspects of the atmospheric cycling of elements, such as metal pollutants, on timescales much longer than the decade or two available to us with atmospheric deposition monitoring programs. The past decade especially has seen a rapid increase in interest in the biogeochemical record preserved in peat, particularly as it relates to environmental changes (e.g. climate and pollution). Importantly, recent studies have shown that carbon dynamics, i.e., organic matter decomposition, may influence the record of atmospherically derived elements such as halogens and mercury. Other studies have shown that under certain conditions some downward movement of atmospherically deposited elements may also occur, which adds complexity to establishing reliable chronologies as well as inherent problems of estimating accurate accumulation rates of peat and past metal deposition. Thus, we still lack a complete understanding of the basic biogeochemical processes and their effects on trace element distributions. While many studies have validated the general temporal patterns of peat records, there has been a limited critical examination of accumulation records in quantitative terms. To be certain that we extract not only a qualitative record from peat, it is important that we establish a quantitative link between the archive and the few to several decades of data that are available from contemporary monitoring and research. The main objective of this doctoral thesis was to focus on improving the link between the long-term paleorecord and the contemporary monitoring data available from biomonitoring and direct deposition observations. The main research questions have therefore been: Are peat archives an absolute or relative record? And how are geochemical signals, including dating, incorporated in the peat archive? What temporal resolution is realistic to interpret by using peat cores?
# List of papers

This doctoral dissertation is based on the following four papers, which are referred to in the text according to their Roman numerals.

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Glossary

Accumulation rate – The rate in which peat or elements accumulate in the peat column.

Acrotelm – The upper, actively growing and aerated layer of a bog. Consists of living parts of sphagnum, litter and partly degraded material, and is only temporarily saturated as it lies above the average water table; most of the decomposition and loss of organic matter occurs here.

Aerosols – A colloid of fine (smaller than 1 μm) solid particles or liquid droplets in air or another gas. Examples of aerosols include clouds, haze, and air pollution such as smog and smoke.

Americium-241 – (241Am), A radioactive isotope associated with, and released to the atmosphere from, nuclear weapon test. 241Am is considered to attach onto organic material to a higher extent than 210Pb and 137Cs and is therefore considered less mobile in peat. Due to its specific origin from nuclear weapon test (occurring during the 1960s), 241Am should show a distinctive peak in the upper peat profile.

Beryllium-7 – (7Be), A short-lived cosmogenic isotope formed in the atmosphere through spallation of nitrogen and oxygen by high-energy cosmic-ray particles, where after it quickly attaches to aerosol particles and deposits through both wet and dry deposition. Has a continuous production in the atmosphere and the mean tropospheric residence time of 7Be is estimated to be 22 – 48 days. Due to its natural origin and short half-life (53.3 days), 7Be is frequently used as a tracer in environmental applications.

Bog – Ombrotrophic mire, which are acidic and poor in nutrients. Can either be raised bog – dome shaped with low mineral content and completely fed by rainwater – or blanket bog – found on lowlands with high rainfall intensities, shallower and forming a blanket-like cover over the underlying soil

Bulk density - The mass of a material divided by the total volume that the mass occupy. Used as an approximation for peat decomposition in geochemical studies. Bulk density increases with depth through the peat column as decomposition results in a loss of strength in the organic matrix, which leads to compaction as more mass is accumulated above.

Carbon/nitrogen ratio – The ratio between Carbon and Nitrogen is often used as an approximation for peat decomposition in geochemical studies. Often abbreviated to C/N. The C/N-ratio will decrease with depth through the peat column as carbon is lost from the acrotelm to the lower catotelm during the decay process while nitrogen is considered generally conservative.

Catotelm – The lower, completely saturated and mostly anoxic peat layer below the acrotelm.

Cesium-137 - (137Cs), A radioactive isotope that, like 241Am, is associated with, and released to the atmosphere from, nuclear weapon tests. 137Cs is also associated with the failures of nuclear power stations, notably the Chernobyl accident in 1986. 137Cs has been shown to be mobile in peat where it is easily incorporated in the vegetation, therefore causing difficulties to accurate date peat records independently, however it is widely used as supportive information in 210Pb-dating techniques.

Copper – A chemical element with the chemical symbol Cu and atomic number 29. Although an essential element to life organisms, Cu can also be found as contaminant metal in peat.

Decomposition – The process by which organic substances are broken down into simpler forms of matter. Similar terms are “rotting” or degradation.

Downwash – the process which 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. Not a question of post-depositional mobility but an extension of the actual deposition itself.

Fen – a minerotrophic mire with a permanent water table close to the surface. It receives input not just through the atmosphere (aerosols, rain, snow, fog) but also from groundwater and surface run-off. Tends to be more alkaline and nutrient rich than ombrotrophic mires (bogs). Can be subdivided into oligotrophic mires or eutrophic mires based on their trophic status.
**Hollows** – The depleted area which is permanently or seasonally filled with stagnating water and where aquatic plants and Sphagnum species are developing.

**Humification** – The process where the organic substrate is broken down (through decomposition) into humus and humic or fulvic acids are released.

**Hummocks** - Hummock is a general geological term referring to a small knoll or mound above ground. On peatlands hummocks are the elevated area (humps) raised by sphagnum colonization.

**Lawn** – referred to here as the homogenous and flat area situated between hummocks and hollows and is covered by mosses.

**Lead** – A chemical element with the chemical symbol Pb and atomic number 82. Regarded as a heavy metal that is generally considered immobile after deposition in peat layers. Often found in peat as a contaminant that is toxic to the environment. Although naturally occurring Pb is usually connected to pollution.

**Lead-210** - \(^{210}\text{Pb}\), a radioactive lead isotope that is formed through the alpha decay of \(^{226}\text{Ra}\) in soil into \(^{222}\text{Rn}\), a noble gas, which escapes to the atmosphere and decays into \(^{210}\text{Pb}\). It has a continuous production, an atmospheric residence time of 4.8±0.3 days and a half-life of 22 years. \(^{210}\text{Pb}\) is widely used to date surficial peat deposits, sediments, and soils providing chronology on a 100-150 year scale.

**Light transmission** – an approximation of humification. During humification (degradation of organic matter into humus), humic or fulvic acids are formed and released which are both dark brown in solution. A darker solution will transmit less light, indicating a higher degree of humic acids and a higher degree of decomposition; that is, the darker the solution the more decomposed material. Light transmission will decrease with depth through the peat column.

**Mercury** – A chemical element with the symbol Hg and atomic number 80. Also known as quicksilver. Hg is heavy metal contaminant that is toxic to the environment. Although naturally occurring Hg is usually connected to pollution.

**Minerotrophic** – See Fen above

**Mire** – An English variation of the Swedish word “myr” that includes all peatland habitats with active peat formation. Similar to the term active peatland.

**Monolith** – In technical terms a geological feature consisting of a single massive stone or rock formed by erosion, here it is referred to the single peat “square” cut out and removed from the peat surface using a handsaw rather than a surface corer, thereby reducing the risk of compaction through coring.

**Oligotrophic** – nutrient poor fens, comes from the Greek words ologos meaning few and trophicos meaning feeding

**Ombrotrophic** – Comes from the Greek words ombro meaning rain and trophicos meaning feeding.

**Ombrotrophic mire** - Usually dome shaped peat or raised bog which receives all its input solely from atmospheric deposition (aerosols, rain, snow, fog). Acidic and poor nutrient content. (See bog)

**Peat** – General term for the matrix in peatlands which is formed by accumulation of partially decayed vegetation under wetland conditions where flooding obstructs flows of oxygen from the atmosphere, slowing rates of decomposition. The major component is Sphagnum moss, although many other plants can contribute. Soils that contain mostly peat are known as a histosol.

**Stratigraphy** (peat-) - a branch of geology which studies rock or peat layers and layering (stratification). Refers here to the various layers throughout the peat column which represents various stages of peat formation and vegetation composition.

**Titanium** – A conservative chemical element, i.e. not involved in biogeochemical processes that will lead to a redistribution of the element and therefore considered immobile, with the symbol Ti and atomic number 22.

