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Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

DAVID BLAIR

PhD THESIS
UNIVERSITY OF EDINBURGH
2013
Declaration

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in part or in whole, for any other degree.

David S. H. Blair

August 2013
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Abstract

Peats and organic-rich soils are a key part of the global carbon (C) cycle due to their sequestration and storage of atmospheric C as organic matter. Atmospheric deposition as a result of human activities has led to increased inventories of lead (Pb) and mercury (Hg) in UK peats and organic-rich soils. Ombrotrophic peat bogs, which receive all their nutrients and pollutants from the atmosphere, provide a historic record of Pb and Hg deposition within their solid phase. Organic-rich forest soil systems can also act as sinks for anthropogenic Pb but vertical transport of Pb can distort these temporal records. The long-term outlook may, however, be affected by processes which lead to decomposition of organic matter e.g. drying out of peatlands and soils due to climatic change, since these may release Pb into the aqueous phase and volatile Hg to the atmosphere. The associations and speciation of Pb and Hg within peats and organic-rich soils are not well understood but are key to understanding both the potential for release of these pollutants into other environmental compartments and the risks to ecosystems and human health posed by such a release. Investigation of 4 sites in central Scotland showed that, depending on vertical depth, ~40-99% of Pb in ombrotrophic peat was in association with large (0.22 µm – 100 kDa) humic molecules. Near-surface regions where intact plant material had not yet undergone complete humification showed the lowest proportion of Pb-humic association. Historical Pb deposition was retained to similar degrees across each site with recorded inventories to 1986 of 0.340-0.561 g m⁻². However, perturbation of the ²⁰⁶Pb/²⁰⁷Pb isotope ratio profile at Glentress forest indicated that limited migration of petrol-sourced Pb may be occurring. Similarly, perturbation of the ²¹⁰Pb profile at Auchencorth Moss, in addition to discrepancies in the apparent
time period in which peak Pb deposition occurred, indicated that Pb may also be subject to migration within this ombrotrophic system. With respect to Hg, between-site differences in speciation were observed. For example, Hg$^{2+}$ represented $<$25% of the total Hg species in the top 10 cm of solid phase ombrotrophic peat but $>$50% of the total in forest soil. In contrast, aqueous phase Hg was entirely in the inorganic form across all sites. The occurrence of a solid phase [Hg] peak in layers corresponding to the ~1955 height of coal burning, in addition to the narrow range of peatland Hg inventories to 1950 (2.20-3.23 g m$^{-2}$) provide evidence that Hg deposition records may be maintained in organic-rich systems to a greater degree than previously assumed. Differences observed in the associations of Pb and the speciation of Hg between the surface vegetation of ombrotrophic bogs and the underlying peat suggests that plants play an integral role in the biogeochemical behavior and sequestration of Pb and Hg in these terrestrial systems.
Lay Abstract

Human activities including mining, industrial processes and combustion of fossil fuels have released large quantities of toxic metal pollutants, such as lead and mercury, into the atmosphere. Atmospheric lead and mercury are transported around the globe before becoming trapped by vegetation and stored in soils and peatlands, including those in the UK. Climate change has increased the risk of some peatland soils drying out and breaking down, potentially causing the toxic lead and mercury stored in the soils to be released back into the environment. The specific components of peat, soil and the overlying vegetation that trap lead and mercury, in addition to the chemical forms these metals take within these systems, are not well understood. This research showed that historical lead deposited in peats and soils is generally well retained through binding to large organic soil molecules. However, two sites in this study showed distributions of lead that were not entirely consistent with expected historical trends, indicating that some Pb may be mobile in these peat and soil systems. The chemical forms of mercury in peats and soils varied between the surface plant life and the underlying soil. Higher levels of toxic organic mercury were discovered in surface plant material whereas less toxic inorganic mercury was the major form in the underlying soils and soil water. These results should enable better prediction of the fate of these metals in the wider environment and the risks they may pose to the environment and ultimately human health.
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<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
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<td>AFS</td>
<td>Atomic fluorescence spectrometry</td>
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<td>AM</td>
<td>The peat bog, Auchencorth Moss</td>
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<td>C</td>
<td>The element, carbon.</td>
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<td>DOC</td>
<td>Dissolved organic carbon</td>
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<td>ED</td>
<td>The peat bog, Easter Deans</td>
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<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<td>FM</td>
<td>The peat bog, Flanders Moss</td>
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<td>GC</td>
<td>Gas chromatography</td>
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<td>GT</td>
<td>The forest, Glentress</td>
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<td>HPLC</td>
<td>High performance liquid chromatography</td>
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<td>ICP</td>
<td>Inductively coupled plasma</td>
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<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
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<tr>
<td>LC</td>
<td>Liquid chromatography</td>
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<tr>
<td>Ligand</td>
<td>An ion or molecule that binds to a central metal atom to form a coordination complex</td>
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<td>L&lt;sup&gt;y&lt;/sup&gt;</td>
<td>A ligand of charge y</td>
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<td>Minerotrophic</td>
<td>Fed by both the atmosphere and groundwater</td>
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<td>Mono-dentate</td>
<td>Singular atom binding to another atom, molecule or ion</td>
</tr>
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<td>MS</td>
<td>Mass spectrometry</td>
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<tr>
<td>Multi-dentate</td>
<td>Binding via multiple atoms to another atom, molecule or ion</td>
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<tr>
<td>M&lt;sup&gt;x&lt;/sup&gt;</td>
<td>A metal of charge x</td>
</tr>
<tr>
<td>NERC</td>
<td>Natural Environment Research Council</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>OES</td>
<td>Optical emission spectroscopy</td>
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<td>OM</td>
<td>Organic matter</td>
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<td>Ombrotrophic</td>
<td>Fed by the atmosphere exclusively</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SIC</td>
<td>Soil inorganic carbon</td>
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<td>SOC</td>
<td>Soil organic carbon</td>
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<td>SOM</td>
<td>Soil organic matter</td>
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<td>SUERCC</td>
<td>Scottish Universities Environmental Research Centre</td>
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<tr>
<td>UNEP</td>
<td>United Nations Environment Programme</td>
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<tr>
<td>UNFCC</td>
<td>United Nations Framework Convention on Climate Change</td>
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<td>USA</td>
<td>The United States of America</td>
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<td>USDA</td>
<td>United States Department of Agriculture</td>
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<tr>
<td>USEPA</td>
<td>The United States Environmental Protection Agency</td>
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<td>USGS</td>
<td>United States Geological Survey</td>
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<td>UV/Vis</td>
<td>Ultraviolet and/or visible</td>
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<td>WEC</td>
<td>World Energy Council</td>
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<td>WHO</td>
<td>World Health Organization</td>
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<td>World Meteorological Organisation</td>
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Chapter 1 Introduction

1.1 Study objective

The objective of this research was to provide new information on associations of specific heavy metals, lead (Pb) and mercury (Hg), in key compartments of near-surface (0-50 cm) podzolic forest soil, ombrotrophic peat and minerotrophic peat systems in Scotland. Ombrotrophic peat bogs receive their inputs of nutrients primarily from the atmosphere whereas minerotrophic peat bogs also receive inputs from groundwater. The compartments of interest within these systems include living vegetation/foliage, fresh and decaying litter, the underlying peats and soils and their associated pore-waters. This new information should allow better prediction of the ultimate fate of Pb and Hg in the wider environment and the risks they may pose to the environment and ultimately human health. The objective can be broken down into specific sub-objectives as follows:

• To provide new information relating to the chemical associations of Pb and Hg in near-surface (0-50 cm) soil and peat layers that correspond to periods of peak deposition of these elements.

• To quantify the partitioning of Pb between soil mineral and organic matter components and to identify differences in partitioning between ombrotrophic peat, minerotrophic peat and forest soil systems.

• To better understand the capability for organic-rich terrestrial systems to sequester contaminants by establishing how Pb and Hg binding may relate to soil organic matter functionality.
To construct robust chronologies to establish the rates contaminant sequestration in relation to depth within the three systems and compare these with historical data to assess recent changes in rates of sequestration of Pb and Hg by these systems.

To investigate the speciation of Hg within near-surface soil/peat environments and the factors that influence the species of Hg present in soil/peat systems.

1.2 Thesis structure and outline

Ombrotrophic peat, minerotrophic peat and organic-rich forest soils are important reservoirs in the global carbon cycle and so Chapter 1 will first introduce the established literature knowledge base surrounding global carbon and pollutant cycles and the interaction of pollutants including Pb and Hg with terrestrial organic and mineral matter. Current gaps in understanding to be addressed in this study will be identified. Chapter 2 gives details of the experimental methods employed throughout the project and their analytical basis is explained where appropriate. Experimental methods that have been developed during this project and the procedures resulting in their optimisation are discussed in detail in Chapter 3. Chapter 4 includes an introduction to the structure, formation and chemistry of soil and peat systems which will be presented before describing the four Scottish sites studied within the project. The geochemical characteristics of these sites are presented to provide a context for the data contained in subsequent chapters. Individual chapters containing the results and discussion relating to Pb, Hg and soil organic carbon then follow (chapters 5, 6}
Introduction

1.3 Global environmental cycles and anthropogenic contaminants

Many of the environmental problems faced by developed countries in the 21st century are a consequence of past human activities. Problems caused by anthropogenic contaminants typically arise some period of time after the release of these pollutants due to the time-lag between release, transport through global environmental cycles, and eventual deposition within an environment where they cause harm (Stigliani et al., 1988). This is perhaps counter-intuitive to the general populace who associate the continued deployment of cleaner and greener technologies and the age of reduced emissions with an immediate improvement in the environment. Examples of such time-delayed problems include long-term sulphur deposition lowering freshwater pH (Schopp et al., 2003) following exhaustion of natural buffers, and increasing Hg concentrations in Swedish fish despite two decades of reduced Hg emission (Haakanson et al., 1990).

The environmental damage caused by an anthropogenic contaminant is linked to the ultimate fate of that contaminant. Those that are eventually removed from
biogeochemical cycles or are otherwise rendered inaccessible are less likely to result in detrimental health effects than those which remain available for ingestion, inhalation or other form of uptake by living organisms. Understanding the fate of these contaminants requires consideration of global environmental cycles. While contamination can occur as a result of localised point sources, large quantities of soil, dust and other particulates are mobilised on a global scale via the atmosphere, or through ocean and river systems, to distant sites. Long range transport processes may be ongoing natural occurrences, i.e. the deposition of Saharan dust particulates across southern Europe (Karanasiou et al., 2012), or alternatively, may be caused by unusual discreet events such as the Chernobyl fallout that was deposited across Europe (Ballestra et al., 1987; Rowan and Walling, 1992; Robbins and Jasinski, 1995) and more distant countries such as the USA (Feely et al., 1988).

This research is concerned with peat and soil systems which themselves form part of the global cycles of Pb and Hg by acting as contaminant reservoirs as will be discussed in Section 1.3.2.2. The peatlands and upland soils considered within this investigation are organic-rich terrestrial systems (Section 4.6) and contain considerable quantities of organic C alongside some inorganic C species. It is therefore important to understand the wider picture including global cycling of C, its relationship to soil and peat systems and the overarching factors that contribute to the current research interest into organic-rich terrestrial systems.
1.3.1 Carbon

1.3.1.1 The C cycle

The C cycle summarizes the exchange of carbonaceous species between the five major pools of global C: (i) oceanic; (ii) geological; (iii) pedologic; (iv) atmospheric; and (v) biotic. Figure 1.1 quantifies the amount of C present in each pool and the annual exchanges between these reservoirs.

![Figure 1.1](image1.png)

The oceanic pool is the largest pool, containing ~38500 Pg C (Lal, 2008) in predominantly inorganic bicarbonate and carbonate forms, although dissolved organic carbon (DOC) species are also present. It is estimated that oceanic C is
increasing at a rate of 2.3 Pg yr\(^{-1}\). Inputs to this pool derive from erosion and
dissolution of C-containing material from the pedologic pool, gas exchange
processes at water surfaces and the dissolution of CO\(_2\) into rainwater with subsequent
precipitation into major water bodies. The biotic pool contains 560 Pg C and includes
plant and animal matter. Photosynthetically produced organic matter is the primary
input of C to this pool with plant respiration, deforestation and decay into soil
systems being the main mechanisms of C loss from the biotic C pool. Taken
together, the biotic and pedologic pools represent the total terrestrial C pool.

The geologic C pool primarily encompasses fossil fuels. The rate of formation of
fossil fuels is negligible in relation to the timescale of the rest of the C cycle and as a
result, the geologic C pool has effectively no inputs. This pool is being actively
depleted via combustion (power station and automotive vehicles) and anthropogenic
atmospheric C emissions to the atmosphere currently stand at \(~7\text{-}9\) Pg yr\(^{-1}\) (Lal, 2008;
Le Quéré et al., 2009) with approximately one third of these emissions originating
from combustion of coal alone (Schrag, 2007). Despite the oceanic pool sequestering
more C than it emits to the atmosphere, the atmospheric C pool is increasing at a rate
of \(~3.5\) Pg yr\(^{-1}\) (Falkowski et al., 2000; Pacala and Socolow, 2004). Emissions from
anthropogenic sources are increasing year-on-year due to the expansion of emerging
economies such as China, India and Korea (Friedlingstein et al., 2010) and the
world’s increasing consumption of fossil fuels. The rate of future increase in
atmospheric CO\(_2\) concentration will depend significantly upon anthropogenic
activities and the rate of depletion of fossil fuel reserves.
Of greater importance to this study, however, is the pedologic C pool. The C content of this pool has been estimated to contain ~3000 Pg C to a depth of 1 m with 1500 Pg stored in soil organic carbon (SOC), 950 Pg representing soil inorganic carbon (SIC), and 450 Pg C stored specifically in peatlands (Batjes, 1996). The two primary input mechanisms of C into the pedologic pool are (i) the death and decay of plants and animals and the waste products thereof forming SOC, and (ii) the erosion and weathering of parent minerals to form primary carbonates coupled with the formation of secondary carbonates via the interaction of atmospheric CO$_2$ with Ca or Mg ions. Transport of soil dust, combined with respiration processes, represents the C losses from the soil to the atmospheric pool. Much of the pedologic C pool is stored in peatlands which predominantly comprise organic C. There are concerns regarding the stability and subsequent longevity of these organic C stores and these issues will be discussed in the following sections.

1.3.1.2 Concerns related to increasing atmospheric C concentrations

Global mean temperatures have increased at a rate of ~0.16°C per decade since the mid 1970s. As of 2012, the previous three decades have each been warmer than the last (IPCC, 2007; 2013; Lal, 2008). The increase in world temperatures has led to reductions in the extent of polar ice, increases in sea levels of ~19 cm (IPCC, 2013) over the period 1901-2010, shifts in ocean ecosystems including the partial desalinisation of previously saline regions, and alterations in the trajectory of major ocean currents (Greene and Pershing, 2007). Temperature increases are attributed to the increased trapping of solar radiation due to a large net increase in emissions of
greenhouse gases which include CO₂ and CH₄. For example, carbon dioxide concentrations have increased from ~290 mg m⁻³ to ~390 mg m⁻³ since 1850 and continue to increase at a rate of 1.7 mg m⁻³ y⁻¹ (WMO, 2006; IPCC, 2013). The available options to mitigate increases in CO₂ include measures to reduce overall CO₂ emissions, the utilization of CO₂ as a chemical feedstock, or storage of CO₂ in geological and environmental repositories (Thomas, 2001). The search for viable CO₂ storage solutions has also resulted in organic-rich terrestrial systems such as peat and upland boreal forests attracting considerable attention as long-term C sinks. Official policy bodies such as the Intergovernmental Panel on Climate Change (IPCC) have recognised the potential for changes in land management practices to cause net decreases in the C that can be easily mobilised from the solid phase into other sections of the global C cycle (IPCC, 2001). The United Nations Framework Convention on Climate Change (UNFCCC) ruled in 2001 that countries could adopt peatlands as a means of C sequestration to assist in reaching net emission reduction targets resulting from the 1997 Kyoto agreement (UNFCCC, 2001). Storage of C within soils and peats is a significant driving force behind current environmental legislation.

1.3.1.3 Importance of peats and organic-rich soils as terrestrial C sinks

Peatlands incorporate increasing quantities of organic matter with time, removing it from the C cycle provided the peatland is accumulating (Malmer et al., 2003) and, therefore, not deteriorating. Peatlands in the northern hemisphere are estimated to
have accumulated 74.8 Pg C yr\(^{-1}\) (Yu, 2012; Gorham \textit{et al.}, 2012) during the hocene; an average of approximately \(\sim 18.5\) g C m\(^{-2}\) yr\(^{-1}\) (Cai and Yu, 2011). Current C stocks in these regions are estimated at between \(\sim 270\) Gt and \(\sim 500\) Gt (Gorham, 1991; Turunen \textit{et al.}, 2002; Yu, 2012) dependent on choice of experimental model and variable assumptions, such as average peat depth.

Boreal forests typically possess organic-rich soil that can also accumulate C. The presence of the tree canopy in boreal forests causes photosynthetically fixed C captured by the canopy to enter the soil through leaf litterfall (e.g. Seely \textit{et al.}, 2002). Furthermore, a recent study (Clemmensen \textit{et al.}, 2013) has implicated the growth, death and decay of root-associated fungal biomass as responsible for \(>50\%\) of organic carbon sequestered in some boreal forest systems. Weathering of underlying or nearby geological material provides an inorganic C component to the soil system. The division of C stocks within soil systems is outlined in Figure 1.2. The proportion of C within each fraction will vary from locality to locality, e.g. grasslands contain less above-ground biomass than boreal forests.
Despite extensive interest, the impacts of climatic change upon the soil and peat C reservoirs themselves are not entirely understood. Of specific concern is that due to the influences of climate change outlined in Section 1.3.2, projected increases in temperature of 1.5-5.8°C during the 21st century (IPCC, 2001, 2013) may result in deterioration of these terrestrial systems due to (i) temperature related effects such as the thawing of permafrost systems, or, (ii) increases in the occurrence and severity of extreme weather conditions such as storm events, periods of high rainfall, or droughts. Under these conditions, a proportion of the stored C would be released via physical transportation of particulates, CO₂ emission to the atmosphere or loss of dissolved carbon through ground and surface water flows. Thus, these systems could be transformed from C sinks to active C sources (Worrall et al., 2003, 2004; Evans et al., 2006). The conversion of natural C reservoirs into C emission sources would act to increase atmospheric CO₂ concentrations which in turn would contribute towards further temperature increases and greater deterioration of peat and soil systems.
Despite global temperature trends implying a shift towards the deterioration of these C accumulating systems, higher yearly C sequestration potential has been predicted in mid-latitude soil systems due to greater uptake by surface biomass (Dilustro et al., 2002). The sink or source nature of a soil or peatland system is dependent upon a range of localized factors and can only be assessed by considering biomass fluctuation, methane flux, net exchange of carbon dioxide, solid particulate loss, and the full characterisation of aqueous C: dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC), and dissolved CO₂ (Dawson et al., 2002). Short-term decreases in accumulation rates within soil or peat systems may act as early indicators of reductions in capability of these ecosystems to store C or could provide warning of imminent degradation and the resultant shift towards the release of C (Lal, 2005). Regardless, peat and organic-rich soils are a key part of the global C cycle and store a large proportion of the pedologic C pool. However, these systems are not completely understood and further research is warranted to assess the long-term stability of these systems in relation to both retention of C and sequestration of anthropogenic contaminants associated with these C reservoirs.

### 1.3.2 Anthropogenic contaminants

Since the onset of the Industrial Revolution in the mid-to-late 1700s, atmospheric release, transport and deposition of anthropogenic contaminants has resulted in markedly increased inventories in soils worldwide (Steinnes, 1987; Callender, 2003; Vestreng et al., 2006; Cloy et al., 2008, 2009). These anthropogenic contaminants
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encompass metals, including radionuclides (Hu et al., 2010), and persistent organic pollutants (Jones and de Voogt, 1999). Persistent organic pollutants will not be investigated within this study.

1.3.2.1 Emission and global atmospheric mobilization of anthropogenic metal contaminants

Heavy metals are loosely defined as a subset of metallic elements consisting of transition metals, some metalloids and members of the lanthanide and actinide series, e.g. (Pb), mercury (Hg), arsenic (As), antimony (Sb), chromium (Cr), cadmium (Cd), nickel (Ni), zinc (Zn), iron (Fe), magnesium (Mg), vanadium (V), copper (Cu), tin (Sn), thallium (Tl), manganese (Mn) and selenium (Se). These elements are often present in the natural environment in small quantities; some are essential for life, some are toxic and others serve no appreciable biological function (Nordberg et al., 2007). Human activities, especially industrial activities, have liberated heavy metals into environments that would otherwise receive few or no natural inputs of such metals. Mining and metallurgical processes, fossil fuel (i.e. coal, oil and gas) extraction and combustion, and waste disposal are primarily responsible. Combustion of fossil fuels in particular represents the major contemporary source of many heavy metal species including: Pb (74%), Hg (66%), Cr (69%), Mn (85%), Sb (47%), Se (89%), Sn (89%), Tl (~100%), Ni (90%) and V (~100%). (Pacyna and Pacyna, 2001). Specific information on the sources, historic emissions, and global transport mechanisms of Pb and Hg are presented in more detail in Chapter 5 and Chapter 6.
respectively. A summary of environmental heavy metal transport is provided here in order to aid a general discussion of contaminant cycles.

Following emission to the atmosphere either through association with fine particulates or through vaporisation, heavy metals are transported via air masses and migration through the ecosystem before deposition onto land surfaces and oceans (Driscoll et al., 1994). The global nature of these transportation processes were evidenced from ice core records in polar regions (Murozumi et al., 1969; Boutron, 1987; Ng and Patterson, 1981; Schuster et al., 2002). Deposition occurs through a combination of dry processes through gravity or scavenging effects and wet deposition through dissolution or association of contaminants with precipitation. Remote locations worldwide exhibit concentrations of metals at enriched levels relative to the concentrations that would be expected from their natural occurrence in the surrounding environment (Nriagu and Davidson, 1986). Anthropogenic sources were implicated in relation to global metal pollution by pioneering studies into ice cores begun by Murozumi et al. (1969). Arctic and Antarctic regions are remote and broadly inhospitable for human life. These conditions result in a dearth of localised contamination sources that would account for elevated metal concentrations within the nearby environment. Ng and Patterson (1981) revealed the extent of anthropogenic emissions and subsequent deposition by discounting the possibility of the 100-fold increase in Pb concentrations in the past 800 years being caused by natural sources. The key pieces of supporting evidence were (i) chronologic peaks in industrial emissions occur within a similar timescale to increases in concentrations within atmospherically fed systems; (ii) established industrial emission Pb mass
inventories suitably account for the observed increases; (iii) natural source emissions including volcanic eruptions and sea spray accumulation when extrapolated leave a 99% deficit when compared with experimentally observed Pb concentrations; and (iv) isotopic tracer data shows deviation from natural ratios and implicates industrial, anthropogenic sources (Shirahata et al., 1980). Further work by Boutron et al., (1988) confirmed that background Pb concentrations were entirely attributable to rock, soil dust and volcanic emissions with no naturally sourced Pb causing the observed excesses above wind-blown dust from crustal rock and soil. The potential exists for anthropogenic heavy metal contaminants to damage ecosystems or harm human health via accumulation within the environment and eventual release into water supplies (Bergvall et al., 2007) and food chains (Ping et al., 2009). These concepts will be discussed further in Section 1.4.

1.3.2.2 Peats and soils as metal contaminant sinks and potential contaminant sources

Accumulating peat and soil systems can act not just as C reservoirs (Section 1.3.1.3) but also as sinks for metal contaminants. Following deposition, contaminants have the potential to become bound to peat and soil solid phase material, becoming effectively immobilized and sequestered within the system. As these terrestrial systems accumulate, their capacity to store metals will also increase resulting in continued removal of metals from environmental cycles.
Both soil organic and mineral matter can sequester metal contaminants although the mechanisms through which they achieve this differ. Mineral matter, including common Scottish clays such as chlorites \(((\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2(\text{Mg,Fe})_3(\text{OH})_6)\) and illites \(((\text{Al,Mg,Fe})_2(\text{Si,Al})_3\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})])\), can bind metals to their surfaces via charge interactions (Wilson et al., 1984). Positively charged metal ions will experience attractive forces with predominantly negatively charged mineral oxide and clay surfaces which may lead to ionic binding. Oxygen-based anionic functionality such as silanols \((\text{R}_x\text{SiOH})\), siloxanes \((\text{R}_x\text{SiO})\) or their aluminium hydroxide \((\text{Al(OH})_x)\), oxide \((\text{AlO}_x)\) and oxyhydroxide \((\text{AlO(OH})_x)\) counterparts are key to providing these negatively charged mineral surfaces (Hohl and Stumm, 1976; Stumm et al., 1980; Matthes et al., 1999). Binding can proceed via either direct surface-metal binding as per Equation 1.1 or via a ligand exchange processes whereby two ions of equivalent charge are exchanged between the mineral surface and solution. An example of ion-exchange and subsequent metal binding is provided in Equation 1.2 (Wypych and Satyanarayana, 2004). In the equations below, ‘M’ represents a metal atom and ‘L’ represents a ligand or, more specifically, an ion or molecule that coordinates to a metal atom.

\[
\text{Surface—OH + M}^{+} \rightleftharpoons \text{Surface—OM}^{(x-1)+} + \text{H}^{+} \quad \text{Equation 1.1}
\]

\[
\text{Surface—OH + M}^{+} + \text{L}^{y-} \rightleftharpoons \text{Surface—L —M + OH}^{-} \quad \text{Equation 1.2}
\]
These examples represent mono-dentate interactions where ligands bind via only one coordinating atom although multi-dentate coordination where individual ligands bind to the metal via multiple atoms is possible via interaction of numerous negative surface species with metal ions. Multi-dentate ligands exhibit a ‘chelate effect’ whereby multi-dentate binding is more favourable and therefore more stable than mono-dentate interactions (Steed and Atwood, 2013).

Binding to soil organic structures and in particular humified organic matter, typically involves either the interaction of negatively charged organic functionality with positively charged metal ions, or the formation of ternary complexes that bind metals to soil organic matter via an intermediate species (Uyguner and Bekbolet, 2004, Matsuda et al., 2009). Negatively charged organic functional groups may be the result of pH controlled proton dissociation, or alternatively the presence of electron donating functionality such as oxygen, nitrogen or sulfur groups (Martinez et al., 2002) can act to stabilise otherwise temporary negative point charges present in an organic structure. Such charges are often further stabilised via resonance stabilisation due to close proximity of aromatic functionalities. Multi-dentate binding of ions including Cu$^{2+}$, Fe$^{2+}$ and Mn$^{2+}$ have also been determined via combinations of techniques including Electron Paramagnetic Resonance (EPR), Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) and Extended Xray Absorbance Fine Structure (EXAFS) spectroscopy (Davies et al., 1997). Figure 1.3 demonstrates a number of theoretical mechanisms through which this may occur.
The deterioration of accumulating peat and soil systems discussed in Section 1.3.1.3 in relation to global change may act to convert metal contaminant sinks into active contaminant sources. Drying and erosion of peat and soil systems, or alterations in system chemistry variables such as pH due to acid rain or increases in dissolved CO$_2$, etc., can lead to the dissociation of previously bound metals species, or the liberation and subsequent transportation of matter with which metals are associated. Loss from contaminant reservoirs can result in pollution of other terrestrial sinks, sediments (Birch and Davey, 1995; Buckley et al., 1995; Estrany et al., 2010), to bioreserviours.
via plant accumulation, the atmosphere, and aquatic systems, dependent on the mechanism and nature of the loss process. Changes in system chemistry variables including pH and redox potential may cause previously insoluble metal species to be converted to soluble, and thus readily dissolvable, forms. For example Chuan et al., (1996) demonstrated that acidic and reducing conditions, respectively, resulted in increases in soluble metal concentrations in soil systems. Soluble species or those that can be suspended colloidal can be subject to transportation through aqueous flow in groundwater, surface water or large aqueous bodies such as rivers, oceans or lakes (Dunnivant et al., 1992; de Weerd et al., 1998; Bekhit et al., 2009). Transport through water systems can move these species into new environments or can expose plants and animals to contaminants as they intake water (Duarte-Davidson and Jones, 1999). Considering temperature increases, some contaminants are subject to volatilisation and are emitted to the atmosphere from near-surface soil and peat layers where temperatures are higher relative to deeper layers and are subject to warming via solar radiation (Galloway et al., 1982). Atmospherically mobilised contaminants are prone to both localised and far-field deposition back into soil or water systems. Solid phase material onto which metals are adsorbed is not immune to environmental mobility. Drying of peatlands in conjunction with storm events and other turbulent weather, natural disasters and human/animal activity can all lead to movement of solid contaminant-bearing material such as soil dust elsewhere (Eggleton and Thomas, 2004; Smith et al., 2003; Wei and Yang, 2010). Solid particulates may be washed or blown away, landslides can shift large quantities of material and human construction/landscaping/landfill can lead to transport of large amounts of solid material and their associated metals across long distances.
1.4 Research questions and wider relevance of this study

Metal contaminants and their ultimate fate in the environment are currently of interest because many are harmful to human health and environmental systems. Organic-rich terrestrial systems are well-known sinks for metal contaminants but climatic change e.g. temperature fluctuations and alterations in weather patterns, may cause previously sequestered metal contaminants to be transferred to receiving aquatic systems. Consequently, there may be increased potential for impacts upon human health, specifically if released into drinking water systems or if bioaccumulated within the human food-chain (e.g. Mudgal et al., 2010; Zhao et al., 2010). The two metals of key interest to this study, Pb and Hg, are among the most toxic and their specific effects and routes of environmental cycling are discussed in more detail in Chapter 5 and Chapter 6, respectively. Both metals are persistent pollutants which has led to their dispersion and deposition across the globe.

Despite considerable depth of literature examining Pb and Hg in the environment, the direct associations of Pb and Hg in the solid and aqueous compartments of soil and peat systems are poorly understood. The surface layers of peat and soil systems, including the overlying vegetation, are the most accessible, exposed, and changeable aspects of terrestrial systems as they lie at the interface between the solid phase, the aqueous phase and the atmosphere. Furthermore, the near-surface layers encompass matter that corresponds to the periods of peak deposition of Pb and Hg (Sunderland and Mason, 2007; Dore et al., 2008). As a result, the soil and peat with, in principle, the greatest concentrations of Pb and Hg is also the most vulnerable to climatic
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change (USDA, 1996). Additionally, the speciation of terrestrial Hg in particular is not well characterized (e.g. AMAP, 2011). Without more information on Pb and Hg’s associations and speciation, it is difficult to model and thus predict their long-term behaviour, the effect of climate change upon the terrestrial reservoirs of these metals, and their ultimate environmental fate (e.g. Turner, 1987; Halim et al., 2005). Furthermore, with the continued deployment of legislation encouraging cleaner fuels and lower emissions, it is important to assess historical changes in the flux of Pb and Hg to peat and soil systems. Such an understanding will reveal the degree to which current emission sources influence, and will continue to influence, the Pb and Hg in peat and soil systems. This study will build upon existing knowledge of environmental Pb and Hg in order to better understand the associations and speciation of these metals in soil and peat systems while also investigating contemporary deposition of these metals compared to historical records.
Chapter 2 Methodologies

2.1 Introduction

This chapter outlines the complete list of methodologies applicable to this work including explanation of the principles of the more complex techniques therein. These methodologies cover field-based techniques followed by those used in the processing and analysis of peat and soil samples and their respective porewaters. All solutions are prepared using deionised water unless otherwise specified.

2.2 Field-based methodologies

2.2.1 Collection of peat and soil samples using a monolith tin

Peat and soil samples were acquired by excavating 60 cm deep pits with 40 x 40 cm surface dimensions and horizontally hammering a 50 x 15 x 7.5 cm vertical steel monolith tin into an undisturbed vertical pit face. Stainless steel knives were used to slice around the monolith block and the peat and soil cores held within the tin were removed as single entities. Cores were sliced on-site at the greatest achievable depth resolution of 1–3 cm dependent on matrix cohesion and water content. Each slice was sealed in an individual labelled polyethylene bag for transport and storage. Monolith sampling prevents the formation of a vegetation ‘plug’ at the top of the core and allows living surface vegetation and associated decaying vegetation to be sectioned alongside the bulk soil matrix.
2.2.2 Collection of peat samples using a Cuttle and Malcolm corer

Spatial variation analysis cores were acquired using a Cuttle and Malcolm (1979) corer. This corer consists of a long rectangular steel box of dimensions 5 x 5 x 100 cm with open ends and one removable side faceplate. First of all the three-sided corer was inserted vertically into the ground and then the faceplate was inserted to complete the box shape of the core. Both were removed together by lifting the apparatus vertically and the peat core was contained therein. The faceplate was removed and the core sliced into 2 cm layers on-site. Each slice was sealed in uniquely labelled polyethylene bags for transport and storage.

2.3 Laboratory-based methodologies

2.3.1 Extraction of peat and soil porewaters

Peat and soil porewaters were extracted via direct centrifugation. Peat/soil samples were packed into 50 ml polypropylene centrifuge tubes and subjected to centrifugation at 5890 x g (Heraeus Instruments Biofuge Primo). The supernatant was collected and the process repeated until 20 ml porewater had been obtained. All collected porewater was filtered through 0.22 µm syringe filters (Millipore, MILEX, PES) to remove suspended particulates (e.g. Graham et al., 2011; Wang et al., 2013) prior to storage at ~4°C and analysis. Where sample matrix did not allow the extraction of porewater via centrifugation (i.e. surface vegetation layers), application of pressure via hand-squeezing the sample inside plastic polyethylene bags was sufficient to liberate sample porewaters.
2.3.2 Sequential ultrafiltration of porewaters

Porewater ultrafiltration (Graham et al., 2008) was performed via addition of 20 ml of filtered porewater to centrifugal ultrafiltration tubes containing polyethersulfone membranes (Sartorius, Vivaspin 20) followed by centrifugation (Heraeus Instruments Biofuge Primo centrifuge) at 5890 x g until <1 ml solution remained in top compartment of the filtration unit. This processes required 10-15 minutes centrifugation for the 100 kDa membrane, 30-40 minutes for the 30 kDa membrane and 60-90 minutes for the 3 kDa membrane. As outlined in Figure 2.1, fractionation was achieved via exposure of the filtrate to sequentially smaller ultrafiltration tubes: 100 kDa, 30 kDa and 3 kDa. Enhanced recovery of the retentate was achieved by gentle agitation of the membranes with modified Pasteur pipettes sliced at the tip to produce a spatula effect, and addition of 1 ml of deionised water. Both filtrate and retentate were collected and weighed and the distribution of DOC material between size sub-fractions determined via UV/Vis absorbance spectroscopy as outlined in Section 2.3.11. Percentage recovery was determined by comparing the mass of DOC in the bulk porewater with the mass of DOC in each sub-fraction (Appendix 1). Samples were stored in a refrigerator at 4°C prior to metal concentration analysis via ICP-MS.
2.3.3 Air drying and homogenisation of solid peat and soil

Following extraction of peat and soil porewaters, each layer’s solid phase material was air dried at room temperature in individual plastic bowls for a period of approximately two weeks. Samples were weighed before drying and weighed again each day to monitor continued mass loss due to moisture evaporation. Samples were assumed to have dried when 48 hours had passed without additional loss of mass.

While drying, samples were covered with paper screens to limit contamination due to atmospheric dust and to block strong direct light. After drying, samples were homogenised by grinding with a mortar and pestle until a fine powder was achieved.

Plant and root material was chopped into fine pieces using scissors where required. Homogenised samples were stored in sealed plastic bags at room temperature until utilised.
2.3.4 Moisture content of peat and soil

Mass loss following drying was adopted as a measure of soil moisture content (Blume et al., 1990). Wet peat and soil aliquots of ~10 g were removed in duplicate from the bulk samples and weighed prior to drying in an oven (Gallenkamp, general protocol oven) at 105°C for 24 hours. Dry samples were weighed following cooling. Moisture content is calculated via Equation 2.1 as a percentage of original wet weight.

\[
\text{Moisture (\%)} = \frac{(\text{wet weight (g)} - \text{dry weight (g)}) \times 100}{\text{wet weight (g)}} \quad \text{Equation 2.1}
\]

2.3.5 Organic matter content of peat and soil

Loss on ignition (LOI) was used to determine soil organic matter content (Blume et al., 1990). In duplicate approximately 0.5 g dry oven-dried (105°C) soil in pyrex beakers, was subjected to ashing at 450°C in a muffle furnace (Carbolite high temperature laboratory chamber furnace) for 4 hours (e.g. Ben-dor and Banin, 1989; NRM, 2013). Beakers were covered with watch glasses to reduce combustion-related loss and contamination within the oven. Upon cooling, the ash residue was weighed and the LOI calculated using Equation 2.2.

\[
\text{LOI(\%)} = \frac{(\text{dry weight (g)} - \text{ash weight (g)}) \times 100}{\text{dry weight (g)}} \quad \text{Equation 2.2}
\]
2.3.6 Concentration of specific organic functionality in soil and peat

Although determination of total organic content is a useful tool in characterisation of peat and soil species, it reveals little about the specific organic matter functionalities of that organic material. The most abundant reactive functionalities in soil organic material are associated with the oxygen-bearing groups. Outlined here are a number of chemical methods adopted in this study for determining the concentration of phenolic, hydroxyl, acidic hydroxyl, carbonyl and carboxyl functional groups within solid phase peat, soil and humic extract samples. Humic extracts were obtained via the methodology presented in Section 2.3.12.

2.3.6.1 Concentration of phenolic functional groups in solid peat and soil

Phenolic functionality concentration was determined via an adapted Folin-Ciocalteau reagent (Folin et al., 1912; 1927) methodology as outlined by Box (1983) and more recently used by Pind et al., (1994) and Freeman et al., (2004).

Peat or soil slurry is created by mixing 0.1 g accurately weighed solid peat or soil with 10 ml deionised water. Solutions containing 1.5 ml of 1.89 M sodium carbonate (prepared from >99% purity Fisher Scientific, laboratory reagent grade) and 0.5 ml 2 M Folin-Ciocalteau reagent (3H₂O₄P₂O₅.14WO₃.4MoO₃.10H₂O, ungraded, lot number: BCBB1845) were added to duplicate 10 ml slurries of selected samples and to a 10 ml deionised water reagent blank. Samples were subjected to sonication for
60 minutes to expose maximum solid surface area to solution-borne reagents. Immediately following sonication, samples were filtered through Whatman 540 hardened ashless filter paper. Absorbance of derivatized phenolic groups was measured on a spectrophotometer (Perkin Elmer, Lambda XLS + UV/Vis) at 750 nm in 1 cm cells exactly 60 minutes after reagent addition. Absorbance at 750 nm is directly proportional to phenolic functionality equivalents. The technique was calibrated using phenol standards of 0-10 mg l\(^{-1}\) (prepared from VWR, NORMAPUR, >99.9%) to generate a linear plot of absorbance at 750 nm against phenolic concentration from which sample phenolic content could be interpolated. Solid phase concentrations were calculated as outlined in Appendix 3.

2.3.6.2 Concentration of acidic hydroxyl functional groups in solid phase peat and soil

Total acidic hydroxyl functionality (COOH, phenolic and enolic –OH) was determined via application of the baryta absorption method (Stevenson, 1994). In duplicate, twenty millilitres of 0.1 M barium hydroxide (prepared from Aldrich, ~95% purity) was added to flasks containing 50–100 mg of selected peat/soil material and to a blank flask, respectively. Each flask was evacuated with nitrogen gas and the contents shaken for 24 hours using a mechanical laboratory flask shaker (Stuart Scientific). The suspension was filtered under gravity (Whatman 540 hardened ashless filter paper). Each flask was rinsed with 5 ml deionised water and the washings filtered as above. The filtrate and washings were combined prior to titration against 0.5 M hydrochloric acid (prepared from Fisher, concentrated grade, 37% w/v). The pH during the titration was monitored using a calibrated pH meter.
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

(Griffin model 50) until the end point of pH 8.4 was achieved. Total acidity in moles kg\(^{-1}\) is calculated by Equation 2.3.

\[
\text{Total acidity} = \frac{(V_{\text{blank}} - V_{\text{sample}}) \times M \times 10^6}{\text{milligrams of peat/soil}}
\]  

Equation 2.3

Where \(V_{\text{blank}}\) and \(V_{\text{sample}}\) represent the titration volume (ml) of hydrochloric acid for blank and sample respectively and \(M\) is the molarity of the acid. The moles of barium hydroxide consumed by the initial reaction equate to the moles of acidic hydroxyl functionality within the soil or peat.

### 2.3.6.3 Total concentration of hydroxyl functional groups in solid phase peat and soil

Total hydroxyl functional group measurement differs from measurement of total acidic hydroxyl functionality concentration as it will detect hydroxyl groups such as alcohols and enols that may not possess acidic character, dependent on their chemical environment, in addition to acidic hydroxyls such as carboxylic acids.

In duplicate, selected samples of peat/soil (0.1 g) were refluxed with 5 ml pyridine (used as supplied, Aldrich, anhydrous, 99.8%) and 5 ml acetic anhydride (used as supplied, Aldrich, ACS reagent grade, ≥98%) for 3 hours under nitrogen gas as per the Schnitzer and Skinner method (1965). After cooling, the mixture was poured into
deionised water and filtered under gravity (Whatman 540 hardened ashless filter paper). The solid precipitate was washed on the filter paper with deionised water and dried under vacuum. Once dry, the acetylated solid was refluxed with 25 ml of 3 M sodium hydroxide (prepared from VWR, analytical reagent grade, >99%) for 2 hours under nitrogen gas. This was followed by addition of 25 ml of 1.5 M sulfuric acid (prepared from Fisher, laboratory grade, 98% w/v) and 25 ml deionised water and the mixture distilled. Subsamples of the distillate were titrated potentiometrically to the pH inflection point against 0.1 M sodium hydroxide (prepared from VWR, analytical reagent grade, >99%) until sample aliquots and the reagent blank titrated equally, indicating that no further reaction product was being formed. The distillation mixture was kept at constant volume by repeated addition of 25 ml portions of deionised water. Total concentration of hydroxyl functional groups (moles kg\(^{-1}\)) was calculated via Equation 2.4.

\[
\text{Total hydroxyl} = \frac{(V_{\text{sample}} - V_{\text{blank}}) \times M \times 10^k}{\text{milligrams of peat/soil}}
\]

Equation 2.4

Where \(V_{\text{sample}}\) represents the titration volume of sodium hydroxide (ml) for accumulated sample aliquots, \(V_{\text{blank}}\) represents the titration volume of sodium hydroxide required for a blank experiment where an identical volume of distillate has been collected and \(M\) is the molarity of the sodium hydroxide titrant. The moles of alkali required to neutralise the unreacted sulphuric acid equate to moles of hydroxyl functionality in the initial soil or peat sample.
A calcium acetate method was used to determine carboxyl functionality concentration (Schnitzer and Gupta, 1965). In duplicate, ten millilitres of 0.5 M calcium acetate solution (prepared from Aldrich, >99%) was added to a flask containing 50–100 mg of a selected peat/soil sample. Flasks were shaken for 24 hours and the mixture samples filtered under gravity (Whatman 540 hardened ashless filter paper) using 40 ml deionised water to wash the apparatus. The filtrate and combined washings were titrated against 0.1 M sodium hydroxide solution (prepared from VWR, analytical reagent grade, >99%) and the pH inflection end point determined potentiometrically. Procedure blanks consisted of identical solutions with 50 ml deionised water. Equation 2.5 is used to determine carboxyl functionality in moles kg\(^{-1}\).

\[
\text{COOH} = \frac{(V_{\text{blank}} - V_{\text{sample}}) \times M \times 10^6}{\text{milligrams of sample}}
\]

Equation 2.5

Where \(V_{\text{blank}}\) and \(V_{\text{sample}}\) represent the titration volume (ml) of sodium hydroxide for blank and sample respectively and \(M\) is the molarity of the alkali. The moles of calcium acetate consumed by the initial reaction equate to the moles of acidic hydroxyl functionality within the soil or peat.
2.3.6.5 Total concentration of carbonyl functional groups in solid phase peat and soil

This method was reported by Stevenson (1994). In duplicate, 5 ml of 0.25 M dimethylaminoethanol (prepared from Aldrich, ≥99.5%) and 6.3 ml of 0.4 M hydroxylammonium chloride solution (prepared from Fisher, SLR grade, >96%) were added to 50 mg peat/soil material. Vessels were heated in a steam bath for 15 minutes and allowed to cool. Following filtration (Whatman 540 hardened ashless filter paper) and addition of 20 ml deionised water, filtrates were titrated potentiometrically to the pH inflection point with 0.4 M perchloric acid (prepared from Aldrich, ACS reagent grade, 70%) solution. A reagent blank was also titrated.