**Zinc** – A contaminant metal with the chemical symbol Zn and atomic number 30. Often considered mobile in the peat column.
Introduction

Environmental changes occurring long-before modern monitoring series need to be assessed using natural archives, such as ice-core, lake sediments and peat bogs, where information about past conditions can be preserved. These natural archives, i.e., cores from soils, lakes, and peatlands, provide us with a powerful means to study past atmospheric deposition and carbon cycling on timescales longer than the years to few decades available from field studies or direct monitoring programs. Since the late 19th century the environmental archive represented by the net accumulation of organic matter preserved in peatlands has been of interest to scientists aiming to reconstruct long-term environmental changes (e.g., Sernander 1892; Weber 1899). Originally the focus of this early peat research was on changes in the peat-forming plant macrofossils and how these reflected the development of the bogs through time (von Post 1913; Granlund 1932), as well as on changes in the pollen assemblage and how they could be used in climate reconstructions (Granlund 1931). But with the groundbreaking study from, e.g., Lee and Tallis (1973), who showed that peat records could be used as a natural archive of past atmospheric contamination, the interest in exploiting the potential of peat records expanded to include geochemistry and the information geochemical records in peat could provide on past environmental changes (Aaby and Jacobsen 1978).

Over longer timescales (decades to millennia) it is now well established that there is a temporal coherence among peat records and between peat and other archives, which supports the utility of peat records for studying long-term environmental changes. The most prominent example is that of lead for which there are now many studies that have shown a cohesive record of atmospheric pollution for the last few thousand years preserved in peat and in other natural archives such as sediment records (Renberg et al 2001). But along with establishing long-term patterns, studies have also tried to quantitatively validate the peat record by comparing it to other media such as moss samples from herbaria collections - at least in terms of matching the isotopic composition of the lead between the peat archive and chronologically well-defined herbaria samples (Weiss et al. 1999; Farmer et al. 2002).

Since the development of biomonitoring based on the use of forest mosses, several studies have shown that the concentrations of many pollutant metals in forest moss are strongly correlated to annual atmospheric wet deposition rates (Ross 1990; Berg et al. 1997; Rühling and Tyler 2001). Because bryophytes (i.e., forest mosses such *Hylocomium splendens* and *Pleurozium schreberi* in Scandinavian biomonitoring) and lichen have a relatively large surface area to intercept deposition, and a strong binding capacity for metals as well as the fact that they lack roots and therefore take up metals supplied essentially via only atmospheric deposition (wet and dry
deposition), they are highly suitable as tools to monitor the deposition of metals (Rühling and Tyler 1968, 1970; Ross 1990; Steinnes et al. 1992). Although the main focus has been on the record of Pb contamination, which includes the use of stable Pb isotopes, the fact that peat records, forest moss and herbaria mosses all show a cohesive pattern of Pb deposition over the last 150 years is an important factor that supports the utility of peat records as an archive of past deposition (Weiss et al. 1999; Farmer et al. 2002; Bindler 2011).

Because ombrotrophic bogs are by definition strongly coupled with the atmospheric supply of many elements, peat records from such bogs are considered particularly useful as a biogeochemical archive for studying the past atmospheric deposition of soil dust (Shotyk et al. 2002; Björck and Clemmensen 2004; Kylander et al. 2007; 2013), pollutant trace metals (Shotyk 1998; Martinez-Cortizas et al. 1999), as well as climate change (Chambers et al. 2007; Martinez-Cortizas et al. 2012). Given the importance of peatlands 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 (Gorham 1991; Fenner et al. 2007; Malmer et al. 2011).

However, a number of studies over the past few decades have also identified several factors that can affect the integrity or temporal accuracy of the recent peat record. These factors potentially include decomposition (Biester et al. 2003, 2012), nutrient cycling (Malmer 1962; Danman 1978; 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; Rydberg et al., 2010; Martínez-Cortizas et al. 2012). During the decomposition process organic compounds
are reorganized and the peat will experience a loss of mass, which might have a strong influence on metal concentrations and their accumulation rates (Biester et al., 2003; Kuhry and Vitt, 1996). An important component of interpreting the geochemical record is therefore to understand the influence of organic matter decomposition and how it affects the geochemical record.

Furthermore, a number of researchers have hypothesized that downwashing or post-depositional remobilization can occur, which could smear the profile of atmospherically supplied elements and even physical particles such as pollen within the uppermost peat layers (e.g., Damman 1978, Clymo and Mackay 1987; Urban et al. 1990; Oldfield et al. 1997; Biester et al. 2007). Of the factors that could affect the integrity and temporal accuracy of the peat record, downwashing is particularly pertinent. Downwashing would have an immediate influence on how and where atmospherically deposited metals are accumulated in the peat record, which would potentially include the atmospherically supplied radiometric isotopes most commonly used for radiometric dating of the recent peat record; for example, lead-210 ($^{210}$Pb), cesium-137 ($^{137}$Cs), and americium-241 ($^{241}$Am). Should these be distributed downwards into the peat during deposition it would thus have a direct effect on age-depth modeling and the establishment of reliable and precise chronologies in short-term peat records (Urban et al. 1990; Mitchell et al. 1992; Oldfield et al. 1995; Lamborg et al. 2002; Bindler et al. 2004; Bindler and Klaminder, 2006; Biester et al. 2007). This would in turn lead to inaccurate estimations of peat accumulation and thus also past deposition rates.

Although a great deal of effort has been placed on establishing the integrity of the long-term accumulation record in peat, we still lack a complete understanding of some of the basic biogeochemical processes and how these may affect trace element distributions. It is still unclear whether peat records fully represent a quantitative record or a qualitative record for the recent past (years to decades). If it is a quantitative record then it should be possible to quantitatively calibrate the peat record with direct monitoring data. The main research questions of this doctoral thesis have therefore been: Are peat archives an absolute or relative record? And, how are geochemical signals, including those relating specifically to dating, incorporated in the peat archive?
Objective

The main objective with this doctoral thesis could best be described by the conceptual sketch in Figure 1, which illustrates the potential to specifically link the long-term paleorecord to the few decades of contemporary monitoring data available from biomonitoring and direct deposition observations, as well as experimental studies. With current knowledge, we know that as the peat record is buried in the catotelm much of the information it contains will be preserved, enabling it as a functional environmental archive of long-term environmental changes. Although discussed initially during earlier studies on peat geochemistry exploring the processes controlling element distributions (e.g., Damman 1978), little focus in subsequent years, however, has been put on the processes in the acrotelm that might affect how the geochemical signals we wish to retrieve are actually incorporated into the archive.

If we want to truly validate the accuracy of the peat archive then we must take advantage of the few decades of monitoring data now available to us and link the peat record to those from contemporary monitoring. But before we can compare long-term paleo records to biomonitoring and direct deposition data, we must first understand the processes that incorporate and ultimately preserve geochemical signals in peat and how these can affect the integrity and accuracy of peat records as atmospheric deposition archives. More specifically: are peat archives an absolute or relative record? And how are geochemical signals, including dating, incorporated in the peat archive? To answer this I have therefore chosen to work solely with surface peat cores (30-50 cm length, spanning ≤500 years) thereby focusing on the transition between the aerated acrotelm and the anoxic catotelm. By doing so I could specifically target the interface between long-term and short-term records, thus enabling me to create a better link between paleo records and monitoring data.

The objective of each of the four papers included in this thesis was therefore to address and respond to the following research questions:

I. Does decomposition in peat bulk density, light transmission and carbon/nitrogen ratios (C/N) reflect the same patterns? Furthermore, how do each of these decomposition proxies relate to other geochemical data?

II. Is there evidence to support the hypothesis of an existing downwash in natural peat cores?

III. How do differences in precipitation intensities affect downwash of commonly studied pollutant metals in peat cores?

IV. How might downwashing affect reconstructions of peat mass accumulation, as well as past metal deposition, and how well will these reconstructions correlate with contemporary monitoring data?
Abstracts of the papers

Paper I.
Evaluating paleoproxies for peat decomposition and their relationship to peat geochemistry

Sophia V. Hansson, Johan Rydberg, Malin Kylander, Kerry Gallagher and Richard Bindler. 2013. The Holocene 23(12) 1666-1671

Abstract
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 change. Importantly, recent studies show that carbon dynamics, i.e., organic matter decomposition, can influence the record of atmospherically derived elements such as halogens and mercury. Most commonly bulk density, light transmission or carbon/nitrogen ratios (C/N) are used as a proxy to qualitatively infer the degree of decomposition in peat, but do these three proxies reflect the same patterns? Furthermore, how do each of these proxies relate to other geochemical data? To address these questions we analyzed bulk density, light transmission and C/N, as well as multi-element geochemistry (WD-XRF), in 3 hummock cores (70 cm in length, ca 500 years) from an ombrotrophic Swedish bog. To compare the proxies we applied principal component analysis (PCA) to identify how the proxies relate to and interact with the geochemical matrix. This was coupled with changepoint modeling to identify and compare statistically significant changes for each proxy. Our results show differences between the proxies within and between cores, indicating each responds to a different part of the decomposition process. This is supported by the PCA, where the three proxies fall on different principal components. Changepoint analysis also showed that the inferred number of changepoints and their depths vary for each proxy and core. This suggests that decomposition is not fully captured by any one of these commonly used proxies, and thus more than one proxy should be included.

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

Sophia V. Hansson, James M. Kaste, Keyao Chen and Richard Bindler
Accepted for publication following minor revision in Biogeochemistry

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 ($t_{1/2}=53.4$ d) 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 the depth of this depends on the properties of the peat, e.g., bulk density and decomposition as well as peatland hydrology.
Paper III.
Testing the downwash of atmospherically deposited metals in peat and the influence of rainfall intensity

Sophia V. Hansson, Julie Tolu and Richard Bindler.
Submitted to Science of the Total Environment

Abstract
Accumulation records of pollutant metals in peat cores have been frequently used to reconstruct past atmospheric deposition rates. While there is good support for peat as a record of relative changes in metal deposition over time, questions remain whether accumulation records represent a quantitative or a qualitative record. Several processes can potentially influence the quantitative record of which downwashing is particularly pertinent as it would have a direct influence on how and where atmospherically deposited metals are accumulated in peat. The aim of our study was two-fold: first, to compare and contrast the retention of Pb, Cu, Zn and Ni in peat cores; and second, to test the influence of different precipitation intensities on the potential downwashing of metals. Four different ‘rainfall’ treatments were applied to 13 peat cores over a 3-week application period, including both daily (2 or 5.3 mm d⁻¹) and event-based additions (37 mm d⁻¹, added over 10 hr or 1 hr). From our results two main trends were apparent: 1) there was a clear difference in retention of the added metals in the surface layer (0-2 cm), i.e. 21-85% for Pb, 18-63% for Cu, 10-25% for Zn and 10-20% for Ni. 2) For all metals and peat types the addition treatments resulted in different downwashing depths, i.e., as the precipitation-additions increased so did the depth at which added metals could be detected. Although the largest fraction of Pb and Cu were retained in the surface layer and the remainder effectively immobilized in the upper peat (≤10 cm), there was a smearing effect on the overall retention, where precipitation intensity exerts a strong influence on the vertical distribution of added trace metals. These results suggest that the position of a deposition signal in peat records would be preserved, but it would be quantitatively attenuated.

Paper IV.
Incorporation of radiometric tracers in peat and implications for estimating accumulation

Sophia V. Hansson, James M. Kaste, Carolina Olid and Richard Bindler
Submitted to Atmospheric Environment

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 five cores from two Swedish peatlands we addressed the consequence for 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 trends based on comparisons to monitoring data (forest moss biomonitoring and wet deposition). After applying the new 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 data from monitoring. We suggest that downwashing can be successfully traced using \(^{7}\)Be, and if this information is incorporated into age-depth models, it allows for a better calibration of peat records with monitoring data and better quantitative estimates of peat accumulation and past deposition.
Materials and methods

Study sites

By definition ombrotrophic bogs (i.e., ombro = rain and trophic = fed) are supplied with their nutrients, and thus also contaminants, only through atmospheric deposition and are essentially isolated from lateral groundwater inputs from surrounding mineral soils. In contrast, minerotrophic peatlands receive inputs not only from the atmosphere but may also be supplied to some extent by lateral groundwater influenced by the surrounding or underlying mineral soils. Most research on pollution records from peat cores has therefore focused on ombrotrophic bogs because of the fact they are supplied exclusively by atmospheric inputs (e.g., rain, aerosols, fog, snow), and thus relating these records directly with the atmospheric signal is simplified in part as compared to other continental archives. However, with careful evaluation many minerotrophic peatlands can also serve as good records of atmospheric metal deposition (cf. Shotyk et al. 1997). In this doctoral thesis, both mire types are included.

Rationale for the choice of study sites

Due to the geographical limitation of ombrotrophic bogs, which have their northern limit in central Sweden (Sjörs 1983, Almquist-Jacobson and Foster 1995), as well as the scientific question at hand, it is not always possible to choose between sites, but rather it is necessary to adjust to the peatlands that are available and assess their applicability. It is therefore important to include different types of peatland systems - and different types of peat - when studying the effects of processes influencing the peat record. For that reason this thesis is based on peat cores collected from two contrasting peatlands; Store mosse, a classic ombrotrophic bog in south-central Sweden, and Rödmossamyran, a minerotrophic fen in northern Sweden that includes a small open sphagnum lawn with some sphagnum hummock features, and denser oligotrophic or poor fen that transitions towards a pine mire at the edges (Korpela 2004). Both sites have also been subject to previous studies on both peat stratigraphy and mire development as well as geochemical studies, which provided detailed background information for both sites. For brevity only a short site description is included here. More detailed description and further details on sampling and sample preparation can be found in papers I-IV and references therein.

Store mosse

Store mosse (Figure 2) 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 (Svensson, 1988a), and peat formation was estimate to have started by 8000 BP (Svensson, 1988a); Kylander et
al. 2013). Extensive studies on the development of Store mosse have been previously published (Malmer et al., 1997; Malmer and Wallen, 1999; Svensson, 1986, 1988a, b,) as well as some geochemical studies e.g. Bindler et al (2004); Bindler and Klaminder (2006), Kylander et al (2013).

Figure 2. Location of Store mosse and Rödmossamyran in Sweden.

**Rödmossamyran**

Rödmossamyran (Figure 2) is a relatively small, ~7 ha, nutrient-poor (or 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.). The boreal forest surrounding the mire is underlain by thin, poorly-to-moderately sorted till re-worked during the isostatic rebound of the region. Based on the basal ages of two other mires in the region – 2400 BP for Stor Åmyran and 3800 BP for Sjulsmyran (Oldfield et al. 1997; Nilsson et al. 2001), which were formed by the same isostatic rebound and emergence from the sea – Rydberg et al (2010) estimated that Rödmossamyran transitioned from a marsh to a mire about 2500–2800 years ago. Rödmossamyran, although being one single site has two contrasting environments separated by a sharp vegetation boundary; a small open sphagnum lawn (~0.3 ha) dominated by *S. centrale* and *S. subsecundum*, and a more oligotrophic fen representing the dominant characteristics of the mire with a mixture of Sphagnum (*S. centrale, S. subsecundum and S. palustre*), shrubs (e.g., *Calluna vulgaris* and *Ledum palustre L.*) and small, thinly spaced pines (*Pinus sylvestris*) that increase in density towards the mire edge. Based on analyses of mercury in a transect from the mire edge in towards the sphagnum lawn, there was no indication of a groundwater influence on the metal inventories (Rydberg et al. 2010).

**Analytical methods**

The analytical techniques used to estimate the various geochemical parameters throughout the work of this doctoral thesis are all well-established, some (e.g. bulk density) even on a very fundamental level, and will therefore only be described here.
in brief as detailed information, including preceding sample preparation work, can be found in paper I-IV respectively.

Analysis of bulk density, light transmission, tot-C/N, Tot-Hg and WD-XRF were all conducted at the geochemical laboratory at Umeå University, Sweden. The instrumentations used was Hitachi U-1100 spectrophotometer with a 1-cm quartz cuvette for light transmission, Perkin-Elmer Series II CHNS/O analyzer 2400 operating in a CHN-mode only for tot-C/N, Perkin-Elmer SMS 100 thermal decomposition atomic absorption spectrometer for tot-Hg and a Bruker S8 Tiger WD-XRF with a Rh anticathode x-ray tube for the XRF analysis. The gamma spectrometry analysis were conducted at the radiometric laboratory at College of William & Mary, Williamsburg VA, USA. $^7$Be, $^{137}$Cs $^{241}$Am and $^{210}$Pb were all measured using a Canberra Broad Energy 5030 with high-purity intrinsic Ge detectors and ultra-low hardware with copper-lined 1000 kg lead shields.

**Statistical calculations**

**Z-scores**

To avoid the effects of scaling and variance between variables, the raw data in paper I were transformed into Z-scores ($Z = (X_i - X_{avg})/ X_{std}$), where $X_i$ is the measured concentration of an element in a sample, and $X_{avg}$ and $X_{std}$ are the average concentration and standard deviation. The purpose of using Z-scores is that it reduces all variables to a similar range of variation, while still keeping the relative variation of the original data.