Carbonyl functionality concentration (moles kg\(^{-1}\)) was determined by application of Equation 2.6.

\[
\text{C=O} = \frac{(V_{\text{blank}} - V_{\text{sample}}) \times M \times 10^6}{\text{milligrams of sample}} \quad \text{Equation 2.6}
\]

Where \(V_{\text{blank}}\) and \(V_{\text{sample}}\) represent the titration volume (ml) of acid for blank and sample respectively and \(M\) is the molarity of the acid. The difference between blank and sample titrant volumes representing the moles of reagent consumed in the initial reaction and therefore the moles of carbonyl functionality in the soil or peat sample.
2.3.7 Determination of (poly)phenol oxidase activity in peat and soil

The development of this procedure is described in Section 3.4 and the optimised methodology presented in Section 3.4.3.

2.3.8 pH measurement of solid phase peat and soil

A solution containing a low concentration of calcium chloride, e.g. 0.01 M, is usually employed to determine solid phase soil pH as it simulates the dissolved species present within a typical soil solution (White, 1969; Kissel et al., 2009). Duplicate homogenised peat/soil aliquots (4 g) were accurately weighed and added to 10 ml of 0.01 M calcium chloride solution (prepared from Fisher, Laboratory grade reagent, >99% purity). The suspension was shaken mechanically using mechanical laboratory flask shakers (Stuart Scientific) for 15 minutes before measurement using a pH meter (Jenway 3505 pH meter). The pH meter was calibrated using pH 4 and pH 7 buffers (Fisher, pH 4 phthalate buffer tablets; Fisher pH 7 phosphate buffer tablets) prior to use.

2.3.9 pH measurement of porewaters from both peat and soil

Porewater pH was measured using an electronic pH meter (Griffin model 50) and carried out in duplicate upon bulk porewater extracted as described in Section 2.3.1. The pH probe was placed into porewater samples contained in 30 ml plastic tubes, allowed to equilibrate to provide a stable pH value and the value recorded. The meter was calibrated using pH 4 and pH 7 buffer solutions from commercially available
buffer tablets (Fisher, pH 4 phthalate buffer tablets; Fisher pH 7 phosphate buffer tablets).

2.3.10 Measurement of porewater conductivity

The conductivity of porewater samples extracted as described in Section 2.3.1 was measured using an electronic multi-meter and probe (Jenway 4200) capable of directly measuring conductivity. The procedure was carried out in duplicate upon bulk porewater samples. The conductivity probe was directly applied to porewater samples in plastic 30 ml tubes until the probe was submerged. Meter readings were allowed to equilibrate and the conductivity recorded. The conductivity meter was calibrated as per manufacturer instructions using 0.01 M KCl (prepared from Fisher, >99%) solution and automatically corrected for temperature. Due to probe construction, in two layers corresponding to surface vegetation where porewater volumes were below 5 ml the probe could not be completely submerged and conductivity could not be reliably determined.

2.3.11 Concentration of dissolved organic carbon in peat and soil porewater

Duplicate porewater aliquots taken from the bulk were transferred to 1 cm quartz spectroscopy cells and their absorbance determined at 254 nm using a Varian 50-SCAN UV-Vis spectrometer. Absorbance at 254 nm is directly proportional to dissolved organic carbonaceous species present if it is assumed that interfering species are in negligible concentration. Concentrations were determined by
comparing sample absorbance to that of calibration standards of stock humic material (prepared from Aldrich H1,675-2, sodium salt, 55%) of 0.003–0.105 mg l$^{-1}$.

2.3.12 Extraction of humic substances from solid phase peat and soil samples
Humic substances were extracted from ground, homogenised solid phase peat and soil samples using 30 ml 0.1 M sodium hydroxide (prepared from VWR, analytical reagent grade, >99% w/w) to 1.0 g of sample matrix for 24 hours. Extracts were centrifuged at 5890 x g and then filtered through Whatman 540 hardened ashless filter papers under gravity. Filtrate was transferred to 3 kDa ultra-filtration filter units (Sartorius, Vivaspin 20; polyethersulfone membrane) and subjected to centrifugation at 5890 x g for ca. 60 minutes. The extracted humic substances residual in the upper compartment of the ultrafiltration apparatus were collected and stored at ~4°C. Sub-samples of this humic extract were dried and used for SEM-EDX analysis as per Section 2.3.15. Additionally, 0.2 ml of each extract was diluted in 0.8 ml 0.045 M tris-HCl (prepared from tris-(hydroxymethyl) aminomethane hydrochloride, VWR Prolabo, 99% purity) solution and used for gel electrophoresis as outlined in Section 2.3.13.

2.3.13 Gel electrophoresis

2.3.13.1 Principles of gel electrophoresis
Gel electrophoresis is a chromatographic technique that separates species on the basis of their size and charge via migration through porous gel materials. Samples
are placed into a well within a flat gel bed surrounded by electrolyte buffer. An electrical potential is placed across the gel and a current applied via electrodes at each end of the gel as shown in Figure 2.2. Highly charged species are driven more rapidly towards their counter-electrode. Steric bulk causes large species to travel shorter distances than their smaller counterparts with equivalent charge density. Molecular size is a greater determinant of distance travelled than charge; small molecules with some charge will still move rapidly through the gel. Current, potential, gel pore size and buffer electrolyte can be adjusted to optimise separation.

![Figure 2.2 Schematic of gel electrophoresis apparatus.](image)

### 2.3.13.2 Gel electrophoresis methodology

Humic substance sub-samples (0.2 ml) were diluted with 0.8 ml of 0.045 M tris-HCl solution and placed into 1 mm wells in gel electrophoresis apparatus (Fisher Gel Electrophoresis plate 13 x 14 x 2 cm, CONSORT E863 power supply). The gel
Microwave-assisted acid digestion aims to transfer all metal elements from a solid sample into the aqueous phase for further analysis, in this case via Inductively Coupled Plasma–Optical Emission Spectroscopy/Mass Spectrometry (ICP-OES/MS). Destruction of organic matter via pre-digestion ashing leaves mineral and metal composites. The use of concentrated acid such as nitric acid (HNO₃), sulphuric acid (H₂SO₄), and hydrochloric acid (HCl) allows for efficient digestion while maintaining the integrity of the metal components. This method is particularly advantageous for samples that are difficult to dissolve using traditional hotplate digestion techniques.

Microwave-assisted digestion also improves the recovery of contaminants, ensuring a more accurate assessment of the metal content in the sample. The use of microwave-assisted digestion is a common method in geochemical analysis, providing a reliable and efficient way to prepare samples for further analysis.

### 2.3.14 Microwave-assisted acid digestion of peat and soil samples

#### 2.3.14.1 Principle of microwave-assisted acid digestion

Microwave-assisted techniques offer numerous benefits over standard hotplate methods: speed, sealed pressurised environments, precise temperature control and operator safety. Acid digestion aims to transfer all metal elements from a solid sample into the aqueous phase for further analysis, in this case via Inductively Coupled Plasma–Optical Emission Spectroscopy/Mass Spectrometry (ICP-OES/MS). Destruction of organic matter via pre-digestion ashing leaves mineral and metal composites. The use of concentrated acid such as nitric acid (HNO₃), sulphuric acid (H₂SO₄), and hydrochloric acid (HCl) allows for efficient digestion while maintaining the integrity of the metal components. This method is particularly advantageous for samples that are difficult to dissolve using traditional hotplate digestion techniques.

Microwave-assisted digestion also improves the recovery of contaminants, ensuring a more accurate assessment of the metal content in the sample. The use of microwave-assisted digestion is a common method in geochemical analysis, providing a reliable and efficient way to prepare samples for further analysis.
acid (H$_2$SO$_4$) and hydrochloric acid (HCl) at high temperature and pressure causes digestion and dissolution of these inorganic species. Nitric acid leaches metals into solution in the form of highly soluble nitrate salts and is widely used to liberate metals from many matrices; sulphuric acid is used due to its ability to destroy almost any organic carbon species when heated to sufficient temperature; and hydrochloric acid is used primarily as a means of stabilising some less stable metals in solution (Sun and Hoffman, 1996). Where high quantities of silicate materials are present, additional acids such as hydrofluoric acid (HF) or hydroborofluoric acid (HBF$_4$) capable of digesting these chemically resilient species must be adopted to facilitate complete sample dissolution.

### 2.3.14.2 Microwave-assisted acid digestion methodology

Soils and peats were digested in duplicate using a modified US-EPA 3052 methodology (USEPA, 1996; Yafa and Farmer, 2006). The method was modified by inclusion of a dry ashing step prior to microwave-assisted acid digestion. More specifically, dried, homogenised soil (0.25 g) was subjected to ashing at 450°C in a muffle furnace (Carbolite high temperature laboratory chamber furnace) for 4 hours. The residues were transferred to HP-500 CEM microwave digestion vessels along with 9 ml concentrated nitric acid (used as supplied, VWR, ARISTAR grade, 69% w/v) and 1 ml concentrated hydrofluoric acid (used as supplied, VWR, ARISTAR grade, 48% w/v). Digestion was carried out using a CEM Microwave Accelerated Reaction System 5 (MARS5) via temperature controlled ramp to 180°C followed by isothermic hold for 15 minutes. After cooling, the solution was transferred to Teflon®
beakers and evaporated to ~1 ml on a hotplate. The remaining 1 ml was made up to 25 ml with 2% (v/v) nitric acid (prepared from VWR, ARISTAR grade, 69% w/v). These samples were stored prior to concentration analysis via ICP-OES/MS as outlined in Section 2.3.16 and Section 2.3.17.

2.3.14.3 Determination of Hg speciation in peats and soils via HPLC-ICP-MS analysis

The background and development of this methodology is discussed in detail in Section 3.3. In duplicate, Hg species were extracted via addition of 9 ml HCl 7.6% v/v (prepared from VWR NORMATOM, 37%) and 1 ml 10% w/v 2-mercaptoethanol (prepared from CALBIOCHEM, molecular biology grade, 99.9%) to 1 g peat/soil. Samples were subjected to sonication in an ultrasonic bath for 45 minutes with regular addition of ice to hold bath temperature at approximately room temperature. Following sonication, samples were centrifuged for 5 minutes at 1077 x g to partition solid and liquid phases. Two ml of supernatant was transferred to a 30 ml PET vial and 15 ml of deionised water added. The resultant solution was adjusted to pH 6.8 using 10% w/v ammonia (prepared from: Fisher, Laboratory grade, 35%) and the mass of total solution made up to 20 g. Solutions were filtered through a 0.22 μm syringe filter prior to HPLC-ICP-MS analysis. HPLC-ICP-MS analysis was carried out as per the configurations in Tables 3.7. and 3.8.
2.3.15 Scanning Electron Microscopy–Energy Dispersive X-ray spectroscopy (SEM-EDX)

2.3.15.1 Principles of SEM-EDX

Scanning electron microscopy-Energy Dispersive X-ray (SEM-EDX) spectroscopy is a combined technique that utilises SEM to create high magnification images of sample surfaces in combination with EDX to assess the elemental composition of specific regions of these surfaces. Both techniques operate by bombarding the surface of solid samples with a high energy electron beam under vacuum. The electrons trigger electromagnetic emissions from the sample due to interaction via both elastic and inelastic collisions: x-ray emissions due to excitation, promotion and relaxation of specimen electrons; secondary electron emissions due to transfer of sufficient energy for near-surface electrons to escape; and back-scattered electrons from the incident beam itself. These signals are shown in Figure 2.3.

Figure 2.3 Surface bombardment and emissions under an SEM-EDX system.

SEM images sample surfaces by scanning a 0.1-40 keV electron beam across the area of interest. Secondary electron emissions are low energy emissions (~50 eV)
that occur due to electron interaction with near-surface atoms and the resulting emissions allow specific imaging of the surface’s depth, edges and topography. Secondary electrons are accelerated towards a scintillator and their interaction detected via a photomultiplier. The photomultiplier output is displayed as a two-dimensional intensity distribution which provides the visual image. Back-scattering emissions are representative of the atoms with which they collided. High atomic number elements such as metals will scatter more readily than low atomic number elements. Backscatter intensity when combined with a secondary electron image provides contrast to the surface image with high density regions appearing brighter than those of low atomic number and thus density.

EDX analysis utilises the inner-electron shell transitions caused by the incident electron beam and the resultant elementally characteristic X-ray emissions. The equipment’s X-ray detector records both number and the specific energy of X-rays emitted. The fingerprint energy bands unique to specific elements allow identification of an element and the intensity provides a measure of the degree to which that element is present. By focusing the electron beam on specific regions of a sample’s surface, elemental composition of discrete areas can be obtained. An example of typical SEM-EDX output is provided below in Figure 2.4.
2.3.15.2 SEM-EDX methodology

Tightly packed, smooth coats of ground homogenised peat, soil or humic extract were fixed to one face of a double-sided tack disk which was then affixed to a steel stub. To ensure that the surface of the sample would be electrically conductive, stubs were subjected to carbon coating via a Denton Vacuum BTT-IV carbon coater at \( x10^{-6} \) Pa and 7-18\% power ramp under low voltage conditions. A conductive surface is essential due to the SEM system’s use of secondary scattered electrons to create a real-time visual representation of the sample surface to the user. SEM-EDX analysis was carried out on a Philips XL30CP with PGT Spirit X-ray analysis and HKL Channel5 Electron Backscatter Diffraction (EBSD) system. Surface images were acquired via manual scanning and secondary image acquisition mode at magnifications between 100x and 10,000x. Multiple regions of interest within each image were selected to provide representative cover of the different morphological microenvironments apparent within each visual SEM image and EDX analysis carried out upon those regions.
2.3.16 Analysis of elemental concentration in porewaters and solid soil and peat samples by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

2.3.16.1 Principles of ICP-OES

Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES) is an analytical technique capable of measuring concentrations of trace elements by energetically exciting atoms via radio frequency discharge and measuring the resultant photon emissions that are characteristic of specific atoms or their respective ions (Atkins, 1988). ICP-OES is capable of analysing a wide array of sample media; liquids are converted into an aerosolised fine mist via a nebuliser, solids are extracted into the aqueous phase via digestion procedures, and gases can be supplied directly to the apparatus. Samples are transferred to a 10000 K Inductively Coupled Plasma (ICP) within the ICP-OES apparatus (Wendt and Fassell, 1965). Within the plasma, aerosolised liquids are vaporised and gaseous molecules become atomised. Once atomised, samples undergo further excitation within the plasma to excited atomic and ionic states. Spontaneous relaxation by these excited states towards electronic ground state releases photons with specific energies dependent on the internal energy levels of the atoms and ions present. Photons are detected via a charge coupled device, also known as a camera chip. The presence of a specific element can be determined by detection of its unique emission peaks. The quantity of photons is directly proportional to the concentration of the originating element and photon ‘counts’ can be converted into concentration units using calibration standards of known concentrations (Hou and Jones, 2000). As elements often possess several characteristic photon emissions, wavelengths are selected to minimise overlapping...
spectral interference effects (Twyman, 2005) from other elements with close or adjacent emission wavelengths. The wavelengths used for specific elements within this project are shown in Table 2.1.

Table 2.1  Wavelengths used for ICP-OES elemental analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral peak wavelengths (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>394.401, 396.153</td>
</tr>
<tr>
<td>Ca</td>
<td>317.933, 422.673</td>
</tr>
<tr>
<td>Cd</td>
<td>214.440, 228.802</td>
</tr>
<tr>
<td>Cu</td>
<td>324.752, 327.393</td>
</tr>
<tr>
<td>Fe</td>
<td>238.204, 259.939</td>
</tr>
<tr>
<td>K</td>
<td>766.490</td>
</tr>
<tr>
<td>Mg</td>
<td>280.271, 285.213</td>
</tr>
<tr>
<td>Mn</td>
<td>257.610, 259.372</td>
</tr>
<tr>
<td>Na</td>
<td>588.995, 589.592</td>
</tr>
<tr>
<td>Ni</td>
<td>341.476</td>
</tr>
<tr>
<td>Pb</td>
<td>217.000, 220.353</td>
</tr>
<tr>
<td>S</td>
<td>180.669</td>
</tr>
<tr>
<td>Si</td>
<td>252.851, 288.158</td>
</tr>
<tr>
<td>Zn</td>
<td>206.200, 213.857</td>
</tr>
</tbody>
</table>

2.3.16.2  ICP-OES methodology

All ICP-OES analysis was carried out using a Perkin Elmer Optima 5300 DV. The standard conditions shown in Table 2.2 were applied throughout unless stated otherwise. The instrumental setup of the Optima 5300 DV comprised a Gem Tip cross-flow nebuliser with Scott-type spray chamber. Argon gas flows were set at 15 l min\(^{-1}\), 0.2 l min\(^{-1}\) and 0.75 l min\(^{-1}\) for plasma, auxiliary and nebuliser flows, respectively. The peristaltic pump flow-rate for sample uptake was set at 1.50 ml min\(^{-1}\).
Table 2.2  Standard ICP-OES operating variables

<table>
<thead>
<tr>
<th>Instrument model:</th>
<th>Perkin Elmer Optima 5300 DV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power:</td>
<td>1400 W</td>
</tr>
<tr>
<td>Spray chamber:</td>
<td>Scott type - polymer</td>
</tr>
<tr>
<td>Nebuliser:</td>
<td>‘Gem Tip’ cross-flow nebuliser</td>
</tr>
<tr>
<td>Plasma flow:</td>
<td>15 l min$^{-1}$</td>
</tr>
<tr>
<td>Auxiliary flow:</td>
<td>0.2 l min$^{-1}$</td>
</tr>
<tr>
<td>Nebuliser flow:</td>
<td>0.75 l min$^{-1}$</td>
</tr>
<tr>
<td>Pump flow:</td>
<td>1.50 ml min$^{-1}$</td>
</tr>
<tr>
<td>Plasma view:</td>
<td>Axial</td>
</tr>
</tbody>
</table>

2.3.16.3  Quality control in ICP-OES analysis

ICP-OES quality control measures including calibration standards, reference materials and additional measures are outlined below. Detection limits are included in Table 2.3 (EAG, 2007). Limits of detection quoted for ICP-OES are for axial view.

Internal ICP-OES software was set to measure each sample three times to generate instrumental errors for each sample analysis (typically <1.5%). Elemental concentration standards were diluted from 1000 mg l$^{-1}$ stock standard solutions (Fisher, Single element standard for ICP analysis: 1000 mg l$^{-1}$ in 1 M nitric acid) with 2% (v/v) nitric acid (prepared from VWR, ARISTAR grade, 48% w/v).
Table 2.3  Element detection limits for ICP-OES and ICP-MS analysis (EAG, 2007)

<table>
<thead>
<tr>
<th>Element</th>
<th>ICP-OES (axial) limit of detection (µg l⁻¹)</th>
<th>ICP-MS limit of detection (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>50</td>
<td>0.005</td>
</tr>
<tr>
<td>Hg</td>
<td>50</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>5</td>
<td>0.002</td>
</tr>
<tr>
<td>Al</td>
<td>20</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn</td>
<td>5</td>
<td>0.0005</td>
</tr>
<tr>
<td>Mg</td>
<td>0.5</td>
<td>0.001</td>
</tr>
<tr>
<td>Cu</td>
<td>5</td>
<td>0.0005</td>
</tr>
<tr>
<td>Zn</td>
<td>5</td>
<td>0.001</td>
</tr>
<tr>
<td>Ni</td>
<td>5</td>
<td>0.002</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5</td>
<td>0.005</td>
</tr>
<tr>
<td>K</td>
<td>100</td>
<td>0.05</td>
</tr>
<tr>
<td>Na</td>
<td>50</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Multielement standards (Merck, ICP multi-element standard solution IV in nitric acid) were employed for simultaneous calibration of over ten elements. A standard blank of 2% (v/v) nitric acid was included as the calibration zero-point. Typical standard concentration ranges were from 0.1–300 mg l⁻¹. Higher concentration standards were added if necessary. Samples exceeding this range were diluted accurately with 2% (v/v) nitric acid (prepared from VWR, ARISTAR grade, 48% w/v) and a repeat analysis carried out. Calibrations were checked via NIST SRM 1643e and M6 certified reference solutions and their concentrations checked against certified values outlined in Table 2.4 and Table 2.5. Concentrations were mainly within 1 s.d. or at worst within 2 s.d. the certified values. Measured CRM concentrations are in good agreement with their certified values. SRM1643e concentrations show ≤5% difference between recorded and certified concentration values, whereas ≤7.5% differences are observed for M6 solution. Unpaired t-tests show p-values in excess of 0.05, implying that measured concentrations and certified concentrations are not statistically different by traditional conventions.
Table 2.4  SRM1643e certified reference solution concentrations analysed by ICP-OES

<table>
<thead>
<tr>
<th>Element</th>
<th>N</th>
<th>Mean µg l⁻¹</th>
<th>s.d.</th>
<th>s.e.</th>
<th>Certified Value µg l⁻¹</th>
<th>s.d.</th>
<th>p-value (t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>17</td>
<td>19.8</td>
<td>1.09</td>
<td>0.26</td>
<td>19.63</td>
<td>0.21</td>
<td>0.153</td>
</tr>
<tr>
<td>Fe</td>
<td>2</td>
<td>99.4</td>
<td>2.31</td>
<td>1.64</td>
<td>99.37</td>
<td>1.64</td>
<td>0.980</td>
</tr>
<tr>
<td>Al</td>
<td>2</td>
<td>147</td>
<td>13.9</td>
<td>9.85</td>
<td>141.8</td>
<td>8.6</td>
<td>0.403</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>22.7</td>
<td>0.44</td>
<td>0.31</td>
<td>22.76</td>
<td>0.31</td>
<td>0.788</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
<td>40.7</td>
<td>0.99</td>
<td>0.070</td>
<td>38.97</td>
<td>0.45</td>
<td>0.431</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>7600</td>
<td>402</td>
<td>285</td>
<td>7841</td>
<td>96</td>
<td>0.360</td>
</tr>
</tbody>
</table>

Table 2.5  M6 certified reference solution concentrations analysed by ICP-OES

<table>
<thead>
<tr>
<th>Element</th>
<th>N</th>
<th>Mean mg l⁻¹</th>
<th>s.d.</th>
<th>s.e.</th>
<th>Certified Value mg l⁻¹</th>
<th>s.d.</th>
<th>p-value (t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>7</td>
<td>9.61</td>
<td>0.89</td>
<td>0.34</td>
<td>10.0</td>
<td>0.5</td>
<td>0.265</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>92.5</td>
<td>9.6</td>
<td>3.8</td>
<td>100.0</td>
<td>5</td>
<td>0.074</td>
</tr>
<tr>
<td>Al</td>
<td>4</td>
<td>9.45</td>
<td>0.75</td>
<td>0.38</td>
<td>10.0</td>
<td>0.5</td>
<td>0.131</td>
</tr>
<tr>
<td>Cu</td>
<td>4</td>
<td>9.85</td>
<td>0.65</td>
<td>0.33</td>
<td>10.0</td>
<td>0.5</td>
<td>0.648</td>
</tr>
<tr>
<td>Mn</td>
<td>4</td>
<td>9.87</td>
<td>0.70</td>
<td>0.35</td>
<td>10.0</td>
<td>0.5</td>
<td>0.700</td>
</tr>
<tr>
<td>Mg</td>
<td>4</td>
<td>9.50</td>
<td>0.77</td>
<td>0.39</td>
<td>10.0</td>
<td>0.5</td>
<td>0.170</td>
</tr>
</tbody>
</table>

Digested samples of NIMT/UoE/FM/001 (Yafa et al., 2004) and CRM 7004 (Kueera et al., 1998), although included primarily as a means of validation of the solid digestion procedures, also provided a quality control reference point where digested solid phase samples were being analysed. Concentration results for the digests of solid phase reference materials are presented in Table 2.6 and Table 2.7. Solid phase CRM concentrations are broadly in agreement with their certified values. The greatest percentage difference between recorded and certified values is seen for Fe in NIMT/UoE/FM/001 where concentrations differ by 15% of the certified concentration. All other metals reported for NIMT/UoE/FM/001 show non-statistically signifigant p-values under t-test of >0.05 and acceptable standard errors. Lead concentrations for CRM7004 are in close agreement with certified values with ~5% difference between reported and certified values.
Table 2.6  NIMT/U0E/FM/001 certified peat reference material concentrations analysed by ICP-OES

<table>
<thead>
<tr>
<th>Element</th>
<th>N</th>
<th>Mean mg kg(^{-1})</th>
<th>s.d.</th>
<th>s.e.</th>
<th>Certified Value mg kg(^{-1})</th>
<th>s.d.</th>
<th>p-value (t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>8</td>
<td>175</td>
<td>18.2</td>
<td>6.44</td>
<td>174</td>
<td>8.0</td>
<td>0.8774</td>
</tr>
<tr>
<td>Fe</td>
<td>16</td>
<td>850</td>
<td>94.1</td>
<td>22.2</td>
<td>921</td>
<td>84</td>
<td>0.0633</td>
</tr>
<tr>
<td>Cu</td>
<td>10</td>
<td>6.08</td>
<td>1.08</td>
<td>0.33</td>
<td>5.28</td>
<td>1.04</td>
<td>0.1088</td>
</tr>
<tr>
<td>Mn</td>
<td>12</td>
<td>6.94</td>
<td>0.82</td>
<td>0.18</td>
<td>7.52</td>
<td>0.41</td>
<td>0.0559</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>616</td>
<td>35.1</td>
<td>10.1</td>
<td>582</td>
<td>168</td>
<td>0.5403</td>
</tr>
<tr>
<td>Al</td>
<td>8</td>
<td>3510</td>
<td>223</td>
<td>70.6</td>
<td>3692</td>
<td>347</td>
<td>0.2179</td>
</tr>
</tbody>
</table>

Table 2.7  Soil reference material CRM 7004–loam concentrations analysed by ICP-OES

<table>
<thead>
<tr>
<th>Element</th>
<th>N</th>
<th>Mean mg kg(^{-1})</th>
<th>s.d.</th>
<th>s.e.</th>
<th>Certified Value mg kg(^{-1})</th>
<th>s.d.</th>
<th>p-value (t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>4</td>
<td>97.8</td>
<td>11.7</td>
<td>5.6</td>
<td>93.4</td>
<td>3.4</td>
<td>0.2783</td>
</tr>
</tbody>
</table>

Over long periods of operation, ICP-OES apparatus can be subject to drift. When drift occurs, internal and detection efficiencies change and can cause repeated analysis of identical solutions to yield different concentration values. A calibration standard solution towards the lower range of standard concentrations was selected and inserted between every 10\(^{th}\) analysis sample to assess drift. This solution was typically 5 mg l\(^{-1}\) in concentration and each drift control sample was followed by a rinse sample of 2% (v/v) nitric acid to prevent carry-over contamination. Drift control samples were monitored during analysis and compared afterwards to ensure consistent measurements across each sample set. Where drift was discovered, samples analysed beyond the latest acceptable drift control standard were repeated in a later analysis run.
2.3.17 Analysis of elemental concentration in porewaters and solid soil and peat samples by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS)

2.3.17.1 Principles of ICP-MS

Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) utilises high temperature argon plasma (~10,000K) as a mass spectrometry ionisation source. Liquid samples are aerosolised via the nebuliser prior to passage to the high density (Ar\(^+\), e\(^-\)) plasma torch where molecules are atomised and atoms become rapidly ionised. These ions are drawn through a series of skimmer cones via a graduated vacuum to focus the ion ingress to approximate linearity as outlined in Figure 2.5. The ion beam is passed to a multi-pole detector where the ions are screened and separated on the basis of their mass to charge (m/z) ratio and the number of ions incident on the detector is recorded. Numerically greater multi-poles provide improved resolution on the atomic mass unit. Further filter and screening apparatus can be fitted between skimmers and multipoles to reduce interference effects. These include an octopole reaction system that applies kinetic energy discrimination and collision-induced separation to remove multiatomic species (Agilent, 2005). Systems are calibrated via elemental standards, certified concentration reference materials or certified isotope dilution references. ICP-MS possesses many advantages over alternative ionisation and detection systems: it is capable of handling entire samples on the atomic as opposed to molecular level, high throughput potential and low detection limits in the µg l\(^-1\) – ng l\(^-1\) range dependent on the element.
2.3.17.2 ICP-MS methodology for determination of trace element concentration

Samples whose concentration fell close to or below detection limits for ICP-OES were analysed using an Agilent 7500ce ICP-MS system incorporating a quadrupole mass analyser and an octopole reaction system. The standard operating conditions shown in Table 2.8 were applied throughout unless otherwise stated. In brief, RF forward power was set to 1540 W with a reflected power of 1 W. Argon gas flow rates were configured to 0.82 l min\(^{-1}\) and 0.2 l min\(^{-1}\) for carrier and makeup flows, respectively. Hardware consisted of a Micro mist nebuliser operating close to free-aspiration conditions at 1.0 ml min\(^{-1}\). Nickel skimmer and sample cones were employed in the interior.
Table 2.8  Standard ICP-MS operating conditions

<table>
<thead>
<tr>
<th>Instrument Model:</th>
<th>Agilent 7500ce ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Power:</td>
<td>1540W</td>
</tr>
<tr>
<td>RF Matching:</td>
<td>1.76V</td>
</tr>
<tr>
<td>Uptake rate:</td>
<td>0.06 rps</td>
</tr>
<tr>
<td>Sampling depth:</td>
<td>8.4 mm</td>
</tr>
<tr>
<td>Carrier gas flow rate:</td>
<td>0.82 l min⁻¹</td>
</tr>
<tr>
<td>Make-up gas flow rate:</td>
<td>0.21 l min⁻¹</td>
</tr>
<tr>
<td>Nebuliser:</td>
<td>Micro mist</td>
</tr>
<tr>
<td>Spray chamber:</td>
<td>Scott-type, glass.</td>
</tr>
</tbody>
</table>

2.3.17.3  Quality control in ICP-MS concentration analysis

ICP-MS quality control measures including calibration standards, reference materials and additional measures are outlined below. Detection limits are included in Table 2.3. Internal ICP-MS software was set to measure each sample three times to generate instrumental errors for each sample analysis (typically ~10% for sub-mg l⁻¹ concentrations and ~1% for µg l⁻¹ concentrations). Elemental concentration standards were diluted from 1000 mg l⁻¹ stock standard solutions (Fisher, Single element standard for ICP analysis: 1000 mg l⁻¹ in 1 M nitric acid) with 2% (v/v) nitric acid (prepared from VWR, ARISTAR grade, 48% w/v). A standard blank of 2% (v/v) ARISTAR nitric acid was included as the calibration zero-point. Typical standard concentration ranges were from 0.1–100 µg l⁻¹. Samples were screened via ICP-OES prior to ICP-MS analysis and samples expected to exceed this range of standards were diluted accurately with 2% (v/v) nitric acid and a repeat analysis carried out. Calibrations were checked via inclusion of NIST SRM 1643e and M4 certified reference solutions inserted into sample sets and their concentrations checked against certified values outlined in Table 2.9 and Table 2.10. Concentrations were mainly within 1 s.d. or at worst within 2 s.d. of the certified values. Measured CRM concentrations are generally in good agreement with certified values. With the
exception of Fe and Al measurements for M4 solution, all reported concentrations are not significantly statistically different from the certified values. However, the statistical difference for Fe and Al is not of concern as these elements are highly abundant in the environment and will be analysed via ICP-OES where no such statistical difference is apparent. Lead concentration measurements for SRM1643e are in excellent agreement with certified values with measured concentration of $19.85 \pm 0.84 \text{ mg l}^{-1}$ compared to the certified value of $19.63 \pm 0.21 \text{ mg l}^{-1}$.

Digested samples of NIMT/UoE/FM/001 (Yafa et al., 2004) and CRM7004 (Kueera et al., 1998), although included primarily as a means of validation of the solid digestion procedures, also provided a quality control reference point where digested solid phase samples were being analysed (Table 2.9). Lead results are in excellent agreement with certified solid phase concentrations and only differ by ~1% from certified values. Results for Hg are acceptable with <13% difference between certified values and those reported in this study. Statistical t-testing showed no significant difference between measured and certified values.

<table>
<thead>
<tr>
<th>Certified reference material</th>
<th>Element</th>
<th>N</th>
<th>Mean</th>
<th>s.d.</th>
<th>s.e.</th>
<th>Certified Value</th>
<th>s.d.</th>
<th>p-value (t-test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM1643e</td>
<td>Pb</td>
<td>2</td>
<td>19.85 mg l$^{-1}$</td>
<td>0.84</td>
<td>0.59</td>
<td>19.63 mg l$^{-1}$</td>
<td>0.21</td>
<td>0.412</td>
</tr>
<tr>
<td>NIMT/UoE/FM/001</td>
<td>Pb</td>
<td>6</td>
<td>175 mg kg$^{-1}$</td>
<td>9.9</td>
<td>4.0</td>
<td>174 mg kg$^{-1}$</td>
<td>8.0</td>
<td>0.828</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>6</td>
<td>0.181 mg kg$^{-1}$</td>
<td>0.03</td>
<td>0.01</td>
<td>0.169 mg kg$^{-1}$</td>
<td>0.01</td>
<td>0.256</td>
</tr>
<tr>
<td>CRM7004</td>
<td>Pb</td>
<td>4</td>
<td>94.4 mg kg$^{-1}$</td>
<td>4.1</td>
<td>2.01</td>
<td>93.4 mg kg$^{-1}$</td>
<td>3.4</td>
<td>0.646</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>4</td>
<td>0.208 mg kg$^{-1}$</td>
<td>0.01</td>
<td>0.007</td>
<td>0.223 mg kg$^{-1}$</td>
<td>0.02</td>
<td>0.185</td>
</tr>
</tbody>
</table>
Table 2.10  M4 certified reference solution concentrations (x1000 dilution) analysed by ICP-MS

<table>
<thead>
<tr>
<th>Element</th>
<th>N</th>
<th>Mean s.d.</th>
<th>s.e.</th>
<th>Certified Value s.d.</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>13</td>
<td>1.05 0.08</td>
<td>0.02</td>
<td>1.0 0.001</td>
<td>0.0627</td>
</tr>
<tr>
<td>Fe</td>
<td>2</td>
<td>1.34 0.005</td>
<td>0.0005</td>
<td>1.0 0.001</td>
<td>0.0001</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>1.15 0.019</td>
<td>0.011</td>
<td>1.0 0.001</td>
<td>0.0001</td>
</tr>
<tr>
<td>Cu</td>
<td>8</td>
<td>1.04 0.07</td>
<td>0.02</td>
<td>1.0 0.001</td>
<td>0.0873</td>
</tr>
<tr>
<td>Mn</td>
<td>8</td>
<td>1.05 0.08</td>
<td>0.03</td>
<td>1.0 0.001</td>
<td>0.0637</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>1.03 0.09</td>
<td>0.06</td>
<td>1.0 0.001</td>
<td>0.2037</td>
</tr>
</tbody>
</table>

Over long periods of operation, ICP-MS apparatus can be subject to drift as operating sensitivity changes over time. When drift occurs, internal and detection efficiencies change and can cause repeated analysis of identical solutions to yield different concentration values. The control measure of incorporating bracketing standards was adopted to assess this effect. A calibration standard solution towards the lower range of standard concentrations was selected and inserted between every 6th analysis sample to assess drift. This solution was typically 5 µg l⁻¹ in concentration and each drift control sample was followed by a rinse sample of 2% (v/v) ARISTAR nitric acid to prevent carry-over contamination. Drift control samples were monitored during analysis and compared afterwards to ensure consistent measurements across each sample set. Where drift was discovered, samples analysed beyond the latest acceptable drift control standard were repeated in a later analysis run.
2.3.17.4 ICP-MS methodology for determination of Pb isotopic ratios

Isotopic analysis measurements were carried out on an Agilent 7500ce ICP-MS with operating conditions as specified in Table 2.8. The instrument was operated in fully quantitative isotope acquisition mode. $^{206}\text{Pb}$ and $^{207}\text{Pb}$ integration occurred for 2 s per point, yielding a total integration time of 6 s per unit mass. $^{208}\text{Pb}$ was integrated for 1 s, providing a total integration time of 3 s.

At the beginning of each day a P/A (pulse/analogue) factor was ascertained across mass range 208-206 amu and the concentration trip-point, i.e. the concentration triggering transition from pulse to analogue mode, determined. This concentration was typically $\sim 25 \mu g \, l^{-1}$ Pb. All samples were diluted to fall within the 15-20 $\mu g \, l^{-1}$ range where they exceeded these concentrations.

2.3.17.5 Quality control in ICP-MS stable Pb isotope ratio analysis

The ICP-MS software was configured to perform five replicate measurements for each sample solution for each isotope to provide both mean values and an indication of instrument-related deviation for isotopic abundances and ratios. Typical standard deviations were $<0.01$ for isotopic ratios.
Isotopic ratio measurements suffer from mass bias effects that arise due to the different inherent masses and thus velocities of the isotopes under analysis. Mass bias in stable Pb isotope ratio analysis was corrected by including serial dilutions of certified reference material NIST SRM 981; typically at 1, 5, 10 and 20 µg l$^{-1}$ Pb concentrations within each analysis set. Alongside isotopic ratio, Pb concentration of each sample was measured. Post-analysis processing was performed by the ICP-MS operating software using the NIST SRM 981 reference material closest in concentration to each individual sample as a reference point providing no noticeable drift had occurred in the measured isotope ratios of the bracketing standard throughout the analytical run.

Lead isotope ratio analysis calibration was checked via inclusion of NIST SRM 981 and NIST SRM 1643e certified reference materials inserted into sample sets and their concentrations and isotope ratios checked against certified values. Isotope values were in good agreement with certified values as shown in Table 2.11. T-test $p$-values (under certified concentrations in the table) show no significant difference between measured and certified values. Simultaneous concentration analysis calibration was carried out as outlined in Section 2.3.17.3 with concentration ranges between 0.01-25 µg l$^{-1}$. 

Methodologies
Table 2.11  Stable isotope ratio results for certified reference materials analysed by ICP-MS

| Reference Material | Measured Values | | | | Certified Values | | | | |
|-------------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                   | $^{206}$Pb/$^{207}$Pb | s.d. | $^{208}$Pb/$^{207}$Pb | s.d. | $^{208}$Pb/$^{206}$Pb | s.d. | $^{206}$Pb/$^{207}$Pb | s.d. | $^{208}$Pb/$^{207}$Pb | s.d. | $^{208}$Pb/$^{206}$Pb | s.d. |
| NIST SRM 981      | 1.094 (n=66)  | 0.002 | 2.369 (n=81)  | 0.007 | 2.163 (n=81)  | 0.009 | 1.0933 (p=0.274)  | 0.0033 | 2.370 (p=0.676)  | 0.008 | 2.168 (p=0.097)  | 0.008 |
| NIST SRM 1643e    | 1.169 (n=12)  | 0.004 | 2.447 (n=12)  | 0.007 | 2.094 (n=12)  | 0.006 | 1.168 (p=0.522)  | 0.003 | 2.452 (p=0.091)  | 0.006 | 2.098 (p=0.087)  | 0.004 |
| NIMT/UoE/FM/001   | 1.177 (n=6)   | 0.002 | 2.462 (n=6)   | 0.004 | 2.092 (n=6)   | 0.005 | 1.176 (p=0.200)  | 0.001 | 2.461 (p=0.577)  | 0.003 | 2.092 (p=1)      | 0.002 |
Machine drift effect was assessed by incorporating bracketing NIST SRM981 standards as a control measure. A calibration standard solution towards the lower range of standard concentrations was selected and inserted between every 6th analysis sample to assess drift. This solution was typically 20 µg l⁻¹ in concentration and each drift control sample was followed by a rinse sample of 2% (v/v) ARISTAR nitric acid to prevent carry-over contamination. Drift control samples were monitored during analysis and compared afterwards to ensure consistent measurements across each sample set. Where isotope analysis drift was discovered, samples analysed beyond the latest acceptable drift control standard were repeated in a later analysis run. Concentration bracketing standards as described in Section 2.3.17.3 were included alongside additional 20 µg Pb l⁻¹ NIST SRM 981 isotope drift control standards to ensure consistency in both concentration and isotopic ratio analysis.

2.3.18 Age determination of peat and soil samples via $^{210}$Pb dating by gamma spectrometry

2.3.18.1 Principles of gamma spectrometry

Gamma spectrometry measures the specific energy of $\gamma$-radiation emissions from a particular source. These emissions occur when a parent radionuclide undergoes decay into a more stable lower energy state, emitting a $\gamma$-ray of approximately keV to 2 MeV. $\gamma$-rays emitted by a specific radionuclide during identical decay processes will possess constant, characteristic energies. Measurement of these characteristic $\gamma$-rays enables the detection of the originating parent radionuclide.
2.3.18.2 Principles of $^{210}\text{Pb}$ dating

Worldwide distribution of $^{238}\text{U}$ decay series radionuclides in geologic minerals causes the generation of $^{222}\text{Rn}$ daughter nuclide gas. The $^{222}\text{Rn}$ is continuously released to the atmosphere where it decays to $^{210}\text{Pb}$ via short half-life intermediates. The $^{210}\text{Pb}$ becomes adsorbed onto atmospheric particulates or dissolved in precipitation and is deposited onto soil or peat surfaces via either wet or dry deposition. This $^{210}\text{Pb}$ forms the ‘unsupported’, excess component and in conjunction with the ‘supported’ $^{210}\text{Pb}$ from long-lived members of the decay series, inherent in the soil and already in secular equilibrium with its surroundings. In peat samples, where mineral content is minimal, the supported $^{210}\text{Pb}$ component is negligible. Where a system is assumed to be accumulating at a constant rate, supported $^{210}\text{Pb}$ is constant with depth, whereas unsupported $^{210}\text{Pb}$ decreases exponentially with increasing soil or peat depth. In order to calculate both the supported and unsupported fractions, it is necessary to measure $^{210}\text{Pb}$ at 46.5 keV, $^{214}\text{Pb}$ at 295 and 352 keV and $^{214}\text{Bi}$ at 609 keV.

Two models can be applied to convert $^{210}\text{Pb}$ activity to ages; the Constant Initial Concentration (CIC) model (Robbins, 1978) or the Constant Rate of Supply (CRS) model (Appleby and Oldfield, 1978). Both models operate on the assumption of a constant rate of supply of unsupported $^{210}\text{Pb}$ and require no post depositional mobility or mixing. Where the models differ is that the CIC model assumes that accumulation rates are also constant; an assumption not easily accepted for peatland systems in particular. The CRS model makes no such assumptions and is therefore the preferred model for extrapolating age information.
The CRS model is used by this project to determine layer ages. Age is calculated via Equation 2.7 where \( t_i \) is the age of layer \( i \), \( \lambda \) is the \(^{210}\text{Pb}\) decay constant (0.03114 y\(^{-1}\)), \( I \) is the total inventory of unsupported \(^{210}\text{Pb}\) within the core and \( I_i \) is the inventory of unsupported \(^{210}\text{Pb}\) inventory below layer \( i \).

\[
t_i = \frac{1}{\lambda} \times \ln \left( \frac{I}{I_i} \right)
\]

**Equation 2.7**

### 2.3.18.3 Preparation and analysis methodologies for \(^{210}\text{Pb}\) dating via gamma spectrometry

Sub-samples weighing 5 g, 10 g, 15 g or 20 g of dried solid peat or soil were weighed for each layer of a core and their masses accurately recorded. Each sample was pressed into disks of 4 cm diameter and equivalent geometry using a hydraulic press and stainless steel template blocks. Sample disks were sealed inside transparent plastic containers of disk geometry and sealed against the air with a coating of epoxy adhesive resins. Sealed containers were allowed to equilibrate with their internal atmosphere for >3 weeks prior to analysis to allow internal atmospheric radon to achieve equilibration. Peat standards of 5 g, 10 g, 15 g and 20 g were spiked with radioisotopes of known activity and processed via identical compression and sealing processes by staff at SUERC. These standards were incorporated into each suite of analysis to verify correct instrumentation function.