**Principal component analysis (PCA)**

Principal component analysis (PCA) is a useful tool for interpreting large geochemical datasets (Biester et al., 2012; Kylander et al. 2013). By reducing the dimensionality of the data, the PCA transforms the interrelated variables into a new set of uncorrelated variables and a smaller number of factors, which provides insight into the structure of the variance of the parameters (Jolliffe 2002). In paper I we therefore applied a PCA to the data using SPSS Statistics v.18 to assess how bulk density, light transmission and C/N-ratio relate to the geochemical composition of the peat.

**Change point analysis**

Change point analysis is a statistical tool to overcome factors that introduce variation or noise within the geochemical records, allowing us to identity significant changes in the data set that might otherwise be clouded by noise (Gallagher et al., 2011). In paper I we therefore applied changepoint modeling to identify the locations of significant changes in each decomposition proxy within each core. Further details on the method can be found in Gallagher et al. (2011) and references therein.
Results & Discussion

While many studies have validated the general temporal patterns of peat records at large, with a focus on pollutant metal accumulations (Shotyk et al., 1996; Weiss et al., 1999; Renberg et al. 2001; Farmer et al., 2002; Novak et al., 2003), there has been a limited critical examination of accumulation records in quantitative terms where the metal accumulation record is expressly compared to data from monitoring (Le Roux et al., 2005). To be certain that we extract not only a qualitative record from peat, it is important that we establish a quantitative link between the archive and the few to several decades of data that are available from contemporary monitoring and research. More importantly: Are peat archives an absolute or relative record? And how are geochemical signals, including dating, incorporated in the peat archive?

Decomposition: Three proxies – one story?

Studies of peat-based environmental change reconstructions have utilized a range of proxies such as fossil lipids, plant macrofossils, testate amoeba, and carbon and nitrogen isotopic ratios to infer the degree of decomposition (humification) in peat (Blackford, 2000; Borgmark and Schoning, 2006; Menot and Burns, 2001; Nott et al., 2000) and, although proven reliable, they are often time consuming, operationally defined or relatively expensive procedures. The most common techniques used to assess the degree of peat decomposition have been bulk density (Chambers et al., 2011; Clymo, 1965; Fenton, 1982; Franzén, 2006; Johnson et al., 1990; Malmer and Wallen, 1993), light transmission or adsorption (reported as %T or %Abs, respectively) (Blackford and Chambers, 1993; Borgmark, 2005; Borgmark and Schoning, 2006; Caseldine et al., 2000; Yeloff and Mauquoy, 2006) or carbon/nitrogen ratio (C/N-ratio) (Kuhry and Vitt, 1996; Malmer and Holm, 1984; Malmer et al., 1997; Malmer and Wallen, 2004), all being relatively inexpensive and time efficient. All three of these proxies are well studied, including the driving mechanisms behind each proxy, yet there are few or any direct comparisons or critical evaluations of all three proxies in relation to each other within a geochemical framework. If they are proxies for one and the same thing, then by default they should also reflect the same information. In paper I we therefore aimed to answer the key question; do these three proxies show the same pattern and do they record the same information regarding the degree of peat decomposition?

Our first step was just to examine the raw data and determine whether we could extrapolate any general trends. All three proxies in all three cores did roughly follow the general behavioral patterns as expected from literature; i.e., bulk density decreased with increasing depth whilst light transmission and C/N-ratio decreased with increasing depth (Figure 3). However, clear variations not just in the absolute values...
but also the depths at which they occurred was evident between all three proxies and among cores. To avoid any effects of scaling or variance between variables, the data were also transformed in Z-scores, yet the differences remained.

**Decomposition proxies vs. PCA**

By including data on major and trace elements from WD-XRF analysis, and applying a principal component analysis (PCA) to the data set, we sought to identify the main factors influencing the geochemical composition, and how the three proxies related to these (Joliffe, 2002; Biester et al. 2012). If the three proxies record and describe the same decomposition pattern then they should group together within the same PC loading plot, yet regardless of whether the proxies were included as active or passive variables, the main component of each of the three proxies consistently placed on different PC loadings. Rather than helping us explain the similarities between the proxies, the differences between them became even clearer once the PCA was applied. Bulk density grouped primarily with the biophilic elements (elements associated with organic matter), light transmission with the relatively mobile or redox-sensitive elements and C/N-ratio with the conservative lithogenic elements. Based on the PCA outcome it therefore became clear that each decomposition proxy did not fully reflect the same signal, however, some common underlying process(es) must exist because the pattern of where the proxies placed within the PCA-scatterplots in relation to the geochemical data remained consistent. We therefore interpreted this as an indication that the proxies do not reflect one decomposition signal but merely different aspects of it.

![Figure 3. Results from the analysis of the three Store Mosse peat cores for a) bulk density (g cm$^{-3}$), b) light transmission (%Trans) and c) C/N-ratio (SM1, filled circles; SM2, gray squares; SM3, open triangles). (Reproduced with permission from SAGE Publishing.)](image)
**Decomposition proxies vs. changepoint analysis**

To further test the cohesiveness of the three proxies within each core and to test whether these three decomposition signals were spatially cohesive or spatially variable (i.e., consistent between cores), we applied a Changepoint model (Gallagher et al. 2011). This model statistically identifies the locations of significant changes in each decomposition proxy within each core. The output confirmed the results as seen in both the raw data and through the PCA; that is, there was a lack of correlation and common pattern in changepoints both within each core and among the cores. This indicated some within-bog spatial variability in the decomposition signal, which has previously been shown for both Pb and Hg as well as plant macrofossils in Store mosse (Bindler et al. 2004). Our conclusion was that although bulk density, light transmission and C/N-ratio all provide valuable information on peat decomposition, our results indicate that the decomposition signal is not fully captured by any one proxy. To get a more representative assessment of long-term biogeochemical changes and responses to environmental factors in peatlands, ideally one should always use a multi-proxy and, when possible, multi-core approach.

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**Paper I in a nutshell:**

Decomposition is not fully captured by any one proxy, as bulk density, light transmission and C/N-ratio reflect different patterns. Thus when studying decomposition patterns of peat bogs, a multi-proxy and multi-core approach should always be used to ensure that the full decomposition process is included in the interpretation.
Downwashing of atmospherically supplied elements in the field: Beryllium-7 as a natural tracer for downwash

Over the last quarter of a century several researchers have hypothesized that the fundamental assumption that $^{210}$Pb is immobile in the peat archive may not be entirely correct. Several studies have suggested with good evidence that some downward movement of atmospherically deposited elements may occur under certain conditions, which may then create difficulties in establishing reliable chronologies as well as inherent problems of estimating accurate accumulation rates of peat and past metal deposition (Damman, 1978; Urban et al. 1990; Mitchell et al. 1992; Oldfield et al. 1995; Benoit el al. 1998; Lamborg et al. 2002; Biester et al. 2007). However, to date no one has sought to actively test the question of a potential downwash of atmospherically deposited elements in peat. In paper II our aim was therefore to specifically address the question: Is there evidence to support the hypothesis of an existing downwash in natural peat cores?

**Beryllium-7 is the key**

In order to address our aim we first had to identify a tool to trace the potential downwash through the peat column, preferably in a natural way without any additions that could influence the results through an operationally defined procedure rather than measuring unimpeded downwash occurring under natural conditions. 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 & Olsen 2009; Kaste et al. 2011a; Kaste et al. 2011b). In the atmosphere $^{7}$Be quickly attaches to aerosols and is delivered to the earth’s surface primarily via wet deposition (Wallbrink & Murray 1996; Whiting et al. 2005). It also has a similar behavior as $^{210}$Pb ($T_{1/2} = 22$ yr, Lal & Suess 1968; Short et al. 2007) and Pb, which has been the foremost focus of previous studies raising the question downward transport/downwash in peat. Based on these characteristics, and the fact that $^{7}$Be can be measured at same time as $^{210}$Pb using gamma spectrometry, $^{7}$Be was an ideal tool to study short-term downwashing of atmospherically deposited elements in peatlands. Any $^{7}$Be activities measured below the peat surface would have to be have deposited on the mire within the past ca. 6 months or less.