To reduce background count rates, sample containers were placed into a Pb, Cd and Cu shielded compartment open to a co-axial n-type high purity germanium HPGe
detectors (Tennelec). Spectra were recorded via an EG & G Ortec multi channel buffer and these spectra were analysed via EG & G Ortec peak search and analysis software. Samples were counted for approximately a week with the accurate detector live time recorded. Cumulative spectra were acquired and the age of each peat and soil sample was calculated as demonstrated in Appendix 7.
Chapter 3 Method development

3.1 Introduction

In this chapter, the development of three key methodologies will be described. These are: concentration analysis of Hg via ICP-MS and speciation of Hg via High Performance Liquid Chromatography–Inductively Coupled Plasma–Mass Spectrometry (HPLC-ICP-MS) and determination of (poly)phenol oxidase activity via UV/Vis spectroscopy.

3.2 Analysis of Hg concentrations in solid soil and peat and associated porewaters by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

3.2.1 Introduction to [Hg] methodology development

Different levels of pre-treatment are required before determining concentrations of trace metals within liquid and solid environmental media. Water samples require little laboratory processing, e.g. filtration followed by instrumental analysis, whereas solid phase media often require drying and homogenisation, destruction of organic matter and dissolution of the solid matrix, filtration and dilution, and finally instrumental analysis. Such extraction processes involve treating soils and peats with acids including HNO₃ and HCl alongside a technique to destroy organic matter such as high temperature ashing or H₂O₂ oxidation as per the USEPA 3050 methodology (USEPA, 1996). When required, acids such as HF, capable of digesting silicates are also incorporated to completely digest the mineral fraction of sample media.
Digestion procedures of this type have already been outlined within Section 2.3.14 of Chapter 2 and these methodologies are applicable to all trace metals of interest to this project with the exception of Hg.

The analysis of Hg in environmental samples poses a number of obstacles. Unless samples have received significant contamination, [Hg] levels are often low and within the µg kg$^{-1}$ – ng kg$^{-1}$ concentration range. These concentration ranges require analytical techniques with low detection limits or that significant pre-analysis concentration is carried out prior to analysis. Furthermore, the unique chemistry of Hg, including its volatility and reactivity, render aspects of the methodologies in Section 2.3.14 and Section 2.3.17 inappropriate. The chemistry of Hg is outlined in greater detail in Chapter 6 but, within this method development, the specific properties of Hg and the problems they pose for sample pre-treatment methods will be discussed.

Dried solid soil and peat certified reference materials were employed throughout the Hg methodology development. The Czech soil reference material (Kueera et al., 1998) CRM 7002 is a light sandy soil with [Hg]: 0.090 ± 0.012 mg kg$^{-1}$ while CRM 7004 is a loam soil with [Hg]: 0.223 ± 0.016 mg kg$^{-1}$. NIMT/UOE/FM/001 ([Hg]: 0.169 ± 0.007 mg kg$^{-1}$) was chosen as a representative peat matrix certified reference material (Yafa et al., 2004).
3.2.2 Selection of analytical technique for [Hg] analysis

Mercury analysis has traditionally been carried out via Flame Atomic Absorption Spectroscopy (FAAS), Cold Vapour-Atomic Fluorescence Spectrometry (CV-AFS), Inductively Coupled Plasma techniques (ICP-OES/MS), or in more recent years via purpose-built CV-AFS Hg analysers designed to give extremely low detection limits in the sub ng l\(^{-1}\) range. The detection limits of these techniques are outlined in Table 3.1.

<table>
<thead>
<tr>
<th>Analytical technique</th>
<th>[Hg] detection limit (µg l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAAS</td>
<td>1000</td>
</tr>
<tr>
<td>CV-AFS</td>
<td>0.0002</td>
</tr>
<tr>
<td>Mercury analyser</td>
<td>0.00002</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>50</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>0.001</td>
</tr>
</tbody>
</table>

The CV-AFS and Hg analyser technologies have the most favourable detection limits but these technologies were not directly available to this project. Accessible in this project was an Agilent 7500ce ICP-MS and a Perkin Elmer Optima 5300 DV ICP-OES system, each with the technical capability to detect Hg with theoretical detection limits of 0.001 µg l\(^{-1}\) and 1 µg l\(^{-1}\) respectively. The considerably lower detection limit of the ICP-MS system made it the favoured option of the two, reducing the need for additional pre-concentration procedures prior to analysis.
3.2.3 Method development for [Hg] analysis of solid peat and soil and associated porewaters by Inductively Coupled Plasma–Mass Spectroscopy (ICP-MS)

The separate steps involved in a standard acid digestion process were assessed from the perspective of [Hg] analysis. These include: the drying and homogenisation process; organic matter destruction and sample dissolution; filtration, volume reduction and re-dissolution; and finally instrumental analysis. The methodology permutations investigated within this development are summarised in Table 3.2.

3.2.3.1 Drying of solid phase soils and peats for Hg concentration analysis

The volatility of Hg raises several concerns surrounding the practices of using (i) heated ovens to dry solid samples prior to homogenisation; (ii) an ashing furnace to destroy organic matter and (iii) hotplates for digestion. The risk of partial loss of Hg vapour during oven-drying of soil at 105°C over a 24 hour period is considerable (Cantle, 1982; Cragin and Foley, 1985). Mercury losses during oven drying vary dependent on sample media and oven temperature; losses of 24%, 40% and 72% have been recorded for sediments, soils and biological materials respectively. To circumvent this potential loss, soils and peats to be analysed for Hg should be air-dried at room temperature and sub-samples placed in a dessicator prior to analysis. As an additional precaution, the risk of Hg undergoing photo-volatilisation (where Hg(II) is first reduced to Hg(0)) should be avoided by ensuring drying samples are not exposed to direct or strong light sources by placing them in a shaded area or via
use of screens to block sunlight. At all stages throughout this method development, all samples were subject to air-drying in the absence of light. The losses of Hg from soil samples during oven-drying and under exposure to sunlight are well-documented (Amyot et al., 1994; Xiao et al., 1995; Carpi and Lindberg, 1997; Lindberg et al., 1998).

Since air-drying can take several weeks, it is helpful to break up the field-moist solid samples to expose the largest possible surface area to the air, and then to store dried samples in a controlled dessicator for additional periods to promote further loss of water and to prevent reacquisition of moisture from the atmosphere.

A consequence of using the air-drying method is, however, that residual moisture may become trapped within the sample bulk yielding inaccurate solid sample mass measurements. High temperature ovens will regularly drive this moisture out whereas air-drying is unlikely to achieve this. Instead, accurate solid sample masses can be obtained by removing sub-samples of the soil after air-drying and subjecting the sub-samples to oven-drying at 105°C in order to obtain the true moisture content. With this value, any residual moisture can be corrected for using Equation 3.1.

\[
\text{Corrected sample mass (g)} = \frac{\text{air-dried sample (g) x oven-dried sub-sample (g)}}{\text{air-dried sub-sample (g)}} \quad \text{Equation 3.1}
\]
3.2.3.2 Destruction of organic matter in solid phase soils and peats for [Hg] analysis

It is necessary to break down and remove the organic components of the peat or soil samples as their continued presence may interfere with the microwave acid-digestion process and with the plasma ionisation within the ICP-MS. Within each approach assessed within this section, all samples were digested via the normal microwave-assisted acid digestion and analysed via ICP-MS as per Section 2.3.17 in Chapter 2. A tabulated comparison of approaches is provided in Table 3.2 and a detailed list of the data and accompanying statistical t-testing is provided in Appendix 4.

Table 3.2 Summary of the drying, organic matter destruction, dissolution and volume reduction configurations adopted during the development of [Hg] analysis

<table>
<thead>
<tr>
<th>Method</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>Oven</td>
<td>Air</td>
<td>Air</td>
<td>Air</td>
<td>Air</td>
<td>Air</td>
<td>Air</td>
</tr>
<tr>
<td>Organic matter destruction</td>
<td>-</td>
<td>Furnace</td>
<td>AR reflux</td>
<td>Cold AR</td>
<td>Cold AR</td>
<td>Cold AR</td>
<td>Cold AR (reduced volume of acid)</td>
</tr>
<tr>
<td>Dissolution</td>
<td>-</td>
<td>Microwave HF/HNO₃</td>
<td>Microwave HF/HNO₃</td>
<td>Hotplate HF/HNO₃</td>
<td>Microwave HF/HNO₃</td>
<td>Microwave HF/HNO₃</td>
<td>Microwave HF/HNO₃</td>
</tr>
<tr>
<td>Volume reduction</td>
<td>-</td>
<td>Low T hotplate</td>
<td>Low T hotplate</td>
<td>Low T hotplate</td>
<td>Low T hotplate</td>
<td>Air evaporation</td>
<td>Low T hotplate</td>
</tr>
</tbody>
</table>

*AR = aqua regia
Table 3.3 Summary of [Hg] and recovery data for methods I-VII for three certified reference materials

<table>
<thead>
<tr>
<th>Method</th>
<th>NIMT/UOE/FM/001 (mg kg⁻¹)*</th>
<th>Recovery (%)</th>
<th>CRM 7002 (mg kg⁻¹)*</th>
<th>Recovery (%)</th>
<th>CRM 7004 (mg kg⁻¹)*</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>n.d.</td>
<td>-</td>
<td>n.d.</td>
<td>-</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>0.004 ± 0.001</td>
<td>2</td>
<td>0.006 ± 0.003</td>
<td>7</td>
<td>0.021 ± 0.018</td>
<td>9</td>
</tr>
<tr>
<td>III</td>
<td>0.112 ± 0.044</td>
<td>66</td>
<td>0.057 ± 0.011</td>
<td>63</td>
<td>0.205 ± 0.031</td>
<td>91</td>
</tr>
<tr>
<td>IV</td>
<td>0.082 ± 0.011</td>
<td>48</td>
<td>0.069 ± 0.022</td>
<td>77</td>
<td>0.136 ± 0.042</td>
<td>61</td>
</tr>
<tr>
<td>V</td>
<td>0.152 ± 0.006</td>
<td>90</td>
<td>0.088 ± 0.011</td>
<td>97</td>
<td>0.186 ± 0.009</td>
<td>83</td>
</tr>
<tr>
<td>VI</td>
<td>0.155 ± 0.004</td>
<td>92</td>
<td>0.075 ± 0.005</td>
<td>83</td>
<td>0.190 ± 0.004</td>
<td>85</td>
</tr>
<tr>
<td>VII</td>
<td>0.165 ± 0.007</td>
<td>98</td>
<td>0.082 ± 0.007</td>
<td>91</td>
<td>0.192 ± 0.026</td>
<td>86</td>
</tr>
<tr>
<td>Certified values</td>
<td>0.169 ± 0.007</td>
<td>-</td>
<td>0.090 ± 0.012</td>
<td>-</td>
<td>0.223 ± 0.016</td>
<td>-</td>
</tr>
</tbody>
</table>

n.d. = not determined          (n=3)

3.2.3.2.1 Ashing of solid samples using a high temperature (450°C) furnace (Method II)

Many sample dissolution methods include an ashing step to destroy organic matter prior to digestion. When applying the ashing procedures outlined in Section 2.3.14.2 of Chapter 2 to 0.25 g sub-samples of certified reference material NIMT/UOE/FM/001, a [Hg] of 4 µg kg⁻¹ was obtained, indicative of a 98% loss of Hg when compared to the certified value of 0.169 mg kg⁻¹. CRMs 7002 and 7004 fared only a little better, with 7% and 9% Hg recoveries, respectively. The almost complete loss of Hg especially from the peat reference material highlights the unsuitability of the ashing procedure where Hg analysis is concerned and removes it from consideration as a viable technique.
3.2.3.2 Aqua regia reflux (Method III)

Aqua regia has been used in some published studies to digest organic matter (e.g. Favilli et al., 2008). Attempts were made to pre-digest soil and peat organic matter by refluxing samples in aqua regia, a mixture of concentrated nitric and hydrochloric acids, prior to a full digestion process. The premise of this technique is that sufficient heat in conjunction with an aggressive chemical environment can be applied to destroy the organic matter in the samples while Hg vapour losses are minimised via condensation within an attached condenser tube. Adsorption of Hg to apparatus surfaces would also be limited via a combination of dissolution and resultant stabilisation of Hg via complexation by chloride ions in the aqua regia.

In this study, the aqua regia reflux was performed with 10 ml aqua regia (prepared from HNO$_3$, ARISTAR, 69% and HCl, NORMATOM, 37% in a 1:3 ratio) on 0.25 g of each of the three certified reference materials in a 25 ml quick-fit round-bottomed flask with condenser attachment. Samples were heated using an electric heating mantle until reflux was achieved and then held under reflux conditions for a period of 4 hours.

This technique suffered from a number of practical issues that limited its applicability. The most evident problem was the violent reaction that consistently occurred when aqua regia was heated in the presence of organic-rich soil or peat samples. Visual assessment indicated that the severity of the reaction increased with increasing organic matter content of the sample. Even when heat was carefully
controlled up to the point of reflux, the unpredictable reaction led to rapid gas formation which caused bumping and bubbling, sometimes resulting in unpredictable loss of sample out of the top of the condenser tube. Visible bumping of solution was dealt with via the immediate cessation of heating, making such losses relatively rare. Operator safety was ensured by the presence of safety screens, leaving only a small access space around waist height to allow manipulation of the temperature controls. Multiple layered gloves, in addition to normal protective equipment, were worn at all times to minimise the risk to hands from accessing the temperature controls. Use of typical mitigation measures such as anti-bumping granules was ruled out due to the risk of contamination.

Where reflux was sustained for 4 hours without evident loss of solution, there were visible indications of significant breakdown of their organic components: reduction in the quantity of solid particulates and discoloration of remaining. However, concentration analysis following digestion showed high variability with mean recoveries for the reference materials ranging from 63–91% relative to certified concentrations as shown in Table 3.3. The wide range in recovery percentages implies variable but often quite significant Hg loss to atmosphere, despite the condenser. A high recovery rate of 91 ± 14% was achieved for CRM 7004 may indicate that with careful control and development this technique could be fit-for-purpose.
3.2.3.2.3 Cold aqua regia treatment (Methods IV-VII)

As direct heating even under reflux conditions appears linked to Hg loss, an alternative consideration was to use cold aqua regia over a longer timescale. A cold aqua regia digestion had been suggested as suitable for total Hg analysis in a published amendment to the USEPA method 1631 (USEPA, 2001). Five millilitres of fresh aqua regia (prepared from HNO$_3$, ARISTAR, 69% and HCl, NORMATOM, 37% in a 1:3 ratio) was added to 0.25 g samples of NIMT/UE/FM/001, CRM 7002 and CRM 7004 in 100 ml beakers covered by watch glasses. After 48 hours a further 5 ml fresh aqua regia was added to the samples and the beakers covered for a further 48 hours. Overall, samples were immersed in cold aqua regia for 96 hours before being transferred to the microwave digestion procedure. Beakers were kept in a shaded area with screens to avoid Hg loss through photochemical volatisation.

Visual inspection of samples after being subjected to cold aqua regia revealed degradation of the sample organic matter: discoloration of the solid particulates, and reduction in the quantity of solid material. Mean recovery percentages ranged from 86–98%, considerably better than any other pre-digestion technique assessed. This method was therefore adopted as the pre-digestion step for the remainder of this study.
3.2.3.3 Digestion of solid phase soils and peats for [Hg] analysis

The digestion step is of key importance to [Hg] analysis as ICP-MS analysis usually requires the analytes to be in the aqueous phase. The primary concern in relation to digestion is that by necessity, such processes require application of heat, therefore risking Hg vapour loss.

3.2.3.3.1 Hotplate digestion (Method IV)

Hotplate digestion is a straightforward technique that relies on readily available laboratory equipment and has been discussed in Section 2.3.13.2 of Chapter 2. In this study, 10 ml concentrated HNO₃ (Aristar) was added to 0.25 g reference material samples in pyrex beakers which were then covered by watch glasses and the contents heated to 80°C and held isothermally for a period of 4 hours until digestion was achieved.

Mean recoveries of 48–77% (Table 3.3) indicated that significant losses of Hg vapour had occurred and that the extent of these losses was highly variable. It is likely that this digestion method embodies many of the same issues as the aqua regia reflux technique in Section 3.2.3.2.2. Samples are open to the atmosphere but do not have the condenser potential of standard reflux apparatus. Furthermore, consistent and careful hotplate temperature control is challenging as controls are often...
imprecise or arbitrary in their scaling and heat distribution across the plate is regularly uneven.

3.2.3.3.2 Microwave-assisted digestion
(Methods V-VII)

Minor adjustments were made to the established microwave digestion method outlined in Section 2.3.14. Specifically, these changes were (i) the inclusion of additional acid volume resulting from the cold aqua regia step that precedes digestion and (ii) a longer lag time of approximately 3 hours following the microwave process to allow complete cooling and condensation of Hg vapour within the microwave digestion vessels. As outlined in Table 3.3, 90 ± 4%, 97 ± 12% and 83 ± 4% recoveries were obtained for NIMT/UOE/FM/001, CRM 7002 and CRM 7004, respectively, using this digestion procedure coupled with the cold aqua region processing step.

Favourable yields from this methodology when compared to the hotplate digestion (Method IV) are most likely the result of microwave-assisted digestion’s one distinct advantage over alternative techniques; digestion vessels are sealed and pressurised, thus excluding them from the atmosphere. The primary concern throughout this development process has been vapour loss and the microwave technique is the only process available to the project that allows direct heating while making atmospheric loss highly unlikely. It therefore appears sensible to adopt this digestion method in the absence of other viable alternatives.
Addition of higher volumes of acid to digestion vessels due to the cold aqua regia step increases the risk of critical pressure building due to liberation of nitrosyl chloride, chlorine and nitrogen oxide gases within vessels. Such an event can lead to safety membranes breaking, causing loss of sample. To reduce the risk of a critical pressure build-up, the procedure was further modified to maintain a total of 10 ml of digest solution in the microwave digestion vessels as per the normal microwave methodology outlined in Section 2.3.14.2. This modification was achieved by adding 1 ml HF (used as supplied, VWR, ARISTAR grade, 48%) to each digestion vessel along with sufficient HNO₃ (used as supplied, VWR, ARISTAR grade, 69%) to make the total volume 10 ml when the sample-bearing aqua regia from the pre-digestion step is taken into account. It is notable that the most favourable overall recoveries were obtained where this modification was adopted (Method VII) when compared to the higher volume methodology (Method V). Furthermore, statistical t-testing (Appendix 4) showed that for only Method VII provided results that could not be statistically differentiated from certified concentrations of the three CRMs used in the development process. Higher recovery rates and reduced risk of critical sample loss due to the lower digest volume cause Method VII to be the preferred microwave digestion configuration for Hg extraction.

3.2.3.4 Post-digestion processing of solid phase soils and peats for [Hg] analysis

It is essential to reduce HNO₃ concentration within digests to below the tolerance threshold of the ICP-MS of ~10 v/v%, while retaining an acidic medium to maintain
digested species in solution. Furthermore, to maintain operator safety, evaporation of any residual HF remaining after the microwave digestion procedure is a necessity. Such a procedure is normally performed via hotplate evaporation. With respect to Hg analysis, the concern with such a procedure is once again the application of direct heat. Two approaches were considered to achieve post-digestion processing; hotplate evaporation and air evaporation.

### 3.2.3.4.1 Hotplate evaporation (Method V)

Following the digestion procedure, standard practice is to transfer digest solutions to Teflon® beakers followed by digestion vessel rinsing with 2% v/v HNO₃ (prepared from VWR Aristar 69% w/v). Sample volume was then reduced to ~1 ml via hotplate evaporation. The evaporation step was immediately followed by filtering and dilution with 2% v/v HNO₃ (prepared from VWR Aristar 69% w/v) to 25 ml in plastic volumetric flasks. Previous stages of this method development showed that, under reflux conditions, significant losses of Hg occurred. Of key importance in this step was that the heat required in order to achieve solution evaporation was considerably lower than that required for either sample digestion or organic matter breakdown.

Hotplate volume reduction was carried out post-microwave digestion in 100 ml Teflon® beakers using the minimum possible heat setting that would achieve evaporation. Mean recoveries for NIMT/UEO/FM/001, CRM 7002 and CRM 7004 were 90 ± 4%, 97 ± 12% and 83 ± 4%, respectively. The low recovery for CRM 7004 is attributed partially to excessive heating due to operator error. Following
evaporation, samples were filtered, diluted to 25 ml with 2% v/v HNO₃ and stored in 30 ml plastic vials at ~4°C in a refrigerator prior to analysis.

3.2.3.4.2 Air evaporation (Method VI)

Due to the issues arising from direct heating of samples in previous sections of the method development, a heatless approach to the evaporation stage was also devised. Prolonged exposure to air at ambient room temperature had been observed in the laboratory to cause evaporation of both 2% v/v HNO₃ (prepared from VWR Aristar 69% w/v) and concentrated acid during the cold aqua regia pre-digestion methodology. To assist in latent evaporation, post-digestion samples in Teflon® beakers were placed exposed to the air in a fume hood with the sash adjusted to maximise airflow across the top of the beakers. Beakers were covered with pierced plastic film in an effort to minimise contamination from falling particulates or dust while still allowing vapour release. When solution volumes were approximately 2 ml and then 5 ml 2% HNO₃ (prepared from VWR Aristar 69% w/v) was used to rinse the beakers’ internal surfaces and to increase sample volume prior to filtration and further washing until the total sample volume was 25 ml. Samples were again stored in 30 ml plastic vials in a refrigerator at ~4°C prior to analysis.

Recovery percentages from air evaporation shown in Table 3.3 were comparable to those from the low-temperature hotplate procedure. Given the comparability of the results, the main factor separating these two procedures is one of time. The air evaporation methodology ranges considerably in the time required to achieve 2 ml
sample volume ranging from a matter of days to up to a week whereas hotplate evaporation requires a matter of hours. Furthermore, the air evaporation technique is questionable in regards to complete evaporation of residual HF. These considerations lead to the low-temperature hotplate step being adopted for the remainder of this study.

### 3.2.3.5 ICP-MS Hg memory effect and stability control

Mercury analysis via the standard ICP-MS procedure outlined in Section 2.3.17 is complicated by the presence of a memory or ‘carry-over’ effect wherein samples following higher concentration Hg standards or samples experience artificial inflation of their [Hg] due to residual Hg retained within the apparatus. The residual Hg added to each subsequent sample by this effect is variable and can range from <1% to >100% of the previous sample’s concentration. The problem arises because Hg adsorbs to the internal surfaces of the plastic sample introduction tubing and the adsorbed Hg is gradually liberated back into solution over time. Table 3.4 demonstrates a trial analysis utilising Hg standard solutions prepared in 2% v/v HNO₃ (prepared from VWR Aristar 69% w/v), blanks (2% v/v HNO₃ (Aristar)), further rinse solutions of 2% v/v HNO₃ (prepared from VWR Aristar 69% w/v). Not only does the memory effect cast doubt over the validity of calculated concentrations for the samples themselves, it raises concern over the credibility of ICP-MS calibration when the relationship between standard concentration and instrumental response is clearly non-linear (Table 3.4).
Table 3.4  Successive ICP-MS analyses of Hg standard solutions using normal methodology

<table>
<thead>
<tr>
<th>Analysis Sequence</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Blank</td>
<td>1 µg</td>
<td>5 µg</td>
<td>10 µg</td>
<td>20 µg</td>
<td>50 µg</td>
<td>100 µg</td>
<td>Rinse</td>
<td>Rinse</td>
</tr>
<tr>
<td>Hg conc. (µg l⁻¹)</td>
<td>0.02 ± 0.00</td>
<td>0.98 ± 0.00</td>
<td>5.0 ± 0.00</td>
<td>12.5 ± 0.02</td>
<td>29.0 ± 0.44</td>
<td>72.3 ± 1.18</td>
<td>185.6 ± 1.68</td>
<td>3.9 ± 0.35</td>
<td>0.9 ± 0.01</td>
</tr>
</tbody>
</table>

(n=1) *Uncertainties are analytically derived errors

Advice provided by Agilent Technologies during the 2008 Sheffield user-group meeting provided insight into curbing the Hg memory effect within the ICP-MS procedure. Addition of chlorine in the form of HCl was trialled to prevent adsorption to plastic surfaces via stabilisation of Hg in solution through complexation with chloride ions (Yu and Yan, 2003) and by actively stripping adsorbed Hg from the plastic surfaces.

Blank and rinse solutions that would traditionally consist of 2% v/v HNO₃ (prepared from VWR Aristar 69% w/v) can be modified by addition of HCl (1 ml c.HCl (37%) to 199 ml 2% v/v HNO₃). The use of this low level chlorine rinse solution can be further incorporated into dilution mediums for standards, samples and reference materials following digestion, maintaining a chlorine influence throughout the entire analytical run. Additionally, the rinse time was increased to 60 seconds between samples to ensure thorough cleaning. These combined adaptations were shown to reduce the influence of carry-over in low concentration samples. However, despite these modifications, Hg standards of 20 µg l⁻¹ continued to impart some memory to rinse solutions that followed these standards (Table 3.5). It is assumed that the low
concentration of chloride present in the samples, standards and rinse solutions became overwhelmed at these higher concentration ranges and was unable to prevent some Hg adsorption. It is conceivable that this could be mitigated through higher concentration spikes of HCl but this measure risks causing increasingly severe polyatomic chlorine interferences that are well documented within ICP systems (Taylor, 2001).

Table 3.5  
Successive ICP-MS analyses of Hg standard solutions using HCl adaptation

<table>
<thead>
<tr>
<th>Analysis Sequence</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Blank</td>
<td>1 µg l⁻¹ Hg std.</td>
<td>2 µg l⁻¹ Hg std.</td>
<td>5 µg l⁻¹ Hg std.</td>
<td>10 µg l⁻¹ Hg std.</td>
<td>20 µg l⁻¹ Hg std.</td>
<td>Rinse</td>
<td>Rinse</td>
</tr>
<tr>
<td>Hg Conc. (µg l⁻¹)</td>
<td>0.01 ± 0.01</td>
<td>1.09 ± 0.03</td>
<td>1.89 ± 0.01</td>
<td>5.43 ± 0.09</td>
<td>10.97 ± 0.48</td>
<td>20.01 ± 0.01</td>
<td>2.37 ± 0.33</td>
<td>1.36 ± 0.21</td>
</tr>
</tbody>
</table>

(n=1) *Uncertainties are analytically derived errors

To reduce the remaining memory effect, a concentration control approach was adopted. Typical post-digestion samples fell within the concentration range of 0.1–5.0 µg l⁻¹. Calibration standards and bracketing standards (Section 2.3.17.3) therefore rarely required to exceed 10 µg l⁻¹. Utilising a lower concentration range of standards solved the memory effects, limiting the carry over to minimal levels as shown in Table 3.6. In the event that a sample was to exceed the 10 µg l⁻¹ upper calibration limit, analysis was repeated with an appropriate dilution to maintain the 0-10 µg l⁻¹ optimum range.
Table 3.6 Successive ICP-MS analyses of Hg standard solutions using HCl adaptation and concentration control approach

<table>
<thead>
<tr>
<th>Analysis Sequence</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Blank</td>
<td>0.1 µg l⁻¹ Hg std.</td>
<td>0.5 µg l⁻¹ Hg std.</td>
<td>1 µg l⁻¹ Hg std.</td>
<td>5 µg l⁻¹ Hg std.</td>
<td>10 µg l⁻¹ Hg std.</td>
<td>Rinse</td>
<td>Rinse</td>
</tr>
<tr>
<td>Hg conc. (µg l⁻¹)</td>
<td>0.03 ± 0.01</td>
<td>0.17 ± 0.07</td>
<td>0.53 ± 0.10</td>
<td>1.01 ± 0.16</td>
<td>5.12 ± 0.62</td>
<td>10.10 ± 0.26</td>
<td>0.07 ± 0.06</td>
<td>0.06 ± 0.05</td>
</tr>
</tbody>
</table>

(n=1) *Uncertainties are analytically derived errors

3.2.3.6 Optimised procedure for Hg concentration analysis in solid phase peats and soils

As a result of the findings presented in Sections 3.2.3.1-3.2.3.5 above, the optimised procedure of [Hg] determination in solid phase peats and soils by ICP-MS was as follows. Air-dried and dessicated soil or peat (0.25 g) in 100 ml beakers was subjected to pre-digestive degradation for 48 hours via addition of 5 ml aqua regia. A further 5 ml aliquot of aqua regia was added and the process continued for a further 48 hours. Beakers were stored behind screens for the 96 hour pre-digestive procedure to shade them from bright or direct light. Aqua regia was freshly prepared before use by mixing concentrated HNO₃ (used as supplied VWR, ARISTAR grade, 69% w/v) and concentrated HCl used as supplied (VWR NORMATOM, 37% w/v) in a 1:3 ratio.

Pre-digestion residues were transferred to HP-500 CEM microwave digestion vessels along with 1 ml concentrated hydrofluoric acid (used as supplied VWR, ARISTAR grade, 48% w/v) and sufficient 9 ml concentrated nitric acid (used as supplied VWR,
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

ARISTAR grade, 69% w/v) to bring the total volume in the vessel to 10 ml. Microwave-assisted digestion was carried out via a temperature controlled ramp to 180°C followed by an isothermic hold for 15 minutes as per USEPA Method 3052 (USEPA, 1996). After cooling for 3 hours to ensure re-equilibration to room temperature and complete condensation within the tubes, the solution was transferred to 100 ml Teflon® beakers and subjected to low-temperature hotplate evaporation to ~1 ml. The remaining 1 ml was made up to 25 ml with 2% v/v nitric acid (prepared from VWR Aristar 69% w/v) and filtered under gravity through Whatman 540 hardened ashless filter papers prior to storage at ~4°C in 30 ml sealed plastic vials. Nitric acid (2% v/v) was prepared by mixing 29 ml concentrated nitric acid (VWR, ARISTAR grade, 69% w/v) with 931 ml deionised water.

Solutions were analysed using an Agilent 7500ce ICP-MS. Operating conditions were as outlined in Table 2.8 in Chapter 2 with the following modifications. Rinse solutions were created via addition of 1 ml c.HCl (VWR NORMATOM, 37% w/v) to 199 ml 2% v/v HNO₃. Rinse times were increased to 60 seconds. Mercury standards of 0.1 µg l⁻¹, 0.5 µg l⁻¹, 1 µg l⁻¹, 5 µg l⁻¹ and 10 µg l⁻¹ were prepared via dilution of 1000 mg l⁻¹ stock standards (Fisher, Single element standard for ICP analysis: 1000 mg l⁻¹ in 1 M nitric acid) with the rinse solution HNO₃ / HCl outlined above. These standards were used to calibrate the ICP-MS and Hg concentrations were calculated following analysis.
3.2.3.7 Concentration analysis of [Hg] analysis in porewaters extracted from peats and soils

Porewater extraction was performed as outlined in Section 2.3.1 in Chapter 2. The drying, pre-digestion, microwave and hotplate evaporation stages involved in solid phase concentration analysis were not required. Porewater was syringe-filtered through 0.22 µm (Millipore Millex Sterile Syringe Filters) filter units and then analysed using the ICP-MS procedure described above without further processing. Standards and rinse solutions were prepared using HNO$_3$ (VWR, ARISTAR grade, 69% w/v) and HCl (VWR NORMATOM, 37% w/v) as described in Section 3.2.3.6. The 10 µg l$^{-1}$ Hg standard solution was omitted during porewater analysis to lower the risk of memory effect on the often <1 µg l$^{-1}$ Hg concentrations in porewater samples.

3.3 HPLC-ICP-MS Hg speciation analysis in peats and soils and their associated porewaters

3.3.1 Introduction

Mercury speciation analysis is complicated by mercury’s tendency to undergo redox conversions both in the environment and in laboratory settings. These redox conversions include photochemical interactions, oxidative chemical reactions (such as oxidation of Hg(0) to Hg(I) and Hg(II) via interaction with chloride), or reductive chemical reactions (such as conversion of Hg(II) to Hg(0)). Photons of wavelength 270–400 nm can be readily absorbed by Hg(II) complexes in solution, triggering
electron transfer reactions that end in reduction to Hg(0) via an Hg(I) intermediate (Nriagu et al., 1994). Photo-oxidation processes involving UV light have also been documented and 254 nm emitters are incorporated into scrubbing Hg(0) from industrial flue-gases (McLarnon et al., 2005). Considering the variety of means through which Hg species may change, care must be taken during speciation analysis to ensure that the true environmental forms of Hg are being identified.

As a consequence, Hg speciation studies have a number of pre-requisites:

(i) Hg species must be removed from the sample matrix where solid samples are involved;

(ii) extraction efficiency must be high; and

(iii) there should be no chemical transformation of Hg speciation during the procedure.

Extraction procedures for total [Hg] analysis are chemically harsh and often involve extremes of pH, e.g. acid extraction via concentrated aqua regia as outlined in Section 3.2.3.2.2 or alkali leaching via hydroxides NaOH or KOH treatment and phase extractions (Lee et al., 2007). Not only do such treatments risk altering the oxidation state of inorganic Hg, some papers also report direct inter-conversion between inorganic (Hg$^{2+}$) and organic species as a result of these methods (Tseng et al., 1997; Hintelmann et al., 1997; Ortiz et al., 2002). Alternative extraction techniques often require additional derivatisation (e.g. Tseng et al., 1998) which, by definition, further transforms the species of interest. However, derivatisation techniques can be used to quantitatively analyse Hg species provided they partially
preserve the original Hg chemical species and that the derivatisation process reacts in a predictable way. Direct alkylation (ethyl-/propyl-/butyl-ation) is one example of such a technique and allows speciation analysis of both methyl and inorganic Hg via GC-ICP-MS with little unintended alkylation of inorganic Hg during the procedure (Fernández et al., 2000). Alkylation techniques are chemically harsh and limit the range of alkyl-Hg species that can be detected. Ethylation, for example, may interfere with detection of native ethylmercury by forming ethylated species from originally inorganic Hg. Considering the possibility that ethylmercury may exist within environmental samples (Yamanaka and Ueda, 1975; Cai et al., 1997; Yin et al., 2012), alternative extractive methods are required.

Mercury has a high affinity for sulfur-based functional groups, particularly the sulphydryl (-SH) group. This has led to the use of 2-mercaptoethanol within extraction methodologies (Cattani et al., 2008). Following Hg extraction by HCl, mercaptoethanol forms complexes with the Hg species as outlined in Equation 3.2 and 3.3, where R represents pre-existing organic functionality such as an alkyl group. The resultant Hg species are thus stabilised against UV degradative processes (Pacheco et al., 2010) and during analysis procedures (Wang et al., 2007).

\[
\begin{align*}
\text{Hg}^{2+} + 2\text{HOCH}_2\text{CH}_2\text{SH} & \rightleftharpoons (\text{HOCH}_2\text{CH}_2\text{S})_2\text{-Hg} + 2\text{H}^+ \quad \text{Equation 3.2} \\
\text{RHg}^+ + \text{HOCH}_2\text{CH}_2\text{SH} & \rightleftharpoons \text{HOCH}_2\text{CH}_2\text{S-HgR} + \text{H}^+ \quad \text{Equation 3.3}
\end{align*}
\]
Separation and analysis of Hg species are often carried out by hyphenated techniques including LC–, GC–, CV– and ICP–AAS (Krull et al., 1986), AES (Palmisano et al., 1993), AFS (Yoshino et al., 1995) among others (Lopéz et al., 2010). Technological advancements in the compatibility of HPLC and ICP-MS systems have seen HPLC-ICP-MS become the forerunner in Hg speciation analysis (Harrington, 2000). The ease of use, availability and variety of column chemical environments makes an HPLC system an ideal medium with which to suitably separate mixed Hg species.

### 3.3.2 HPLC set-up and configuration

The methodology of Chen (2005) was used as the basis for this method development. Chen (2005) used an Agilent 1100 HPLC system and Agilent 7500a ICP-MS coupled as outlined in Figure 3.1. Both pieces of equipment were available at Edinburgh and were utilised by this project. Polyether-ether-ketone connections, as employed by Chen, were used throughout the HPLC and ICP-MS systems and at equipment interface points. The recommended HPLC column is a ZORBAX Eclipse XDB-C18 2.1 mm diameter x 50 mm length with 5 µm bead size. This column was not available to the project although a longer, wider ZORBAX Eclipse XDB-C18 4.5 mm x 150 mm with 5 µm particle size was accessible and used throughout the methodology. Although both column stationary phases have the same densely packed silanols shown in Figure 3.2, the difference in column dimensions will alter the retention times and separations achieved during the HPLC process. The recommended smaller column should theoretically achieve a higher sensitivity as the concentration of analyte will be higher within the lower volume of mobile phase.
required to traverse one length of the column. Considering the complexity of this technique and the differences in recommended and available HPLC columns, it was necessary to evaluate the application of the Agilent (Chen, 2005) method using the HPLC and ICP-MS instrumentation available in Edinburgh.

Figure 3.1 HPLC-ICP-MS schematics and connectivity using an Agilent 1100 series HPLC and Agilent 7500 series ICP-MS (Chen, 2005).

Figure 3.2 Column surface structure of ZORBAX Eclipse XDB range HPLC columns (Agilent, 2009).
3.3.3 Method development

3.3.3.1 Extraction and pre-analysis processing of Hg species from solid phase peats and soils

The methodology of Cattani et al. (2008) was adopted for Hg extraction without modification. Mercury was extracted via addition of 9 ml HCl (7.6% v/v) and 1 ml 2-mercaptoethanol (10% v/v, prepared from CALBIOCHEM, molecular biology grade, 99.9%) to 1 g of peat or soil. To ensure the greatest possible solid surface area was exposed to the extractant, samples were subjected to sonication in an ultrasonic bath for 45 minutes with regular addition of ice to hold the bath temperature at approximately room temperature. Samples were centrifuged for 5 minutes at 1077 x g following sonication to partition solid and liquid phases allowing simple decanting of the aqueous extract. 2 ml of the supernatant was transferred to a 30 ml PET vial and the pH adjusted to 6.8 with 10% v/v ammonia solution (prepared from: Fisher, Laboratory grade, 35%). The resultant solution was made up to 20 ml with deionised water and filtered through 0.22 µm syringe filters (Millipore Millex Sterile Syringe Filters) prior to analysis.

3.3.3.2 HPLC-ICP-MS configuration

The HPLC was configured as per Table 3.7 below, in line with the operating conditions of Chen (2005). The mobile phase consisted of 0.06 M ammonium acetate, 3% (v/v) methanol, 0.1% v/v 2-mercaptoethanol, pH 6.8. In order to improve peak resolution, the HPLC column was chilled to 4°C as suggested by Cattani et al. (2008). Prior to use HPLC grade methanol was run through the column as a cleaning
measure at 0.4 ml min\(^{-1}\) for ~2 hours. Following methanol treatment, the column was allowed to equilibrate with the mobile phase for 30 minutes at 0.2 ml min\(^{-1}\) prior to introduction of samples. ICP-MS tuning and configuration was performed by a technician to achieve optimum sensitivity. The experimental settings are outlined below in Table 3.8. Operating and data acquisition software was run in time-resolved mode.

**Table 3.7**  Experimental configuration of HPLC system

| Machine model: | Agilent 1200 series |
| Column: | ZORBAX Eclipse XDB C-18 4.6 mm x 150 mm, 5µm |
| Mobile phase: | 0.06 M ammonium acetate, 3% (v/v) methanol, 0.1% 2-mercaptoethanol |
| Flow rate: | 0.4 ml min\(^{-1}\) |
| Injection volume: | 100 µl |

**Table 3.8**  Experimental configuration of ICP-MS system for HPLC-ICP-MS

| Machine model: | Agilent 7500ce ICP-MS |
| RF power: | 1540 W |
| RF matching: | 1.76 V |
| Uptake rate: | 0.06 rps |
| Sampling depth: | 8.4 mm |
| Carrier gas flow rate: | 0.82 L min\(^{-1}\) |
| Make-up gas flow rate: | 0.21 L min\(^{-1}\) |
| Nebuliser: | Micro mist |
| Spray chamber: | Scott-type, glass. |

**3.3.3.3 Standard analysis and elution time determination**

Individual Hg species solutions of 100 µg l\(^{-1}\) were prepared from MeHgCl (Alfa Aesar, 1000 mg l\(^{-1}\)), EtHgCl (Alfa Aesar, >99% purity), Hg(I)Cl (Acros Organics, >99% purity) and Hg(II)Cl (Acros Organics, 99.5% purity) as outlined in Appendix
5. These solutions were subjected to HPLC-ICP-MS analysis and the species elution peak times recorded as outlined in Table 3.9. Output graphs are shown in Figure 3.3.

<table>
<thead>
<tr>
<th>Method development</th>
<th>Hg(I)</th>
<th>Hg(II)</th>
<th>MeHg⁺</th>
<th>EtHg⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method development</strong></td>
<td>271 ± 4</td>
<td>143 ± 22</td>
<td>111 ± 2</td>
<td>806 ± 35</td>
</tr>
<tr>
<td>Chen (2005)</td>
<td>N/A</td>
<td>194</td>
<td>153</td>
<td>392</td>
</tr>
<tr>
<td>Cattani et al. (2008)</td>
<td>142</td>
<td>279</td>
<td>192</td>
<td>558</td>
</tr>
</tbody>
</table>

The elution order of MeHg → Hg(II) → EtHg obtained using this methodology was consistent with that in the published literature. However, the elution order of Hg(I) in this case, in between Hg(II) and EtHg, does not agree with that reported by Cattani et al. (2008) who observed that Hg(I) eluted first when 2-mercaptoethanol was used. It is evident that elution times are variable and highly sensitive to minor variations in instrumental set-up configuration such as column dimensions or mobile phase composition (Yin et al., 1998; Hashempur et al., 2008). For example, Cairns et al. (2008) adopted a 100×2.1 mm Alltima HPC-18 3 µm column and observed elution of Hg(II) at ~100 seconds and then MeHg at ~130 seconds, the reverse of the elution order observed within this study and those by Chen (2005) and Cattani et al. (2008). Method-dependent variations in elution times highlight the importance of consistent experimental configuration prior to analysis. As a consequence, standards must be run prior to every set of sample analyses to correctly identify the different Hg species.
Concentration calibration and measurement were achieved by running multiple concentrations of Hg species standards through the HPLC-ICP-MS procedure and integrating to acquire graph peak areas. Peak areas are proportional to the concentration of Hg passing through the ICP-MS system as shown in Figure 3.4. ICP-MS sensitivity is variable from day to day and therefore these calibration lines are subject to change. New calibrations must be performed prior to each quantitative analysis.
Figure 3.4 Linear relationship between total concentration of Hg standards and total integrated output area from HPLC graph (n=4 where each replicate is a solution of identical [Hg] but a different speciation, i.e. Hg(I), Hg(II), MeHg and EtHg).

Overall percentage recovery for the developed method was determined via extraction and analysis of certified peat reference material NIMT/UOE/FM/001 ([Hg] = 0.169 ± 0.007). Recoveries of 85.8% were obtained with the total [Hg] split among MeHg, EtHg and Hg(II) species, as shown in Table 3.10. This percentage agrees favourably with those reported elsewhere in literature where recoveries of 90–110% for Hg species in soil samples have been reported (Chen 2005; Wang et al., 2007; López et al., 2010).

<table>
<thead>
<tr>
<th>[Hg] (mg kg⁻¹)</th>
<th>MeHg</th>
<th>EtHg</th>
<th>Hg(II)</th>
<th>Hg(I)</th>
<th>Total</th>
<th>Certified Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.035 ± 0.003</td>
<td>0.093 ± 0.005</td>
<td>0.017 ± 0.003</td>
<td>N/A</td>
<td>0.145 ± 0.007</td>
<td>0.169 ± 0.007</td>
</tr>
</tbody>
</table>

Method development
3.3.3.4 Bismuth isotope mobile phase tracer spike

An additional stage of the method development was that the HPLC mobile phase was spiked with \(^{209}\text{Bi}\). Once stabilised, this provides a continuous level of background counts on the ICP-MS detector. When the non-spiked samples are injected and reach the detector, a transient drop in the \(^{209}\text{Bi}\) background is observed. Spiking with bismuth was employed by Chen (2005) to monitor long-term instrument stability but it can also be utilised for two additional purposes:

(i) while testing the method it allowed us to confirm the time period from column injection to detector; and

(ii) it allows comparison of the drop in the \(^{209}\text{Bi}\) background with Hg peaks to confirm that observed Hg spikes are the result of sample progress through the column and not due to sudden intra-system release of adsorbed Hg from cumulative memory effect.

3.3.3.5 Mercury memory effect assessment

The HPLC-ICP-MS methodology exhibits surprisingly limited, if any Hg memory effects. Background Hg counts return to the values obtained for reagent blanks and the stabilised mobile phase rapidly following sample analysis and only minor residual tailings can be seen on the time-resolved species peaks themselves as exemplified by Figure 3.3. The inclusion of 2-mercaptoethanol in the mobile phase is likely the cause of this. Not only is the extracted Hg bound to the 2-mercaptoethanol, its continued presence can act to scavenge any ‘free’ or dissociated Hg. Uncomplexed 2-mercaptoethanol will further act to push the equilibria outlined in
Equation 3.2 and 3.3 to the right and thus will stabilise the complexed Hg species. Mercaptoethanol could be utilised in future determination of total [Hg] due to its stabilising influence and may act as a suitable replacement to HCl within rinse solutions or potentially extraction methodology.

### 3.3.3.6 Assessment of species inter-conversion

Of great concern in speciation studies is the potential for the inter-conversion of Hg species during either the extraction or analysis steps of the procedure. Single species test solutions shown in Figure 3.3 (Appendix 5) yield only the one expected peak, confirming that conversion does not occur during the LC separation phase of the procedure. In order to confirm species stability during extraction it would be necessary to either assess certified speciation references or to spike uncontaminated soils with known concentrations of Hg species. Certified reference materials for Hg speciation were not available to the project at the time of experimental assessment and prevented this being carried out. However, recent publications (Cattani et al., 2008; Lopéz et al., 2010) have detailed such tests and have demonstrated no observable changes in certified species distribution following extraction with mercaptoethanol and HCl.
3.3.4 Optimised procedure for Hg speciation in solid phase peat and soil samples using HPLC-ICP-MS

As a result of the findings presented in Sections 3.3.3.1-3.3.3.6 above, the optimised procedure of Hg speciation analysis in solid phase peats and soils by ICP-MS was as follows. Mercury was extracted via addition of 9 ml HCl (7.6% w/v) (VWR NORMATOM, 37%) and 1 ml 2-mercaptoethanol (10% w/v) (prepared from CALBIOCHEM, molecular biology grade, 99.9%) to 1 g peat/soil. Samples were subjected to sonication in an ultrasonic bath for 45 minutes with regular addition of ice to hold bath temperature at approximately room temperature. Following sonication, samples were centrifuged for 5 min at 1077 x g to partition solid and liquid phases. Two ml of supernatant was transferred to a 30 ml PET vial and 15 ml of deionised water added. The resultant solution was adjusted to pH 6.8 using ammonia (10% w/v) (prepared from: Fisher, Laboratory grade, 35%) and the solution made up to 20 g with deionised water. Solutions were filtered using 0.22 µm syringe filters (Millipore Millex Sterile Syringe Filters) prior to HPLC-ICP-MS analysis. HPLC-ICP-MS analysis was carried out as per the configurations in Tables 3.7 and 3.8.

3.4 Phenolic oxidase enzyme assay for solid phase peat

3.4.1 Introduction

(Poly)phenol oxidases (PO) are copper based enzymes produced by plants and microorganisms (Sinsabaugh, 2010) that can be used as indicators of total microbial activity in soil and peat systems (Giai and Boerner, 2007; Hamman et al., 2008). The
enzyme and its relevance to this study are discussed in detail in Chapter 7. Presented here is the development of a technique to measure PO activity in solid phase peat samples.

Despite its existence being recorded for over a century, a literature consensus on appropriate assay techniques for PO is lacking. Spectrophotometric analysis of PO is the most common assay technique and 3,4-dihydroxy-L-phenyl-alanine (L-DOPA) has become the substrate of choice due to its availability, ease of use and low cost. The adoption of substrate methodologies has recently been favoured over alternative techniques as spectrophotometer technology (and thus sensitivity) has advanced. The first synthesis of 3,4-dihydroxy-L-phenyl-alanine (L-DOPA) was published over a century ago (Funk, 1911). When oxidised, L-DOPA undergoes conversion to 3-dihydroindole-5,6-quinone-2-carboxylate (DICQ) which has an orange colour in solution. This orange pigmentation, and thus DICQ concentration, can be measured via UV/Vis spectrophotometry at 460 nm. Over the course of a number of hours DICQ undergoes further reactions to form melanin (Robinson and Smyth 1997).

Alternative substrate methodologies such as guaiacol (Nanniperi et al., 1991), 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfononic acid) diammonium salt (ABTS) (Terrón et al., 2004; Floch et al., 2007) and pyrogallol (Allison and Vitousek, 2004) have been assessed in literature. However, these techniques suffer from either higher costs or increased experimental complexity than the L-DOPA methodology. These alternative substrate methods still reportedly provide comparable values to those
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems
determined via DOPA (Sinsbaugh et al., 2008) although they are not commonly adopted as there is no apparent benefit to their use that outweighs their cost and complexity issues.

Application of the L-DOPA assay to solid phase peat samples is not without its own limitations. The technique is unable to separate tyrosinase and lacasse activity, sub-classifications of POs, into their separate components, although there is no need to do so for the purposes of this study. Furthermore, literature has focused upon PO in the aquatic medium. L-DOPA analysis techniques have not been extensively applied to solid phase material due to organic-rich soil, and in particular peat, samples resulting in high concentrations of soluble and suspended organic material in the reagent extracts. This organic matter will absorb across broad spectral wavelengths, including in the blue region of the visible spectrum in which the assay product, DICQ, absorbs. While L-DOPA remains the preferred substrate, its applicability to the peats in this study must be confirmed before this technique can be adopted as a reliable measure of PO activity. To these ends, a further examination of the methodology was made.

3.4.2 Method development

The basis for this development process is the L-DOPA methodology of Pind et al. (1994) as it has been adopted more extensively in the analysis PO activity in peat material than other techniques (Williams et al., 2000; Jones and Power, 2012; Kang et al., 2009). Individual variables of the PO – L-DOPA reaction were explored in
relation to PO activity and solution colour development to allow practical optimisation of the technique. The parameters explored were L-DOPA substrate concentration, sample mass, pH, incubation time and reaction termination methods.

### 3.4.2.1 Bulk peat development material

Peats used exclusively in the development of the L-DOPA PO methodology were taken from Tyndrum, Scotland on 9th July 2009 by staff at SUERC using the Cuttle and Malcolm procedure described in Section 2.2.2.2. Cores were not sectioned and instead were homogenised to provide a consistent development medium. Tyndrum peat was used for development to avoid depleting stocks of material from other sites.

### 3.4.2.2 Definition of activity

PO activity is defined as nmol of DICQ min⁻¹ g of sample⁻¹ calculated by application of Beer’s law to the molar absorbance coefficient of DICQ: 3.7x10⁴. (Mason, 1948). Activity is therefore calculated via Equation 3.4.

\[
\text{Activity} = \frac{A}{3.7 \times 10^4} \times \frac{\text{time(min)}}{\text{soil mass(g)}} \times 10^9
\]

**Equation 3.4**

### 3.4.2.3 Substrate Concentration

L-DOPA has limited solubility in aqueous solution of ~3.3 mg ml⁻¹ (Sigma Aldrich, 2009). The 10 mM L-DOPA solution concentration applied by Pind *et al.* (2004) was
found to be difficult to prepare consistently therefore a more dilute substrate solution is proposed. In practice, 5 mM concentrations proved consistently achievable. Theoretically, a 5 mM concentration is greatly in excess considering the typical evolution of nmol of DICQ min\(^{-1}\) (Mason, 1948; Pind et al., 2004; Sinsabaugh et al., 2010) and the 1:1 molar ratio of L-DOPA:DICQ. It should be noted that L-DOPA solution is prepared using deionised water and not buffer solution unless otherwise specified.

### 3.4.2.4 Optimum pH for PO measurement

The rate of o-hydroxylation of monophenols and subsequent oxidation to o-diphenols by PO reportedly reaches a maximum between pH 5 and pH 9 (Kazandjian & Klibanov, 1985; Pind et al., 1994; Sinsabaugh et al., 2010). To check the activity of PO across this pH range, universal buffers were created from pH 5 to pH 9 at 0.5 unit increments by mixing 0.1 M citric acid (Sigma-Aldrich, ACS reagent, \(\geq 99.5\%\)) and 0.2 M dibasic potassium phosphate (Sigma Aldrich, ACS reagent, \(\geq 98\%\)) as outlined in Appendix 6 (Pearse, 1980). Three millilitres of buffer solution was mixed with 2 ml of 5 mM L-DOPA solution (Sigma Aldrich, \(\geq 98\%\)) and 0.2 ml of 10 mg l\(^{-1}\) PO mushroom tyrosinase standards (Sigma Aldrich, from agaricus bisporus, lyophilised powder >1000 unit mg\(^{-1}\)). Exactly 10 minutes after addition of the PO enzyme standard, evolution of DICQ was measured via UV/Vis absorbance spectrophotometry at 460 nm. Results are shown in Figure 3.5.
Figure 3.5  Absorbance as a measurement of PO activity across pH scale 5-9.

These data show the activity maximum to be in the region of pH 7.5–pH 9.0 with activity decreasing rapidly with decreasing pH. These results are consistent with other literature for similar peat mediums (Kazandjian & Klibanov, 1985; Pind et al., 1994; Sinsabaugh et al., 2010). Carrying out the DOPA reaction within this pH range is undoubtedly advantageous as numerically higher absorbance values increase the signal in relation to analytical error and improves overall precision. However, at pH values above 7, the 5 mM L-DOPA solution was observed to undergo rapid conversion to a black substance, presumed to be melanin. This conversion does not appear to interfere with absorbance measurement at 460 nm. However, under these conditions, the increasing inconsistencies in substrate concentration developed over time cast doubt over the credibility of repeated measurements unless undertaken simultaneously. Additionally, measurement at alkaline pH values will provide an over-estimated measurement of PO activity within the acidic peats in this study discussed in more detail in Chapter 4. It is therefore proposed that despite the
optimum activity region of 7.5-9.0, no buffer be employed for application to peat systems where adopting the natural sample pH will provide a more realistic measure of true activity within the system and allowing better comparison between sample sites. It should be noted that although pH can vary with depth, this technique measures the activity of the PO and not the quantity of PO present in the soil. Adopting the natural pH of the sample will therefore better reflect the true activity of a given sample.

### 3.4.2.5 Soil mass and interference of soil particulates

In order to assess the effects of changes in peat mass upon the L-DOPA methodology, 0-2 g solid peat (fresh weight) was added to various volumes of 50 mM pH 5 acetate buffer with and without the presence of L-DOPA. This was achieved as outlined below. Acetate buffer was created by addition of 7.4 ml of 0.2 M acetic acid (prepared from VWR, glacial, ≥99%) to 17.6 ml 0.2 M sodium acetate solution (prepared from Sigma Aldrich, anhydrous, ≥99%) and 75 ml deionised water. Buffer solution was used throughout this section to remove the effect of pH variation from results. Peat samples (0-2 g) were added to (i) 3 ml of 50 mM pH 5 acetate buffer and 2 ml of 5 mM L-DOPA solution (prepared from Sigma Aldrich, ≥98%), (ii) 5 ml of 50 mM pH 5 acetate buffer, and (iii) 6 ml 50 mM acetate buffer and 4 ml of 5 mM L-DOPA solution. Absorbance was measured at 460 nm via UV/Vis spectroscopy 200 seconds after the mixing of reagents. Results are presented in Figure 3.6.
Each of the three test conditions demonstrates an initial linear increase in absorbance at 460 nm with increasing masses of peat in the slurry mixtures. Beyond 0.5 g peat solid in experiment (i), and 1.5 g peat solid in experiments (ii–iii), additional increments of solid impart little, if any, additional increase in absorbance at 460 nm after 200 seconds. It is assumed that at these masses, absorbance plateaus due to particulate saturation of the reaction mixtures (Berberan-Santos, 1990).

Comparison of experiments (i) and (ii) shows a more rapid increase in absorbance relative to mass in the presence of L-DOPA solution when compared to the mixture with peat slurry alone. This comparison shows that the development of DICQ can be observed above and beyond the natural coloration imparted to solution by peat alone. It also confirms for the first time in this development procedure that this bulk peat possessed PO activity capable of generating DICQ. In the presence of L-DOPA the
linear trend plateaus at 0.5 g wet soil mass as opposed to 1.5 g when L-DOPA is not added. As opposed to the particulate saturation effect mentioned previously, the change in absorbance trends at 0.5 g for experiment (i) is believed to be due to saturation of the sample to the point that additional peat particulates (and thus PO) are unable to physically access the L-DOPA in solution to the same degree as previous peat quantities. This hypothesis was explored by repeating the experiment in double the sample volume, experiment (iii), while maintaining consistent L-DOPA concentration. A greater mass of peat was required to achieve the plateau point in a greater volume of peat, as would have been predicted if particle saturation (Berberan-Santos, 1990) is responsible for the plateau.

When selecting an appropriate peat mass for an optimised methodology, it is obviously unfavourable to use a mass of peat that would cause either of the saturation effects observed in this study. It is also beneficial to obtain the highest possible absorbance values to maximise the signal to background ratio Optimal sample masses are in the region of ~0.35 g for 5 ml reaction volumes and ~0.7 g for 10 ml reaction volumes. These masses would allow for inherent variations in the solid content of fresh peat samples while avoiding saturation.

### 3.4.2.6 Reaction incubation time

Literature methodologies have employed a range of potential incubation times for the PO–L-DOPA reaction from between 1 and 3 minutes (Robinson and Smyth, 1997) to 5 hours (Pind et al., 1994). The production of DICQ across 10 minutes was assessed
via kinetic analysis on a Perkin Elmer, Lambda XLS + UV/Vis spectrometer with additional readings across longer timescales measured via default acquisition mode. Reaction mixtures contained 2.8 ml volume of 50 mM pH 5 acetate buffer stock created by addition of 7.4 ml of 0.2 M acetic acid (VWR, glacial, >99%) to 17.6 ml of 0.2 M sodium acetate solution (Sigma Aldrich, anhydrous, ≥99%) and 75 ml deionised water, 2 ml of 5 mM L-DOPA solution (Sigma Aldrich, ≥98%) and 0.2 ml of 10 mg l⁻¹ PO mushroom tyrosinase standard (Sigma Aldrich, from *agaricus bisporus*, lyophilised powder >1000 unit mg⁻¹). Results are shown in Figure 3.7.

![Figure 3.7](image)

**Figure 3.7** Absorbance at 460 nm due to DICQ development over 0-10 minutes then subsequently at 10 minute intervals.

An initial linear reaction-phase during the initial 10 minutes shows rapid development of DICQ. Beyond 10 minutes, the increase in absorbance is less pronounced over time as the graph quickly transitions into a linear phase with a reduced gradient from 10-70 minutes. The calculation of enzyme activity outlined in Section 3.4.2.2 operates on the assumption that a direct linear relationship between
absorbance and time exists for a given sample. The activity calculation therefore
would provide a poor estimate of enzyme activity if a singular measurement was
adopted from any time beyond this transition time in DICQ evolution as the true
relationship is clearly not linear. Measurements must therefore consistently be taken
for all samples at a time before this transition takes place.

Further kinetic studies were employed to further investigate the time at which the
reaction shifts from its rapid phase to its slower phase. Reaction mixtures outlined
above, but containing varied concentrations of enzyme standard were used and the
kinetic study repeated. The times at which the initial linear graph phase ended are
summarised in Table 3.11.

<table>
<thead>
<tr>
<th>Enzyme Stock (mg l⁻¹)</th>
<th>Duration of rapid DICQ evolution phase (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5</td>
<td>9.79</td>
</tr>
<tr>
<td>10.0</td>
<td>10.41</td>
</tr>
<tr>
<td>6.0</td>
<td>11.83</td>
</tr>
<tr>
<td>4.5</td>
<td>12.90</td>
</tr>
<tr>
<td>2.0</td>
<td>14.91</td>
</tr>
</tbody>
</table>

These results clearly show that as enzyme concentration, and thus PO activity in
solution decreased, the time at which the rapid production phase of DICQ ends
increased. It is therefore suggested that a measurement time of 8 minutes is
appropriate as the linear transition will be consistently beyond this time for natural
peat samples which will possess lower activity than the standard solutions presented
here.
3.4.2.7 Temperature

The activity of PO can change in relation to temperature with 20°C reported as optimal for the functionality of the enzyme (Zufelato et al., 2004). Natural daily and seasonal temperature variations make selecting a temperature baseline from which to judge ‘true’ PO activity in the environment problematic. Unlike peat pH which tends to remain consistent over short timescales, temperatures can fluctuate markedly across 24 hour periods and will also change from locale to locale. Measurement at a consistent temperature representative of a peat system would be highly impractical and require significant expenditure to ensure ambient conditions were maintained for samples from field sampling through to activity analysis. Instead, to permit better comparison and to allow straightforward incorporation into a range of laboratory configurations, the procedure will be carried out under ambient conditions in an air-conditioned temperature controlled laboratory at 21 °C which approximates the enzyme’s optimum activity region (Zufelato et al., 2004).

3.4.2.8 Reaction termination

The ability to halt the oxidation of L-DOPA and resultant development of DICQ is crucial to the viability of taking consistent repeated measurements within a practical timescale. Viable termination options include centrifugation, filtration and addition of enzyme denaturing agents.
3.4.2.8.1 Filtration

Filtration is essential to the methodology; the presence of soil particulates in the final analytical solution greatly compromises the credibility of a spectrometer reading. Furthermore, filtration acts to remove the bulk mass of soil from contact with the L-DOPA solution. This contributes towards the cessation of the reaction by removing the source of PO from the substrate and preventing further interaction of surface adsorbed enzymes with the L-DOPA solution. The solubility of PO (Sanchez-Ferrer et al., 1993; Mchedlishvili et al., 2000) means that further measures are required to stop the reaction, as PO passes through the filter in the absence of other measures and DICQ will still be produced post-filtration.

3.4.2.8.2 Centrifugation (Methods II, IV and VI)

Centrifugation can serve to hinder the DOPA reaction by either removing PO-bearing particulates from the bulk solution or by damaging cell walls to modify cellular PO dynamics. The effect of centrifugation was assessed by addition of 2 ml of 5 mM L-DOPA solution (Sigma Aldrich, ≥98%) and 0.2 ml of 10 mg l\(^{-1}\) PO mushroom tyrosinase standard (Sigma Aldrich, from agaricus bisporus, lyophilised powder >1000 unit mg\(^{-1}\)) to 2.8 ml of 50 mM pH 5 acetate buffer prepared as described in Section 3.4.2.6. Centrifugation was performed exactly 4 minutes and 30 seconds after reagents were mixed. Samples were subject to centrifugation at 1077 x g for exactly 3 minutes. Absorbance at 460 nm was measured 10 minutes, and 15 minutes after the mixing of reagents. Results are shown in Table 3.12. The results for
solvent addition experiments presented in this table will be discussed in Section 3.4.2.8.3. Experiment (I) was untreated and functioned as a control.

Table 3.12 Influence of reaction termination techniques on DICQ production 10 minutes and 15 minutes after addition of L-DOPA

<table>
<thead>
<tr>
<th>Centrifugation</th>
<th>Acetone</th>
<th>Chloroform</th>
<th>Absorbance-10 min</th>
<th>Absorbance-15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-</td>
<td>-</td>
<td>0.0142 ± 0.0002</td>
<td>0.0196 ± 0.0002</td>
</tr>
<tr>
<td>II</td>
<td>X</td>
<td>-</td>
<td>0.0128 ± 0.0001</td>
<td>0.0222 ± 0.0003</td>
</tr>
<tr>
<td>III</td>
<td>-</td>
<td>X</td>
<td>0.0132 ± 0.0001</td>
<td>0.0170 ± 0.0002</td>
</tr>
<tr>
<td>IV</td>
<td>X</td>
<td>X</td>
<td>0.0108 ± 0.0001</td>
<td>0.0162 ± 0.0001</td>
</tr>
<tr>
<td>V</td>
<td>-</td>
<td>-</td>
<td>0.0193 ± 0.0002</td>
<td>0.0215 ± 0.0001</td>
</tr>
<tr>
<td>VI</td>
<td>X</td>
<td>-</td>
<td>0.0117 ± 0.0001</td>
<td>0.0148 ± 0.0001</td>
</tr>
</tbody>
</table>

(n=3)

Comparison of DICQ development rates in samples exposed and unexposed to centrifugation demonstrated that the process does cause reduction in DICQ development until the 10 minutes point. Comparison of the control sample (Method I) with the centrifuged sample (Method II) demonstrates a 0.0014 decrease in absorbance at the 10 minute point when centrifugation takes place. Similar reductions in absorbance after 10 minutes are seen when centrifuged and non-centrifuged samples are compared for the solvent methods to be discussed in the following section. However, when samples that have undergone centrifugation are measured 5 minutes later, their absorbance has increased more rapidly across this 5 minute time period than the samples that have not. The reasoning for this observation is unknown but it is clear that centrifugation is not a valid means of halting the production of DICQ. Centrifugation does, however, greatly accelerate the filtration-step by allowing decanting of the solvent, free from peat residue. If the enhanced reactivity brought about by centrifugation can be addressed, such a step would be useful in optimising sample throughput times.
3.4.2.8.3 Denaturing solvents (Methods III–VI)

Organic solvents such as acetone and chloroform are known to denature protein structures. (Khmelnitskyl et al., 1991; Schellman 2002). Both of these solvents were tested experimentally for their suitability to denature PO and thus halt the production of DICQ as outlined in Table 3.12. The methodology outlined in Section 3.4.2.8.2 was employed with 200 µl volumes of acetone (Fisher Scientific, HPLC grade) or chloroform (Fisher Scientific, certified analytical reagent grade, conforms to ACS) added exactly 8 minutes after mixing of the other reagents.

Acetone and chloroform were found to significantly, but nevertheless incompletely, inhibit the development of DICQ from 10 minutes to 15 minutes following the initiation DICQ production. Acetone proved less effective than chloroform with the acetone sample showing an increase in absorbance from 10 minutes to 15 minutes of 0.0038 whereas the chloroform sample exhibited an increase of only 0.0022 during that timeframe; the lowest increase of any termination method tested. Similar trends are observed when solvents are added to centrifuged samples with acetone showing less effectiveness than chloroform. Chloroform is clearly more fit-for-purpose and will be adopted as a means of halting the development of DICQ to reduce variability over successive measurements.
3.4.2.9 Reaction volume

Low reaction volumes can lead to difficulties in filtration that can compromise sample throughput times due to the moisture adsorption capabilities of solid peat residue preventing solution from passing through filter papers. For this reason it is advised that 10 ml total reaction volumes be adopted to facilitate rapid filtration of sufficient solution to allow a spectrophotometer reading while maintaining reasonable sample throughput times.

3.4.3 Optimised procedure for determination of PO activity in peat

A 0.7 g weight of homogenized peat (fresh weight) was placed into replicate 50 ml centrifuge tubes. A 6.0 ml volume of deionised water was added to each tube and the contents shaken by hand to mix. Subsequently, 4 ml of 5 mM L-DOPA solution (prepared from Sigma Aldrich, ≥98%) was added to each tube to initiate the reaction. Blanks were prepared via addition of 4 ml deionised water in place of the L-DOPA solution. After 4 minutes 30 seconds, each tube was subject to centrifugation for 3 minutes at 3500 RCF (Sanyo MSE Harrier 15/80). Immediately following centrifugation, the tubes were transferred to a fume cupboard and 200 µl chloroform (used as supplied, Fisher Scientific, certified analytical reagent grade, conforms to ACS) was added, with mixing, to terminate the reaction. Each sample was then subjected to filtration under gravity (Whatman, No 1) and the filtrate absorption measured spectrophotometrically at 460 nm on a UV/Vis spectrophotometer (Perkin Elmer, Lambda XLS + UV/Vis). The activity of PO was calculated by deducting the
blank absorbance values before application of Beer’s law, using the molar absorbance coefficient for the reaction product DICQ (3.7x10^4). Activity of PO is expressed as nmol of DICQ min^{-1} g of sample^{-1}.
Chapter 4 Classification of peats and soils

4.1 Introduction

This chapter will provide an overview of soil and peat systems including their structure, formation, constituent phases and fractions, classifications and relevant chemistry. The field sites involved in the project will be introduced and discussed and the initial results relating to moisture content, organic matter (OM) content, density, solid and aqueous phase pH, porewater conductivity, porewater dissolved organic carbon (DOC) content and [Fe] and [Mn] will be presented and discussed. The primary aim of this chapter is to provide a foundation for the discussion of the Pb, Hg and more detailed organic matter data contained within chapters 5, 6 and 7.

4.2 Soil formation and structure

Soils comprise living and decaying organic matter, weathered and unweathered rock and other mineral phases. It forms on the uppermost part of the regolith as a consequence of interactions between unconsolidated rock material and the atmosphere, water and living biological entities. The impact of soil upon humankind cannot be understated due to its supporting role in the food chain. Plants use soil as a source of nutrients and as a matrix in which to grow. Humans in turn eat these plants or utilise them to feed livestock that in turn is eaten. In the absence of soil, the entire biosphere/ecosystem would be significantly different. Soils comprise three main phases, i.e. solid matter, solution phase and gas phase, and the processes controlling the composition of each will be described in turn.
4.2.1 Soil solid phase

The soil solid phase can be broadly separated into two categories: organic and mineral matter. The majority of solid phase material consists of large organic/inorganic-humic aggregates although both organic and inorganic carbon species can also be found as smaller, discrete solid phase particles (Dawson and Smith, 2007). These species are discussed in more detail in the following sections. The proportion of organic and inorganic species, size classifications, and overarching structure can vary greatly dependent on soil geological influences, local flora and geography.

4.2.1.1 Soil solid mineral fraction

Most types of soil comprise primarily of mineral matter sourced from the weathering and comminution of parent rock material. Parent rock material can either be underlying bedrock or material transported from further afield by such as glacial drift (Campbell and Claridge, 1987). Mineral particles are classified by their grain size, although precise definitions vary across official bodies. These classifications are compared in Figure 4.1. The clay size fraction which includes clays and metal oxide is the smallest classification (<2 µm) with silt (~2-50 µm) and sand (~50-2000 µm) making up the larger size classifications.
Many minerals are siliceous inorganic structures consisting of repeating bulk crystal units comprised of Si$^{4+}$ and O$^{2-}$ with some structures incorporating Al$^{3+}$. Hydrogen ions and other metal cations balance some of the dominant negative ionic charges. Weathering of the larger-sized primary minerals including quartz (SiO$_2$), feldspars (KAlSi$_3$O$_8$, CaAl$_2$Si$_2$O$_8$, etc), Fe-bearing silicates ((Mg, Fe)$_2$SiO$_4$, K(Mg,Fe)$_3$(AlSi$_3$O$_10$)(F,OH)$_2$, etc) and calcite (CaCO$_3$), through exposure to groundwater, rainwater and acids leads to formation of the smaller-sized secondary minerals. There are numerous secondary minerals including Fe (hydr)oxides such as goethite (FeO(OH)), hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$), Al oxides and hydroxides including gibbsite (Al(OH)$_3$), and clays encompassing illite (K$_2$H$_3$O)(Al,Mg,Fe)$_2$(Si,Al)$_4$O$_10$(OH)$_2$, kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) and montmorillonite (Na,Ca)$_0.33$(Al,Mg)$_2$(Si$_4$O$_10$)(OH)$_2$ among others (Greenland, 1978).

The crystal structure of illite is shown in Figure 4.2 as an example of a typical clay crystal. Clay particles play an important role in soils due to their propensity to form
charged surface layers. In silicate clays, isomorphic substitution in the crystal structure often results in permanent charges at the mineral surface. Furthermore, some clays, e.g. kaolinite, and metal oxides possess pH dependant surface charges. At low pHs surfaces can become protonated granting net positive charge, whereas, high pHs result in sorption of hydroxyl groups causing net negative surface charges. Thus soil mineral species can adsorb both anionic and cationic species dependent on ambient pH (Barrow, 1993).

![Crystal structure of illite](image)

**Figure 4.2** Crystal structure of illite, adapted from USGS (2001).

### 4.2.1.2 Soil solid organic fraction

In contrast to the origins of the soil mineral fraction, the organic matter fraction is sourced from deposited litter from living plants and animals. The organic fraction itself can be categorised as living biomass, fresh and partially decomposed detritus, humic material and black carbon (e.g. Magdoff et al., 1996; Lal, 2005).
Humic material is formed via humification, the process whereby the carbon of organic residues is transformed and converted to humic substances through biochemical and abiotic processes (e.g. Buscot and Varma, 2005). Humification is part of the cycling process experienced by soil organic matter as outlined in Figure 4.3.

It encompasses the decomposition of detrital carbohydrates, proteins and subsequent synthesis reactions of the low molecular weight units produced by these processes. In the majority of environments, the primary parent molecules will therefore consist of partially decomposed plant-cellulose and hemicellulose, non-decomposed lignins, tannins, and proteins (Stevenson, 1994). Less abundant secondary inputs are typically derived from fauna and include carcasses and faeces. The decomposition
processes typically involve partial oxidation reactions carried out by chemical interactions with the soil aqueous phase or via interaction with soil fauna (Wolters, 2000). The majority of the decomposition of these primarily polymeric structures is performed through catabolism by living biomass in the soil, i.e. microorganisms, fungus and living plants. These biota, including many prokaryotes and eukaryotes, assimilate other soil molecules as nutrient sources. Biota-induced catabolism is capable of inducing complex enzyme-catalysed chemical transformations that would be otherwise chemically unfavourable. Traditionally, it was believed that assimilation of organic matter by biota in combination with the abiotic oxidation of polyphenols and deamination of amino acids provided molecular fragments capable of undergoing polycondensation processes to form new polymeric chains with concentrations of carboxylic acid (R–COOH) typically higher than in the parent material (e.g. Qi et al., 2012). These polymeric chains result in dark brown coloured, high molecular weight humic macromolecules that possess no standardised structure and for which no general chemical formula will suffice. Figure 4.4 provides one traditional theoretical example of a humic acid for illustrative purposes only.

![Figure 4.4 Traditional theoretical structure of a humic acid including quinone, phenol, catechol, carboxylic acid and chain alcohol functionalities (Yikrazuul 2009).](image)

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Recent publications, however, have proposed that humic substances are in fact supramolecular clusters where hydrogen bonding, dipole interactions and hydrophobic effects link clusters of smaller and highly chemically varied organic species (Sutton and Sposito, 2006). Utilising gel permeation and high-pressure size-exclusion chromatography, Piccolo et al. (2001) provided evidence of aggregation and disaggregation effects that conflicted with the traditional polymeric macromolecular description of humic matter. Piccolo’s observations were supported by the work of Simpson et al. (2001a; 2001b) who adopted a multidimensional nuclear magnetic resonance approach to observe the aggregation and disaggregation of these supramolecular species. Evidence that humic species exhibited micelle behaviour and had functional group distributions that were inconsistent with a polymeric structure further reinforced this theory.

Due to the emergence of these two conflicting humic structure theories, there remains a current focus within literature on analysis and characterisation of humic material. The supramolecular model is relatively new and the functional group distributions of the individual components of these aggregates fractions have not yet been adequately explained. Additional information is also required to resolve the hydrophobic and hydrogen-bonding interactions that link the aggregates. Thus, contemporary publications continue to apply a plethora of analytical techniques to characterise humic substances including NMR spectroscopy (Chiu and Tian, 2011; Mao et al., 2011), HPLC-fluorescence spectroscopy (Gora et al., 2012), wet chemical derivatisation methods including esterification (Rozenbaha et al., 2002),
Composition is important because it controls the behaviour of humic substances in the environment. For example, the solubility of humic molecules depends on molecular size and the concentrations of functional groups such as carboxylic acids (R-COOH) and hydroxyl (R-OH) groups relative to hydrophobic entities such as aliphatic chains and aromatic structures. Traditionally, humic substances were operationally fractionated on the basis of their solubility. Humic acids are insoluble under acidic conditions due to insufficient capacity to form the hydrogen bonds to create a functional solvation shell, either due to large molecular size or poor dipole availability. Fulvic acids are soluble at all pH values and are often smaller than their humic counterparts with a higher proportion of oxygen containing functional groups relative to molecular mass. The structure of humic substances is also important with respect to their interactions with other solid phase soil components and, more generally, the properties of the soil as a whole. Acidic groups such as R-COOH and phenol groups can be adsorbed onto the surfaces of minerals and mineral oxides at low pHs. The resulting aggregates are conducive to formation of pore spaces within the soil. These ionisable groups also make a highly significant and pH-dependent contribution to soil cation exchange capacity, an important parameter in relation to bioavailability of plant nutrients.
4.2.2 Soil aqueous phase

Soils contain significant quantities of water that is held within pore spaces; this is either termed the porewater or soil solution. Transmission pores (>50 µm diameter) act to facilitate the passage of this water throughout the structure whereas smaller pores may only trap water. A hypothetical structure of soil showing pore spaces is presented in Figure 4.5. The aqueous soil phase contains organic and inorganic entities, both truly dissolved (<1 nm) and colloidal (~1 nm – ~1 µm). Truly dissolved entities encompass metal cations (Fe$^{2+}$, Mn$^{2+}$, K$^+$, etc), inorganic anions (SO$_4^{2-}$, H$_2$PO$_4^-$, etc), neutral species (dissolved O$_2$) and polar or hydrogen bonded organic molecules including fulvic acids. Some soil components, including humic molecules and inorganic Fe and Al species, are known to exhibit colloidal characteristics (Tombacz, 2005; Pokrovsky et al., 2006).

![Figure 4.5 Soil macrostructure showing pore spaces proximal to both mineral and organic matter (DPI, 2011).](image)

The aqueous phase is of key relevance to the reactions of species within soil as many processes require that the aqueous phase be in contact with the solid phase soil.
order to occur. Ion exchange, redox processes, complexation reactions, hydration/hydrolysis and precipitation/dissolution all influence the solid phase via the action of the aqueous phase upon it. These equilibrium processes influence soil parameters such as pH and reduction potential ($E_h$).

The transport of nutrients and other chemical species into soils is controlled partially by aqueous phase soil processes. Dissolved species, colloids and suspended particulates can be transported by lateral groundwater flow and rainwater input. Laboratory studies (Dunnivant et al., 1992) and in-situ field studies (Watanabe et al., 2012) have concluded that humic colloids are both significant contributors to dissolved organic matter (DOM) and are potentially mobile throughout a soil-water system.

### 4.2.3 Gaseous phase

The soil gas phase refers to the gaseous species present within soil pore spaces. The gas within the pore spaces strives to reach equilibrium with the atmosphere where facilitating diffusion processes are possible. Where pore networks are not readily connected or pore volume is low relative to the bulk soil (<10%) diffusion processes are hampered and the composition of the soil gas phase may differ significantly from the atmosphere (Bolt and Bruggenwert, 1978).
The respiration of biological entities including microorganisms and plant root structures further influences soil gas phase composition. There is a general trend of increasing deviation from atmospheric composition, decreasing oxygen concentration with depth (e.g. Limpens et al., 2008) and a corresponding increase in CO₂ levels. At depths where atmospheric diffusion is limited, the oxygen concentration can tend towards zero.

### 4.2.4 Depth, structure and horizons

Soil can be classified by the layered structure that represents the transformation, decomposition and changes in composition of the soil material in relation to depth. These layers or ‘horizons’ are often distinguishable visually and encompass different degrees of organic matter decomposition and humification, and different mineral content and composition. Localised conditions can modify the thickness of horizons or can eliminate their presence entirely. A unique Scottish soil classification system has been developed (Macauley institute and SNH, 2009) and will be adopted for the explanations in the following sections.

In general terms, the uppermost layer is the ‘O’ horizon and contains fresh, slightly decomposed, fragmented and highly decomposed OM. However, it should be noted that the ‘O’ horizon is not present in all soil types. Underlying the ‘O’ horizon is the ‘A’ horizon, or topsoil layer, which is characterised by an intense dark colour. This layer consists of a mix of mineral and humified material. Below the ‘A’ horizon lies the illuvial ‘B’ horizon comprising of partially weathered clays, Fe- and Al- oxides
in addition to some humus. Between the bedrock and the ‘B’ horizon lies the ‘C’ horizon comprised of mineral material subjected to only slight chemical alteration. These horizons are representative of a mineral/organic soil and are outlined in Figure 4.6. The horizon structure of soil is greatly dependent on the presence of mineral matter and so mineral horizons are not applicable to peatlands due to the deficit of mineral material within these organic-rich systems. The structure of peatlands is described in more detail in Section 4.3.1.

![Soil horizon profile showing typical O, A, B, C and R horizons.](image)

**Figure 4.6** Soil horizon profile demonstrating typical O, A, B, C and R horizons.

### 4.3 Soil classification

Of particular interest to this project are three specific categories of soil: ombrotrophic peats, minerotrophic peats, and forest podzols. Although they all have organic-rich substrates, these soils differ with respect to their mineral contents: ombrotrophic peat (~1-15% mineral content) < minerotrophic peat (~5-35% mineral content) < forest podzols (~25-95% mineral content) (SCWG, 1998; Huat et al., 2011). Ombrotrophic
peat bogs and hilltop forest soils both receive their inputs of nutrients primarily from the atmosphere whilst other forest soils and minerotrophic peat bogs also receive inputs from groundwater. These three terrestrial environments are outlined in more detail in the following sections.

### 4.3.1 Peat

Peat bogs account for approximately 10–14% of Scotland’s surface area (Taylor, 1983, WEC, 2004). This percentage translates to ~1.1 million hectares of peat; approximately 2.5 times the surface area of England and Wales’ peat resources combined. Within Europe, only Russia, Finland, Sweden, Norway and Belarus possess larger areas of peatlands than Scotland with total European peat occupying around 190 million hectares.

Peat is an organic-rich, highly waterlogged histosol consisting primarily of decayed plant material together with low concentrations of deposited minerals (USDA, 1999). Peat is characterised by its greatly expanded ‘O’ horizon. Peat bogs possess two distinct layers. The aerobic ‘acrotelm’ (approx 30-50 cm deep depending on hummock/hollow topography) comprises surface vegetation and mostly stems of living *Sphagnum* moss. (Quinty and Rochefort, 2003; Lindsay, 2010). This is the zone in which fluctuations in the water table occur. The underlying layer, the ‘catotelm’ contains the collapsed and decomposing mass of *Sphagnum* fragments and usually lies below the water table as shown in Figure 4.7. Water can travel quickly through the acrotelm but moves slowly through the catotelm (~1 metre per day).
under normal environmental conditions. The acrotelm is increasingly permeable towards the surface, a property that acts to stabilise water table levels in response to abnormally high levels of rainfall (Bragg and Tallis, 2001).

The formation of peat bogs begins when surface waters become isolated. Weeds and vegetation gradually encroach upon these waters until no open water remains. Upon death, plant components are preserved in the resulting swamp and ultimately form a layer of peat on the swamp-bed. As peat continues to accumulate, additional vegetation can no longer root in the underlying mineral soils. The plants around the swamp’s edges typically absorb all available nutrients where there is a supply of groundwater to provide for them. This creates a nutrient deficient zone in the centre of the water. Species of *Sphagnum* begin to dominate the vegetation and continued accumulation of peat results in bog formation (DOENI, 2005). Within the catotelm, peat degrades slowly and anaerobically. To maintain bog stability, the system must accumulate more peat than is lost or degraded over time. If the balance is negative,
Vegetation across mires is highly dependent on hydrological factors. *Sphagnum* or ‘bog moss’ is key to the very formation of the system, whereas the other species of peat surface vegetation can vary. Botanists for the UK national vegetation classification project have classified over 38 distinct varieties of flora on peat bogs (Rodwell, 1999). Such variation is facilitated by microforms within the continuous *Sphagnum* carpet (convex hummocks, concave hollows, lawns etc) that provide a range of heights above the water table at which different plants can grow.

The aqueous phase of peat is of considerable importance as water comprises the majority of the mass of the peat. Indeed, some peatlands can exceed 95% water content by mass (Hayes, 1978). It is therefore important that such systems are treated not simply as solid entities but as hydrological systems. Peat falls into one of two categories dependent on its respective sources of water and nutrient inputs: minerotrophic, groundwater fed; and ombrotrophic, rainwater fed. Typically, minerotrophic fen peat is alkaline in nature with a pH ~7-8 while ombrotrophic bog peat is generally acidic with pH values in the range ~3-5. Ombrotrophic bogs can be further categorised as ‘raised’ or ‘blanket’. Raised bogs exhibit an elevated dome shape in the centre that is notably absent on blanket bogs. Systems seldom lie truly at the ombrotrophic or minerotrophic extremes and occupy a point on the spectrum somewhere in between. Completely ombrotrophic systems are somewhat rare as

the bog is vulnerable to long-term degradation, erosion and destruction (Clymo, 1984).
some nutrient input will often occur through groundwater flow during surface surges and abnormal weather events.

In contrast to conventional soils, the highly anaerobic conditions combined with low pHs in typical peatlands results in the loss of activity, deactivation, or death of many species of soil microorganisms. The metabolism of the microorganisms that remain alters to less energy-efficient fermentation, methane formation or nitrate and sulfate reduction reactions (Haider 1992). Under these conditions, the oxygen-dependent breakdown of high order aromatic ring structures and phenolic substances is not favourable and these compounds accumulate in peatlands.

4.3.2 Podzolic forest soils

Forest soils globally typically possess a greater percentage of mineral components in comparison with peats but remain highly organic with up to ~75% organic matter content (SCWG, 1998). In Scotland the majority of upland coniferous forest soils fall under the category of podzols. Podzols are formed in cool, damp climates where heath or forest vegetation dominates (e.g., Wilding et al., 1983). Aerobic conditions and coarse existing soil texture are also essential (Lundstrom et al., 2000). Podzols are normally acidic, offer high water permeability and possess a high C:N ratio. Low nitrogen availability in the decomposition cycle results in a low overall fertility. Structurally, podzols conform closely to a typical horizon configuration. When covered by forest, these soils exhibit a thick (>5 cm) ‘O’ horizon organic layer comprising litter, slowly decomposing organic matter and humus. Below the ‘O’
horizon lies the ‘A’ horizon which consists of a mix of humic material and mineral matter which results in a distinct brown colour. At greater depth lies a grey-coloured, structureless eluvial ‘E’ horizon which has high silica but low Fe and Al content. Below this is sometimes a layer of redeposited organic matter that may or may not overlie a iron hard pan. The thickness of these layers can vary considerably from soil to soil. At further depth is an enriched illuvial ‘B’ horizon of humus and Fe/Al followed by underlying relatively unaltered mineral layers. This is illustrated in Figure 4.8.

![Figure 4.8 Structure of a typical forest podzol.](image)

Forest soil formation is based on a succession of processes. Initially, soluble metal-humus complexes become mobilised and pass from the surface layers to greater depth, thus forming the illuvial Fe/Al horizon. Humus and Fe/Al oxides subsequently
accumulate within the subsoil (Macauley Institute, 2008) giving rise to the structure outlined above. Dependent on eluvial horizon thickness, Fe:C ratios, organic matter properties and gleying properties, podzols can be sub-classified into haplic, cambic, ferric, carbic, gleyic and gelic categories.

4.4 Peatland and forest soil as archives of atmospheric deposition of metals

Undisturbed accumulating organic-rich systems can act as sinks for atmospherically deposited metal contaminants from both diffuse and localised sources. These concepts are outlined and in Figure 4.9, although a more detailed discussion of historical pollution records relating specifically to Pb is presented in Chapter 5. Peatlands and accumulating upland soil systems, where the predominant input mechanism is via the atmosphere and rainwater, are examples of environments where atmospheric deposition history of metals may be reconstructed. As layers are accumulating, each layer of peat or soil represents a record of the atmospheric inputs to the soil during the time period in which that layer was accumulating. (e.g. Stewart and Fergusson, 1993; MacKenzie et al., 1998a, 1998b; Blackford, 2000; Shotyk et al., 2002; Farmer et al., 2005; 2009; Cloy et al., 2008; Bindler, 2011; etc). For example, Pb that entered a peatland through windborne particulates in 2000 will be present in the surface layer in 2000, but will be at a depth of a few cm by 2012 as additional layers of peat have accumulated. This is only true if species deposited from the atmosphere are immobilised in the soil or peat matrix following deposition as any vertical mobility will perturb the historical record. Layers can be dated
through processes such as $^{210}\text{Pb}$ dating and identification of key radionuclide dating markers from nuclear weapons testing and disasters such as Chernobyl in 1986 (e.g. Rowan and Walling, 1992; Robbins and Jasinski, 1995). The $^{210}\text{Pb}$ dating process is discussed in additional detail in Chapter 2 and Chapter 5.