**The hypothesis of downwash**

Our hypothesis was that if rapid downwashing occurred then dissolved $^{7}$Be would follow the percolating rainwater, thereby reaching deeper into the peat column before being immobilized through binding to the organic matter substrate. Originally the study only included the triplicate hummock cores from Store mosse, but in order to
meet some critique that was raised at an early stage regarding spatial variability and the representativity of the initial results for peat cores in general, we also later included two cores from Rödmossamyran. By doing so we could gain a more comprehensive view of downwash in peat, because our results would then be based on a total of five peat cores from two contrasting peatlands which, more importantly, represented three different types of peat; sphagnum hummocks in ombrotrophic bogs, and sphagnum lawn and fen-peat in an oligotrophic mire. We hypothesized that the open environment and well-aerated peat structure found on the sphagnum hummocks on Store mosse would facilitate a deeper gradient of downwashing, whereas on Rödmossamyran with a more compacted and dense fen peat would show an accumulation gradient of $^7$Be downcore more similar to those found in soils. For the sphagnum lawn, which has a high water table (at or near the surface), it was uncertain as to whether downwashing would be of a similar scope as for the hummocks, because of the open structure of the peat with a low degree of decomposition or whether the high water table would inhibit downwashing as shown in experimental additions in the laboratory (Wieder et al. 2010). It should be noted though, that at this point in time the aim of our study was to empirically study downwashing and was not implicitly mechanistic because we first had to address the hypothesis of downwash itself before delving into which processes that could cause it. The results from the gamma-spectrometry, however, confirmed our hypothesis on all accounts, yet both the depth at which $^7$Be could be detected, as well as the within site variability of the $^7$Be distribution were greater than anticipated.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Distribution with depth shown as \% of the total $^7$Be inventory in the three hummock cores from Store mosse and the sphagnum-lawn and fen core from Rödmossamyran.}
\end{figure}

**Empirical evidence**

Due to its high affinity to bind to organic matter, which leads to strong bonds with oxygen atoms on surfaces of organic compounds and inorganic minerals, $^7$Be is rapidly bound to soil and organic particles once deposited (Hawley et al. 1986; You
et al. 1989; Taylor et al. 2012). Experimental studies have also indicated that $^7$Be is not readily remobilized after deposition (Taylor et al. 2012). Thus, any $^7$Be measured at depth in peat must have been rapidly transported to these underlying levels, especially considering the short half-life of only 53.4 days. The deepest level at which we could detect $^7$Be activities ranged from only 2–4 cm in the fen core down to as deep as 18–20 cm in one of the sphagnum hummock cores, indicating variable degrees of downward movement in different peat environments. Even more interesting was the distribution pattern (Figure 4) that clearly showed that although the largest fraction (25-80%) was measured in the top 0-2 cm slice, the remaining $^7$Be was distributed down to the approximate height of the water table in two of three hummock cores and well below the water table in the sphagnum lawn, where the water table was at the lawn surface at the time of sampling. In addition, two of the hummock cores also exhibited an almost bi-modal distribution with secondary peaks found in the 12-20 cm depth interval. The implications of this are two-fold; first, some downward movement within the peat must exist in order for $^7$Be to be located at those depths, and second, the differences in distribution between cores and between sites indicates that there is a spatially variable component.

**If not downwash, then what?**

During the initial review process of this study, a critical concern was the differences in $^7$Be distributions between cores, particularly the two secondary peaks found in 2 of 5 cores. The critique put forward was that the differences in distribution undermined our conclusions of an existing downwash, i.e. since the depths of downwash was not conclusive between cores our result could not be interpreted as evidence for downwash. Yet, the question of spatial variability is not novel as several studies have shown that variations in geochemistry (as well as plant macrofossil composition) can occur even within very small distances. Considering the current knowledge on the spatial variability of geochemistry in peatlands (Benoit et al. 1998, Bindler et al. 2004, Coggins et al. 2006, Rydberg et al 2010), one cannot and should not expect that each core should show record the exact same distribution with depth. Since the design of this study was empirical rather than mechanistic in nature, we could only speculate as to why the second peak in activity occurred in 2 of 5 cores; however, the fact that any $^7$Be could be detected below the surface is strong evidence to indicate that a significant downward redistribution of recently deposited $^7$Be occurs. One could of course invoke a range of additional hydrologic processes and argue, for example, that lateral flow may be a possible explanation for the secondary peaks, but given the short half-life of $^7$Be, that alone cannot give a full explanation of the exponential decline of $^7$Be found throughout the cores. These deeper peaks are also a lesser component of the total $^7$Be inventory – the bulk of the inventory is retained in the upper aerated zone. Any relocation of $^7$Be by lateral flow still requires that recently deposited $^7$Be must first be rapidly transported to the groundwater table and transferred rapidly laterally (without
binding) through the peat. Whether this transport is downward or lateral would support our hypothesis in either case.

Based on the behavioral characteristics of $^7$Be, including its short half-life, we interpret our results as direct evidence that downwashing of atmospherically supplied elements does occur in certain environments, regardless of whether the $^7$Be was transported vertically through percolating rainfall or secondarily through horizontal redistribution by lateral flow. The differences in depths between the various peat types, indicates that the extent of downwash must be dependent upon peat characteristics, such as bulk density, fragmentation (and thus connectivity of pore spaces) and vegetation composition. The latter two would have implications for binding based on increasing surface area and the properties of the organic matter compounds present.

**Paper II in a nutshell:**

Yes, downwash of atmospherically deposited elements in peat does exist based on empirical evidence from five peat cores showing that $^7$Be can be measured as far down as 20 cm in well-aerated Sphagnum peat. The extent of this downwash will depend upon the properties of the peat (e.g. density, fragmentation) yet mechanistic processes e.g. hydrology cannot be excluded.
**Downwash in the laboratory:**
Retention of metals in relation to rainfall intensities

Based on the natural \(^{7}\text{Be} \) results of the five cores from Store mosse and Rödmossamyran, we had empirical evidence verifying our hypothesis that downwashing can occur in peatlands. However, we wanted to test to what extent this applies to other elements as well, in particular pollutant metals that are frequently studied using peat cores, and that we did not “just got lucky” with our field data, as was implied by one anonymous reviewer. We therefore conducted an additional experiment in the laboratory based on that used by Vile et al. (1999) and Wieder et al. (2010), who conducted their studies to demonstrate the immobility of atmospherically supplied elements. In those experiments they added dissolved Pb (Vile et al.) and dissolved Be (Wieder et al.) to ombrotrophic peat cores with different water table levels (3 cm, 15 cm and varying between 3 and 15 cm depth) to study the retention or mobility of these elements throughout the peat column.

**CuBr-addition**

With the assistance of a master’s student, four peat monoliths were collected from Rödmossamyran and placed in Plexiglas-boxes fitted with a mesh-bottom and brought back to the laboratory. Over a three week treatment period, a solution of 0.15g CuBr\(_2\) dissolved in 300 ml deionized water was gently added to two cores over ~1 hour - a rate equivalent to 14 mm of rain – and the additions occurred on a weekly basis over a three-week period. An equal amount of water was added to two control cores. We specifically chose CuBr\(_2\) as it completely dissolves in water and also that it would give us two separate tracers; Cu\(^{+2}\), a metal cation that binds rapidly to the organic matrix (Bunzel et al. 1976; Qin et al. 2006) and Br\(^{-}\) an anion that is bound to organic matter through interaction with humic substances and exists in peat mainly in organic form (Yamada 1968; Maw and Kempton 1982; Bietser et al. 2004; Zaccone et al. 2008).

This treatment yielded a total addition of 0.13 g Cu and 0.32 g Br, which were excessive concentrations of Cu and Br, 1000-fold greater than the ambient concentration; however, the resulting concentrations are similar to those found in the vicinity of metal smelters (Ukonmaanaho et al. 2004) after decades of loading. The reason for this high concentration addition was that we wanted to better capture the tail end of the downwashing, which we predicted would occur from the Vile et al. (1998) and Wieder et al. (2010) studies. This came at the cost of unrealistically high concentrations of Cu and Br. Recognizing that these high Cu treatment could potentially exceed the binding capacity of the peat, we re-performed the laboratory addition on a third monolith using a lower Cu concentration (2.523 mg over three weeks, further details see paper II). Despite the high addition in the first Cu treatment,
the new results showed distributions comparable to both the first Cu treatment, but also the distribution of Be shown by Wieder et al. (2010), i.e. 49 ±1 % of the added Cu was retained in the upper 0-2 cm section whereas the rest showed an exponential decline down to the height of the water table. The results of our laboratory treatments, in combination with the results presented previously by Vile et al. (1999) and Wieder et al. (2010), therefore became indicative that the hypothesis of downwashing would include not just ⁷Be, but Cu, Pb and total Be as well. Whereas the studies of Vile et al. and Wieder et al. had concluded the treatments provided evidence for limited mobility, and thus confirmation of a central premise in age-depth modelling that the dating radioisotopes are immobile, our field study and first experimental study together indicated that initial downwashing has a substantial effect on how some atmospherically supplied elements are distributed.