![Diagram](image)

Figure 4.9 Example of peat behaving as a contaminant sink.

### 4.5 Introduction to properties of peats and soils

A brief summary of peat and soil organic percentage and moisture content, DOC, conductivity, and Fe and Mn cycling are outlined here to provide context for the results that follow in Section 4.7. These descriptions will focus on the relevance of such measurements to this project.

#### 4.5.1 Organic matter and moisture content

The quantity of organic matter within a peat or soil environment is important in relation to its classification within the ombrotrophic, minerotrophic and mineral soil
spectrum within this study. Measurement of peat or soil organic matter is also a means through which the mineral content can be determined; in this study the mineral content is defined as the amount of solid material remaining after the organic content has been removed by ashing at 450°C. The relative proportions of organic to mineral content will influence the mechanisms through which Pb, Hg and other metals might be retained within the peat or soil. This in turn will influence the potential re-release of metals into the aqueous phase. The amount of organic matter in a soil or peat environment can also be used as an estimate of carbon stock as the two factors are directly related (e.g. Leifeld and Kögel-Knabner, 2005).

Peat/soil moisture content is an important measurement for several reasons. Moisture content exerts a controlling influence on oxygen availability and correspondingly redox potential (e.g. Rubol et al., 2012), microbial activity (e.g. Baldrian et al., 2010) and the decomposition rate of soil organic matter (e.g. Craine and Gelderman, 2011). Furthermore, a moisture content profile provides an indication of the level of the water table at a particular location.

### 4.5.2 Dissolved organic carbon (DOC)

Dissolved Organic Carbon (DOC) has been introduced previously in Section 4.2.2. Measurement of DOC is important to this study for a number of reasons. Primarily, DOC provides a measurement of the quantity of organic matter in the aqueous phase; total DOC concentrations are essential for humic colloid sub-fractionation experiments detailed in Chapter 7. Mobility of DOC represents one of the mechanisms through which both carbon and species associated with the DOC itself
can be transported throughout a soil or peat environment (e.g. Neff and Asner, 2001). High concentrations of DOC may indicate a propensity for organic matter to become dissolved or suspended in the aqueous phase within a particular soil or peat, potentially providing an indication of the likelihood of loss of organic matter and associated contaminants from a system.

4.5.3 Conductivity

Porewater conductivity provides a crude qualitative indication of dissolved inorganic species. Ionic strength (I) and conductivity are directly linked e.g. \( I \approx 1.6 \times 10^{-5} \text{ SpC} \) (e.g. Langmuir, 1969; Lind, 1970; Russell, 1976). In relation to this study, the effect of ionic strength on double layer thickness around humic substances can directly influence the capability for metals to adsorb onto the surfaces of these humic substances (e.g. Sekaly et al., 1991). It has also been proposed that the degree of humic aggregation (according to the supramolecular humic theory) or humic coiling (according to the traditional polymer theory) will increase with ionic strength, resulting in reduced access of metals and other ligands to viable binding sites and transfer of aggregated molecules to the solid phase.

4.5.4 Iron and manganese cycling

At neutral to acidic pHs, Fe can exchange between solid and aqueous phases depending on the redox conditions within a soil profile. At the surface at near-neutral pHs where conditions are oxic and \( E_h \) values are >0.77 V, Fe\(^{II}\) in solution is oxidised and precipitates into the solid phase as insoluble Fe\(^{III}\) species (e.g. Deutsch, 1997).
However, it should be noted that under acidic conditions, Fe$^{II}$ will be stable in solution. When $E_h$ values drop sufficiently to $<0.77$ V, insoluble Fe$^{III}$ is reduced to soluble Fe$^{II}$. This Fe remains in solution until it migrates via diffusion upwards where the more oxic conditions cause it reoxidise and precipitate therefore repeating the cycle (e.g. Deutsch, 1997; Song and Muller, 1999). Manganese undergoes similar redox cycling within acidic soils. Insoluble Mn$^{IV}$ is reduced to soluble Mn$^{II}$ where soils become sufficiently anoxic while in the near-surface oxic environments the Mn$^{II}$ is oxidised to Mn$^{IV}$. In soil environments, the reduction of Fe and Mn is largely driven by microorganisms that use the reduction to, in turn, oxidise organic functional groups such as aromatic rings, or sulphur bearing moities. Typically, Mn$^{IV}$ is reduced before Fe$^{III}$ where electron donors are available. Conversely, Fe$^{II}$ is oxidised in preference to Mn$^{II}$ except where the oxidation of Mn$^{II}$ is catalysed via interaction with soil mineral surfaces (Fendorf, 2012).

4.6 Field-sites

In the initial phase of the project, three Scottish sites were chosen in order to encompass a spectrum of organic-rich terrestrial systems incorporating varied proportions of mineral matter. As discussed in Section 4.3, podzolic forest soil possesses more mineral matter than minerotrophic peat, which in turn has higher concentrations of mineral matter than ombrotrophic peat. To include each of these systems in the project, the following sites were selected: the ombrotrophic raised dome bog at Flanders Moss (FM), approximately 8 miles west of Stirling; the minerotrophic bog at Easter Deans (ED), approximately 5 miles south of Penicuik; and the raised hillside forest at Glentress (GT), 1 mile east of Peebles. Following
access discussions with the NERC Centre for Ecology and Hydrology (CEH) at Bush Estate, a 4th site, Auchencorth Moss (AM), 3 miles southwest of Penicuik was included later in the project due to the availability of atmospheric deposition data for Hg. Figure 4.10 shows the location of these sites around Scotland. The FM and ED sites have been investigated previously (Sugden 1993; Cloy et al., 2005; 2008; 2009; Farmer et al., 1997a; 2005; 2009; MacKenzie et al., 1997) thus providing past data for comparison. Details of the cores taken from each site are presented in Tables 4.1 and 4.2 using the monolith method discussed in Section 2.2.1 or the Cuttle and Malcolm coring method outlined in Section 2.2.2. Cores presented in Table 4.2 were used exclusively for $^{210}$Pb dating whereas Table 4.1 details cores that were used for general analysis, including $^{210}$Pb dating for GT and AM cores. Depth resolution of cores across sites varies due to a number of considerations. Nature of the matrix including density, wetness and integrity following extraction sometimes prevents slicing in 1 cm increments. All areas chosen for core sampling appeared to be undisturbed and unmixed at the time of sampling. As explained in Section 1.4, the project focused on the uppermost 50 cm at these sites as these layers represent post-industrial deposition in which the majority of anthropogenic deposition of Pb and Hg is contained whilst also representing the sections of peat and soil most vulnerable to the influence of climate change, e.g. drying out degradation during prolonged dry periods and erosion in subsequent wet periods etc.
4.6.1 Flanders Moss (FM)

Flanders Moss is the largest remaining intact area of raised ombrotrophic bog in the UK. Acquired gradually by Scottish Natural Heritage since 1980, the site is now an established nature reserve. The bog is located in central Scotland approximately 10 miles West of Stirling (56.137°N 4.318°W). Three cores were collected from FM in March 2009; one near the edge of the bog to assess minerotrophic tendencies around the site’s perimeter and two from the dome area itself for general analysis and dating.

4.6.2 Easter Deans (ED)

Easter Deans is a bog of more minerotrophic character than the others assessed within this project (Sugden, 1993). Located approximately 2 miles south of Penicuik (55.773°N 3.222°W), the bog lies adjacent to Easter Deans farm. Two cores were
taken from the site in November 2010; one for characterisation and the other for dating analysis.

### 4.6.3 Glentress Forest (GT)
Located approximately 1.5 miles east of Peebles, Glentress Forest (55.661°N, 3.133°W) is a Forestry Commission site popularized by an abundance of mountain biking trails. Soil cores were collected in November 2008 and 2009 from ~300 m above sea level and from Dunslair Heights peak ~600 m above sea level. Dunslair Heights is the location of a rural DEFRA – UK Air Quality Network monitoring station.

### 4.6.4 Auchencorth Moss (AM)
Auchencorth Moss is an ombrotrophic peatland area located approximately 1.5 miles south of Penicuik (55.803°N 3.281°W). The site hosts an air quality monitoring station maintained by the Centre for Ecology and Hydrology (CEH) that forms part of the Department for Environment, Food and Rural Affairs (DEFRA) - UK Automatic Rural and Urban Air Quality Network. The site’s rural location qualifies it as one of the official background stations for the network. Seven cores were taken from the site in April 2011 for a combination of general analysis, dating and spatial variability assessment.
Table 4.1  Sampling, layer and dimension information for cores used for general analysis

<table>
<thead>
<tr>
<th>Corer type</th>
<th>Area (cm x cm)</th>
<th>Depth (cm)</th>
<th>Sampling interval (cm)</th>
<th>FM</th>
<th>AM (Centre1)</th>
<th>AM (Centre2)</th>
<th>AM (North)</th>
<th>AM (East)</th>
<th>AM (South)</th>
<th>AM (West)</th>
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</thead>
<tbody>
<tr>
<td>AM (Centre1)</td>
<td>15 x 10.5</td>
<td>46</td>
<td>1*</td>
<td>AM</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td></td>
</tr>
<tr>
<td>AM (Centre2)</td>
<td>5 x 5</td>
<td>38</td>
<td>2</td>
<td>AM</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
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<tr>
<td>AM (North)</td>
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<tr>
<td>AM (East)</td>
<td>5 x 5</td>
<td>50</td>
<td>2*</td>
<td>AM</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td></td>
</tr>
<tr>
<td>AM (South)</td>
<td>5 x 5</td>
<td>50</td>
<td>2</td>
<td>AM</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td></td>
</tr>
<tr>
<td>AM (West)</td>
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<td>2</td>
<td>AM</td>
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<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td>Cuttle &amp; Malcolm</td>
<td></td>
</tr>
</tbody>
</table>

*Deepest section exceeded regular sampling interval due to changes in core composition with depth.

Table 4.2  Sampling, layer and dimension information for cores used exclusively for \(^{210}\)Pb-dating

<table>
<thead>
<tr>
<th>Corer type</th>
<th>Area (cm x cm)</th>
<th>Depth (cm)</th>
<th>Sampling interval (cm)</th>
<th>FM</th>
<th>AM</th>
</tr>
</thead>
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<td>Monolith</td>
<td>15 x 15</td>
<td>40</td>
<td>2*</td>
<td>AM</td>
<td>Monolith</td>
</tr>
</tbody>
</table>

*Deepest section exceeded regular sampling interval due to changes in core composition with depth.

4.7 Preliminary field-site characterisation and classification

Characterisation data for each site is presented and discussed within this section.

Extraction of peat and soil porewaters was carried out via hand-squeezing or centrifugation (Section 2.3.1). Solid phase moisture content was determined as per Section 2.3.4. Solid phase organic matter content was assessed as outlined in Section 2.3.5. The pH of solid phase material was ascertained via the methodology presented in Section 2.3.8 whereas aqueous phase pH was evaluated as per Section 2.3.9. Solid phase [Mn] and [Fe] profiles were obtained using microwave-assisted acid digestion (Section 2.3.14) followed by ICP-OES analysis (Section 2.3.16). Porewater conductivity was determined using a conductivity probe as discussed in Section
2.3.10. Dissolved organic carbon concentration of porewaters was measured spectrophotometrically under the conditions described in Section 2.3.11.

4.7.1 Characterisation results

4.7.1.1 Flanders Moss (FM)

The FM dome core extended to a depth of 50 cm, the greatest depth allowed by the monolith tin sampling method. It should be noted that the depth of peat in the dome itself may approach ~7 m (SNH, 2011). The upper layers of the core comprised plant material down to approximately 15-16 cm; below this decomposition was evident and the humified peat material was found. Surface vegetation across the bog was dominated by *Sphagnum* species including *S. magellanicum*, *S. tenellum*, *S. papillosum* and *S. cuspidatum* with hummock/hollow micro-topography allowing varied surface environments to support wide ranges of plant life. Other, less prevalent plant species include bog rosemary, bog cranberry and bog cotton.

Initial solid phase characterisation for the FM core is presented in Figure 4.11. Overall, the organic matter content changed little throughout the core. Percentage organic matter was consistently ~99% from the surface until ~17.5 cm, below which it dropped to a minimum of ~93% at 24.5 cm before rising again to ~99% at 30 cm depth. Moisture content showed a little more variation with values ranging from 79-91%. There was an increase from the surface down to a band of high moisture from 8–16 cm with a maximum at 13.5 cm, close to the transition between the living vegetation and the peat material. The moisture content profile suggests that the water
Solid phase pH ranged from 3.0-4.3 with the highest pH being detected 5-6 cm depth. The overarching trend within the pH profile is a gradual decrease of around 0.5 units from the surface to 30 cm depth. Solid phase density decreased from 0.61 g cm\(^{-3}\) in the uppermost layer to 0.25 g cm\(^{-3}\) at 3-4 cm cm. Below this depth, density generally increased down the core to 1.55 g cm\(^{-3}\) at 25-26 cm, below which a rapid decrease was observed to 0.40 cm\(^{-3}\) at 29-30 cm. [Fe] and [Mn] profiles were not determined for the FM core.

The FM aqueous profile data is presented in Figure 4.12. The range of aqueous phase pH was ~3.3-4.5, similar that for he solid phase and again there was a general decrease from the surface to 20-21 cm, below which depth the pH remains constant at ~3.5. Conductivity increased from its lowest value of 42.7 µS m\(^{-1}\) at the surface, to a peak of 203 µS m\(^{-1}\) at 20-21 cm. Below this depth, conductivity values varied somewhat but there was an overall decrease down to a depth of ~40 cm. The DOC profile showed a sharp decrease from the surface concentration of 52 mg l\(^{-1}\) to ~15 mg l\(^{-1}\) with a minimum concentration within this near surface region of ~11 mg l\(^{-1}\). The concentration returned to 51 mg l\(^{-1}\) at 13-14 cm depth before gradually decreasing to a minima of 27 mg l\(^{-1}\) at 22-23 cm. Below this, concentrations again returned to ~50 mg l\(^{-1}\) and remained constant until the base of the core.
Classification of peats and soils

Figure 4.11  FM solid phase profiles showing moisture content, LOI, pH, and density.

Figure 4.12  FM aqueous phase profiles showing pH, conductivity, and DOC concentration.
4.7.1.2 Glentress Forest (GT)

GT comprises primarily Norway and Sitka spruce (*picea abies* and *picea sitchensis*, respectively) species with underlying vegetation consisting of moss carpets, bracken and needle litter deposited from the canopy above. The vegetation layer within the GT core was restricted to the uppermost surface 1-2 cm of the core although partially decayed litter was apparent to a depth of ~5-6 cm (Figure 4.13).

The upper 0-6 cm of the core was a highly organic (>80%) O-horizon consisting of freshly decomposing litter. The overall decrease in organic matter content down the core mimics the trend observed in the solid phase moisture content which decreased from ~81% at the surface to ~49% at 20 cm. This relationship between organic matter content and moisture is not surprising due to the organic matter’s ability to form water-retaining pores. Solid phase pH was ~5.5 at the surface and decreased somewhat towards the base of the core to approximately ~4.5. Soil density increased from ~0.23 g cm\(^{-3}\) in the uppermost 3 cm to ~0.41 g cm\(^{-3}\) at depths of 7-11 cm. Towards the base of the core, density decreased to ~0.19 g cm\(^{-3}\) at 15-19 cm. The solid phase [Fe] and [Mn] profiles in Figure 4.14 showed identical trends below 7 cm with gradual increases in the concentrations of both elements with increasing depth. The [Fe] was low in the upper layers when compared to the deeper mineral rich layers. In contrast, [Mn], greatest in the surface layer at 235 mg kg\(^{-1}\). Below a broad minimum from 3-9 cm depth, the [Mn] increased again towards the bottom of the core.
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Figure 4.13 GT solid phase profiles showing moisture content, LOI, pH and density.

Figure 4.14 GT solid phase profiles showing [Fe] and [Mn].

Classification of peats and soils
The aqueous phase pH profile (Figure 4.15) showed a similar trend to the solid phase pH profile but across a wider scale. The surface layer was close to neutral at pH 6.9 but the pH then decreased rapidly over the top 0-6 cm of the core to ~4.5. Below this layer, aqueous phase pH was similar to that of the solid phase, and values were within the range of ~4.3 to ~4.9. Porewater conductivity showed a surface maximum of 271 µS m\(^{-1}\) and then decreased rapidly with depth to 56 µS m\(^{-1}\) at 7 cm. From 9 cm to the base of the core, conductivity remained constant at ~115 µS m\(^{-1}\). DOC concentrations changed little in relation to depth with the surface layer concentrations of 32-33 mg l\(^{-1}\) decreasing by ~10 mg l\(^{-1}\) over the entire core to ~20 mg l\(^{-1}\) at the core’s base.

### 4.7.1.3 Easter Deans (ED)

Cores taken from ED extended to a depth of 30 cm and both solid and aqueous phases were characterised over the full depth. Surface plant cover consisted of
Sphagnum carpets with dead and decaying tree matter over the entire area. Living vegetation was present to a depth of ~7 cm. The water table was presumed to lie at ~10 cm due to the decrease in moisture content towards the surface of the core from this depth. As with FM, no underlying bedrock or mineral horizons were visible down to the base of the core. The solid phase moisture content, organic percentage, pH and density for the ED core are shown below in Figure 4.16. The [Fe] and [Mn] profiles are presented in Figure 4.17. Aqueous phase characterisation data are displayed in Figure 4.18.

In the solid phase, moisture content, organic matter proportion and pH exhibited little variation throughout the core. Moisture content increased from ~83% at the surface to a peak value of 88% at 10 cm where the water table lay. Below the water table, moisture content slowly decreases to a value of ~80% at 28.5 cm at the base of the core. Percentage organic matter content remained within the range of ~94-97% throughout the entirety of the core. Solid phase pH showed a decrease with depth spanning less than half a unit from 3.4 at the surface to 3.0 at 28-29 cm. Peat density increased from 0.35 g cm\(^{-3}\) at 1.5 cm to 1.06 g cm\(^{-3}\) at 10.5 cm. From 10.5-25.5 cm density fluctuated between 0.7 g cm\(^{-3}\) and 1.06 g cm\(^{-3}\) before decreasing to 0.34 g cm\(^{-3}\) at 28.5 cm depth. The [Fe] and [Mn] profiles showed near-identical trends.
Figure 4.16  ED solid phase profiles showing moisture content, LOI, pH and density.

Figure 4.17  ED solid phase profiles showing [Fe] and [Mn].
The concentrations of both elements increased from 0.19% w/w Fe and 23 mg kg$^{-1}$ Mn at the surface to maximum values of 0.34% w/w Fe and 28 mg kg$^{-1}$ Mn at 7-8 cm. Below these peaks, there was a general decrease in concentration towards the base of the core, with concentrations of 0.23% w/w Fe and 10 mg kg$^{-1}$ Mn at the base of the core.

Aqueous phase pH showed effectively no variation down the core profile. All values are within the range of 3.4-3.7. DOC concentrations were in the range of ~68-75 mg l$^{-1}$ and there was little variation with depth. Porewater conductivity decreased from a surface value of 184 µS m$^{-1}$ to 135 µS m$^{-1}$ at 16-17 cm before increasing at greater depth to 154 µS m$^{-1}$ at 18.5 cm.

![Figure 4.18](image)

**Figure 4.18**  ED aqueous phase profiles showing pH, conductivity, and DOC concentration.

### 4.7.1.4 Auchencorth Moss (AM)

The surface of AM is largely flat but still possesses a *Sphagnum* layer with minor hummock/hollow topography. Other plant species on the site include *Deschampsia*
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*flexuosa*, *Eriophorum vaginatum*, *Juncus effusus*, *Erica tetralix*, *Calluna vulgaris*, and *Vaccinium myrtillus* (CEH, 2011). Auchencorth had the greatest proportion of non-moss surface vegetation of any of the sites sampled in this study. Total monolith core depth was 46 cm and living vegetation material was present to a depth of 15–16 cm with the water table presumed to lie somewhere in the 5–10 cm depth region based upon the decrease and minimum in moisture content that occurred in this depth range (Figure 4.19).

The solid phase characterisation profiles for AM are shown in Figure 4.19 with [Fe] and [Mn] profiles presented in Figure 4.20. Organic matter content decreased gradually from a surface value of ~96% to ~90% at 37.5 cm. The layers below 37-38 cm were clay-rich and a mineral content of ~85% of the total solid matter was evident at 45 cm depth. The moisture content generally followed the organic matter trend with a range of 79-86% in the upper 0-6 cm before increasing to ~90% at 7-8 cm, within the region of apparent water table fluctuation. Below 8 cm, moisture percentage gradually decreased to 81% at 39-40 cm before the presence of the clay layers caused a rapid decrease to 46% at 45 cm depth. Solid phase pH decreased from a surface value of 4.0 to a value of 3.3 at 18-19 cm. The deeper layers of the core showed a small increase with depth to a value of 3.9 at 45 cm. Solid phase density showed an increase from 0.25 g cm\(^{-3}\) at 0.5 cm to ~1.9 g cm\(^{-3}\) at 7.5 cm. From 8-43 cm, density fluctuated from 0.7 g cm\(^{-3}\) to 2.2 g cm\(^{-3}\) with layers of high densities at 11-12 cm, 23-24 cm and 40-41 cm. The [Fe] profile showed an increase from a surface concentration of 0.11 % w/w to a peak of 1.54% w/w at a depth of 11-12 cm. In the deeper layers, [Fe] decreased to ~0.61% w/w at 18.5 cm before.
increasing to the greatest concentration recorded for the core of 2.02% w/w at 35.5 cm. Towards the base of the core at 45 cm, the [Fe] dropped to 1.06% w/w. Manganese shows a very different concentration profile when compared to Fe. The largest [Mn] of 315 mg kg\(^{-1}\) was observed at the surface from where it decreased to ~50 mg kg\(^{-1}\) at 18.5 cm and remained almost constant to the base of the core.

The aqueous phase pH profile showed a narrow range of 4.2-4.6 with lower values being obtained for the 5-22 cm sections. Porewater conductivity increased from a surface value of ~106 µS m\(^{-1}\) to a maximum of ~165 µS m\(^{-1}\) at 5-6 cm. Below this, conductivity dropped to 114 µS m\(^{-1}\) and continued to decrease progressively with depth to a value of 30 µS m\(^{-1}\) at the base of the core. The DOC concentrations were in the range 125-140 mg l\(^{-1}\) across the upper 0-16 cm of the core and decreased to 48 mg l\(^{-1}\) at a depth of 17-18 cm. The DOC concentration increased to 105 mg l\(^{-1}\) at 24-25 cm before a concentration minimum of 43-50 mg l\(^{-1}\) was observed in the region of 26-34 cm. The porewaters from the bottom 10 cm of the core, where the solid phase became increasingly mineral-rich, exhibited some variation in DOC concentration from 50 mg l\(^{-1}\) to 120 mg l\(^{-1}\). Porewater pH, conductivity and DOC concentration profiles are shown in Figure 4.21.
Classification of peats and soils
4.7.2 Discussion

4.7.2.1 Site classification

The sites surveyed in this study correspond broadly to the preliminary classifications assigned in Section 4.6. In the case of FM, the dome structure visible on the bog itself, in combination with the high organic matter content of 98.2 ± 2.6% and acidic pHs in the range 3.0-4.3 are consistent with those of an ombrotrophic bog. Soil at GT has previously been reported to be an acidic brown earth with peaty-podsolic tendencies (Kerr et al., 2009). The data in this study seem consistent with this interpretation due its high mineral content (7-62%) in relation to peat material and acidic pH range (~4.5-5.5). On first assessment, ED appears to possess some minerotrophic character due to its mineral matter content of ~5.2 ± 0.9%, higher than the 1.8 ± 2.6% seen in the dome of FM. High porewater conductivity of 150 ± 15 µS m⁻¹ at ED also indicates some minerotrophic character (APTHQ, 2013). However, ED is highly acidic with mean solid phase pH of 3.13 ± 0.13 and mean aqueous
phase pH of 3.54 ± 0.05. These pH ranges are more in line with an ombrotrophic system since minerotrophic peats tend to possess less acidic pH ranges than their ombrotrophic counterparts (e.g. Sjors, 1959). Thus ED does not fit the typical criteria of either ombrotrophic of minerotrophic classifications and its characteristics lie somewhere in between these two categories. However, this discovery does not adversely influence the project as ED remains more minerotrophic than FM, which is entirely ombrotrophic. AM is located on a slope towards the Black Burn and resulting lateral groundwater transport down the slope apparently causes it to exhibit a greater mineral matter content and higher [Fe] and [Mn] than would be expected for a bog of ombrotrophic character. In terms of porewater parameters, however, the site still remains nearest the ombrotrophic end of the spectrum due to low mean porewater conductivity of 57.5 ± 17.8 µS m⁻¹ in the bulk peat layers, alongside a mean aqueous pH of 4.42 ± 0.20, corresponding to the typical ranges that would be expected of an ombrotrophic bog (APTHQ, 2013). These findings are consistent with literature assertions that AM is an ombrotrophic bog (Dinsmore et al., 2009, Drewer et al., 2010).

4.7.2.2 Comparison between sites

A tabulated comparison of the key features of the profiles in Figures 4.11-4.21 is presented below in Table 4.3 and Table 4.4. The three peat systems all possess solid phase and aqueous phase pHs ~3-5 and broadly show decreasing pH values with increasing depth. A greater difference in pH values between ombrotrophic and minerotrophic peats was expected although the similarities in structure, composition and surface Sphagnum-dominated vegetation at each peatland may account for the
similarities in pH ranges. The climatic conditions at each site will also be broadly similar due to the sites’ geographic proximity, causing the pH of rain incident upon the peats to impart similar influence upon their pH profiles. There were no obviously abnormal factors influencing the pH of these systems leaving acidic rain input and cation exchange processes as the primary control factors (Clymo, 1984) alongside the partial influence of litter and vegetation decomposition by-products upon the deeper peats/soils. The less acidic pH range of GT of 4.25-6.9 is characteristic of an upland forest soil where the basicity of mineral matter will counteract the acidic organic matter and the influences of acidic rainfall to a greater degree than mineral deficient peatlands (e.g. Zoltan, 2010).

GT possesses a considerably higher proportion of mineral matter in the bulk material, 39.6 ± 20.9%, than FM, ED or AM which possess mean mineral contents of 1.8 ± 2.6%, 5.2 ± 0.9% and 10.3 ± 5.2%, respectively. These percentages are in reasonable agreement with values reported by Sugden (1993) for FM (~3%) and ED (~9%). The ranges of organic matter percentages were also similar across each peatland site with the only abnormality being the low minimum value of 15% at AM, accounted for by the clay-rich layer at the base of the core. The three peatlands had similar mean moisture contents in their bulk peat, excluding clay layers, of 83-85% with the GT soil exhibiting on average ~20% less overall water than the peatlands due to lower retention capacity resulting from the forest’s lower organic matter content.
Table 4.3  Summary of key solid phase profile features from Flanders Moss (FM), Glentress Forest (GT), Easter Deans (ED) and Auchencorth Moss (AM)

<table>
<thead>
<tr>
<th></th>
<th>Mean organic content (%)</th>
<th>Organic content range (%)</th>
<th>Mean moisture content (%)</th>
<th>Moisture content range (%)</th>
<th>Solid pH range</th>
<th>Depth of soil pH maximum (cm)</th>
<th>Depth of soil pH minimum (cm)</th>
<th>[Fe] range (%)</th>
<th>[Fe] maximum depth (cm)</th>
<th>[Fe] minimum depth (cm)</th>
<th>Depth of [Mn] range (mg kg⁻¹)</th>
<th>[Mn] maximum depth (cm)</th>
<th>[Mn] minimum depth (cm)</th>
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</thead>
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<td>FM</td>
<td>98.2±2.6</td>
<td>93-99</td>
<td>84.3±3.5</td>
<td>79-91</td>
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</tr>
<tr>
<td>GT</td>
<td>60.4±20.9</td>
<td>38-93</td>
<td>64.6±10.8</td>
<td>48-93</td>
<td>4.3-5.5</td>
<td>1</td>
<td>11</td>
<td>0.16-1.60</td>
<td>18.5</td>
<td>1</td>
<td>50-234</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>ED</td>
<td>94.8±0.9</td>
<td>93-97</td>
<td>83.3±2.6</td>
<td>80-88</td>
<td>3.0-3.4</td>
<td>1.5</td>
<td>19.5</td>
<td>0.19-0.34</td>
<td>7.5</td>
<td>1.5</td>
<td>9.7-28.2</td>
<td>7.5</td>
<td>28.5</td>
</tr>
<tr>
<td>AM</td>
<td>89.7±5.2</td>
<td>15-96</td>
<td>84.8±7.6</td>
<td>46-91</td>
<td>3.3-4.0</td>
<td>0.5</td>
<td>18.5</td>
<td>0.11-2.02</td>
<td>35.5</td>
<td>0.5</td>
<td>42-315</td>
<td>0.5</td>
<td>27.5</td>
</tr>
</tbody>
</table>

Table 4.4  Summary of key aqueous phase profile features from Flanders Moss (FM), Glentress Forest (GT), Easter Deans (ED) and Auchencorth Moss (AM)

<table>
<thead>
<tr>
<th></th>
<th>DOC conc. range (mg l⁻¹)</th>
<th>DOC conc. maximum depth(cm)</th>
<th>DOC conc. minimum depth(cm)</th>
<th>Conductivity range (µS m⁻¹)</th>
<th>Conductivity maximum depth (cm)</th>
<th>Conductivity minimum depth (cm)</th>
<th>Porewater pH range</th>
<th>Porewater pH maximum depth(cm)</th>
<th>Porewater pH minimum depth(cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM</td>
<td>11-57</td>
<td>41.5</td>
<td>3.5</td>
<td>43-203</td>
<td>20.5</td>
<td>3.5</td>
<td>3.3-4.5</td>
<td>3.5</td>
<td>19.5</td>
</tr>
<tr>
<td>GT</td>
<td>18-33</td>
<td>3</td>
<td>13</td>
<td>56-271</td>
<td>1</td>
<td>7</td>
<td>4.3-6.9</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>ED</td>
<td>68-75</td>
<td>13.5</td>
<td>10.5</td>
<td>135-184</td>
<td>4.5</td>
<td>16.5</td>
<td>3.5-3.6</td>
<td>13.5</td>
<td>22.5</td>
</tr>
<tr>
<td>AM</td>
<td>43-150</td>
<td>8.5</td>
<td>28.5</td>
<td>30-167</td>
<td>4.5</td>
<td>43</td>
<td>4.1-4.7</td>
<td>13.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>

Classification of peats and soils  150
Across all field sites, the [Fe] minimum occurred within the surface layers of the cores that correspond to layers of living plant matter. The [Fe] in the GT core was in line with the expectation that it would possess high [Fe]; here concentrations of ~1.0-1.6% w/w were found for the most mineral-rich 10 cm of the core. Concentrations of 0.2-0.5% w/w Fe within the organic-rich upper 0-5 cm of GT are comparable to the [Fe] at the equivalent depths of both ED and AM. The AM solid phase [Fe] peak of >2.0% w/w is greater than expected as it is higher in magnitude even than the GT [Fe] peak of ~1.6% w/w, and several times higher in concentration than the ED core maximum of ~0.35% w/w. The high [Fe] at AM is attributable to the mineral-rich layer visible at the base of the core feeding Fe into the upper peat layers. Without accompanying porewater [Fe], it is not possible to unambiguously identify the redox cycling zones within these sites. However, the solid phase ED [Fe] peak at ~8 cm, near the water table, is likely the Fe(II)$\rightarrow$Fe(III) oxidation zone. AM exhibits a similar solid phase peak at ~11 cm which may also be attributed to Fe oxidation-reduction processes. GT shows a poorly pronounced [Fe] peak at ~7 cm in the solid phase which may correspond to a region of Fe redox activity although no clear indication of an iron pan at this depth was observed.

The [Mn] profiles were similar across all sites with surface or near-surface maximum concentrations and a subsequent decrease in [Mn] with depth. GT does not entirely match this trend and exhibits a [Mn] peak of ~210 mg kg$^{-1}$ at the core’s base, close in value to the surface maximum of ~230 mg kg$^{-1}$. Whether this peak corresponds to the presence of Mn-bearing minerals, Mn accumulation by plant material or a region of precipitation of solid Mn out of the aqueous phase cannot be completely resolved.
AM exhibits a [Mn] peak of ~315 mg kg\(^{-1}\), higher than the peak concentration in GT. As discussed in the case of Fe, the high [Mn] at AM would not typically be expected in an ombrotrophic bog and may be due to the clay layers underlying the surface peats at this site.

GT showed the lowest overall DOC concentrations across the sites of 18-33 mg l\(^{-1}\) compared to the 11-57 mg l\(^{-1}\) at FM, 68-75 mg l\(^{-1}\) at ED and 43-150 mg l\(^{-1}\) at AM; this is consistent with GT being the site with the least overall solid phase organic matter content. GT also showed the highest porewater conductivity of the four sites with a peak value of 271 µS m\(^{-1}\), likely a result of its relatively high inorganic content (~40%) imparting high ion concentrations to solution. Conversely, AM possesses the highest porewater DOC with peaks of 150 mg l\(^{-1}\), but the lowest overall conductivity with a range of 30-167 µS m\(^{-1}\). The low conductivity values could be considered to conflict with the high [Mn] and [Fe] present within the site’s solid phase profile and its >10% apparent mineral content. These abnormalities could be explained if the inorganic species present were in low charge-high molecular weight forms and therefore not subject to dissolution and unable to contribute to conductivity, although there is insufficient evidence to confirm this hypothesis. The high concentrations of DOC of ~145 mg l\(^{-1}\) within the upper layers of AM correspond to the zone of living and freshly decaying plant matter imparting organic matter to solution. FM and ED both show similar levels of DOC and conductivity with ranges of 40–200 µS m\(^{-1}\), ~60 mg l\(^{-1}\) and 130–180 µS m\(^{-1}\) and ~50 mg l\(^{-1}\), respectively, attributable to the similarities in overlying plant matter and concentrations of mineral matter at each site.
Classification of peats and soils

4.8 Chapter conclusions

The four sites investigated in this study were characterised and classified. The domed structure, high organic matter content (mean: 98%) and acidic pH range (3.1-4.5) of Flanders Moss (FM) indicates that it is ombrotrophic in character. Soil from Glentress Forest (GT) was found to conform to a peaty acidic brown earth with podsolic tendencies due to its overlying O-horizon, high mineral matter content (mean: 40%) and mildly acidic-acidic pH range (4.3-6.9). Easter Deans (ED) peat bog lies between an ombrotrophic bog and a minerotrophic bog in character as it demonstrated mineral content (mean: 5%) and porewater conductivity (135-184 µS m⁻¹) consistent with a minerotrophic bog but an acidic pH range more typical of an ombrotrophic system (3.0-3.6). Auchencorth Moss (AM) exhibited characteristics typically associated with an ombrotrophic bog but showed higher than expected [Fe] and [Mn] (0.11-2.02% w/w Fe; 42-315 mg kg⁻¹ Mn) more comparable to the forest soil at GT (0.16-1.60% w/w Fe; 50-234 mg kg⁻¹ Mn) than the ED peatland (0.19-0.34% w/w Fe; 9.7-28.2 mg kg⁻¹ Mn). These high metal concentrations at AM were attributed to the influence of groundwater flow due to the sloped geography of the site.

Flanders Moss, ED and AM peat bogs show general similarities in the shapes of their pH, moisture and organic matter profiles due to the overarching similarities in their Sphagnum-dominated surface vegetation and the acrotelm/catotelm structure such vegetation imparts. In the GT forest environment characterisation profiles showed more pronounced features and greater degrees of variation in relation to depth. Near-
surface decreases in moisture content suggest that the water table rests at a depth of ~10 cm at FM, 10-12 cm at GT, ~10 cm at ED and ~5-10 cm at AM.
Chapter 5 Lead

5.1 Introduction

Lead, Pb, is a group 14 metal element with atomic number 82. It has a melting point of 327.5°C, a boiling point of 1740°C and a density of 11.3–11.4 g cm\(^{-3}\) (e.g. Emsley, 2003; Kabata-Pendias and Mukherjee, 2007). The standard atomic weight of Pb is 207.2 and its average atomic radius is 181 pm. The metal in its pure form is a dull grey or blue-tinted malleable solid although it is not typically found in the environment in this state. Lead’s malleability, high density, ease of extraction from its ores, bulk inertness and straightforward purification make it highly versatile. The average concentration of Pb within the Earth’s crust is estimated to be within the range of 10–16 mg kg\(^{-1}\) although crustal distribution is uneven. Lead in the environment is discussed in more detail in Section 5.3.

5.2 Toxicity and risk to human health

Lead is a non-essential element with no known biological function. With respect to human health, its toxicity is well-documented with harmful effects having been acknowledged since around the second century B.C. (Hernberg, 2000). LD50 values, the median lethal dose (50% lethality), are unconfirmed for humans although 70 mg kg\(^{-1}\) body weight has been reported for rats (Thornton et al., 2001). At sub-lethal doses, long-term accumulation of Pb in the human body leads to numerous detrimental effects. Pb affects humans as a chronic, cumulative poison and cases of acute poisoning are uncommon. The presence of Pb in the human body disrupts the
action of the ALA-dehydrase enzyme and prevents the subsequent formation of prophobilinogen, leading to haemoglobin formation failure. Additional effects include inhibition of mental functions, nervous system damage, increased blood pressure, kidney damage and eventual death (WHO, 1995). The human body cannot distinguish between Pb and Ca, resulting in transfer and storage of Pb to bones and teeth (Rabinowitz et al., 1991; 1993). Under stress or abnormal long-term physical duress, this Pb can be remobilised into the blood stream causing further damage (Thornton et al., 2001).

Inhalation of airborne Pb, ingestion or inhalation of Pb-bearing dust (Mielke and Reagan, 1998), or ingestion of food or water contaminated with Pb are the predominant routes of human exposure to Pb (Figure 5.1). Human bioavailability of Pb changes depending on intake route. Airborne and inhaled Pb species have an estimated uptake rate of ~50% whereas ingested Pb is mainly excreted by the body with a retention rate around 5% (Goyer, 1996). A typical adult human living in a large USA or western European city is estimated to ingest 200–300 µg Pb day\(^{-1}\) with around 25 µg Pb day\(^{-1}\) stored in bones and 200 µg Pb day\(^{-1}\) excreted by the body (De, 2003).

Widespread dissemination of anthropogenic Pb coupled with the continued trend of population concentration within urban environments led to increased daily human intake of Pb in the decades following industrialisation.
Figure 5.1  
Lead exposure pathways from sources and reservoirs to humans (Paustenbach and Galbraith, 2006).

Analysis of modern day and pre-industrial human teeth demonstrates an increase in tooth [Pb] of 1-2 orders of magnitude (Grandjean and Jørgensen, 1989). Research has focused on the links between low-level Pb exposure and the behavioural and intellectual development of children. Greater concentrations of Pb within bones, teeth (Needleman et al., 1979) and blood (McMichael et al., 1988) correlated with decreased IQ, lower educational attainment and mental focus (Lanphear et al., 2003). Figure 5.2 demonstrates the decreasing ability scores of 4-year-olds as their blood [Pb] increased.
Since the mid 1980s, blood [Pb] has generally decreased. From 1986 to 2006, the mean blood [Pb] in adult women in the EU declined from ~65 µg l\(^{-1}\) to ~25 µg l\(^{-1}\) (Smolders et al., 2010). Similarly, [Pb] in the blood of children in the US and the EU has decreased from a peak concentration of 80 µg l\(^{-1}\) in 1982 (Smolders et al., 2010) to a mean of 10 µg l\(^{-1}\) in 2006 (Birdsall et al., 2010). Despite these decreases in blood Pb levels, research continues to focus on areas where Pb contamination still poses a risk to human health, such as urban environments in the US (e.g. Mielke et al., 2011; Zahran et al., 2013), China (e.g. Luo et al., 2012) and India (e.g. Chabukdhara and Nema, 2013). In some urban locations, Pb soil concentrations continue to exceed the DEFRA concentration safety threshold of 450 mg kg\(^{-1}\) (DEFRA, 2002) for residential land.
5.3 Speciation, geochemical behaviour, and environmental forms of Pb

Speciation is defined by IUPAC as ‘the atomic or molecular form of an analyte’ and is an assessment of the chemical form of an element (Hill, 1997). The term is wide-ranging and encompasses molecular structures, steric conformations, ligands, isotopes and electronic configurations such as oxidation states. While total concentration of a given contaminant is undoubtedly important, the form(s) that the contaminant takes is far more indicative of its environmental effect. Differences in speciation can alter an element’s toxicity, solubility, bioavailability, environmental mobility and its use as an environmental tracer. The specific form of Pb present within a soil system is dependent upon factors including ambient pH, the system’s redox chemistry, the available counter-ions in the system and to some degree, the origin of the Pb itself. Common Pb compounds occurring in soils are Pb(OH)$_2$, PbCO$_3$, PbS, PbO and Pb$_3$(PO$_4$)$_2$ (Fergusson, 1990). Sections 5.3.1 and 5.3.2 will discuss the isotopes, chemical compounds and geochemical behaviour of Pb.

5.3.1 Pb Isotopes

5.3.1.1 Stable Isotopes

There are four naturally occurring stable Pb isotopes: $^{204}$Pb, $^{206}$Pb, $^{207}$Pb and $^{208}$Pb. The $^{208}$Pb isotope is the most naturally abundant (51-56%) with $^{206}$Pb and $^{207}$Pb comprising 20–28% and 17–24%, respectively. $^{204}$Pb, although stable, comprises <1% of the world’s Pb pool (Komarek et al., 2008). The three highest abundant isotopes are each daughter products of a radiogenic decay series (Figure 5.3): $^{238}$U →
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

$^{206}\text{Pb}, \, ^{235}\text{U} \rightarrow ^{207}\text{Pb}$ and $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$ with the parent nuclides possessing half-lives of $4.468 \times 10^9$ years, $0.70381 \times 10^9$ years and $14.0100 \times 10^9$ years, respectively (Bourdon et al., 2003).

Over time, the environmental abundance of $^{207}\text{Pb}$ has not altered greatly as the short half-life of $^{235}\text{U}$ in comparison to $^{238}\text{U}$ and $^{232}\text{Th}$ has led to the majority of the Earth’s $^{235}\text{U}$ having already undergone radioactive decay. The Earth’s $^{238}\text{U}$ has not undergone decay to such an extent and so over time, the proportion of $^{206}\text{Pb}$ can only increase relative to $^{207}\text{Pb}$. Older Pb ore deposits (1000 million years) were formed before the decay of U or Th could influence their composition and are generally characterised by a lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ($^{206}\text{Pb}/^{207}\text{Pb}: \leq 1.10$) than comparatively younger radiogenic formations ($^{206}\text{Pb}/^{207}\text{Pb}: \geq 1.18$) that experienced a greater influence of the decay of U and Th into Pb (e.g. Maring et al., 1987; Bacon, 2002). As a result, the stable Pb isotope ratios in different geological bodies can vary dramatically from locale to locale.
5.3.1.2 Unstable isotopes and $^{210}\text{Pb}$

There are over twenty unstable radioisotopes of Pb and the majority are short-lived decay intermediates with half lives in the region of minutes and seconds and thus of relatively little interest to this project. The most important radioisotope in the context of this research is $^{210}\text{Pb}$ which is used as a tool in the radionuclide-dating process (Section 2.3.18). $^{210}\text{Pb}$ is a radioactive decay intermediate in the $^{238}\text{U}$ decay chain with a half-life of 22.3 years. Decay of $^{226}\text{Ra}$ releases a continuous supply of $^{222}\text{Rn}$ gas to the atmosphere. The decay of $^{222}\text{Rn} \rightarrow ^{210}\text{Pb}$ ($t_{1/2} = 3.831$ days) and eventual fallout either via wet or dry deposition causes a constant flux of $^{210}\text{Pb}$ to the Earth’s surface. The deposited $^{210}\text{Pb}$ is described as unsupported. Where soil or peat surfaces
are undisturbed and the nuclide is immobile (as discussed in Section 5.3.3), concentration of unsupported $^{210}\text{Pb}$ decreases exponentially with depth. Supported $^{210}\text{Pb}$, where present, arises from the $^{238}\text{U}$ decay series and is produced continuously from the decay of $^{226}\text{Ra} \rightarrow \rightarrow \rightarrow \rightarrow ^{210}\text{Pb}$. Since these radionuclides are at secular equilibrium, $^{226}\text{Ra}$ can be used to determine the activity of supported $^{210}\text{Pb}$ which can then be subtracted from total $^{210}\text{Pb}$. The two models used to calculate layer dates from $^{210}\text{Pb}$ activity are discussed in more detail in Section 5.3.5.2.