**Downwash and rainfall intensities**

During the review process of paper II critique was raised against not only the high concentrations applied in the experiment but also to the rate of addition, which was determined to be “a weakness that could not be overlooked”. Considering that our experimental set-up was based on that of Vile et al. (1999) and Wieder et al. (2010), and that the rate of addition (14 mm h⁻¹), in fact was in close agreement with naturally occurring rainfall events (see paper III), this comment was surprising. However, as we ourselves had begun to think of the effect various rainfall intensities might have on the extent of downwash, the idea of a new and more extensive experimental set-up, which would address this critique that was raised, came to life.

A total of 13 peat cores were collected from adjacent sides of the vegetation boundary on Rödmossamyran and placed in Plexiglas core boxes (designed and assembled solely for the study at hand). The cores were then randomly selected and subjected to 4 different rainfall treatments: Steady-low, Steady, Event and Flush, which were applied over a 3-week application period and consisted of both daily (2 or 5.3 mm d⁻¹) and event-based additions (37 mm d⁻¹, added over 10 hr or 1 hr). The artificial rain that was added to the cores followed that of Wieder et al. (2010) but was adjusted to the precipitation chemistry of the Umeå region with a pH of 4.7. In addition, the bulk artificial rain also included EPA Method 200.7 spiking standards 3 and 5, which contained four metals commonly studied in peat records and which we had chosen to study in terms of retention in peat (Pb, Cu, Zn and Ni).

Besides considering differences in mobility between the metals, the design of the experiment was set up to test how various rainfall intensities would influence the retention of metals in peat. Based on the knowledge that most rainfall is episodic and does not occur at an evenly distributed rate (SMHI.se; Hellström and Malmgren, 2004), but also that previous studies had ignored this factor (Vile et al. 1999; Wieder
et al. 2010) we wanted to capture a range of intensities varying from the annual daily average of the region (2 mm d$^{-1}$, i.e., Steady-low) to high, yet not extreme, episodic addition (37 mm 10 h$^{-1}$, i.e., Event). The hourly distribution of this Event treatment followed a rainfall event on 27 September 2012, as recorded at the weather station maintained by the Department of Applied Physics and Electronics, Umeå University (http://www8.tfe.umu.se/weather/1024/1440/10/sv-SE/history.htm). Similar events have been recorded at SMHI’s weather station at Holmön, 4 km east of Umeå, where hourly rainfall data are also available. In addition, we also wanted to trace any difference in downwash between different types of peat, hence the inclusion of both sphagnum lawn and fen cores.

The results from our study were two-fold: First, there was a clear difference in the depth to which elevated concentrations of each of the added metals could be detected with the order from the shallowest to the deepest being Pb<Cu<Zn≤Ni. This pattern is consistent with earlier studies on adsorption rates of metals in peat (e.g. Bunzl et al. 1976; Kerndorff and Schnitzer, 1980). This difference is also reflected in the retention of the added metals in the surface layer (0-2 cm), i.e., 21-85% for Pb, 18-63% for Cu, 10-25% for Zn and 10-20% for Ni, with the range in values dependent upon the varying treatment. Second, our results also showed that for both peat types and all metals the different treatments resulted in different downwashing depths, i.e., as the precipitation increased so did the depths of downwashing (Steady-low≤Steady<Event<Flush). From these results we can conclude that downwashing, in connection to rainfall events with higher intensities, exerts a strong influence on the vertical distribution of recently deposited metals in the upper, aerated, section of the peat. Although the largest fraction of Pb and Cu were retained in the surface, there was still a smearing effect on the overall retention. This suggests that the general position of a deposition signal, i.e., past metal pollution, would be preserved in peat records but that this signal would be quantitatively attenuated.

Paper III in a nutshell:

Based on results from 13 peat cores and 4 rainfall treatments, the retention of metals decreases in the order Pb<Cu<Zn<Ni. Higher precipitation, in terms of both quantity and intensity, leads to deeper downwashing of metals. It is unambiguously shown that downwashing during intense rainfall events exerts a strong influence on the vertical distribution of metals in peat.
The effect of downwash: Implications on estimated accumulation rates

Based on the empirical evidence in paper II and the experimental evidence in paper III, we concluded that we had sound evidence to support our hypothesis of downwashing of atmospherically supplied elements in peat. The continuance of this was, of course, to see what implications this would have on interpretations of the time trends for geochemical data in peat. For instance, as previous work had shown, difficulties in establishing reliable chronologies in peat records based on $^{210}$Pb age-depth models were believed to be caused by a downward transport or movement, which could also include remobilization (Malmer and Holm, 1984; Urban et al. 1990; Mitchell et al. 1992; Lamborg et al. 2002). We therefore wanted to address the consequence for estimating accumulation rates in the light of downwashing of atmospherically supplied elements, as previously shown by the analyses of $^7$Be; but also to look further at the representativity of single cores and the incorporation of atmospheric signals in peat. Our specific question was: How might downwashing of the radioisotopes used for age-depth modeling influence our quantitative estimates of peat mass accumulation rates and accumulation rates of metal pollutants?

To facilitate this we analyzed $^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^7$Be as well as total concentrations of Pb and Hg in five peat cores from Store mosse and Rödmossamyran ($^7$Be are also included in paper II). The results from these analyses are presented in Figure 5. A more detailed discussion regarding the distribution of these elements can be found in paper IV, but a brief synopsis follows here. Based on the results of our analyses, i.e., the lack of well-defined peaks in $^{241}$Am activities and the non-monotonic decline of $^{210}$Pb, we concluded that a rapid downwashing or smearing of atmospherically deposited radionuclides occurred not only for $^7$Be as shown previously in our cores (paper II), but for $^{210}$Pb as well. $^{241}$Am may likewise have been downwashed at the time of deposition or re-mobilized at a later time, but this cannot be separated here. The downwashing shown by $^7$Be and as we suggest from the initially increasing $^{210}$Pb activities in the upper layers contradicts a main assumption of conventional $^{210}$Pb dating models, e.g., the constant rate of supply (CRS) model (Appelby and Oldfield, 1978) which is the most applied dating model, that the radioisotopes upon which the model relies are immobile. To test this specifically, we applied two age-depth models to our data set: the conventional constant rate of supply (CRS) model (Appleby and Oldfield, 1978), as well as a new age-depth model, the so-called initial penetration CRS (IP-CRS) (Olid et al. In revision), which considers an initial downward movement in the upper section of the peat. To test the quantitative accuracy of our accumulation records we compared our data to reported peat mass accumulation rates for similar sites (and including previous work on Store mosse) and to deposition data available from monitoring programs (forest moss biomonitoring and wet deposition; IVL.se).
Figure 5. Bulk density, activities of $^{210}$Pb, $^{137}$Cs, $^{241}$Am and $^7$Be, as well as total concentrations of Pb and Hg as measured in the three cores from Store mosse (upper panel) and in the two cores from Rödmossamyran (lower panel).

**Monitoring data – the “facit”**

Previous studies in Sweden and Norway have shown that concentrations of trace metals in forest mosses can be directly related to absolute deposition rates (Ross, 1990; Berg et al., 1995; Rühling and Tyler, 2001). Using the equations relating the metal concentrations of the moss to annual wet deposition of the metals (Rühling and Tyler 2001), it was possible to reconstruct the past Pb deposition trend for the period from 1970 to 2010, based on biomonitoring moss data from southern Sweden (data host, IVL.se), which could then be extended back to 1870s based on analyses of Pb in herbaria samples (Naturvårdsverket Monitoring 1987). These results could then be compared to our accumulation rates from the five cores from Store mosse and Rödmossamyran. The monitoring data indicates a threefold increase (3.2 – 10.3 mg m$^{-2}$ y$^{-1}$) in lead deposition from the 1870’s to the maximum peak recorded in 1970 (the timing of which is supported by varved sediments from northern Sweden; Brännvall et al. 1999), after which Pb deposition decreased by >90% to 0.4 mg m$^{-2}$ y$^{-1}$. Wet deposition measurements of Pb (IVL.se) show a decline from about 20–50 mg m$^{-2}$ y$^{-1}$ in the late 1980’s to about 0.2–0.3 mg m$^{-2}$ y$^{-1}$ in present time. Mercury was not regularly included in monitoring programs until the mid-1980’s and therefore fewer data points are available for comparison (Munthe et al., 2001; Munthe et al., 2007).
However by comparing a limited forest moss survey in ca. 1970 to regular monitoring from 1985, there is indication that mercury deposition had declined about 50% over this period (from 186 to 78 ng g\(^{-1}\), Rühling and Tyler 2001). Wet deposition of Hg in the late-1980s was 10–27 µg m\(^{-2}\) y\(^{-1}\) (Iverfeldt et al., 1995) and about 5–10 µg m\(^{-2}\) y\(^{-1}\) in the 1990’s–early 2000’s.