5.3.2 Pb in the environment

Small amounts of Pb are present in all rocks with average concentrations of around 25 mg kg$^{-1}$ (Lovering, 1976). Lead ores generally exist in conjunction with other metals and mining operations often extract Zn, Cu, Ag or Au alongside Pb. Naturally occurring ores of Pb, enriched relative to crustal abundances, exist predominantly as sulphides, alongside a number of less common oxide species. Galena ($\text{PbS}$) is the most abundant Pb ore comprising approximately 55-85% Pb dependent on impurities and region of origin (Baba et al., 2011; Peng et al., 2002). The predominance of PbS is typical of the reactivity of Pb$^{II}$ as Lewis acid-base theory dictates a preference for soft bases such as S$^{2-}$. Cerrusite ($\text{PbCO}_3$) and anglesite ($\text{PbSO}_4$) are weathering products that occur where galena has been oxidised. Cerrusite and anglesite, in addition to galena, have been found in sufficient abundance to have been subject to human mining activities. Less common ores include minium ($\text{Pb}_3\text{O}_4$), pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) and mimetesite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$), phosgenite ($((\text{PbCl}_2)\text{CO}_3$), linarite ($\text{PbCuSO}_4(\text{OH})_2$) and crocoite ($\text{PbCrO}_4$) (Schumann, 1993). Solid phase metallic Pb$^0$
Lead is found in low concentrations within the environment and is considered stable under standard temperature and pressure conditions once its surface layer has formed a protective coating of oxides, carbonates and hydroxycarbonates. Metallic Pb$^0$ is rapidly oxidised to Pb$^{II}$ in the presence of oxygen from where it can undergo a number of other chemical reactions (e.g. Powell et al., 2009) such as conversion to hydroxides or carbonates (Equation 5.1–5.2).

\[
Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2 + 2H^+ \quad \text{Equation 5.1}
\]

\[
Pb^{2+} + H_2CO_3 \rightleftharpoons PbCO_3 + 2H^+ \quad \text{Equation 5.2}
\]

Naturally occurring Pb exists predominantly in the +2 and +4 oxidation states. The largest proportion of environmental Pb exists as the Pb$^{II}$ state which typically forms energetically favourable complexes due to a 6s outer electron shell configuration with two electron lone pairs available for bonding. Tetravalent, Pb$^{IV}$ is also found in the environment and occurs most commonly in inorganic complexes (Manceau et al., 1996). Lead valencies as high as +XII have been recorded, although these species are not encountered in significant quantities outside of forced laboratory conditions.

The solubility of Pb varies considerably dependent upon its oxidation state and coordinated species. For example, Pb$^0$ is insoluble whereas Pb$^{2+}$ is soluble. At pH values lower than ~7.7, Pb$^{2+}$ becomes hydrated by a sphere of water molecules and is present as the free hydrated ion. Where the solution pH exceeds this threshold, Pb$^{2+}$ undergoes hydrolysis and cleaves the water molecule forming a proton and Pb(OH)$^+$, which is itself soluble (Essington, 2005). In the aqueous environment, the speciation...
of Pb is driven by both pH and the redox conditions present within a system. Hydroxides, carbonates, sulphates and chlorides are commonly encountered. The major aqueous species are summarised in Table 5.1 and an example of the pH dependence of Pb speciation within a typical freshwater environment is shown in Figure 5.4. Although these species are soluble, within a soil system, the solubility of Pb is limited due to its strong associations with both organic and mineral surfaces. Phosphate and carbonate minerals are key solubility controlling solid phase species due to their direct or indirect effects on Pb (e.g Badaway et al., 2002). Surface interactions between Pb and mineral species will directly control the amount of Pb in solution whereas the mineral phases may also indirectly influence the pH of an environmental system itself (Papadopoulos and Rowell, 1988). Lead’s solubility is greatly influenced by pH. Higher pH values reduce Pb solubility by encouraging sorption to solid phase matter (Harter, 1983; Rooney et al., 2007). Martinez and Motto (2000) demonstrated that Pb undergoes its most rapid rate of change in solubility across the pH range 5.0–6.0 in a range of natural soil systems.

Table 5.1 Predominant aqueous Pb species at various pH and redox conditions (Sanmanee, 2002)

<table>
<thead>
<tr>
<th>Lead</th>
<th>pH = 4</th>
<th>pH = 7</th>
<th>pH = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Oxidizing</td>
<td>Reducing</td>
<td>Oxidizing</td>
</tr>
<tr>
<td>PbSO₄²⁻</td>
<td>PbOH⁻</td>
<td>PbOH⁻</td>
<td>PbCO₃</td>
</tr>
<tr>
<td>PbHCO₃⁻</td>
<td>PbHCO₃⁻</td>
<td>Pb(CO₃)²⁻</td>
<td>Pb(CO₃)²⁻</td>
</tr>
<tr>
<td>PbCl⁻(sw)</td>
<td></td>
<td></td>
<td>PbCl⁻(sw)</td>
</tr>
<tr>
<td>PbSO₄²⁻(sw)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(sw) indicates seawater
5.3.3 Pb binding to solid environmental media

Within terrestrial systems, Pb is generally considered to be immobile (e.g. Shotyk, 1997; Farmer et al., 1997a; Shotyk et al., 2002; 2004, Weiss et al., 1999a; 1999b; MacKenzie et al., 1997a; 1998b) as it binds stably to both solid phase minerals and organic matter (e.g. Logan et al., 1997). Even in environments where loss, or mobility of Pb has been reported (e.g. Urban et al., 1990; Biester et al., 2012), the considerable majority of Pb is still demonstrably retained with the peat system.

The sorption mechanisms of Pb onto both clay and oxide-rich mineral structures are complicated by the large variety of possible mineral structures. Oxygen-containing functionalities are usually implicated as the primary point of interaction where Pb is bound directly to solid mineral surface functionalities. X-ray absorption spectroscopy (XAS) studies have shown Pb adsorbing via a bidentate inner-sphere mechanism on
Al₂O₃ structures (Strawn et al., 1998) and via both inner- and outer-sphere mechanisms dependent on the specific surface site involved (Bargar et al., 1996). Alternative binding mechanisms are possible and ternary interactions between Pb and mineral surfaces through Cl-Fe bridges have also been reported (Bargar et al., 1998). The prevalent mechanism appears to be controlled by ionic strength and pH, with low pH ranges encouraging ion exchange processes and low ionic strengths encouraging greater Pb adsorption onto mineral surfaces from solution (Strawn and Sparks, 1999; Matocha et al., 2001).

The binding of Pb ions to soil organic matter has been studied extensively with specific focus on interactions with humic material. As discussed previously in Chapter 1, general consensus is that Pb²⁺ binds via ionic or electrostatic interaction with exposed anionic functional groups within the humic macrostructure. Deprotonated acidic OH (carboxyl and phenolic) groups are most often implicated. Davies et al. (1997) and Xia et al. (1997) indicated that metal-HA association was primarily through multi-dentate interactions with carboxyl and phenolic groups dominating, giving rise to idealised interactions such as Figure 5.5. More recent spectroscopic studies by Orsetti et al., (2013) support this assertion. Monodentate interactions are predicted by some models, but always representing a less favourable interaction than the multidentate alternative (Tipping and Hurley, 1992; Orsetti et al., 2013). Amino, sulfhydryl and quinine groups are also implicated as potential binding sites although their concentration within humic material is often considerably lower than that of the carboxylic and phenolic functionality (Perdue et al., 1984; Benedetti et al., 1995). As a result, many predictive models of metal-HA binding often
consider only carboxylic and phenolic humic functionality as relevant (Tipping and Hurley, 1992).

Concentration of Pb\(^{2+}\) in the aqueous phase and pH are considered controlling factors in determining preference for and uptake of Pb\(^{2+}\) by specific binding sites. For the majority of metal ions, higher ambient pH within the range 4-8 reportedly increases the importance of phenolic binding sites although carboxylic functionality always appears to dominate (Benedetti et al, 1995). Low concentrations of metal ions also appear to promote phenolic binding which may indicate uptake by more thermodynamically favourable, phenolic stabilised binding sites in preference to purely carboxyl alternatives.

### 5.3.4 Anthropogenic Pb

Natural inputs of Pb into soil and water systems from weathering of Pb-containing parent geologic sources or atmospheric deposition following natural fires or volcanic activity are negligible in comparison to worldwide inputs of anthropogenic sourced Pb. Lead’s malleability, high density, ease of extraction from its ores, bulk inertness and the low technological requirement for its purification have led to its widespread...
practical adoption by civilisations past and present. As a result, the primary sources of Pb to the atmosphere, soil and water systems across the past two millennia are predominately anthropogenic.

5.3.4.1 Historical production of Pb (Ancient–1920)

Human adoption of Pb in day-to-day activities is estimated to have begun in approximately 4000 BC (Settle and Patterson, 1980; Hong et al., 1994) but did not become prevalent until ~3000 BC upon the discovery of cupellation and the smelting of Pb and Ag (Nriagu, 1978). During the Copper (5000-3000 BC), Bronze (3000-1200 BC) and Iron ages (1200 BC-200 AD), the use of Pb steadily increased to ~1-10 kt yr$^{-1}$ and was adopted by Greek civilisation for use in coinage. The Romans appear to have been the first truly large-scale users of Pb. It is estimated that Romans extracted in the region of 60 kt Pb yr$^{-1}$ for around 400 years (Herberg, 2000) with production peaking at 80 kt yr$^{-1}$. Archaeological studies have unearthed Roman cooking utensils, pottery glazes, and piping incorporating the metal. During the fall of the Roman Empire, worldwide production of Pb experienced a sharp decline encompassing medieval times until ~1000 AD where Europe experienced resurgence in Pb and Au mining. Discovery of the Americas and subsequent colonisation by the Spanish around 1500 AD acted to further increase global Pb production but not sufficiently to match peak Roman output levels. The greatest rate of increase in worldwide Pb production occurred during the boom of world industry, metallurgy and technology that occurred during the Industrial Revolution. Britain and central Europe were the first adopters of widespread industrial scaling of material extraction,
processing and commercial manufacturing from around 1750 with the majority of Europe and the USA utilising industrial scale metallurgical processes by 1850. Global Pb production surpassed peak Roman production in the late 1700s (Nriagu, 1978). Around 1800, ore mining, extraction, smelting and refining, and adoption of large scale fossil fuel combustion became the primary sources of anthropogenic Pb. Historical Pb production is outlined in Figure 5.6.

### 5.3.4.2 Modern Anthropogenic Pb (1920–Present)

Until the early 1920s, increases in worldwide Pb production were driven primarily by increasing demand for large scale industry and the increases in ore extraction, smelting and fossil fuel combustion that such an upscaling required. In 1923, the DuPont Corporation began marketing automobile petroleum containing the tetraethyl-Pb anti-knock additive which dramatically improved fuel performance. Worldwide proliferation and the effective monopoly of Pb-additive petrol resulted in dramatic increases in demand for Pb, production of petrol Pb-additives and subsequent release of Pb to the atmosphere. Nriagu and Pacyna (1988) published detailed estimates of Pb atmospheric emissions for the year 1983 where totals were in the region of 289–376 kt yr\(^{-1}\) with 4–21.5 kt yr\(^{-1}\) from fossil fuel combustion, 31–84 kt yr\(^{-1}\) from mining and metallurgical processes, 1.5–3.1 kt yr\(^{-1}\) from waste streams and 248 kt yr\(^{-1}\) due to combustion of leaded petrol; the latter accounting for around ~75\% of the emission total. Unleaded fuel was introduced in the US and in Japan in the 1970s, with the US banning leaded fuel in 1986 and much of Europe following in 2000 (UNEP, 2009).
Figure 5.6  History of Pb production (Nriagu, 1978).
Lead additives were not banned, however, in the aviation fuel sector with approximately 0.5 kt of Pb contained within fuel additives allocated to US airports released to the atmosphere in 2002 alone (USEPA, 2008). Despite bans on leaded petroleum, the use of Pb remains widespread with modern application in radiation shielding, noise attenuation, Pb-oxide batteries, PVC/polymer additives, electrical cable sheathing and alloying. The leading commercial extractors of lead ore are China, Australia, the United States of America, Peru and Mexico, accounting collectively for 78.5% of total worldwide production during 2009 and 2010 (USGS, 2012). Developed countries including the USA, Canada, and the UK have all seen primary domestic Pb production decrease year on year since the early 2000s. This decrease, however, has not offset the rising demand of developing countries who continue to drive the increases in worldwide Pb production from 3,600 kt yr\(^{-1}\) in 2006 to 4,200 kt yr\(^{-1}\) in 2010 (Brown et al., 2012., USGS 2012). Production trends from 2006-2010 are shown in Table 5.2.

With a focus on the UK specifically, Pb usage and emissions have decreased drastically over the past few decades. In the 1970s to mid 1980s, emissions were 7–9.5 kt yr\(^{-1}\) whilst by 1986-1990, they had almost halved to 3.5–4 kt yr\(^{-1}\) (Dore et al, 2008). This was achieved through legislation forcing reductions in the amount of Pb in petrol and the introduction of unleaded petrol in 1986. From the 1970s until the mid 1990s, road traffic consistently contributed 70–89% of the UK’s atmospheric Pb emissions with an immediate decrease to <5% contribution from petroleum following the banning of leaded petrol in 2000 (Figure 5.7). As of 2006, the UK’s
total atmospheric Pb emissions had decreased to around ~90 tonnes yr\(^{-1}\); <1% of the world’s combined emissions in that year (Dore et al., 2008; MSC-E, 2012).

Table 5.2 Worldwide Pb production 2006–2010 for selected countries (in tonnes).
Adapted from USGS (2012)

<table>
<thead>
<tr>
<th>Country</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>15,764</td>
<td>24,574</td>
<td>24,600</td>
<td>24,800</td>
<td>25,000</td>
</tr>
<tr>
<td>Canada</td>
<td>83,096</td>
<td>75,135</td>
<td>98,974</td>
<td>68,761</td>
<td>64,859</td>
</tr>
<tr>
<td>United States</td>
<td>429,000</td>
<td>444,000</td>
<td>410,000</td>
<td>406,000</td>
<td>369,000</td>
</tr>
<tr>
<td>China</td>
<td>1,330,000</td>
<td>1,410,000</td>
<td>1,500,000</td>
<td>1,600,000</td>
<td>1,850,000</td>
</tr>
<tr>
<td>Mexico</td>
<td>120,450</td>
<td>120,000</td>
<td>100,725</td>
<td>143,838</td>
<td>158,206</td>
</tr>
<tr>
<td>UK</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>World Total</td>
<td>3,360,000</td>
<td>3,720,000</td>
<td>3,880,000</td>
<td>3,900,000</td>
<td>4,140,000</td>
</tr>
</tbody>
</table>

Figure 5.7 Breakdown of UK Pb emissions 1970–2006 (Dore et al., 2008).
5.3.5 Applications of Pb isotopes

5.3.5.1 Isotopic ratio as a tracer of Pb origin

Lead isotopes have been widely employed as indicators of the source of Pb within the environment. In particular, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio has been adopted towards these ends (e.g. Bacon and Bain, 1995). The geogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in ore bodies are region-dependent. As discussed previously in Section 5.3.1.1, ore bodies of different age and location result in varying $^{206}\text{Pb}/^{207}\text{Pb}$ signatures depending on the amount of $^{238}\text{U}$, $^{235}\text{U}$, and $^{232}\text{Th}$ associated with the Pb over geological timescales, in addition to the length of time that the Pb and its radioactive parent nuclides were together in the Earth’s mantle before that Pb became segregated into a body of ore (Maring et al., 1987). Regional variation in geogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios is notable even within countries; for example, Shotyk and Weiss (1998) record Swedish geogenic $^{206}\text{Pb}/^{207}\text{Pb}$ signatures of ~1.22 whereas values of >1.30 have been reported elsewhere in Sweden (Klaminder et al., 2005, 2006, 2008).

Due to the global import and export of goods and raw materials, the isotopic signature of Pb emissions from countries are increasingly representative of a mixture of native and non-native Pb sources rather than their local ore bodies alone. Both native and imported ores are commonly used in metallurgical extraction processes, coal and other Pb-bearing fuels are sourced both domestically and abroad, and secondary Pb emissions such as those from waste incineration encompass goods and waste material from internationally sourced products. Between the introduction of alkyl-Pb petroleum additives in 1923 and their phasing out towards 2000,
combustion of automobile petrol also contributed significantly to the $^{206}\text{Pb} / ^{207}\text{Pb}$ ratio of atmospheric Pb (e.g. Sugden et al., 1993). The combination of Pb sources to the atmosphere leads to a composite $^{206}\text{Pb} / ^{207}\text{Pb}$ signature for a particular location. For example, in the late 1980s, Africa’s atmospheric aerosols exhibited a $^{206}\text{Pb} / ^{207}\text{Pb}$ of 1.156 whereas the ratio for aerosols from Marseilles was 1.118 (Table 5.3).

Considerable numbers of studies have been undertaken within the UK to record $^{206}\text{Pb} / ^{207}\text{Pb}$ ratios of sources of atmospheric Pb relating to the industrial and post-industrial era where Pb emissions were at their peak. A summary of these sources is outlined in Table 5.4. The $^{206}\text{Pb} / ^{207}\text{Pb}$ ratios in UK petros, coals, ores and from incinerator sources in nearby Europe are broadly distinct. Petrol sampled from UK pumps exhibits a $^{206}\text{Pb} / ^{207}\text{Pb}$ range of 1.059-1.093 (Delves and Campbell, 1993; Krause et al., 1993; Sugden et al., 1993; Monna et al., 1997; Farmer et al., 2000). The gradual phasing out of leaded petrol began in 1986 but remained a considerable source until the outright ban in 2000. The 1986 legislation included a reduction in the maximum permitted concentration of Pb in petrol from 0.40 to 0.15 g l$^{-1}$. In 1989,
$^{206}\text{Pb}/^{207}\text{Pb}$ values for petrol directly from commercial pumps were ~1.05-1.06. This value rose gradually with time to ~1.08-1.09 a decade later in 1998 prior to the leaded petrol ban. The low ratios are reflective of Octel importing Australian Pb (Day and Tylecote, 1991) whose geological $^{206}\text{Pb}/^{207}\text{Pb}$ value is ~1.04 and mixing it with British Columbian Pb of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio ~1.16. This mixing yielded anti-knock Pb additives with a ratio of ~1.07.

<table>
<thead>
<tr>
<th>Source Type</th>
<th>$^{206}\text{Pb}/^{207}\text{Pb}$</th>
<th>Relevant Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaded petrol</td>
<td>1.060–1.067</td>
<td>Delves and Campbell (1993)</td>
</tr>
<tr>
<td>Leaded petrol</td>
<td>1.060–1.070</td>
<td>Krause et al. (1993)</td>
</tr>
<tr>
<td>Leaded petrol</td>
<td>1.056–1.093</td>
<td>Sugden et al. (1993)</td>
</tr>
<tr>
<td>Leaded petrol</td>
<td>1.076 ± 0.011</td>
<td>Farmer et al. (2000)</td>
</tr>
<tr>
<td>British Coal</td>
<td>1.184 ± 0.006</td>
<td>Farmer et al. (1999)</td>
</tr>
<tr>
<td>Coal</td>
<td>1.17–1.19</td>
<td>Sugden et al. (1993)</td>
</tr>
<tr>
<td>Tyndrum ore</td>
<td>1.146 ± 0.004</td>
<td>MacKenzie and Pulford (2002)</td>
</tr>
<tr>
<td>Leadhills ore</td>
<td>1.170–1.178</td>
<td>Sugden et al. (1993); Rohl et al. (1996); Farmer et al. (1999)</td>
</tr>
<tr>
<td>Scottish Galenas</td>
<td>1.110-1.186</td>
<td>Moorbath (1962)</td>
</tr>
<tr>
<td>Incinerator (French)</td>
<td>1.143-1.155</td>
<td>Monna et al. (1997)</td>
</tr>
<tr>
<td>Incinerator (German)</td>
<td>1.142-1.159</td>
<td>Hamester et al. (1993)</td>
</tr>
</tbody>
</table>

*All sources are UK based unless otherwise stated

The isotopic signature of UK coals is significantly different from that of UK petrol with a $^{206}\text{Pb}/^{207}\text{Pb}$ range of 1.17-1.19 recorded (Sugden et al., 1993; Farmer et al., 1999). The study of Sugden et al., (1993) only examined a small number of coal samples (N=3) whereas Farmer et al’s 1999 study was more comprehensive and included coals from Scotland, England and Wales (N=65). The mean $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for UK coals reported by Farmer et al, (1999) was 1.184 ± 0.006. Scottish Pb ores exhibit a wide range $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.110-1.186 (Moorbath, 1969; Sugden et al., 1993; Rohl et al., 1996; Farmer et al., 1999; 2002; MacKenzie and Pulford
2002), dependent on age of the deposit. Historically most of the Pb extracted in Scotland originated in the Leadhills deposit at Wanlockhead ($^{206}\text{Pb}/^{207}\text{Pb}$ ratio: 1.170 ± 0.003) with other mining operations contributing comparably insignificant quantities of ore to the Scottish total. Emissions from domestic waste incinerators, albeit from the European mainland, are also individually distinct but demonstrate a wide $^{206}\text{Pb}/^{207}\text{Pb}$ range of 1.140-1.159 (Hamester et al., 1993; Monna et al., 1997).

The Pb isotope ratios characterising these sources have been used to estimate the relative contributions of these sources to atmospheric Pb in the UK, although the use of such estimates in the time period following the phasing out of Pb-petrol has been questioned in the literature (Ellam, 2010). Flament et al. (2002) estimated the proportion of petrol-derived Pb in the UK atmosphere as 14-62% in 1995-1996 while alternative measurements by Bolhöfer and Rosman (2001) suggested that the contribution of petrol Pb was ~50%. The majority of the remaining atmospheric Pb was attributed to industrial sources. Farmer et al. (2000) measured the $^{206}\text{Pb}/^{207}\text{Pb}$ composition of Scottish rainwater and reported car exhaust sourced Pb contributions to Scottish atmospheric Pb of 53-61% in the late 1980s falling to 32-45% during 1997-1998. This change was attributed to the uptake of unleaded petrol and reductions in car exhaust Pb emissions in the UK. This demonstrates that the contribution of each Pb source to the atmospheric pool has changed over time.
5.3.5.2  

**210Pb-dating of peat and soil layers**

The activity of the $^{210}$Pb isotope can be measured in order to calculate peat/soil layer dates corresponding to the past 150 years (~7 half lives for $^{210}$Pb) via one of two models, the constant initial concentration (CIC) and constant rate of supply (CRS) models (Appleby and Oldfield, 1978; Robbins, 1978; Oldfield and Appleby, 1984). The CIC model operates on the assumption that a constant initial unsupported $^{210}$Pb concentration is present within an environmental system whereas the CRS model assumes of a constant rate of supply of unsupported $^{210}$Pb to the soil or peat, in addition to no post depositional mobility or mixing. The CRS model is the more widely adopted and is still subject to refinements to improve the accuracy of determined chronologies (MacKenzie et al., 2011). However, not all peatlands render Pb completely immobile and Pb loss from some peat systems has been reported (Damman, 1978; Urban et al., 1990; Biester et al., 2012). The early work of Damman (1978) demonstrated considerable loss of Pb, ~90%, from solid phase matter below the water table. These Pb losses were judged relative to the Pb content of the organic matter in the acrotelm, during a period of time where deposition of Pb to the vegetation of the acrotelm was around its peak (Section 5.3.4.2). Such a comparison made without current knowledge of Pb deposition history, alongside the contextualisation of the past 30 years of research, may have resulted in an overestimation of Pb loss from this peat environment. The work of Urban et al. (1990) and Biester et al. (2012) demonstrate loss, or mobility of Pb within peat systems which would render $^{210}$Pb-dating unreliable if applied to the peatlands they studied. The Pb loss demonstrated by Urban et al. (1990) was attributed to organic-rich groundwater flow and must be assumed to be due to site-specific influences as
such Pb mobility would be more widely reported in literature if it were applicable to peatlands in general. The smearing of the peatland Pb profile reported by Biester et al. (2012) is attributed to the mass loss during peat mineralization and increasing particle density with the break-down of the plant material’s structure during decay. Such a smearing effect would clearly distort the Pb distribution, and importantly, the $^{210}$Pb distribution in the uppermost layers of a peat profile, although it should be noted that this distortion will have been occurring continually throughout the bog’s lifetime. As the plant matter breakdown and the humification progresses, the peat layers become compacted; accumulation is relatively slow and so the effect of the distortion processes occurring in the uppermost vegetation sections may have limited impact on the $^{210}$Pb dating process. This may be why, as discussed in Section 5.3.3, Pb is generally considered to be immobile in many peatland environments (e.g. Shotyk, 1997; Farmer et al., 1997a; Shotyk et al., 2002; 2004, Weiss et al., 1999a; 1999b; MacKenzie et al., 1997a; 1998b). In particular, previous studies at the Flanders Moss and Easter Deans sites investigated in this project have presented strong evidence supporting the immobility of Pb in these Scottish peatland environments (Farmer et al., 1997a; MacKenzie et al., 1997). Moreover, the integrity of profile dates derived from $^{210}$Pb-dating can be confirmed by comparison of the calculated dates with key core features that correspond to fixed dates, e.g. the peak in $^{241}$Am activity that corresponds to the 1963 peak in nuclear bomb fallout (Clymo et al., 1990; MacKenzie et al., 1997). Calculation of layer ages from unsupported $^{210}$Pb measurement is outlined in Appendix 7.
5.3.6 Environmental archives of atmospheric Pb deposition

No exposed surface area of the Earth is unpolluted by atmospheric Pb (Southwood, 1983). Even where no localised Pb source is present, the release of Pb to the atmosphere through both natural and anthropogenic combustion processes, followed by atmospheric particulate transport have mobilised Pb across the globe. Accumulating solid phase environmental media such as ice cores, lake sediments and ombrotrophic peat bogs have the potential to provide historical records of atmospheric Pb emissions assuming that: (i) atmospheric deposition is the only input of anthropogenic Pb; (ii) Pb is immobilised within the ice or peat; and (iii) there is no post-depositional mixing within these systems. A means of determining the age of layers within the peats, soils and lake sediments is required and dating via $^{210}$Pb as outlined in Sections 2.3.18 and 5.3.5.2 is often used.

Ice core research has been the key to reconstruction of long-term Pb deposition chronologies via environmental archives. Studies pioneered by Murozumi *et al.*, (1969) followed by considerable effort over several decades, accurately measured and explained historical [Pb] in these remote Arctic systems. Prior to major anthropogenic inputs, atmospheric Pb fallout to the Arctic region was dominated by silicate dusts and volcanic ash (Boutron, 1987). Ng and Patterson (1981) revealed the extent of anthropogenic contamination by discounting the possibility of the observed historic increases in Pb deposition beginning around 1000 BC being caused by natural sources. Chronological peaks in industrial emissions from 1000 BC onwards occur within a similar timescale to increases in concentrations within
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems (Figure 5.8). Established industrial emission Pb mass inventories where such values can be calculated and modelled suitably account for the observed increases across the past 3000 years; natural source emissions including volcanic eruptions and sea spray accumulation when extrapolated leave a 99% deficit when compared with experimentally observed [Pb]; and isotopic tracer data shows deviation from natural ratios and implicates industrial, anthropogenic sources (Shirahata et al., 1980).

Figure 5.8 Comparisons of Pb chronological archives in peat cores, lake sediments and glacial ice (Bindler, 2006).
Historical records of Pb and its atmospheric emissions have been further compiled through extensive study of lake sediments and peat cores. Accumulating lake sediments experience a continual flux of Pb due to a combination of wet and dry deposition to lake surfaces, association with particles and subsequent downward settling through the water column to the sediment. However, lake systems do not receive their inputs solely from the atmosphere and will often be fed by streams or rivers in addition to groundwater flow from the catchment, raising doubt over deposition chronologies derived from lake sediments. Post-depositional mixing in both the water column and of the uppermost sediment layers can also affect the integrity of atmospheric records constructed from sediment studies. Where these problems have not been encountered, lake sediment research has shown historic trends comparable to those in both peat and ice cores (Figure 5.8). Extensive work has been performed in Sweden and Scotland over the past two decades to demonstrate anthropogenic influence and historical trends recorded within lake sediments (e.g. Sweden: Brannvall et al., 1999; Renberg, 1994; 2002; Bindler, 2011; Scotland: Farmer et al., 1994; 1996; 1997a; Eades et al., 2002). Scottish lake sediment studies involving Pb have shown chronological markers and historical trends consistent with peat and soil profiles discussed later in this section. Studies at Lochs Lomond (Farmer et al., 1994; 1996), and Ness (Eades et al., 2002) each provide records of inputs corresponding to local industry, coal combustion and petrol-related sources. In addition to inputs of atmospherically deposited Pb from the surrounding terrestrial catchment, lake sediment archives may also be susceptible to Pb inputs via riverine transport of particulate material from local mining-related activities. A study at Loch Tay (Farmer et al., 1997b) found evidence of a limited
input of locally sourced material, identified using source apportionment calculations and the known $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of nearby Tyndrum Pb ore (Table 5.4). The Loch Tay sediment $^{206}\text{Pb}/^{207}\text{Pb}$ ratio profiles from Loch Tay are very different from those obtained for other Scottish lochs, highlighting the potential problems in the use of cores from a single location for regional scale extrapolation of historical records.

Ombrotrophic peat cores were established as a means of tracking historical Pb atmospheric deposition in the mid-to-late 1960s when cores from locations in northern Europe were observed to possess high [Pb] in the near-surface layers in comparison to the deeper layers; the latter were presumed to be indicative of background concentrations (Hvatum, 1965; Salmi, 1969). Accumulating peatlands experience a continual flux of Pb due to a combination of wet and dry deposition to their uppermost layers. Ombrotrophic bogs receive all their inputs solely from the atmosphere making them good records of historical deposition. Minerotrophic bogs do not receive their inputs solely from the atmosphere and will often be fed by local groundwater flow, although the general immobility of Pb in peatlands often renders the groundwater Pb contribution negligible when compared to the anthropogenic input. Lead concentration peaks in UK peats relating to Roman mining activities (Lee and Tallis, 1973) alongside similar discoveries in other parts of Europe (Van Geel et al., 1989) were the first indicators that these systems had the potential to act as historical archives of Pb. Historical Pb records have been obtained at many peatland locations, including Scotland (Cloy et al., 2005; 2008; 2009; Farmer et al., 1997b; 2006; MacKenzie 1997; 1998a; Weiss, 2002; Shotyk 1997; 2004), England (West et al., 1997), Switzerland (Weiss et al., 1997; Shotyk et al., 1998b), Germany
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems (Le Roux et al., 2005), Spain (Martínez Cortizas et al., 1997), the USA (Norton et al., 1997) and Sweden (Klaminder et al., 2003). European peatlands exhibit broadly comparable [Pb] with historic peaks corresponding to Roman mining, medieval mining and more contemporary industrialisation and petrol influences. Environmental archive research in Scotland is of specific relevance to this project due to the Scottish study sites involved. Recent Scottish research is discussed in more detail in Section 5.3.8.

Bindler (2006) presented side-by-side comparison of Pb deposition (Figure 5.8) reconstructions from varied environmental media, demonstrating remarkable agreement and synchronicity between ice-cores, peat cores and lake sediments. The archival records all demonstrate a peak in Pb deposition that occurs approximately 2000 years ago during the height of the Roman Empire followed by a decline and subsequent resurgence in deposition during the medieval period that continues through the Industrial Revolution, culminating in the maximum deposition of Pb in the 1970–1980s. These trends are in good agreement with worldwide historical production estimates outlined previously in Figure 5.6 (Nriagu, 1978). Differences in [Pb] profiles observed between bogs in Germany (Le Roux et al., 2005), Sweden (Klaminder et al., 2003) and Switzerland (Shotyk et al., 1998b) are attributed to differences in accumulation rates in individual bogs. In spite of these differences in [Pb] profiles, isotope ratios in bogs across Europe are remarkably similar from site-to-site (Novak et al., 2003). The effects of spatial variation between core Pb profiles is discussed in more detail in the following section.
5.3.7 Spatial deposition variability and the use of point cores as estimates of wider deposition

Detailed analysis of only single or closely paired cores for the reconstruction of historical deposition trends leaves some uncertainty surrounding the degree of within-site variability. A question has been raised as to whether a core can be assumed to adequately reflect an entire peatland, a small radius around the core or merely the exact surface area of the core. In Swedish bogs, Malmer and Wallén (1999) observed variation in peat structure and nutrient distribution due to hummock/hollow microgeography. Hummock samples exhibited ~200 g m$^{-2}$ N more than hollows and, in addition, there were variations in other factors such as bulk density and the thickness of surface vegetation layers. Urban et al. (1990) also observed spatial differences in Pb depletion in hummock and hollow microtopography within bog systems. Bindler et al. (2004) observed variation in concentrations and inventories of Pb across 9 cores within a single bog approximating a factor of 2, dependent on localised microtopography; this was greater than the variation between two cores taken ~90 km apart within the south-central Sweden. Importantly, each core examined by Bindler et al. (2004) showed similar historical trends and characteristics but the magnitudes of key features differed considerably. In Scottish bogs, Cloy et al. (2008) observed similar shaped depth profiles for a set of bogs across Scotland. However, post-1800 Pb deposition intra-site inventories within these Scottish bogs also varied by a factor of about 2 when the two cores each taken from Carsegowan Moss (Pb$_{\text{inv}}$: 2.7-5.0 g m$^{-2}$), the Red Moss (Pb$_{\text{inv}}$: 2.5-4.5 g m$^{-2}$) and Flanders Moss (Pb$_{\text{inv}}$: 2.1-3.6 g m$^{-2}$) were compared. Rothwell et al. (2007) examined 10 cores across 0.1 km$^2$ in the UK’s Pennine region.
Comparing individual cores, the upper 20 cm Pb-inventories ranged from 5.27 g m$^{-2}$ to 13.09 g m$^{-2}$, varying by a factor of about 1.5 when considering the lowest and highest values. Thus, remarkably similar magnitudes of intra-site variability have been reported in the literature. Intra-site variability in the context of this study is discussed in more detail in Section 5.5.2.3.

5.3.8 Environmental Pb research in Scotland

Over the past two decades considerable Pb-related research has been performed in Scotland involving a variety of matrices and sites including some of those adopted within this study and others within close geographical proximity. These studies have focused primarily upon reconstruction of archival Pb deposition, historical identifiers and source apportionment via [Pb] profiling and isotopic studies. Matrices and sites include Scottish organic-rich upland soils at the Glensaugh catchment, NE Scotland (Bacon and Bain, 1995; Bacon 2002; Bacon et al., 2004; Vinogradoff et al., 2005; Farmer et al., 2005); multiple Scottish peatland sites including Flanders Moss, central Scotland (Cloy et al., 2005; 2008; 2009; Farmer et al., 1997a; 2006), the Red Moss, near Edinburgh, Turclossie Moss, NE Scotland, Carsegowan Moss, SW Scotland (Cloy et al., 2009), Mugdock, near Glasgow, Uist, Outer Hebrides, Easter Deans, south of Edinburgh (MacKenzie et al., 1997; 1998a; 1998b), and the Shetland Isles (Shotyk, 1997, Shotyk et al., 2004); sediment studies at Lochs Lomond (Farmer et al., 1994, 1996), Ness (Eades et al., 2002), and Tay (Farmer et al., 1997b); historical trend reconstruction via archival mosses (Farmer et al., 2002); and tree bark and vegetation assessment (Patrick and Farmer, 2007; Farmer et al, 2010).
As discussed previously in Section 5.3.5.1, major sources of Pb emissions in the Scottish environment can be summarised as follows: Scottish Pb-mining, notably at Wanlockhead in the Leadhills in southwest Scotland, produced ores with $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of $\sim$1.170-1.178 (Sugden et al., 1993; Rohl, 1996; Farmer et al., 1999); ore from Tyndrum, although mined much less extensively than at the Leadhills, possessing a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.146 ± 0004 (MacKenzie and Pulford, 2002). Scottish coals possess a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.181 ± 0.011 (Sugden et al., 1993, Farmer et al., 1999). The isotopic ratio of Scottish leaded petrol changed over time within the range 1.059-1.093 (Delves and Campbell, 1993; Krause et al., 1993; Sugden et al., 1993; Monna et al., 1997; Farmer et al., 2000).

Bacon’s work on soils from Glensaugh, NE Scotland (Bacon et al., 2004), determined the isotope signature of Pb present in different chemical soil fractions via a modified BCR extraction procedure (Quevauviller et al., 2004). The lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, indicative of a higher contribution from petrol-derived Pb, corresponded to the most soluble, most labile fractions. It was hypothesised that Pb from different input sources is linked to association with different soil fractions and that distributions may have changed in the years following the leaded petrol ban in 2000 relative to those prior. The key outcomes of the Bacon et al. (2004) study were that there was no discernible change in isotopic composition of each of the soluble, oxidisable, reducible and residual fractions over the span of a decade, implying either a lack of exchange processes between compartments or that such processes only occur over longer timescales.
Work at the University of Edinburgh has previously assessed long-term historical trends at Flanders Moss (Cloy et al., 2005), a site also adopted for this study. Peat Pb-inventories from 1700–2004 were ~2.10 g m$^{-2}$ with peak flux of ~22 mg m$^{-2}$ yr$^{-1}$ around 1960. The $^{206}$Pb/$^{207}$Pb ratio was ~1.17 for layers corresponding to 210 BC until 1876 AD with the petrol related minima towards the surface in the mid-1970s of ~1.13 (Figure 5.9). Pb deposition chronologies, accounting for local and national influences, were consistent with other European studies (Renberg et al., 2002; Bindler, 2006), some of which were discussed previously in Section 5.2.5. Further publications on the Flanders Moss site (Farmer et al., 2006; Cloy et al., 2005; 2008; 2009) confirmed that the Pb records were consistent with known deposition data derived from mosses, air and wet deposition. Other Scottish peatlands, Turclossie Moss and the Red Moss (Cloy et al., 2005; 2008) had $^{206}$Pb/$^{207}$Pb minima of ~1.12, similar to that observed at FM, with post 1800 inventories of 1.2–5.0 g m$^{-2}$.

Alternative long-term Scottish chronologies by Shotyk et al., (2004) and Weiss et al., (2002) demonstrated broadly consistent chronological trends. Cloy et al. (2005; 2008) established that between the 17$^{th}$ and early 20$^{th}$ century, the burning of coal and processing of native Pb ores were the most important input into soils and peats around southern and central Scotland. MacKenzie et al. (1997; 1998a; 1998b) reported chronological markers based on $^{210}$Pb dating, Pb fluxes, $^{206}$Pb/$^{207}$Pb ratio trends consistent with those of Cloy et al. (2005; 2008). A direct comparison of Flanders Moss cores with Scottish lake sediment cores (Farmer et al., 1997a) concluded that there was good agreement between the main isotopic and historic markers within each system.
Additional evidence, independent of soil, ombrotrophic peat bog and lake sediment records, for the changes in the isotopic signature of Scottish atmospheric Pb has been obtained. Bacon and Bain (1995) assessed isotopic signatures of rain and streamwaters in the Glensaugh catchment, NE Scotland, from 1989–1991. Rainwater exhibited a $^{206}\text{Pb}/^{207}\text{Pb}$ signature of $1.119 \pm 0.013$ while streamwater had a $^{206}\text{Pb}/^{207}\text{Pb}$ value of ~$1.114 \pm 0.018$. Publication of rainwater data for 1997-1998 by Farmer et al., (2000) demonstrated that the isotope ratio of rainwater had increased to mean $^{206}\text{Pb}/^{207}\text{Pb}$ values of $1.145 \pm 0.014$ and $1.144 \pm 0.026$ for 1997 and 1998, respectively. Other Scottish studies also show evidence of the gradually changing isotope ratios in Scotland. Separate work by Bacon (2002) with Glensaugh grass data spanning 1989–2002 demonstrated a shift in $^{206}\text{Pb}/^{207}\text{Pb}$ isotope signature from ~$1.11–1.15$ consistent with the decreasing contribution from $^{206}\text{Pb}$-deficient anti-knock alkyl-Pb petrol additives produced using Australian Pb-ores.

It was further concluded that >90% Pb in surface vegetation was derived from atmospheric sources, a claim reinforced by investigation of Glensaugh heather (Farmer et al., 2010). More contemporary assessment of Scottish rainwater and vegetation over the period 2007-2008 (Farmer et al., 2010) has shown deposition isotope ratios for this period of between $1.146 \pm 0.004$ and $1.148 \pm 0.017$ in vegetation and rainwater, respectively. However, tree bark has not proved a suitable medium for measuring contemporary atmospheric Pb deposition.
Figure 5.9  \([\text{Pb]}\) and \(^{206}\text{Pb}/^{207}\text{Pb}\) profiles from Flanders Moss (Cloy et al., 2005; 2008).
Patrick and Farmer (2007) and Farmer et al. (2010) both concluded that the surface layers of tree bark contained Pb accumulated across a number of years. This was emphasised by a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of $1.134 \pm 0.006$ for 2007 tree bark corresponding to values derived for older peat layers ($1.134 \pm 0.001$) from 1995-1999. Despite the issues surrounding the application of bark, the comparable findings from rainwater, moss, heather and grass analysis act to increase the confidence in the integrity of peat-derived archives. A further important point is that studies carried out on archival media taken around the turn of the millennium demonstrate upturns in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the most recent chronological samples e.g. the near-surface layers of peat (Farmer et al., 2006), soil cores (Farmer et al., 2005) and archival mosses (Farmer et al., 2002). This trend mimics the gradually increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratio observed in Glensaugh rainwater from ~1990-2000 (Farmer et al., 2010). It is currently unknown whether this increasing $^{206}\text{Pb}/^{207}\text{Pb}$ ratio trend is due to the continued reduction in atmospheric petrol-derived Pb due to deposition from the atmospheric reservoir coupled with further reductions in the number of countries where leaded petrol is sold (UNEP, 2011). If the increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratio continues to the current day, the sources of Pb to the atmosphere causing this increase would be poorly understood. It is further unknown whether this continued increase in $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is also reflected in current Scottish rainwater or whether ratios remain broadly constant at ~1.15 as shown from ~2000-2005 at Glensaugh (Farmer et al., 2010).

5.4 **Current Pb research needs**

With respect to environmental records and continued study of chronologies, a need exists to continue collecting archival peat data and to analyse both the upper peat
layers, and the surface vegetation to determine current Pb fluxes and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to identify changes in Pb source composition affecting Scotland.

Traditionally, many coring techniques have diminished the viability of surface vegetation analysis by either discarding the vegetation outright or by compacting it into a plug. The evidence presented in Section 5.3.8 highlighting the importance of vegetation as a measure of contemporary Scottish atmospheric Pb presents a need to better study Pb within the vegetation itself and not just the underlying bulk peat and soils. The vegetation layers are increasingly recognised to play an important role (e.g. Biester et al., 2012) in the fundamentals of how Pb is incorporated into the peat material; deposition occurs on the vegetation at the surface of the moss and how Pb is being held and subsequently incorporated into the peat has not been satisfactorily established.

In the context of global change and predicted shifts in global weather patterns, the fate of Pb sequestered within near-surface sections of upland organic-rich soils and peatlands is not entirely understood. Surface layers of peat/soil systems are typically the most exposed and therefore most susceptible to both changes in environmental chemistry and the impacts of severe weather events such as storms. The studies of Vinogradoff et al. (2005) and Graham et al. (2006) demonstrate that Pb released into receiving streamwaters was mainly from the top 0-2 cm sections of the soil. Although most of the Pb in streamwater was mobilised during storm events either in association with large particles (>25 µm) or organic-rich colloids (3 kDa-0.2 µm),
there is a deficit of knowledge regarding exactly what this Pb is associated with and as a result, the potential for these Pb reservoirs to impact upon aquatic and even human health cannot be evaluated. While the sequestration mechanisms of Pb can be modelled within ideal environments such as highly organic ombrotrophic peatlands, the exact mechanisms of sequestration in more complicated, mineral incorporating systems is unclear. Schroth et al. (2008) indicated that Pb and Fe were linked in forest soil environments and this assertion is supported by in other research publications. For some highly contaminated soils, Karczewska (1996) observed a relationship between soluble Fe and Pb in close proximity to a Cu smelter. Covelo et al. (2007) reported positive correlations between Pb sorption/retention and presence of humic matter, kaolinite clays and importantly, Fe-oxides. Dong et al. (2000) also highlighted the chemical similarities between Pb and Fe and the potential for them to compete for favourable ionic binding sites on both organic and inorganic species, with the ratio of aqueous/sorbed Fe apparently correlating to Pb solubility within experimental laboratory settings. Peat systems are, however, comparatively deficient in Fe and mineral matter yet Pb is still well-retained in these systems. Several studies have implicated ternary complexes involving a humic component, a metal ion (in this case Pb) and Fe-oxides and demonstrate evidence to support the formation of humic substance–iron oxide complexes (Varadachari et al., 2000; Saito et al., 2005; Fu and Quan., 2006). Orsetti et al. (2006) published results that indicate Pb^{II} promotes humic acid binding to Fe-oxides by acting as a bridge between the two species. The ternary complex was considered to be stabilised via proton displacement. In environmental systems, these ternary binding mechanisms appears to contradict the purely organic functionality model predictions of Perdue et al. (1984), Benedetti et
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al. (1995), Davies et al. (1997), Xia et al. (1997) discussed in Section 5.3.3 as these earlier models do not broadly consider the simultaneous interaction of both organic and inorganic species with Pb. Additional information and study is required before the binding behaviour of Pb can be understood.

In the context of the remaining unknowns surrounding environmental Pb, the objectives of this study are to investigate Pb associations in the near-surface sections (including surface vegetation) of both peat and soil systems so that its behaviour and ultimate environmental fate can be better understood. This goal will be achieved by quantification of the partitioning of Pb between soil mineral and organic matter components and by identifying differences between ombrotrophic peat, minerotrophic peat and forest soils since these systems encompass a spectrum of organic-rich sites with varied mineral matter proportions. The chemical associations of Pb within peat/soil environments will be assessed alongside the continued capacity for these environments to act as long-term Pb sinks. Furthermore, with the decline of the historically dominant petrol anthropogenic emissions sources, contemporary flux of Pb to peat and soil systems and the \(^{206}\text{Pb}/^{207}\text{Pb}\) profile of these sites will be determined to examine changes in deposition and the potential impact of remaining emission sources to the wider environment.
5.5 Results and discussion

5.5.1 Solid phase $^{210}$Pb activity, [Pb] and $^{206}$Pb/$^{207}$Pb ratios in the upper sections of cores from Flanders Moss (FM), Glentress Forest (GT), Easter Deans (ED) and Auchencorth Moss (AM)

The $^{210}$Pb activity profiles for FM, GT, ED and AM cores are presented in Figure 5.10. Layer dates were established via $^{210}$Pb-dating using the CRS model (Section 2.3.18). Dates for layers from FM and AM cores were extrapolated from the dating performed on sister cores taken directly adjacent to the cores used for concentration and isotope ratio analysis. To facilitate this dating process, it is assumed that a given depth for adjacent cores corresponds to the same age in each of those cores. Layer depths and corresponding dates are tabulated in Appendix 8. The solid phase [Pb] and $^{206}$Pb/$^{207}$Pb profiles for the upper sections of cores from four sampling sites are shown in Figures 5.11-5.14. Concentration and isotope ratio data was acquired via acid digestion and ICP-OES/MS analysis (Section 2.3.14 and Sections 2.3.16 and 2.3.17, respectively). An overview of results is presented here and discussed in more detail in Section 5.5.2.
5.5.1.1  $^{210}$Pb activity profiles

Figure 5.10 shows the supported and unsupported $^{210}$Pb profiles for FM, GT, ED and AM. Supported and unsupported $^{210}$Pb activities were measured to depths of 23 cm at FM, 18.5 cm at GT, 22.5 cm at ED, and 35 cm at AM. Unsupported $^{210}$Pb activity decreases exponentially with depth in the vegetation layers at FM (0-15 cm) and GT.
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(0-1 cm) until both supported and unsupported $^{210}$Pb activity are approximately equivalent in the deeper layers of each core. Surface activity maxima are different in magnitude between FM and GT at 536 Bq kg$^{-1}$ and 3290 Bq kg$^{-1}$, respectively. The ED profile differs from those of FM and GT insofar as the unsupported $^{210}$Pb activity remains consistently ~100 Bq kg$^{-1}$ larger than the supported $^{210}$Pb activity below ED’s vegetation layer (0-10 cm). The surface activity maximum at ED is 221 Bq kg$^{-1}$, smaller than the maxima at FM and GT. The $^{210}$Pb activity profile at AM is much flatter than those at the other 3 sites. While surface $^{210}$Pb activity at AM is similar to that at ED (~200 Bq kg$^{-1}$) and the unsupported $^{210}$Pb activity at depth does become broadly equivalent to the supported $^{210}$Pb, unsupported activity in the uppermost 20 cm only decreases gradually with depth, and not exponentially as observed at FM, GT and ED. Furthermore, unsupported $^{210}$Pb maximum, 270 Bq kg$^{-1}$, occurs at a depth of 7 cm and not at the surface as per the other cores.

The constant rate of supply (CRS) model (Appleby and Oldfield, 1978; Robbins, 1978; Oldfield and Appleby, 1984) was applied to $^{210}$Pb inventories calculated from the unsupported $^{210}$Pb data as outlined in Section 2.3.18.2 to generate dates for the layers from each core. Example calculations are provided in Appendix 7. Uncertainties in layer dates are greater towards the base of each core due to low proportion of total unsupported $^{210}$Pb inventory at greater depth.
5.5.1.2 Flanders Moss peat core (0-30 cm)

The FM [Pb] profile (Figure 5.11) reveals low and near-constant concentrations of ~50 mg kg\(^{-1}\) Pb for the uppermost 0-15 cm vegetation layers sections. Within the peat, [Pb] increased rapidly to a concentration maximum of 267 ± 6.7 mg kg\(^{-1}\) at ~20 cm which corresponds to the peak in atmospheric Pb output due to coal burning in the 1950s. Below 25 cm, [Pb] decreased rapidly to ~50 mg kg\(^{-1}\) at the bottom of the core.

The \(^{206}\)Pb/\(^{207}\)Pb ratio further reflects these historical trends. From the surface down to a depth of 7.5 cm, the \(^{206}\)Pb/\(^{207}\)Pb ratio remains relatively uniform at 1.12–1.14. Below 7.5 cm, the \(^{206}\)Pb/\(^{207}\)Pb ratio decreases at a rate of ~0.004 cm\(^{-1}\) to a minimum value of 1.095 ± 0.002 at 15.5 cm, representing the peak contribution of Pb from
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petrol combustion (Table 5.4). The ratio then increases sharply below 22 cm to 1.161 ± 0.003 at ~25 cm depth and then remains approximately constant to the base of the core.

5.5.1.3 Glentress Forest soil core (0-30 cm)

Once again, the lowest [Pb] (6.1 mg kg⁻¹) was obtained for the vegetation layer. As for FM, [Pb] increased rapidly within the organic-rich soil at GT (Figure 5.12) and reached a maximum value of 135 ± 0.3 mg kg⁻¹ at 9 cm depth. In contrast with FM, there was then a decrease in concentration to ~70 mg kg⁻¹ at 13 cm followed by a sharp increase to 135 ± 0.2 mg kg⁻¹ at 15 cm depth. Concentrations then decreased towards the bottom of the core. No dates are available for the bottom sections of the core but the high concentrations at 15 cm probably correspond to the pre-20th century industrialisation.
While the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio value of ~1.139 for the uppermost layer (vegetation) of the GT soil were in good agreement with those for the vegetation layers at FM (1.13-1.14), the ratio values remained within the range 1.136-1.144 and thus showed no increase towards the bottom of the core. Some influence of Australian Pb ore (geological $^{206}\text{Pb}/^{207}\text{Pb}$: ~1.04) may be expected in the deeper core layers due to its import and use in UK smelters in the south of England in the late 19th century (Eades et al., 2002) although it would not be expected to have such a large effect over such a large span of time. Alternatively, as these low $^{206}\text{Pb}/^{207}\text{Pb}$ values were observed for sections dating prior to the 1920s, it must be considered that a proportion of petrol-derived Pb may have been transported down the soil profile and this will be discussed in Section 5.5.2.1.2 and Section 5.5.5.2.

5.5.1.4 Easter Deans peat bog (0-30 cm)

![Graph showing Pb and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles for Easter Deans Moss including layer dates.](image)

Figure 5.13  [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles for Easter Deans Moss including layer dates. N=3. Dashed line represents vegetation/peat interface.
At the ED site, \([\text{Pb}]\) increased with depth from the surface concentration of 27.7 ± 1.5 mg kg\(^{-1}\), reaching a maximum concentration of 95.6 ± 0.1 mg kg\(^{-1}\) at 16.5 cm (Figure 5.13). This broad \([\text{Pb}]\) maximum again relating to peaks in coal burning and leaded petrol Pb emissions during that period. From ~22 cm, the \([\text{Pb}]\) decreases to 38.5 ± 0.7 mg kg\(^{-1}\) at the base of the core. The \(^{206}\text{Pb}/^{207}\text{Pb}\) ratio generally increases with layer depth from a minimum of 1.149 ± 0.004 to a maximum of 1.179 ± 0.003. The characteristic decrease in \(^{206}\text{Pb}/^{207}\text{Pb}\) ratio just above the concentration maximum again corresponds to the increased contribution of Australian Pb petrol additives to the total Pb emissions.

### 5.5.1.5 Auchencorth Moss peat bog (0-45 cm)

Figure 5.14 \([\text{Pb}]\) and \(^{206}\text{Pb}/^{207}\text{Pb}\) profiles for a peat core from Auchencorth Moss including layer dates extrapolated from an adjacent sister core. \([\text{Pb}]\): N=3. \(^{206}\text{Pb}/^{207}\text{Pb}\): N=5. Dashed line represents vegetation/peat interface.
The AM profile (Figure 5.14) exhibited a general increase in [Pb] from a surface concentration of $10.4 \pm 3.5 \text{ mg kg}^{-1}$ to a peak of $178 \pm 2.2 \text{ mg kg}^{-1}$ at a depth of 19.5 cm, corresponding to the mid 1960s. The broad region of high [Pb] from 19.5 cm to 22.5 cm again corresponds chronologically to maximum coal burning and leaded petrol Pb emissions. From 22.5 cm, the [Pb] decreases with increasing depth until the 35-45 cm sections of the core where concentrations reach a near-constant value of $\sim 30 \text{ mg kg}^{-1}$. With respect to the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, the values for the 0-12 cm vegetation layers were generally within the range of 1.13–1.14. Unlike the FM core, there is no sharp minimum in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio relating to the maximum emissions from leaded petrol. Instead, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio increased gradually down the core to a value of $\sim 1.18$ at 26.5 cm depth and remains approximately constant down to a depth of $\sim 33$ cm. Below 33 cm, the ratio values increased to $\sim 1.2$ towards the bottom of the core. It should be remembered that there is a major change in composition below 40 cm from peat to clay.

5.5.2 Discussion of Solid Phase [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles

5.5.2.1 Comparison of profiles with published literature

5.5.2.1.1 Flanders Moss (FM)

As described above, the FM solid phase [Pb] profile exhibited a consistent [Pb] of $\sim 50 \text{ mg kg}^{-1}$ in the vegetation layer that comprises the uppermost 15 cm of the core. Below 15 cm, where the peat layer begins, the [Pb] increases with depth to a peak value of $267 \pm 8 \text{ mg kg}^{-1}$ at 20 cm before decreasing back to $\sim 50 \text{ mg kg}^{-1}$ at 30 cm depth. Over the entire core, the $^{206}\text{Pb}/^{207}\text{Pb}$ values were in the range 1.095-1.162. The
The near constant [Pb] of ~50 mg kg\(^{-1}\) recorded for the uppermost 13.5 cm of FM’s vegetation layer is not repeated in either of the FM cores of Cloy \textit{et al.} (2005; 2008). There are a number of reasons that may account for this. First, the FM core in this study was taken 5 years later than those of Cloy \textit{et al.} (2005; 2008) and the
uppermost layers are representative of Pb deposition during these interim years. Second, the Cuttle & Malcolm core presented by Cloy et al. (2005; 2008) was missing its vegetation section, resulting in the layers corresponding to ~2000 to be lost. The latter point also explains the differences between the surface [Pb] of the C&M core (~75 mg kg$^{-1}$) reported by Cloy et al. (2005; 2008) and the corresponding value in this study (~50 mg kg$^{-1}$). With the vegetation layers removed, the uppermost core layers will consist of peat rather than vegetation material which would be expected to possess a larger [Pb] than the overlying plant material. However, the FM monolith core of Cloy et al. (2005; 2008) may show the beginnings of this constant [Pb] region in its uppermost 5 cm, starting in the layer dated to 1994 ± 2. For this study, however the start of the near-constant [Pb] corresponds to the mid-1980s. The good agreement between profile dates in this study and the literature for the deeper sections of the core would suggest that small differences between the surface topography and vegetation thickness between the core used for elemental analysis and that used for dating will have caused additional offset in the dates of the vegetation layer, resulting in it appearing to be older than it really is.

**Minimum value of $^{206}$Pb/$^{207}$Pb isotope ratio**

With regard to the $^{206}$Pb/$^{207}$Pb ratios, minimum values of ~1.134 and 1.130 were reported by Cloy et al. (2005; 2008). Farmer et al. (1997a) reported a $^{206}$Pb/$^{207}$Pb minimum of ~1.12 with MacKenzie et al. (1997) presenting a $^{206}$Pb/$^{207}$Pb minimum of 1.150 ± 0.002. Thus the minimum $^{206}$Pb/$^{207}$Pb value of 1.095 ± 0.002 reported in this study is at least ~0.025 lower than the minima in the published FM cores described above. However, isotope ratios of ~1.11 have been recorded for other
Scottish bogs (Cloy et al., 2008) and thus the value of 1.095 ± 0.002 reported here is not significantly out of line with these values. It is important to remember that there can be sampling-related reasons for such differences. For example, (i) the sectioning interval will affect the resolution of vertical profiles; e.g. sectioning of 2 cm was used by MacKenzie et al. (1997) in contrast to the 1 cm sectioning of Cloy et al. (2005; 2008); (ii) the date on which the core was collected in combination with the removal/or not of vegetation may mean that the trends in isotope ratios over recent decades are not recorded (Farmer et al., 2006); (iii) the type of corer that has been used may compact the vegetation layer and therefore the resolution of vertical profiles may be affected (Farmer et al., 2006); (iv) even for cores sectioned at similar intervals using the same coring method, small differences in vertical profiles attributable to the precision of sectioning may also arise (Cloy et al., 2005; 2008). In addition to these operator-induced factors, the topographical and plant compositional features of the bog may affect the particle trapping capability of the bog (Bindler et al., 2004) contributing not only to differences in concentration but also to differences in stable isotope ratios. The most likely explanation for the differences in the minimum $^{206}\text{Pb}/^{207}\text{Pb}$ reported by this study and that of Cloy et al. (2005; 2008) is the large sectioning interval (3 cm, monolith core) they adopted and resultant lack of depth resolution this bestows. Thicker sections result in greater averaging within those sections and may have caused the more pronounced minimum in this study to have been lost. Although the above has highlighted differences in the minimum ratio value, the layer dates at which previous studies report the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio minimum, e.g. 1976 ± 7 for FM01-CM1 (Cloy et al., 2008), ~1980 (MacKenzie et al., 1997) are in good agreement with those reported here (1966-1982).
Vegetation $^{206}\text{Pb}^{207}\text{Pb}$ isotope ratios

The vegetation layers (0-15 cm) of the FM core presented in Section 5.5.1.2 showed an upturn in $^{206}\text{Pb}/^{207}\text{Pb}$ from the minimum of $1.095 \pm 0.002$ at the vegetation/peat interface to a near-constant value of 1.13-1.14. The monolith core of Cloy et al. (2005; 2008) also shows an upturn in $^{206}\text{Pb}/^{207}\text{Pb}$ in the uppermost layers however the region of near-constant value is not present. This difference is likely reflective of the 5 year time difference between collection of this study’s core that of Cloy et al. (2005; 2008). It is notable that chronological $^{206}\text{Pb}/^{207}\text{Pb}$ Scottish rainwater trends reported by Farmer et al. (2010) demonstrate a similar upturn from ~1.11 from when records began in the early 1990s to a near-constant value of ~1.15 from around 2000 until 2007. The upturn for rainwater reported by Farmer et al. (2010) is in reasonable chronological agreement with those reported for peat cores in this study and by Cloy et al. (2005; 2008) within the limitations of the dating of the peat cores.

5.5.2.1.2 Glentress forest (GT)

As described in Section 5.5.1.3, the GT core exhibited a [Pb] minimum of $6.1 \pm 1.1$ mg kg$^{-1}$ in the uppermost layer. This layer comprised a thin carpet of moss at the surface of the core. Within the peaty soil, [Pb] peaks of ~135 ± 1 mg kg$^{-1}$ at both 9 cm and 15 cm were evident and there was a narrow range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values (1.136-1.144).
Maximum [Pb] and range of $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio values

There are no existing publications for [Pb] at the GT site and so a direct comparison cannot be made. However, there have been several studies on Swedish boreal forests which provide a point of comparison for this study (Brännval et al., 2001; Klaminder et al., 2008). The [Pb] maxima reported by these studies ranged from ~10 mg kg$^{-1}$ to ~140 mg kg$^{-1}$ although the majority of profiles had maximum [Pb] values of 75-125 mg kg$^{-1}$. The maximum of ~135 mg kg$^{-1}$ observed in this study was at the upper end of the values obtained in Swedish forests. Elevation is another factor which influences the extent of contaminant deposition to soils. Thorter Hill, at ~500 m asl is the most elevated part of the Glensaugh catchment, NE Scotland, and is at comparable elevation to the location sampled at GT (~600 m asl). However, the maximum concentration in soil profiles at Glensaugh was ~500 mg kg$^{-1}$, more than three times greater than those obtained at GT (Farmer et al., 2005). Thus, factors other than elevation and afforestation are important in determining the extent of Pb contamination in upland areas. Brännval et al. (2001) and Klaminder et al. (2008) determined a wide range of $^{206}\text{Pb}/^{207}\text{Pb}$ (~1.11-1.18) values within these Swedish boreal forest systems. However, the majority of these forest cores show a $^{206}\text{Pb}/^{207}\text{Pb}$ range of 1.13-1.15 at depth, comparable with the range of 1.136–1.144 obtained within this study.

[Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ isotope profile trends and shape

The [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles of Brännval et al. (2001) showed several differences to the GT profiles in this study. The Swedish forest soils had high [Pb] in the uppermost layers, rapidly decreasing with depth to near-constant values of <10
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mg kg$^{-1}$ at depths of 3-10 cm. In contrast, the lowest [Pb] was in the surface layer at GT, with values increasing to 50-135 mg kg$^{-1}$ at depth. The presence of a low surface concentration at GT are likely reflective of the reductions in Pb emissions and subsequent deposition across the decade since the cores of Brännval et al. (2001) were taken. The complete ban on leaded petrol across Europe in 2000 (Section 5.3.4.2; UNEP, 2009) will not have affected cores taken in 1998 however sufficient time will have passed to allow the influence of the ban to be visible in the uppermost layers of the 2009 GT core due to the accumulation rate of ~2 cm soil decade$^{-1}$. The lack of any decrease in [Pb] with depth at GT may be a result of the shallow depth of the core (21 cm) and the resulting ages of the layers collected. The oldest dated GT layer corresponded to ~1947 and so the [Pb] concentration would be expected to continue to decrease in the deeper layers beneath the core’s lower limit.

The $^{206}$Pb/$^{207}$Pb profiles reported by Brännval et al. (2001) showed minima of ~1.11 at the surface of the core followed by rapid increases with depth across the uppermost ~15 cm to a near-constant value of 1.13-1.15. The near-surface change in isotope ratio and the surface ratio minimum values of ~1.11 were not observed in the GT profile, even in the GT layers that corresponded to similar dates to the surface layers of the Swedish cores. However, isotope ratios of ~1.14 at GT are in good agreement with the 1.13-1.15 range reported for depths of >15 cm in the Swedish forest. The near-surface ratio minimum was attributed by Brännval et al. (2001) to the penetration and influence of leaded petrol-sourced Pb. The ratios at depths up to 60 cm were accounted for by the penetration of historical anthropogenic Pb into deeper soil layers. The lack of agreement between the near-surface layers of this
study and those of Brännval et al. (2001) could be presumed to due to mixing or migration processes. Mixing process due to afforestation or deforestation activities at GT are unlikely to be responsible due to the preserved exponential decrease in $^{210}$Pb activity with depth (Section 5.5.1.1) and the apparent agreement of [Pb] profiles with established chronologies (Section 5.5.1.3). Migration of Pb within forest soils is not without precedent in the literature. Brännval et al. (2001) discussed the potential for decomposition of organic matter to transport Pb bound to organic decomposition products down a profile into the mineral soil, a process also discussed by Wang and Benoit (1996). Furthermore, Bacon et al. (2004) demonstrated that petrol-derived Pb, with its characteristic low $^{206}$Pb/$^{207}$Pb ratio in the UK, was the most labile fraction of Pb in soils from Glensaugh, NE Scotland. Application of source apportionment calculations (e.g. Farmer et al., 2005; Appendix 11) to the GT core suggests that petrol-sourced Pb equivalent to ~30-35% of total layer [Pb] would be required to shift $^{206}$Pb/$^{207}$Pb from the ~1.17-1.18 maximum reported at depth in this study’s peatland archives (Section 5.5.1) and the literature (e.g. Cloy et al., 2005; 2008; MacKenzie et al., 1997) to the ~1.14 values observed across the GT core. For the upper layers of GT where [Pb] was ~5 m kg$^{-1}$, this equates to a small amount of Pb (~1.5 mg kg$^{-1}$), whereas in deeper layers where concentrations are ~135 mg kg$^{-1}$ and the $^{206}$Pb/$^{207}$Pb maximum would be predicted from historical records, the quantity of petrol-derived Pb required to cause the 1.18-1.14 shift is a considerable ~45 mg kg$^{-1}$ Pb. The potential mobility of petrol-derived Pb fractions at GT will be discussed in more detail in relation to aqueous phase data in Section 5.5.3.
5.5.2.1.3 Easter Deans (ED)

As described in section 5.5.1.4, the ED peat core had a [Pb] of ~26 ± 1 mg kg\(^{-1}\) in the uppermost layer, rising to ~51 ± 1 at ~10 cm, the base of the vegetation layer. Within the peat, concentrations increased to a broad [Pb] peak of ~91 mg kg\(^{-1}\) before decreasing to ~34 mg kg\(^{-1}\) at the base of the core. The \(^{206}\)Pb/\(^{207}\)Pb ratio increases with depth down the core from 1.149 ± 0.004 at the surface to 1.179 ± 0.003 towards the bottom of the core.

**Maximum [Pb] and range of \(^{206}\)Pb/\(^{207}\)Pb isotope ratio values**

MacKenzie *et al.* (1997) previously published [Pb] and isotopic data for a peat core from the Easter Deans bog. In that study, the solid phase [Pb] peak of 92 ± 6 mg kg\(^{-1}\) was determined for a layer corresponding to ~1960 whilst the \(^{206}\)Pb/\(^{207}\)Pb ratios were in the range 1.148–1.179 down the core. The data presented within this study shows remarkable agreement with these key core features. Specifically, the profiles shown in Figure 5.11 had a [Pb] maximum of ~91 ± 1 mg kg\(^{-1}\) in a section corresponding to 1960 ± 18 and the \(^{206}\)Pb/\(^{207}\)Pb ratio values over the 0-30 cm depth sections ranged 1.148–1.179, almost identical to the MacKenzie *et al.* (1997) data. This similarity would suggest that Pb deposition at ED has not changed significantly in \(^{206}\)Pb/\(^{207}\)Pb composition during the two decades between the sampling of MacKenzie’s (1997) core and the core in this study.
Surface Vegetation [Pb] and $^{206}$Pb/$^{207}$Pb isotope ratios

The surface vegetation [Pb] values reported by MacKenzie et al. (1997), 50 ± 6 mg kg$^{-1}$ at 1 cm and 92 ± 6 mg kg$^{-1}$ at 3 cm, were greater than the values of 26 ± 1 mg kg$^{-1}$ and 32 ± 2 mg kg$^{-1}$ for equivalent layers in this study. The lower [Pb] in more contemporary vegetations layers following the post-2000 banning on leaded petrol (UNEP, 2009) reflect the decreases in Pb emissions since the core of MacKenzie et al. (1997) was sampled in the 1990s.

Isotope ratio values for the uppermost two sections of the MacKenzie et al. (1997) ED core, 1.148 ± 0.004 and 1.157 ± 0.004, respectively, are statistically indistinguishable from the $^{206}$Pb/$^{207}$Pb range of 1.148-1.155 in the vegetation layers of this study’s ED core. The absence of any discernible change in $^{206}$Pb/$^{207}$Pb values in the surface vegetation layers between this study and that of MacKenzie et al. (1997) provides further evidence, alongside the FM vegetation data (Section 5.5.2.1.1) and the rainwater data of Farmer et al. (2010), that $^{206}$Pb/$^{207}$Pb deposition has become relatively constant in recent times. The decrease in [Pb] in the surface vegetation layers of this study’s core, attributed to decline in petrol derived Pb since the 2000 ban, would suggest that the $^{206}$Pb/$^{207}$Pb of deposition would have perhaps increased in the time period between the sampling of the MacKenzie et al. (1997) core and the core reported here. Whilst the $^{206}$Pb/$^{207}$Pb of the sources of contemporary atmospheric Pb are not entirely established, the known contributors to total atmospheric [Pb] have changed across the past two decades (Figure 5.7; Dore et al., 2008). As a result, it is conceivable that with the decline in leaded petrol-sourced Pb post-2000, the variations in anthropogenic sources have caused the overall
$^{206}\text{Pb}/^{207}\text{Pb}$ signature of deposition to remain broadly constant. Detailed characterisation of current atmospheric sources of Pb, their $^{206}\text{Pb}/^{207}\text{Pb}$ and a comparison with recent deposition is required to explore this hypothesis.

### 5.5.2.1.4 Auchencorth Moss (AM)

As discussed in Section 5.5.1.5, the profile for the AM core exhibited an increase in $[\text{Pb}]$ from a surface concentration of $\sim 10 \pm 4 \text{ mg kg}^{-1}$ to a peak of $\sim 178 \pm 2 \text{ mg kg}^{-1}$ at a depth of 19.5 cm. The increase started from the surface of the vegetation layer, continued through the vegetation-peat interface at a depth of 10 cm, and then through the peat to a depth of 19.5 cm. From there, the $[\text{Pb}]$ decreased with increasing depth down to the 35-45 cm sections of the core where concentrations reached $\sim 30 \text{ mg kg}^{-1}$. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the uppermost 15 cm layers were within a consistent range of 1.13–1.14 before increasing deeper down the core until 37.5 cm, below which $^{206}\text{Pb}/^{207}\text{Pb}$ values fluctuated between $\sim 1.190$ and $\sim 1.24$. There are no known publications that report Pb data for AM. As a result, other Scottish sites are the only available points for comparison.

**Maximum $[\text{Pb}]$ and range of $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio values**

The maximum $[\text{Pb}]$ of $\sim 178 \pm 2 \text{ mg kg}^{-1}$ at AM is higher than the ED $[\text{Pb}]$ maximum value reported by MacKenzie *et al.* (1997) of $92 \pm 6 \text{ mg kg}^{-1}$. However, the AM $[\text{Pb}]$ maximum is lower than the FM $[\text{Pb}]$ maxima reported by MacKenzie *et al.* (1997) ($388 \pm 49 \text{ mg kg}^{-1}$), Farmer *et al.* (1997a) (200-300 mg kg$^{-1}$) and Cloy *et al.* (2005; 2008) (264 mg kg$^{-1}$; 193 mg kg$^{-1}$). The close proximity of AM to the ED site
suggests that the flux of atmospheric Pb incident upon both sites would be broadly similar. It is therefore unsurprising that the AM [Pb] maximum is closer to those reported for ED than those for FM. The minimum $^{206}\text{Pb}/^{207}\text{Pb}$ values reported for FM (Cloy et al., 2005; 2008: 1.13; Farmer et al., 1997a: ~1.12) are in good agreement with the 1.13 lower boundary in the AM profile. The upper AM $^{206}\text{Pb}/^{207}\text{Pb}$ value (~1.20) is somewhat higher than the maximum $^{206}\text{Pb}/^{207}\text{Pb}$ value of ~1.18 reported by MacKenzie et al. (1997), Farmer et al. (1997a) and Cloy et al. (2005; 2008) at both FM and ED. The $^{206}\text{Pb}/^{207}\text{Pb}$ maximum at AM occurred in the deepest section of the core where clay-rich layers were present, suggesting that the ratio of ~1.20 is indicative of the geogenic $^{206}\text{Pb}/^{207}\text{Pb}$ signature at that location. The difference between this AM signature and that of Tyndrum ores (~1.146 ± 0.004; MacKenzie and Pulford, 2002) and Leadhills ores (1.170-1.178; Rohl et al. 1996) further demonstrates the variability in geogenic $^{206}\text{Pb}/^{207}\text{Pb}$ across Scotland.

**Surface vegetation [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios**

The ~10-100 mg kg$^{-1}$ [Pb] in AM’s vegetation layers is considerably higher than at the FM, ED and GT sites in this study. The surface section [Pb] values reported by MacKenzie et al. (1997) of 50 ± 6 mg kg$^{-1}$ and 92 ± 6 mg kg$^{-1}$ are both within the AM vegetation [Pb] range but it is unclear whether these surface sections reflect vegetation or the peat proper. The broadly constant ~75 mg kg$^{-1}$ [Pb] reported by Cloy et al. (2005; 2008) at FM is also within AM’s vegetation [Pb] range. However, the vegetation [Pb] profile at AM showed an increase in concentration from 10-50 mg kg$^{-1}$ in the upper sections to ~100 mg kg$^{-1}$ in the deeper vegetation layers, in contrast to this study’s FM vegetation profile where a near constant [Pb] was
recorded throughout the entire vegetation section. The reasons for this difference will be explored in more detail in Section 5.5.2.2.

The $^{206}$Pb/$^{207}$Pb ratios in the uppermost 15 cm layers were within a consistent range of $1.13\text{--}1.14$, in close agreement with the $^{206}$Pb/$^{207}$Pb range of $\sim1.12\text{--}1.14$ in vegetation layers of FM, the Red Moss of Balerno and Turclossie Moss reported by Cloy et al. (2008). The ED vegetation $^{206}$Pb/$^{207}$Pb values in this study and those reported by MacKenzie et al. (1997) were however higher than the AM ratios in this study, at $1.148\pm0.004$ and $1.157\pm0.004$ in the uppermost two ED core layers.

The reasoning behind the differences between AM, FM, ED and literature cores is not entirely clear. In order to better explain these differences a direct inter-site comparison of the cores in this study must be made. Furthermore, the degree to which intra-site variation can influence Pb profiles must be made as it is conceivable that these influences, where present, may contribute to inter-site disparities. Inter-site variation will be discussed in Section 5.5.2.2 whereas intra-site variation will be addressed in Section 5.5.2.3.

### 5.5.2.2 Inter-site comparison and further discussion

Key features of the solid phase cores from FM, GT, ED and AM are presented in Table 5.5. The features presented include the peak solid phase [Pb], $^{206}$Pb/$^{207}$Pb ratio maximum values, $^{206}$Pb/$^{207}$Pb ratio minimum values, the surface $^{206}$Pb/$^{207}$Pb ratio and
Pb inventories to the layer dated 1986, and to 20 cm depth. Lead inventories are a measure of the amount of Pb present in a given surface area of land to a specific depth. Inventories are calculated using layer concentrations, masses and the core dimensions, as outlined in Appendix 9. The inventories were calculated to the layers corresponding to 1986, as this date represents the beginning of widespread decline in atmospheric Pb emissions (Section 5.3.4.2). Additionally, inventories were calculated to 20 cm since this was represented the approximate length of the shortest core (GT).

Table 5.5 Key solid phase Pb core features for FM, GT, ED, and AM

<table>
<thead>
<tr>
<th>Core</th>
<th>Length (cm)</th>
<th>[Pb] maximum (mg kg(^{-1}))</th>
<th>(^{206}\text{Pb}/^{207}\text{Pb}) maximum</th>
<th>(^{206}\text{Pb}/^{207}\text{Pb}) at surface</th>
<th>Pb-inventory; to 1986 (g m(^{-2}))</th>
<th>Pb-inventory; to 20 cm (g m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM</td>
<td>31</td>
<td>267.2 ± 6.7</td>
<td>1.095</td>
<td>1.162</td>
<td>1.127</td>
<td>0.516</td>
</tr>
<tr>
<td>GT</td>
<td>21</td>
<td>135.2 ± 0.3</td>
<td>1.136</td>
<td>1.144</td>
<td>1.139</td>
<td>0.425</td>
</tr>
<tr>
<td>ED</td>
<td>30</td>
<td>90.5 ± 0.5</td>
<td>1.148</td>
<td>1.179</td>
<td>1.149</td>
<td>0.491</td>
</tr>
<tr>
<td>AM</td>
<td>50</td>
<td>132.0 ± 4.7</td>
<td>1.130</td>
<td>1.199</td>
<td>1.145</td>
<td>0.340</td>
</tr>
</tbody>
</table>

\([\text{Pb}],^{206}\text{Pb}/^{207}\text{Pb}\) ratios and Pb inventories

FM exhibited the highest \([\text{Pb}],\) double that of the other cores Whilst the maxima for GT, ED and AM were in the range 90.5–135.2 mg kg\(^{-1}\). The low minimum \(^{206}\text{Pb}/^{207}\text{Pb}\) value at FM (1.095) is attributable to FM being the only site in this study to be located to the north of Scotland’s main industrial belt; prevailing wind directions will have resulted in greater transport and deposition of near-field Pb and central-belt automobile-sourced petrol to this site than to GT, ED or AM (MacKenzie et al., 1997). The surface isotope ratios across the sample sites are similar to those reported by Farmer et al (2010) for 2006-2007 surface vegetation which demonstrated a \(^{206}\text{Pb}/^{207}\text{Pb}\) value of 1.146 ± 0.004. Surface isotope ratios will be
discussed in more detail in relation to aqueous phase profiles in Section 5.5.3. Variation in core inventories to 1980 in this study of ~1.5 between sites is of a similar magnitude to the variation of ~1.3-1.8 in post-1800 inventories reported by Cloy et al., (2008) when FM, the Red Moss, and Carsegowan Moss sites in Scotland were compared.

FM and ED demonstrate almost identical Pb inventories to 1986, 0.516 g m$^{-2}$ and 0.491 g m$^{-2}$, respectively. GT and AM possess lower Pb inventories to 1986 with 0.425 g m$^{-2}$ at GT and 0.340 g m$^{-2}$ at AM. Calculated inventories to 20 cm show considerable differences between the four sample sites. The thickness of core vegetation layers is also a large contributor to differences in depth based inventories due to the 10-15 cm vegetation layers in the peatlands compared to the 1 cm thick surface vegetation at the GT site. The large GT inventory to 20 cm (4.834 g m$^{-2}$) is reflective of the lower accumulation rate of the forest soil when compared to peatlands. A depth of 20 cm at AM is dated to 1960 ± 6.5 whereas the same depth at GT corresponds to pre-1891; approximately 100 additional years of Pb deposition are retained within the 0-20 cm depth range at the GT site. Comparison of concentration profiles and inventories from different sites based upon depth alone is of limited value; surface vegetation and peat/soil accumulation rates can alter the magnitude, thickness and depths of the [Pb] maximum and other features (e.g. Mighall et al., 2002). Thus the sub-section that follows takes into account the accumulation rates at each location.
Layer dates in relation to [Pb], $^{206}$Pb/$^{207}$Pb ratios and Pb flux

To allow better comparison of sites, [Pb], $^{206}$Pb/$^{207}$Pb ratios and annual Pb flux were plotted against date (Figure 5.15-5.16). In relation to the historical Pb emissions and deposition chronologies, the trends for FM are in good agreement with those in the existing literature (Farmer et al., 1997b; MacKenzie et al., 1997; Cloy et al, 2005; 2008). Lead concentrations decrease from ~240 mg kg$^{-1}$ around ~1949-1966 until reaching a generally constant ~50 mg kg$^{-1}$ in the vegetation layers corresponding to 1982-2003. These sections represent the period during which there were lower emissions due to reductions in the use of leaded petrol and its eventual banning, alongside heightened environmental legislation. $^{206}$Pb/$^{207}$Pb isotope ratios decrease from 1.151 in ~1900 to minimum of 1.095 in 1973, at the height of the influence of petrol-derived Pb. The GT [Pb] date plot showed a similar chronological trend to FM. The [Pb] maximum corresponded to a date of 1959 ± 9.2, within the period when coal burning was at its maximum.
Figure 5.15  [Pb] (○) and 206Pb/207Pb ratio (●) plotted against layer date for FM, GT, ED and AM cores.

A [Pb] of 52 mg kg\(^{-1}\) in ~1983 decreased towards the current day until a concentration of 6.1 mg kg\(^{-1}\) corresponding to ~2003 in the vegetation section of the core, attributable to the post-2000 banning of leaded petrol. Plotting 206Pb/207Pb ratio against date does not highlight any new features in the isotope ratio profile of GT due to the narrow range of 206Pb/207Pb values (1.136-1.144) throughout the core. The ED core showed a decrease in [Pb] from 95.6 ± 0.1 mg kg\(^{-1}\) in the layers corresponding to ~1950-1970 to a contemporary minimum of ~26 mg kg\(^{-1}\). The 206Pb/207Pb fluctuates but demonstrates a small overall decrease in 206Pb/207Pb over time. The [Pb] in the AM core again decreased from ~118 mg kg\(^{-1}\) in the 1948 midpoint layer to ~41 mg kg\(^{-1}\) in ~2009 in the surface vegetation section. There was a concomitant change in 206Pb/207Pb ratio from 1.168 to 1.132. The most rapid 206Pb/207Pb ratio
decrease from 1.20-1.15 did, however, occur between the late 1960s and the late 1970s, a little later than the core’s [Pb] maximum.

All four sites exhibited reasonable agreement in [Pb] trends in relation to date although the rapid drop observed in AM’s [Pb] near the surface is unique amongst these plots. ED and AM, whilst both showing a [Pb] peak associated with coal burning and petrol emissions, demonstrated a less pronounced $^{206}$Pb/$^{207}$Pb minimum than observed at FM. However, AM and ED do show a decrease in $^{206}$Pb/$^{207}$Pb until ~1975-1985, beyond which $^{206}$Pb/$^{207}$Pb values remain approximately constant. The GT $^{206}$Pb/$^{207}$Pb in relation to date is different from the other sites; there is very little change in $^{206}$Pb/$^{207}$Pb ratio across the GT date plot. Notably, values of ~1.14 were observed for GT sections dating from before the introduction of leaded petrol. The approximately constant $^{206}$Pb/$^{207}$Pb at GT suggests that the historical $^{206}$Pb/$^{207}$Pb deposition signature has not been preserved at this site. It should be remembered that the GT [Pb] plot in relation to dates does generally agree with trends that would be predicted from the literature (e.g. Farmer et al., 1997b; MacKenzie et al., 1997; Cloy et al., 2005; 2008). Distortion of the $^{206}$Pb/$^{207}$Pb signature suggests that some Pb may be transported throughout the core or that the isotopic signature of Pb deposition incident on the site has become distorted through mixing or similar effects. Distortion of $^{206}$Pb/$^{207}$Pb could be explained by interception and mixing of Pb by the canopy (e.g. Lindberg et al., 1982) although this explanation seems unlikely as [Pb] profiles would also be notably impacted if such a process were occurring. Thus the most likely explanation for GT’s $^{206}$Pb/$^{207}$Pb profile is the selective transportation of a Pb throughout the core and this will be discussed in more detail in Section 5.5.5.2.
Peak Pb flux was greatest at FM (74.5 g m$^{-2}$ yr$^{-1}$ corresponding to ~1957) followed by GT (70.6 g m$^{-2}$ yr$^{-1}$ corresponding to ~1973), AM (36.5 g m$^{-2}$ yr$^{-1}$ corresponding to ~2002) and ED (29.0 g m$^{-2}$ yr$^{-1}$ corresponding to ~1960). Thus, with the exception of AM where maximum Pb flux was observed in 2002, the time period across which the maximum fluxes occurred was generally 1940-1980. Previous studies also had peak fluxes at FM and ED in close chronological agreement with those in this study. Farmer et al. (1997) and Cloy et al. (2005) reported peak fluxes at FM corresponding to the mid-1950s of ~60 g m$^{-2}$ yr$^{-1}$ and 21 g m$^{-2}$ yr$^{-1}$, respectively. MacKenzie et al. (1997) reported a peak flux at ED of 10.5 g m$^{-2}$ yr$^{-1}$ around 1965.

Overall, the cores across the four sites show broadly similar overarching trends in [Pb] and $^{206}$Pb/$^{207}$Pb in relation to depth. The magnitudes, ranges and degrees to
which historic maxima and minima are evident are, however, different from site-to-site when plotted against date. Additionally, the dates at which peak [Pb], peak Pb flux and $^{206}\text{Pb}/^{207}\text{Pb}$ maximum and minimum values occur can vary considerably. It is apparent that cores from sites in close geographical proximity cannot be assumed to be representative of each other. The vegetation layers and their different thicknesses (1-15 cm) from site-to-site appear to play a role in how these inter-site differences manifest.

**Influence of vegetation upon inter-site differences**

In general, the [Pb] in peatland and soil vegetation layers is typically lower than that of the underlying peat and soil material, although concentrations vary based upon species-specific considerations and a plant’s ability to uptake and accumulate Pb (e.g. Kovalevsky, 1987; Reimann et al., 2007; 2008). Moss species have been shown to intercept and uptake between 63% (Ceburnis et al., 1999) and 100% (Berg et al., 1999) of atmospheric Pb deposition, resulting in the vegetation layer playing a key role in the mechanisms through with Pb is incorporated into the underlying peat/soil where atmospheric deposition is the primary source of Pb. The [Pb] and the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the vegetation layers of each site in this study were not uniform and there was no common trend evident across all sites (Figure 5.11-5.14). With the exception of the AM core, the $^{210}\text{Pb}$ activity profiles (Figure 5.10) show decay with depth that is broadly in line with the constant deposition and decay of $^{210}\text{Pb}$, with much of the $^{210}\text{Pb}$ activity, and consequently the region of most rapid decrease in activity, occurring in the vegetation layers of the peat cores. The existence of this typically exponential $^{210}\text{Pb}$ activity decay trend within the vegetation demonstrates
that deposited $^{210}\text{Pb}$ is being retained by the vegetation surface. The progressively lower $^{210}\text{Pb}$ activities with depth imply that there is no additional input of $^{210}\text{Pb}$ to sub-surface layers.