**Conventional CRS model**

After applying the conventional CRS modeling (Appleby and Oldfield, 1987), the maximum peat mass accumulation rates in the uppermost layers of our cores were calculated to be in the range of 415-629 g m\(^{-2}\) y\(^{-1}\) in Store moss and 415-427 g m\(^{-2}\) y\(^{-1}\) in Rödmossamyran. These values, however, appeared unrealistically high because they are more than twice those typically reported for ombrotrophic bogs, based mostly on direct measurements of moss growth (30 to 300 g m\(^{-2}\) yr\(^{-1}\), Clymo, 1970; Malmer and Wallen, 1999; Kempter and Frenzel, 2007). Based upon our \(^{7}\)Be-data, our interpretation of the mass accumulation rates estimated by the CRS model in our cores, was that our two-fold higher mass accumulation rates were caused by downwashing of \(^{210}\)Pb below the peat surface, which resulted in an underestimation of the ages of the upper layers. This problem of underestimating ages was previously observed by Oldfield et al. (1997) in a study of a peat core from Stor Åmyran in northern Sweden (~10 km from Rödmossamyran), where a tephra layer, identified as originating from the AD 1875 eruption of Askja, had a CRS date of 1927.

The underestimation of peat ages in the CRS model output resulted in overestimates of peat accumulation rates, but also, more importantly, inaccurate estimations of past Pb and Hg accumulation rates. By comparison to the biomonitoring data, the conventional CRS-modeled accumulation records show two main differences. First, the CRS-model output suggests an increasing accumulation trend for both Pb and Hg in recent peat, which is opposite of the declining trend known from biomonitoring and wet deposition data (IVL.se; Rühling and Tyler 2001). The decline in Pb and Hg accumulation in the peat cores is not consistent with the established temporal pattern for deposition indicated by moss monitoring since ca. 1970 (and by sediment studies, cf. Renberg et al. 2001). Second, the conventional CRS model shows a ~two-fold higher (18 mg m\(^{-2}\) y\(^{-1}\)) Pb accumulation than the Pb deposition estimated from biomonitoring (10 mg m\(^{-2}\) y\(^{-1}\)). The accumulation rates based on the conventional CRS model therefore appear unrealistically high in comparison.

**Adjusted (IP)-CRS model**

By applying the IP-CRS model, which takes an instantaneous downwashing of atmospherically deposited elements into account, our estimated peat mass accumulation rates in the uppermost layers was reduced to 105-132 g m\(^{-2}\) y\(^{-1}\) in Store
mosse and to 103 and 198 g m\(^{-2}\) y\(^{-1}\) in Rödmossamyran, which are in closer agreement with published values for these mire types. Although the Pb accumulation still remained higher (4 -18 mg m\(^{-2}\) y\(^{-1}\)) than biomonitoring (10 mg m\(^{-2}\) y\(^{-1}\)) the IP-CRS model yielded accumulation rates of Pb and Hg that were in better agreement with the temporal trends and deposition rates from the biomonitoring data than those estimated from the conventional CRS-model. More importantly the increasing trend in deposition during recent years as seen in the CRS-model output, which is not supported by monitoring or direct deposition data, is no longer evident in the IP-CRS model output. However, for both Pb and Hg, the IP-CRS chronology of metal accumulation still indicates a lag relative to monitoring data. Further to this the peaks of Hg accumulation are not perfectly synchronous, particularly in Rödmossamyran. Two possible explanations for the remaining difference between monitoring and our reconstructions are: 1) that our one sampling occasion and the depth of downwashing indicated at this time by the \(^{7}\)Be does not perfectly capture the redistribution caused by downwashing; and 2) that the IP-CRS model does not include a redistribution of \(^{210}\)Pb that matches the complexity of the \(^{7}\)Be distribution, particularly as seen in the two Store mosse cores also having higher activities near the water table, which could underestimate the complete extent of downwashing. In spite of this, the IP-CRS model is still a first important step towards addressing the occurrence of downwashing in peat and it provides a valuable framework for moving forward to make better quantitative comparisons of peat records with the increasing number of years of monitoring data.

Based on the output from the two models, and from the comparison to monitoring data, we concluded that applying a conventional CRS model without considering the possibility of downwashing can lead to an overestimation of peat mass accumulation rates – and thus also inaccurate trace metal accumulation rates and incorrect temporal patterns. Our results also suggest that more reliable chronologies and accurate estimates of past metal accumulation rates could be obtained if downwashing was considered within the age-depth modeling process. However, a continued development of age-depth models is still required to fully account for downwash in peat.
Paper IV in a nutshell:

$^{210}\text{Pb}$, $^{137}\text{Cs}$, $^{241}\text{Am}$ and $^{7}\text{Be}$, along with tot-Pb and Hg were measured in five peat cores. Two age-depth models were applied yielding different peat mass accumulation - and metal deposition - rates which was compared to monitoring data. The conventional CRS-model lead to unrealistic peat mass accumulation rates and inaccurate estimations of past Pb and Hg deposition trends. The new IP-CRS-model, which considers downwash, rendered in mass accumulation comparable to published values and temporal trends of metal accumulation in better agreement with monitoring data. More reliable chronologies and accurate peat mass accumulation rates – thus also trace metal accumulation - can therefore be obtained if the possibility of downwash is considered in the age-depth model used.
Conclusions

The main research questions of this doctoral were: how are geochemical signals, including those relating specifically to dating, incorporated in the peat archive? And, are peat archives an absolute or relative record? The answers to these are neither precise nor simple. In answer to the first, there is a general consistency regarding the incorporation of decomposition signals and also deposition signals of atmospheric metal pollutants, exemplified through lead and mercury. Regarding decomposition proxies, the data indicate that they are not fully interchangeable and that decomposition as a process is reflected in different ways. Given the differences between the three proxies for decomposition evaluated here, the ideal would be to include more than one both for studies of past decomposition, and how this relates to climate changes, and for studies aimed at geochemical questions. For the second question, peat archives can be considered as both a qualitative and a quantitative record depending on the temporal resolution required. The qualitative aspects for past trace metal deposition and for soil dust are well established, but as it pertains to quantitatively matching the recent peat record to measurements performed in monitoring programs the answer is less clear. The aim of this thesis and each paper has not been to question the fundamental utility of peat as an archive. Numerous studies, based on sound evidence, have validated peat as an archive (Shotyk 1998; Weiss et al. 1999; Renberg et al. 2001; Farmer et al. 2002), and our general results here do not contradict previous work. However, some critical questions have been raised in terms specifically regarding whether peat is a relative or absolute record. The precise accuracy and temporal resolution in recent time remains unclear. As an archive on millennial, centennial or even decadal scale peat records preserve a consistent record of patterns in past deposition, and the data presented here are consistent with the established patterns, but with regard to a higher temporal resolution, i.e. annual scale, several processes can affect the integrity of the signal being incorporated thereby altering the accuracy of the record. As the combined results of this thesis have shown, care must be taken as to which processes are involved in the incorporation and preservation of geochemical signals (exemplified in this doctoral thesis by decomposition and downwashing), because these may alter the signal and thereby the integrity of the record.

From the results and conclusions of the four papers this doctoral thesis is based upon, the following two conclusions can be made. First, decomposition is not fully captured by any one proxy (paper I). Although bulk density, light transmission and C/N-ratio are all informative they represent different aspects of the decomposition process. More work is required before we can determine exactly which aspects these might be and how this influences, or is influenced by, other geochemical data. Second, the combined results of paper II – IV proves that downwashing, that is, the rapid
advection of atmospherically deposited elements downwards through the surface layers of peat, does exist and that the extent of it will depend upon precipitation and peat characteristics. Although there are many questions that remain unanswered, such as the influence of pH, within-site hydrological flow and the precise peat structure (i.e. vegetation composition, density and compaction) that will specifically influence the extent to which downwashing may occur, the results here from field and laboratory studies provide convincing evidence that downwashing does occur in bogs and in fens, in hummocks and in lawns, and that this has implications for studies interested in accumulation rates of any element – pollutant metals as well as carbon.
Future perspectives

The logical next steps from this studies combined can be summarized into the following bullet points;

- **Within-site hydrology:** Water movement is obviously a key mechanism of downwashing and as pointed out in our discussion, the influence of within-site hydrology may be more important than just downward movement as studied in this thesis. It would be useful to consider the rapid movement of rainwater and potential short-term fluctuations in the water table due to major rainfall events, which would be a potential factor for downward transport/redistribution of atmospherically deposited elements in peat. More work is therefore needed which would entail a mechanistic study design enabling studies of peat wetness, water table height, lateral flow as well as monitor rainfall, DOC and water chemistry.

- **Influence of pH/DOC on $^7$Be:** Although experimental studies on the adsorption rates and retention of metals in peat extends back to the early 1970’s (e.g., Rashid 1974; Bunzel et al. 1976; Kerndorff and Schnitzer, 1980) little work has been done, with the exception of Taylor et al (2012), on the behavior of $^7$Be in in peat. Taylor et al. showed that the sorption time of $^7$Be is almost instantaneous at pH levels of 4.5, after which it is not readily remobilized. However, because many peatland environments have pH-ranges below this (e.g., pH 3.7-6.5, Sjörs 1950; pH 3.4-5.8, Malmer, 1986) more work is required to know in which cases $^7$Be is a good analogue to trace the movement of $^{210}$Pb and in which cases it is not.

- **Isotopic labeling through artificial addition under natural field conditions:** Without undermining the results of our (and others’) experimental studies, it still has to be said that no laboratory experiment can ever fully capture the complexity that reigns under natural conditions. If we really want to test downwashing using additions, we should do so directly onto controlled field plots using isotopically labeled metals (e.g., Kaste et al. 2003). The addition levels could then be held to a level comparable to ambient levels of metal atmospheric deposition rates as measured by monitoring data. With isotopic labeling, such as with stable Pb isotopes, this would facilitate the separation of small additions of metals from those already present in the peat, which would provide a more natural assessment of downwashing in natural field conditions.
Author contributions

Paper I

JR, MK and RB carried out the fieldwork; SH prepared all samples and performed the laboratory analysis (except CN together with JR); KG carried out the change point modeling analysis; SH performed all other data analysis and wrote the manuscript. All co-authors contributed with comments during the writing.

Paper II

SH, KC and RB performed the fieldwork on Rödmossamyran (for the Store Mosse-cores see Paper I); SH prepared the Rödmossamyran samples; JK carried out the radiometric measurements (SH took part in some of the analyses); KC performed the initial high Cu-addition experiment including XRF analysis with RB; SH performed the low Cu-addition experiment and those XRF analysis; SH performed the data analysis with input from RB and JK; SH wrote the manuscript with input and comments from JK and RB.

Paper III

SH planned the experimental set-up; SH and RB carried out the fieldwork; SH performed the laboratory experiment, prepared all samples and ran the XRF-measurements; SH analyzed the data with input from JT and RB; SH wrote the manuscript with comments from JT and RB.

Paper IV

SH and RB performed the fieldwork on Rödmossamyran (for the Store Mosse-cores see Paper I); SH prepared all samples and carried out the XRF and Hg analyses; JK performed the radiometric analysis (SH took part in some of the analyses) and calculated the conventional CRS-model, CO calculated the IP-CRS model, SH analyzed the data with input from RB; SH wrote the manuscript with input and comments from all co-authors.

Authors:

Tusen tack...

First and foremost; Rich – where do I even begin? You are truly an inspiration in so many ways. As a supervisor, a boss, a teacher, a co-worker and a mentor – I couldn’t have wished for a better supervisor even if I had tried. So thank you. Thank you for giving me the opportunity and for introducing me to the world of science. Thank you for never, ever turning me away no matter how busy you were or how stupid my question was. For guiding me through the scientific process - fieldwork to submission to “stupid” reviews - you were always ready to lend a helping hand or a sound advice. Thank you for all the conversations ranging from science, teaching, and communication to music, food and coffee. Thank you for believing in me even in the times when I didn’t. Thank you! Thank you! Thank you!


Tusen tack till Francois - The third part of the holy supervision-trinity. Thank you for showing me the value of networking, for taking me in and giving me the opportunity to work in Toulouse, and above all for always sharing your larger-than-life personality and passion when it comes to food, wine and fashion. You are a great scientist, a great supervisor and a great friend. Merci beaucoup!

Tusen tack till Jon & Carsten – my academic kid-brothers! Tack för att ni stått ut med mitt svängiga humör i stressade stunder, för alla gånger ni fått vika servetter och måla blompinnar, för hjälp med idéer och fältarbete och it-support. Tack för alla luncher, alla middagar och alla pubrundor. Tack för att ni alltid, alltid funnits där! "My life is a little bit better because of you”… I’m doooooin sciiiiienceeeeee…

Tack till Lovisa för tiden i BM, alla drinkar och för alla välbehövliga lång-luncher! A huge thank you to everyone in the Paleogroup: Dominique, Julie, Ingemar, Christian, Åsa, Carolina, Marina, Wenting, Manuela, Erik and Erik. Och tack till Johan för att du tog mig under dina vingar då jag började (och förlåt för alla miljoner frågor innan jag fått kläm på EMG-admin-systemet…).

Tusen tack till alla medförfattare; Johan, Malin, Kerry, Jim, Keyao, Julie, Carolina and Rich!

Tusen tack till Antonio – “Martinez Cortizas et al.” Thank you for showing me that being a big-shot-name can still equal modesty and humbleness. Thank you for unwaveringly teaching me PCA no matter how stupid my questions were. Thank you for opening your home to me, showing me the enchanting streets of Santiago and for introducing me to the “real” tapas. Muchas gracias!

Tusen tack till Malin – You are my academic role model! Thank you for showing me that you can be a woman with a family AND be a successful researcher who rock as scientist! “When I grow up I wanna be like you…” So thank you for just being you!
A great big thanks also goes to Gael LeRoux for acting as an objective mentor throughout these years. Your comments and insights, no matter how critical, have truly been helpful and I appreciate it tremendously!

Ett stort tack till Ingrid och Ann-Sofie och alla andra av EMGs administratörer. Utan er skulle EMG stanna på en dag!

Thank you “Klassiker-gänget” for sharing hours of training and competition, sweat and frozen fingers, laughter and tears. It was a great experience and I’m so happy that I got to shear it with you all.

Till Kristina och Helena; Vänner är som stjärnor, man ser dem inte alltid men man vet att de finns där! Tusen tack till Helena för att du påminner mig om att det finns en hel värld utanför Universitet (till och med i Umeå!) och för att du alltid ger din ärliga åsikt. Tusen tack till Kristina för att du alltid finns där redo för nya äventyr i vått och torrt! Ni två är helt underbara och jag är så tacksam över att få ha er som vänner.

Henke – Tack för 14 år av vänkamp och för alla fika-stunder där teman om allt mellan himmel och jord har avhandlats! Kraaam! En fika-date så snart jag kommer hem?

Tusen tack till Moster Gun & ”Morbror” Leif för att ni visat er uppmuntran och stolthet från dag 1, det har fungerat som en sporre i alla stunder det känts motigt.

Tusen tack till Linda, min stora idol, för att du finns och att du är du. Jag är så oerhört stolt över att få vara din syster! (Och väntar med spänning på din nästa bok!) Skrufsan och Doffe förtjänar också tusen och åter tusen tack för all glädje de sprider omkring sig. Moster Iia lovar att komma och hälsa på igen snart! Tusen tack till Janne för att du alltid håller mig alert med dina snabba kommentarer och dråpliga kommentarer.

Tusen tack till Lucifer & Chino: Vad vore jag utan er? Ni är min klippa, mitt bollplank, min uppväxt och min frizon. Tack för allt ert stöd, ert uppmuntran och er stolthet. Tack för att ni tar hand om mina gudbarn och för att ni gör min jorden så lycklig. Tusen tack till Charlie för att du accepterar mina tokigheter, mina knasiga regler och allt som hör Cirkus-Hansson till. Tack för att du är och att du är bäst. Och på begäran; “I want to say a special thank you to the person who fought, sweated, cried, and laughed at my side during this amazing period in my life, Thank you Karl-Christian Högbom!” Din tok-stolle…

People have asked how I can have a cat and a dog while living alone and doing a Phd, yet the answer is quite simple; it’s for the sake of my sanity. So to Lucifer & Chino:

Tusen tack! Tack för er odelade uppmärksamhet, er obevekliga lojalitet och er villkorslösa kärlek. Ni är värda varenda håruss, dregel och missad sovmorgon! Finally I’d like to thank someone who may not even remember me but whose impact made a long lasting impression for which I am forever grateful: my old social science teacher Tomas Frank. Tack för att du vågade ställa krav, för att du fick mig att sätta höga mål och för att du gav mig viljan att arbeta för att nå dem. Jag är nära nu…

Tusen tack!
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