**Influence of mixing processes upon AM**

The AM core profile showed a number of features that were not in accordance with the other cores in this study. AM’s vegetation layer showed the $^{210}\text{Pb}$ activity trend least consistent with exponential decay across the four sites with broadly constant $^{210}\text{Pb}$ activity in the uppermost 20 cm of the core. The peak $^{210}\text{Pb}$ activity at AM was also at 7 cm, in contrast to the surface layer $^{210}\text{Pb}$ activity maximums reported at the other sites. Furthermore, a peak Pb flux in the early 2000s at AM is unlikely to be true reflection of atmospheric deposition as the other study sites agree with literature assertions (Section 5.3.4) that peak Pb deposition across Scotland occurred around 1940-1980. Finally, the vegetation [Pb] of $\sim$100 mg kg$^{-1}$ from $\sim$7 cm depth to the vegetation/peat interface at 15 cm is considerably larger than the vegetation [Pb] reported at the FM, GT and ED sites. The differences observed in the AM core may be explained via comparison with the site characterisation data presented in Section 4.7.1.4. The depth at which the previously described perturbations in the $^{210}\text{Pb}$ activity and [Pb] profiles are apparent is generally in the 7-15 cm depth region within the core’s vegetation. The moisture content profile (Figure 4.19) suggests that the water table also typically rests at $\sim$5-10 cm depth. Furthermore there is a wide peak in [Fe] from 7-12 cm (centred on 10 cm depth; Figure 4.20). The combination of the [Fe] maximum in close proximity to the water table suggests that these depths are the redox boundary at which the Fe$^{II}$ is becoming oxidised to Fe$^{III}$ and removed from
solution onto the solid phase (Section 4.5.4). It is therefore conceivable that redox cycling of Fe is also transporting small amounts of Pb upwards through the core, resulting in the high vegetation [Pb] below the water table shouldering the [Pb] maximum and causing mixing of $^{210}$Pb. Such a mixing process would also account for the comparatively flat $^{206}$Pb/$^{207}$Pb profile in Section 5.5.1.5 as higher $^{206}$Pb/$^{207}$Pb value Pb is moved from deeper sections into the near-surface sections where $^{206}$Pb/$^{207}$Pb ratios are typically lower due to the influence of Australian Pb (e.g. Section 5.3.5.1 and Section 5.3.8). Despite the apparent transportation and mixing processes occurring at AM, at the FM and ED sites, where no such processes are evident, the preserved $^{210}$Pb profiles in addition to the good agreement between [Pb] profiles and other archival records (e.g. Shotyk, 1997; Farmer et al., 1997a; Shotyk et al., 2002; 2004, Weiss et al., 1999a; 1999b; MacKenzie et al., 1997a; 1998b) suggest that Pb is well-retained and generally immobilised in the cores’ vegetation and underlying peat layers.

5.5.2.3 Intra-site spatial variation analysis

As discussed in Section 5.5.2.2, cores taken from different geographic sites demonstrated some inter-site variations in Pb inventories, [Pb] profiles and $^{206}$Pb/$^{207}$Pb ratios. Cores at specific sites have to this point been assumed to be broadly representative of Pb deposition across their immediate locale. It is however important to assess the strength of this assumption. For a core to be representative of its immediate vicinity there must be no evidence that two cores taken short distances apart have significantly different [Pb] or $^{206}$Pb/$^{207}$Pb. In order to assess the validity of this assumption, Cuttle and Malcolm cores were taken at AM adjacent to, and at 20
m distances from, the central monolith coring site to the north, south, east and west, creating two perpendicular transects as shown in Figure 5.17. One transect ran 40 m from north to south with the other spanning 40 m from east to west. Both transects incorporate both the monolith core presented in Section 5.5.1.5 and a shared Cuttle and Malcolm core at their centre points. Results for the cores were examined for within-site spatial variation in [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ in the solid phase. Cuttle and Malcolm cores were utilised in preference to additional monolith cores due to the increased ease and speed of coring and on-site processing when compared to the monolith method.

**Comparison of the central monolith and Cuttle & Malcolm cores**

The two directly adjacent central cores of the transect, the monolith core and CM1, are compared in Figure 5.18. The vegetation layer of CM1 comprised the uppermost ~13 cm of the core, apparently compacted in contrast to the 15-16 cm thick
vegetation layer previously reported for the adjacent monolith core. In the solid phase, [Pb] profile trends are similar between cores. Lead concentrations increased with increasing depth from the surface until a narrow region of high [Pb] towards the middle of the cores from where concentrations decreased with increasing depth. The [Pb] peaks in each core are comparable at 177 mg kg\(^{-1}\) and 211 mg kg\(^{-1}\) for the monolith and CM core, respectively. The slightly greater [Pb] in the CM core is most likely attributable the greater compaction from the CM corer resulting in a narrower depth range across which the Pb peak occurs when compared with the monolith. The depths at which peak [Pb] occurs are offset by \(\sim4\) cm with the CM peak occurring nearer to the surface than the monolith core. The Pb peak offset is once again attributed to compaction of the surface vegetation and low density peat layers by the CM corer during sampling, therefore reducing the apparent thickness of surface and near-surface layers by \(\sim3-4\) cm. The CM1 core also showed a near-surface [Pb] profile shoulder at \(\sim5-10\) cm depth, a feature observed in the monolith core from \(\sim5-15\) cm. In the monolith core, this feature was attributed to the transport of Pb due to the influences of redox cycling of Fe (Section 5.5.2.2), suggesting that a similar process is also occurring in the adjacent CM core. The influence of these cycling processes appears less pronounced in the CM core as the [Pb] of the CM profile’s shoulder is 55-85 mg kg\(^{-1}\), lower than \(\sim100\) mg kg\(^{-1}\) in the monolith core.

The two central cores appear to show considerable differences in their \(^{206}\text{Pb}/^{207}\text{Pb}\) profiles at first assessment, although on closer examination, the monolith and CM1 \(^{206}\text{Pb}/^{207}\text{Pb}\) profiles are remarkably similar. The minima in \(^{206}\text{Pb}/^{207}\text{Pb}\) are almost identical (monolith \(^{206}\text{Pb}/^{207}\text{Pb}\)\(_{\text{MIN}}\): 1.132; CM \(^{206}\text{Pb}/^{207}\text{Pb}\)\(_{\text{MIN}}\): 1.134) although the
maximum $^{206}\text{Pb}/^{207}\text{Pb}$ value (monolith $^{206}\text{Pb}/^{207}\text{Pb}_{\text{MAX}}$: 1.203; CM $^{206}\text{Pb}/^{207}\text{Pb}_{\text{MAX}}$: 1.173), and therefore the range of $^{206}\text{Pb}/^{207}\text{Pb}$ in each core are quite different.

![Figure 5.18](image)

Figure 5.18 Comparison of AM monolith core (left) and central Cuttle and Malcolm core (right) solid phase [Pb] (top) and $^{206}\text{Pb}/^{207}\text{Pb}$ (bottom) profiles.

However, if the extra depth of the monolith core over the CM core (the 37-47 cm section) is removed from consideration, the maximum $^{206}\text{Pb}/^{207}\text{Pb}$ values are similar (monolith $^{206}\text{Pb}/^{207}\text{Pb}_{\text{MAX}}$: 1.180; CM $^{206}\text{Pb}/^{207}\text{Pb}_{\text{MAX}}$: 1.173). Both profiles also showed similar $^{206}\text{Pb}/^{207}\text{Pb}$ profile shapes although the monolith core’s features are
flatter and less pronounced. The flatter $^{206}\text{Pb}/^{207}\text{Pb}$ profile of the monolith was previously attributed to the redox cycling of Fe (Section 5.5.2.2). The apparently smaller influence of these Fe-cycling processes upon the CM core’s [Pb] profile would also account for the smaller degree of flattening apparent in the CM $^{206}\text{Pb}/^{207}\text{Pb}$ profile.

**Spatial variation analysis of north-south and east-west transects**

[Pb] profiles and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles for the five Cuttle and Malcolm cores are provided in Figure 5.19. Inventory and key feature comparison data is presented in Table 5.6. Two key features of the cores at AM are the solid phase peak in [Pb] attributed to peak coal burning and petrol consumption ~1955 and the rapid decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ that occurred alongside the use of Australian Pb in UK petrol additives around the 1930s. On the assumption that these profile features each represent layers corresponding to approximately equivalent dates, core inventories to the depths of these profile features, the magnitude of the coal and petrol-sourced [Pb] peak, the minimum $^{206}\text{Pb}/^{207}\text{Pb}$ value, and the current surface $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio will be compared as measures of intra-site variability. Inventories to 30 cm and the $^{206}\text{Pb}/^{207}\text{Pb}$ shift point will also be adopted as a comparison measure as 30 cm represents the deepest sampling point shared by all cores. The $^{206}\text{Pb}/^{207}\text{Pb}$ shift point represents the layer in which the historical sloping decrease in $^{206}\text{Pb}/^{207}\text{Pb}$ begins and this point is also assumed to be a common chronological marker across each core. Vegetation inventories are included to allow comparison with similar data from the literature discussed later in this section. The shoulder feature in the 5-10 cm regions of [Pb] profiles caused by the influence of Fe redox-cycling at CM1, CM4 and to a
lesser extent CM2 and CM3 will not greatly compromise the use of the selected features as points of comparison. The zone affected by redox-related processes occurs above each core’s [Pb] maximum, but below the surface layer and therefore should not greatly perturb the [Pb] maximum point, or distort the surface $^{206}$Pb/$^{207}$Pb in any way. In regard to inventories as comparison measures, although some Pb may be mobilised throughout the core, Pb is unlikely to be completely removed from the system to a great extend due to Pb’s high affinity for solid phase matter (Section 5.3.2 and Section 5.3.3).

The [Pb] profiles and $^{206}$Pb/$^{207}$Pb profiles exhibit remarkable similarity in trends with all five cores exhibiting a [Pb] maximum within the uppermost 25 cm for both solid and aqueous phase, and each ratio profile showing the characteristic point of inflection associated with the rise and fall of leaded petrol discussed previously within this chapter. Key profiles features are, however, offset by as much as 6 cm. For example, the ~1955 coal burning peak midpoint lies at ~11 cm for CM4 but at ~17 cm for CM3. The statistical signifigance of core key features from north → south and east → west, and subsequently the statistical signifigance of core position in the transects, were assessed statistically via one-way ANOVA tests, where $H_0$ represents non-variant means and $H_1$ variation due to position. Variability assessment measures include magnitudes of variation alongside ANOVA fitting to north → south and east → west transects.
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

CM1 | CM2 | CM3 | CM4 | CM5
--- | --- | --- | --- | ---

**Figure 5.19** Solid phase [Pb] and $^{206}$Pb/$^{207}$Pb profiles across five comparison cores in AM with across two transects CM1 (central), CM2 (N), CM3 (W), CM4 (S), CM5 (E).
Table 5.6  Comparison of key features of Auchencorth spatial variability cores and accompanying ANOVA analysis data for N→S and E→W transects

<table>
<thead>
<tr>
<th>Core identifier</th>
<th>Location</th>
<th>Solid [Pb] maximum (mg kg⁻¹)</th>
<th>²⁰⁶Pb/²⁰⁷Pb minimum</th>
<th>²⁰⁶Pb/²⁰⁷Pb surface</th>
<th>Inventory to 30 cm (g m⁻²)</th>
<th>Inventory to bottom of ²⁰⁶Pb/²⁰⁷Pb slope region (g m⁻²)</th>
<th>Inventory to coal burning [Pb] peak (g m⁻²)</th>
<th>Vegetation inventory (g m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM1</td>
<td>Central</td>
<td>211</td>
<td>1.134</td>
<td>1.154</td>
<td>2.74</td>
<td>1.80</td>
<td>0.957</td>
<td>0.760</td>
</tr>
<tr>
<td>CM2</td>
<td>North</td>
<td>173</td>
<td>1.135</td>
<td>1.159</td>
<td>2.46</td>
<td>1.35</td>
<td>0.731</td>
<td>0.560</td>
</tr>
<tr>
<td>CM3</td>
<td>West</td>
<td>115</td>
<td>1.138</td>
<td>1.158</td>
<td>2.81</td>
<td>1.27</td>
<td>0.909</td>
<td>0.544</td>
</tr>
<tr>
<td>CM4</td>
<td>South</td>
<td>157</td>
<td>1.152</td>
<td>1.157</td>
<td>2.84</td>
<td>2.49</td>
<td>0.979</td>
<td>0.310</td>
</tr>
<tr>
<td>CM5</td>
<td>East</td>
<td>131</td>
<td>1.130</td>
<td>1.160</td>
<td>3.03</td>
<td>2.35</td>
<td>0.777</td>
<td>0.491</td>
</tr>
<tr>
<td>Monolith</td>
<td>Central</td>
<td>177</td>
<td>1.132</td>
<td>1.145</td>
<td>2.07</td>
<td>1.84</td>
<td>1.120</td>
<td>0.590</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>160</td>
<td>1.137</td>
<td>1.156</td>
<td>2.657</td>
<td>1.85</td>
<td>0.912</td>
<td>0.543</td>
</tr>
<tr>
<td>Magnitude of variation</td>
<td>1.83</td>
<td>1.17*</td>
<td>1.10*</td>
<td>1.46</td>
<td>1.96</td>
<td>1.53</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>N→S p-value</td>
<td></td>
<td>0.712</td>
<td>0.250</td>
<td>0.868</td>
<td>0.556</td>
<td>0.008</td>
<td>0.370</td>
<td>0.500</td>
</tr>
<tr>
<td>E→W p-value</td>
<td></td>
<td>0.851</td>
<td>0.044</td>
<td>0.877</td>
<td>0.783</td>
<td>0.001</td>
<td>0.620</td>
<td>0.814</td>
</tr>
</tbody>
</table>

*Magnitude of variation calculated from decimal places alone as only these values change or are of significance within this context
The magnitude of variation is a unitless measure that expresses the magnitude of difference between the lowest and highest values in a data set, allowing comparison in the variability sets of data that may possess different units. Variation across the AM site is remarkably low with magnitudes of variation across [Pb], $^{206}\text{Pb}/^{207}\text{Pb}$ and inventory features of ~1.1-2.5. These results are in good agreement with similar spatial variation studies in literature (Bindler et al., 2004; Farmer et al., 2005; Rothwell et al., 2007) that report ~1.5-4.0 fold variation between intra-site cores with respect to maximum [Pb] and core inventories. Rothwell et al’s 2007 study examined 450 m transects in the Peak District of the UK and took paired cores every 50 m along the transect. Cores were taken using a Russian type corer, equivalent in principle to the Cuttle and Malcolm corers used at AM. The Peak District transects demonstrated 2-fold differences in inventories to 30 cm. The study concluded that 15 cores from a given region were required to provide an accurate mean inventory. Bindler et al. (2004) reported ~2-fold variation in the magnitude of [Pb] maximums and ~3-fold variations in core Pb inventories. The study of Farmer et al. (2005) demonstrated ~1.5-4 fold variation in inventories in peaty soil cores sampled approximately 100 m apart from Thorter hill, Glensaugh in Scotland (Table 5.7). Generally good agreement was found in the inventories of 5 cores measured to 10 cm (1.8-fold variation), the greatest depth of detectable anthropogenic Pb (1.5-fold variation), and to the bottom of each core (1.5-fold variation). Cores taken from similar altitudes demonstrated good agreement in inventories, although higher altitude cores exhibited larger inventories than those at lower altitudes. However, Farmer et al. (2005) reported higher variability in vegetation inventories (~4-fold variation), and inventories measured to the start of the $^{206}\text{Pb}/^{207}\text{Pb}$ shift (~4-fold) than
the variation in comparable inventories in this study (2.5- and 2-fold, respectively). It should also be noted that the profiles of Farmer et al. (2005) demonstrated broad similarities in profile shape and overall trend.

The somewhat higher variability observed in some of these literature studies is likely attributable to the differences in distances involved between sampling instances. The closer proximity (20 m apart) of the AM cores relative to those taken in the Peak District (50 m apart; Rothwell et al., 2007) and Glensaugh (100 m apart; Farmer et al., 2005) provides a shorter distance across which ambient conditions, topography and chemical conditions can change between cores. Hydrology, underlying geology, surface vegetation and surface microtopography are more likely to change across increasing distances, accounting for the higher variation between distant cores in comparison with those sampled in closer proximity.
One-way ANOVA testing does not demonstrate any significant influence of transect compass position upon most of the key characteristics of these cores. The mean p-value of all [Pb], $^{206}$Pb/$^{207}$Pb and inventory directional trend analyses falls at 0.518, suggesting that there is not a statistically significant influence of compass position within the transect upon Pb distribution at AM. However, on first assessment, ANOVA analysis does suggest that $^{206}$Pb/$^{207}$Pb minimum values are influenced by its E→W position ($p$-value E→W:0.044) and that Pb inventories to the bottom of the $^{206}$Pb/$^{207}$Pb slope region are affected by their positioning within the transect ($p$-value N→S: 0.008; E→W: 0.001). The explanation for these apparently significant trends lies once again in the Fe redox-cycling processes occurring within the AM site. The $^{206}$Pb/$^{207}$Pb minimum value will become distorted to different degrees depending upon the severity of these cycling processes. It should also be highlighted that the magnitude of variation within the $^{206}$Pb/$^{207}$Pb minimum measurement is very low across the E→W transect (1.06). In regards to the apparently significant influence of transect position upon Pb inventory trends, it should be remembered that the inventory to the $^{206}$Pb/$^{207}$Pb shift point will encompass the depth region of the profiles in which [Pb] has become inflated due to Fe-cycling and Pb migration. Each core appears to have been impacted to a different degree by these redox processes as different thicknesses and magnitudes of [Pb] profile peak shoulder features are apparent in the 5-10 cm region of the profiles (Figure 5.19). Inventories to 30 cm are not significantly different from core-to-core as previously shown in Table 5.6. The core with the greatest inventory to its $^{206}$Pb/$^{207}$Pb shift point (CM4: 2.49 g m$^{-2}$) is not the core with the greatest inventory to 30 cm (CM5: 3.03 g m$^{-2}$) suggesting, for example, that transportation of Pb into surface layers is artificially inflating the
inventory to the $^{206}\text{Pb}^{207}\text{Pb}$ shift point at CM4. Compass position within the AM transects appears to impart different levels of Pb transportation due to redox-cycling which distorts measurements that rely heavily upon the Fe redox zone of the core and results in their comparison being an unreliable measurement of spatial variability.

**Corer-derived offset of Pb profiles**

As discussed earlier in this Section, the Cuttle & Malcolm coring methods adopted in this spatial variation study can cause compaction of the vegetation and upper peat layers of the cores. Variable compaction in each core due to the human role in the sampling process, in addition to the minor topographical differences in vegetation thickness across the surface of the bog, may have resulted in a small offset in the depths at which historical peaks in [Pb] and $^{206}\text{Pb}^{207}\text{Pb}$ are apparent in each profile. If this offset can be satisfactorily accounted for, the apparent variation between CM cores may be reduced. To investigate this effect, the profiles presented in Figure 5.19 were adjusted in a similar manner to the offset profiles of Farmer *et al.*, (2006). In the absence of layer dates for the CM cores, the depths of the $^{206}\text{Pb}^{207}\text{Pb}$ shift points, adopted previously in this section for inventory calculations, were aligned as they were assumed to represent the same period of time. These adjustments resulted in downward offsets of 2 cm, 2 cm, 0 cm, 2 cm and 4 cm for CM1, CM2, CM3, CM4 and CM5, respectively. Offset graphs are presented in Figure 5.20.
Offset adjustment demonstrates that the shapes and profile features of CM1, CM2 and CM3; and CM4 and CM5, are very similar. From the base of the core upwards, the increase in [Pb] starts in all cores at ~30 cm with a [Pb] peak at ~18 cm shared by all cores. Similarly, CM1-3 showed remarkable agreement in their $^{206}\text{Pb}/^{207}\text{Pb}$ profiles across the entire core when the offset is in effect, with the low $^{206}\text{Pb}/^{207}\text{Pb}$ region from 5-15 cm shared by all three cores in both shape and magnitude. The highest variations in profile shape between offset cores occurs in the near-surface core sections. This observation is in agreement with the main inter-site variations.
observed primarily reported in the near-surface core sections between the cores in this study (Section 5.5.2.2) and when this study’s cores are compared with the literature (Section 5.5.2.1). In this particular case, the differences in profiles observed in the upper core sections may also stem from the Fe-cycling related transportation of Pb and, in particular, the influence this has upon the 5-10 cm section of the cores where the most pronounced differences in profile shape are apparent. The maximum profile offset of 4 cm is representative of two CM core layers. Such an offset is not excessive considering the compaction potential of the surface ~15 cm of vegetation present in the monolith core (e.g. Section 5.5.1.5). The influence of CM coring practices upon these cores highlights the importance of consistent coring methodology in order to preserve historical records. However, once accounted for, the remarkable agreement between these offset cores clearly shows that the Pb depositional record is both similar and well preserved across the entire AM transect despite the influence Fe redox-cycling processes upon some of the profiles.

**Key results from the intra-site variation study**

Intra-site variation recorded at AM (~1.1-2.5 fold variation) is slightly lower than ~1.5-4-fold variation reported by similar studies in the literature (Bindler et al., 2004; Farmer et al., 2005; Rothwell et al., 2007). The agreement between this study’s AM cores, in combination with the remarkable agreement between literature and the FM and ED cores in this study discussed previously in Section 5.5.2.1, provides a degree of reassurance that cores taken in close proximity are indeed indicative of their surrounding area. Given the span of the AM transects, the project can only conclude that singular cores are approximately representative of a circular area of radius 20 m
where the singular core forms the centre point and no obvious topographical changes occur within the area of the circle. Such a circular area will encompass 1257 m$^2$. The significance of this area will obviously vary dependant on the total area of a given sampling site. In the context of AM however, the bog itself possesses a surface area over an order of magnitude greater than this. A larger number of cores would require to be taken across a greater area of the bog to assess reproducibility over a larger area or to provide accurate inventories for the entire location, as per the indication of Rothwell et al. (2007).

However, this intra-site study has highlighted several other important results. Core compaction due to choice of coring techniques and resulting offsets caused by coring methodology must be considered. Corers that require downward pressure in order to penetrate the soil and collect the core are particularly vulnerable to these compaction effects. Only if these offsets are adequately accounted for can core-derived Pb records be correctly interpreted. Furthermore, the AM cores have demonstrated varying degrees of perturbation in their [Pb], $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{210}\text{Pb}$ profiles (Section 5.5.2.2) linked to the redox-cycling of Fe. The severity of these perturbations varies considerably on an intra-site level although it should be noted that below the depths around the water table where Fe is oxidised, core features are generally comparable once corer-related offsets have been taken into account. Cores which show little-to-no perturbation due to Fe-cycling also show comparable features at an inter-site level. For example, CM5, which showed the least influence of redox-related Pb transport, demonstrated a more pronounced minimum in $^{206}\text{Pb}/^{207}\text{Pb}$ than any of its counterparts, a feature profile feature also observed at FM where no Fe-related
perturbation is apparent. Having now individually assessed the degrees of inter- and intra-site variability between Pb profiles, the two types of variability themselves can be compared.

### 5.5.2.4 Intra-site variability compared to inter-site variability

The magnitudes of variation employed in Section 5.5.2.3 were applied to the inter-site and intra-site variation measures common to both Section 5.5.2.2 and Section 5.5.2.3 to allow comparison of the variation in data sets from the AM intra-site analysis and the overall inter-site analysis. Inter-site variations are calculated from the extreme values within each data set. This comparison is presented in Table 5.8.

<table>
<thead>
<tr>
<th></th>
<th>Inter-site variation</th>
<th>Intra-site variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pb] maximum</td>
<td>2.95</td>
<td>1.83</td>
</tr>
<tr>
<td>$^{206}$Pb/$^{207}$Pb minimum*</td>
<td>1.55</td>
<td>1.17</td>
</tr>
<tr>
<td>$^{206}$Pb/$^{207}$Pb at surface*</td>
<td>1.14</td>
<td>1.10</td>
</tr>
<tr>
<td>Pb inventory to depth**</td>
<td>2.88</td>
<td>2.45</td>
</tr>
<tr>
<td>Mean Variation</td>
<td>2.13</td>
<td>1.63</td>
</tr>
</tbody>
</table>

*Magnitude of variation calculated from decimal places alone as only these values change or are of significance within this context

**Determined by maximum shared core depths: 20 cm for inter-site variation, 30 cm for intra-site variation

Mean inter-site variation is 2.13, higher than the mean intra-site variation of 1.63. The inter-site magnitudes of variation are greater for [Pb] maximum, $^{206}$Pb/$^{207}$Pb minimum, surface $^{206}$Pb/$^{207}$Pb and Pb inventory to depth than those shown for the intra-site values. The level of variation in $^{206}$Pb/$^{207}$Pb values is broadly equivalent on
both an inter- and intra-site level. The comparatively greater variation between different sites when compared to within-site variation is in agreement with data in the literature. Despite the apparently large range of inventories and [Pb] maximum values across the localised transects reported by Rothwell et al. (2007), an assessment of inter-site variability in maximum [Pb] and Pb inventories (Table 5.9) throughout literature highlights far greater variability than observed on an intra-site in the studies of Novak et al. (2003); Bindler et al. (2004); Farmer et al. (2005); Rothwell et al. (2007); and Cloy et al. (2008). The literature comparisons demonstrate a 71-fold magnitude of variation between the smallest and largest [Pb] maxima and 8.8-fold differences between the smallest and largest Pb inventories to 100 cm depths.

### Table 5.9

<table>
<thead>
<tr>
<th>Location</th>
<th>Maximum Pb concentration (mg kg⁻¹)</th>
<th>Site description</th>
<th>Sampling depth (cm)</th>
<th>Pb inventory (g m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenska, Scania, forest-tundra zone, Russia</td>
<td>1650</td>
<td>Past</td>
<td>80</td>
<td>21.00 ± 5.63</td>
</tr>
<tr>
<td>Gota d’Iago, Switzerland</td>
<td>1528</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ringsburg Bog, Peak District, England</td>
<td>1230</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parissow Fell, Forest of Bowland, England</td>
<td>845</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tinsley Park Bog, Lower Don Valley, England</td>
<td>827</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gassington Moor, North Yorkshire, England</td>
<td>800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ringinglow Bog, Peak District, England</td>
<td>700</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Snake Pass, Peak District, England</td>
<td>570</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ringinglow Bog, Peak District, England</td>
<td>548</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kola Peninsula, Russian Arctic</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thores Hill, Grampian Highlands, Scotland</td>
<td>489</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bolf Dar, Czech Republic</td>
<td>479</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lochmuir, Scotland</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yetholm Valley, Cardiganshire, Wales</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmoor Bog, Morpeth, Britain</td>
<td>230</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haydavila, South Wales</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rouyn-Noranda, Quebec, Canada</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Miramar, Faroe Islands</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ovejero Valley, Andean Royal Belt, Bolivia</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adapted from Rothwell et al. (2007)
5.5.3 Aqueous phase [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the upper sections of cores from FM, GT, ED and AM

5.5.3.1 Flanders Moss (0-30 cm)

![Figure 5.21](image)

Figure 5.21 [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ aqueous profiles for FM. Dashed line represents vegetation/peat interface.

The FM aqueous [Pb] profile (Figure 5.21) shows an approximately constant [Pb] in the uppermost layer of the core of ~1.5 µg l$^{-1}$. Below 10.5 cm, porewater [Pb] increased until it reached a maximum value of ~97 µg l$^{-1}$ at 19.5 cm. Although there was considerable variability between adjacent layers, the porewater [Pb] remained at ~60-70 µg l$^{-1}$ over the depth range 15-25 cm. Continuing deeper down the profile, concentrations decreased to ~4 µg l$^{-1}$ at 29.5 cm. The aqueous phase $^{206}\text{Pb}/^{207}\text{Pb}$ ratios increased with depth within in the vegetation layers from 1.137 in the uppermost layer to 1.180 at a depth of 8.5 cm. From 8.5 cm the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio decreases until a midpoint of 1.083 at 16.5 cm from where it increased to a value of ~1.18 at 22.5 cm before decreasing to 1.17 at the base of the profile.
5.5.3.2 Glentress Forest (0-30 cm)

The GT [Pb] profile (Figure 5.22) exhibits a general decrease in concentration from 27.8 µg l$^{-1}$ in the surface vegetation layer down to 6.838 µg l$^{-1}$ at the base of the core. The profile shows no distinct peak maxima or concentration minima distinct from the overall trend of decreasing concentration. The aqueous phase $^{206}\text{Pb} / ^{207}\text{Pb}$ profile is not available for GT.
ED’s aqueous phase [Pb] profile (Figure 5.23) shows a consistent concentration of ~20 µg l⁻¹ throughout the core’s vegetation layers, continuing until 13.5 cm into the peat itself. Below 13.5 cm, aqueous [Pb] increases to 78.53 µg l⁻¹ at 22.5 cm before decreasing further into to core to a value of 18.77 µg l⁻¹ at 28.5 cm. The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio profile is not available for the ED aqueous phase.
5.5.3.4  Auchencorth Moss (0-45 cm)

Figure 5.24  [Pb] and $^{206}$Pb/$^{207}$Pb aqueous profiles for Auchencorth Moss. Dashed line represents vegetation/peat interface.

The AM aqueous [Pb] profile demonstrates (Figure 5.24) a narrow range of concentrations down the entire profile. Concentrations decrease from the surface value of 23.7 $\mu$g l$^{-1}$ to 3.3 $\mu$g l$^{-1}$ at 4.5 cm. Deeper into the vegetation layer, concentrations again increase to a concentration peak of 35.95 $\mu$g l$^{-1}$ at 10.5 cm before decreasing into the peat layer to a concentration of 5.81 $\mu$g l$^{-1}$ at 28.5 cm. From 28.5 cm, [Pb] is approximately constant to the base of the core. The aqueous $^{206}$Pb/$^{207}$Pb profile exhibits a decrease from the surface layer value of 1.17 to 1.14 at 5.5 cm depth. Below 5.5 cm, the $^{206}$Pb/$^{207}$Pb ratio gradually increases with depth to a value of 1.167 at 32.5 cm.
5.5.4 Discussion of aqueous phase [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ profiles

5.5.4.1 Comparison of aqueous and solid phase Pb profiles

The aqueous-phase [Pb] profiles for peat/soil porewater are presented in Figure 5.25, alongside their solid phase counterparts for ease of comparison. Peak porewater [Pb] was 97 µg l$^{-1}$ at 19-20 cm for FM, 28 µg l$^{-1}$ in the 0-1 cm section at GT, 79 µg l$^{-1}$ at 22-24 cm for ED and 36 µg l$^{-1}$ at 20-22 cm for AM.

Overall, the majority of Pb in the uppermost layers of peat and soil systems is sequestered by the solid phase with only comparatively small concentrations of Pb (<100 µg l$^{-1}$) present in the aqueous phase. The FM and ED porewater profiles show broad agreement between their solid phase and aqueous phase [Pb]. At FM, maximum [Pb] in both phases occurred in the 19-20 cm region with the wide band of high [Pb] occurring between 15 cm and 30 cm depth in each case. In the uppermost 0-15 cm vegetation layers, concentrations in both phases of FM were approximately constant with the porewater [Pb] not exceeding 2.5 µg l$^{-1}$. For ED, the broad peak in the solid phase [Pb] profile at 17-23 cm depth is matched by a similarly broad but more pronounced concentration peak in the aqueous phase. The maximum value of 79 µg l$^{-1}$ occurred at ~23 cm but elevated porewater concentrations of 44-55 µg l$^{-1}$ were observed across the 17-23 cm region; [Pb] of ~20 µg l$^{-1}$ was measured in the porewaters of all the other layers of the core.
In contrast with the two sites described above, the solid phase and porewater [Pb] profiles for the GT did not exhibit close agreement between its solid and aqueous phase. The GT porewater profile showed only a gradual decrease in [Pb] from 27 ± 6 µg l\(^{-1}\) at the surface to 7 ± 1 µg l\(^{-1}\) at 18.5 cm in contrast to the overall [Pb] increase in the solid phase. At the depths of GT’s two peaks in solid phase [Pb], two of the lowest porewater [Pb] in the core are observed, 11 ± 3 µg l\(^{-1}\) and 9 ± 1 µg l\(^{-1}\).
porewater profile for AM showed a similar overarching trend to its solid phase counterpart although [Pb] peaks seldom occur at identical depths in both profiles. The porewater [Pb] maximum at ~10 cm occurs 3-4 cm above the solid phase [Pb] maximum and furthermore, occurs in the region of the core where Fe-cycling processes have been implicated in perturbing the solid phase [Pb] profile. It is conceivable that the region of high porewater [Pb] above this maximum is the result of transportation of Pb from deeper core sections and its subsequent removal from the aqueous phase back into the solid phase results in the Pb shoulder feature ~5-10 cm in the solid phase profile.

The porewater and solid phase $^{206}\text{Pb}/^{207}\text{Pb}$ ratio profiles for the FM and AM cores are presented side-by-side in Figure 5.26. Porewater $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio profiles are not available for the GT and ED cores. The $^{206}\text{Pb}/^{207}\text{Pb}$ profiles for FM both exhibit similar trends although the porewater profile had more pronounced features, as a consequence of the greater range of isotope ratio values. However, the profiles for both had maximum $^{206}\text{Pb}/^{207}\text{Pb}$ ratio values at ~25 cm depth and minimum values at 15-17 cm. The minimum $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the porewater was 1.083 ± 0.001, lower than the solid phase minimum of 1.095 ± 0.002. There was a larger discrepancy between the maximum ratio values with 1.196 ± 0.005 measured in the porewaters compared to the solid phase maximum of 1.161 ± 0.003.
At AM, there was good agreement between the solid and porewater $^{206}\text{Pb}/^{207}\text{Pb}$ profiles at depths of 20-35 cm where values increased from $\sim1.16$ to $\sim1.18$ with increasing depth. However, in the uppermost 20 cm of the core, the porewater ratios are considerably greater in value than those for the solid phase. This difference is most pronounced in the near-surface layers where the porewater possesses a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of $1.170 \pm 0.003$ in contrast with a value $1.127 \pm 0.003$ in the solid
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The difference in ratios between phases decreases as depth from the surface increases until the 20 cm point where the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the two phases converge. The range of porewater $^{206}\text{Pb}/^{207}\text{Pb}$ values was also reduced (1.140 ± 0.004 to 1.179 ± 0.002) in comparison to the solid phase range of 1.153 ± 0.022 to 1.243 ± 0.016.

Where porewater $^{206}\text{Pb}/^{207}\text{Pb}$ profiles exist in this study, porewaters in the uppermost layers of the FM and AM cores have greater $^{206}\text{Pb}/^{207}\text{Pb}$ ratios than the solid phase matter at the same depth. This may indicate a time lag between deposition via rainwater and adoption by the solid phase. The largest surface $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of either phase is present in the aqueous phase of AM, 1.170 ± 0.003. Otherwise when contemporary Pb inputs are considered, the surface $^{206}\text{Pb}/^{207}\text{Pb}$ value of 1.137 in the aqueous phase of FM is in agreement with recent publications that report $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for deposition in Scotland. Rainwater from 1998 possessed a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of ~1.140 (Farmer et al., 2000). Farmer et al. (2010) reported a more recent $^{206}\text{Pb}/^{207}\text{Pb}$ values for 2007 rainwater of 1.111-1.182, the upper limits of which closely approximates the surface AM aqueous phase $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and implying that the $^{206}\text{Pb}/^{207}\text{Pb}$ of current rainwater has not changed considerably since that study was performed.

The GT aqueous profile is remarkably different from its solid phase counterpart. The aqueous concentration peak of 27.8 µg l⁻¹ occurs at the surface as opposed to the solid phase maximum around 8 cm depth. It should, however, be highlighted that the
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Porewater [Pb] in the forest site is, on average, lower than the peatland peaks despite the solid phase [Pb] being equivalent to that at AM, and in excess of that at ED. Similarly to the GT profile, the AM solid and aqueous phase [Pb] peaks occur 9 cm apart, with the solid phase peak at 19.5 cm and the porewater peak at 10.5 cm. The aqueous phase profile at AM does not reflect atmospheric deposition history. The uppermost 25 cm of AM’s aqueous phase also exhibits $^{206}\text{Pb}/^{207}\text{Pb}$ ratios considerably different to those in the solid phase although both profiles are also flat with no distinct peaks. These differences between phases at GT and AM are again likely attributed to Fe redox processes causing transportation and mixing of Pb via the aqueous phase. The higher porewater $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in the near-surface sections in comparison to the solid phase will result in a gradual increase and overall contraction of solid phase $^{206}\text{Pb}/^{207}\text{Pb}$ in the profile section (layers corresponding to ~1925-2000) where low ratio petrol-derived Australian Pb would be presumed to have the most influence (c.f. Cloy et al., 2005; 2008; MacKenzie et al., 1997; Section 5.5.2; etc).

Overall the AM and GT sites are quite different in their composition by virtue of one being a forest soil and the other being an ombrotrophic bog and so share few characteristics that would account for the perturbation of their [Pb] profiles by Fe-cycling that are not also shared by the FM and ED sites. Conductivity, pH and organic percentage (Section 4.7.1) are all unremarkable in relation to the [Pb] profiles with GT and AM exhibiting no apparent comparable features that are not shared by the other sites. One notable feature that GT and AM do share is their high [Fe] in the solid phase (Table 4.3). As a forest soil, GT would be assumed to possess...
a high [Fe] due to its mineral rich nature; its [Fe] peak of 1.6% w/w agrees with this assumption. The high concentration of Fe at AM, over 2.0% w/w in some layers, is unusual considering it contains only ~5-10% mineral content (Figure 4.19) across the majority of the core. Comparatively, the maximum ED solid phase [Fe] is 0.34% w/w and, while no data from FM exists in this study, Farmer et al., (2006) reported a [Fe] maximum at FM of 0.2-0.3% w/w. The hypothesis that Fe may be influencing the interactions between Pb and solid phase matter within GT and AM requires further investigation as it appears to agree with the implications of Schroth et al. (2008) highlighted in Section 5.4 that Fe plays a controlling role in Pb association within some terrestrial systems. Although peatlands with [Fe] comparable to forest environments will be uncommon, it is also conceivable that peatlands with high [Fe] will experience similar degrees of Fe-cycling.

5.5.4.2 Comparison of AM transect porewater [Pb] profiles

Porewater [Pb] profiles for the AM monolith core and five Cuttle and Malcolm cores used previously for spatial variation analysis in Section 5.5.2.3 are provided in Figure 5.27. Porewaters were extracted as per the methodology in Section 2.3.1 and analysed via ICP-MS (Section 2.3.17).
Figure 5.27 Aqueous phase [Pb] profiles across six comparison cores in AM with across two transects monolith (central); CM1(central), CM2(N), CM3(W), CM4(S), CM5(E).
The aqueous phase [Pb] profiles each demonstrate a region of high [Pb] (monolith: 10.5; CM1: 17 cm; CM2: 23 cm; CM3: 19 cm; CM4: 17 cm CM5: 13 cm), with some cores possessing secondary [Pb] peaks within 10 cm depth of their [Pb] maximum (monolith: 5.5-8.5 cm; CM2: 15-17 cm, CM3: 23 cm; CM4: 23 cm). The magnitude of each cores’ [Pb] maximums are 24.5-44.4 µg l⁻¹. It is notable that the aqueous phase porewater [Pb] peaks do not all occur at depths that correspond to a solid phase [Pb] peak. For example, CM3’s solid phase [Pb] maximum occurs in the 5-15 cm region (Figure 5.19) whereas its porewater [Pb] peaks occur at 19 cm and 23 cm. The lack of agreement between porewater and solid phase profiles is further suggestive of the mobilisation of solid phase [Pb] via Fe-cycling processes. In some cores the Pb appears to be mobilised at depths below the solid phase [Pb] maximum (c.f. CM3 and CM4) and removed nearer the surface in the 5-10 cm region where porewater [Pb] becomes low and the solid phase ‘Pb shoulder’ discussed in Section 5.5.2.2 is visible in the solid phase profile. The variation in porewater [Pb] profile shapes is likely due to the variations in the degree to which Fe-cycling is mobilising Pb into the aqueous phase. Section 5.5.2.3 has already established that this process is occurring to different degrees across the AM site.

This Section and Sections 5.5.2.2, 5.5.2.3, 5.5.3.5 have all highlighted the possible influence of Fe-redox cycling upon Pb profiles and mobilisation of Pb via the aqueous phase. In order to investigate these processes further, and in order to resolve the traditional organic-Pb association approach alongside the hypothesised Pb-Fe interactions, the specific associations of Pb in peat and soil environments requires further investigation.
5.5.5 Characterisation of Pb associations

5.5.5.1 Pb associations with solid phase humic matter

The literature discussed previously in Section 5.3 and Section 5.4 in addition to the results of this study presented in Section 5.5.1-5.5.4 has highlighted the importance of achieving a greater understanding of the associations of Pb within peat/soil systems. Sub-samples of ~10 layers distributed within the uppermost 30 cm of each of the FM, GT and ED cores were selected to determine the changes in Pb association with humic substances down the vertical profile. Humic material was extracted via the methodology outlined in Section 2.3.12 and the concentration of Pb in the extracts was compared to the total [Pb] for each selected layer. AM cores were not analysed in this way as this part of the study was performed prior to access being granted to the site. Profiles showing Pb associations with humic substances are presented in Figure 5.28.

![Figure 5.28 Percentage Pb-humic associations (*) in cores from FM, GT and ED. [Pb] concentration profile is shown in accompanying bar plots.](image-url)
The uppermost layers of FM showed poor association between total Pb and humic matter with the overall humic association increasing with depth excepting the 7.5 cm and 8.5 cm layers with % associations of 17.1% and 18.6%, respectively. In the vegetation layers, the Pb association with humic matter fluctuates and ranges between 9.8% and 99.9%. In the peat layer itself, % association is comparatively higher, ranging between 64.5-99.9%. GT exhibits 99.9% Pb association with humic substances in the uppermost 5 cm of the core. Below this depth, association decreases to a minimum of 39.5% at 15 cm before increasing to 99.9% in the 18.5 cm layer. The ED humic association profile is similar in shape to the GT profile. In the uppermost 13.5 cm at ED, Pb-humic association % is broadly constant from 96.7-99.9%. Below 13.5 cm, association decreases to 51.5% at 19.8 cm before increasing back to 99.9% association at 28.5 cm.

The low association in the surface sections of FM relative to the other sites likely arises from it possessing the greatest thickness of vegetation at the bog’s surface; GT and ED both have thinner layers of compact surface flora. Living vegetation layers have a low concentration of humic substances as much of the organic matter is still contained within living plant material. Each core shows high Pb-humic association immediately below vegetation layer in the uppermost layers of peat/soil itself; these layers corresponding to the layers where solid phase [Pb] begins to increase. Despite the presence of some layers where peak [Pb] corresponded to minimum Pb-humic associations (17.5 cm at FM, 15 cm at GT, and 19.5 cm at ED), concentrations
around these layers are high and often corresponded to high degrees of Pb-humic association. Fractions with <50% Pb-humic association at FM also possess low (~10 mg kg\(^{-1}\)) solid phase concentration and only one layer at ED possesses <50% Pb-humic association. Otherwise, all layers investigated show the majority of Pb (>50%) associated with humic substances. Applying layer masses and solid phase concentrations to humic association percentages, a considerable proportion of each core’s total solid-phase Pb inventory is stored within the humic matter fraction with only ~20% contained within other compartments. Considering the solid phase material of the entire core, an approximate 79%, 81% and 83% of the total Pb is associated with humic matter for FM, GT and ED, respectively. Taking each core as a whole, it is clear that a considerable majority of total [Pb] is associated with humic matter in the solid phase of all three sites. In order to gain a complete understanding of the mechanisms controlling Pb-humic association, it is necessary to further characterise the humic matter to which Pb is associated and its associated Fe. Organic matter characterisation will be addressed further in Chapter 7.

### 5.5.5.2 Aqueous phase Pb characterisation via sequential ultrafiltration

Following characterisation of the solid phase environment, it was necessary to investigate the associations of Pb within peat/soil porewaters in an attempt to better explain the trends observed in the aqueous phase profiles presented in Section 5.5.3. To these ends, porewaters from FM, GM and ED were subject to sequential ultrafiltration as outlined in Section 2.3.2. Layers within each core were selected to
represent a range of depths within the core while retaining moderate to high [Pb] to facilitate detection following the fractionation process. Figure 5.27 demonstrates the distribution of Pb across porewater molecular size fractions >100 kDa, 100-30 kDa, 30-3 kDa, and <3 kDa following ultrafiltration with combined bars representing combined fraction totals and dot plot representing totals from the unfractionated porewaters.

The procedure provided acceptable recovery rates across all sites with 72% mean recovery for FM samples, 93% mean recovery for GT and 99% for ED. Across all sites, the highly coloured colloids bind the majority of aqueous phase Pb. The >100 kDa molecular size fraction is the most important as it consistently contains between 40–75% of the Pb within each layer. The 30–100 kDa size fraction contains very low [Pb] across all investigated samples. At FM and GT, the 3-30 kDa fraction also contains 10-45% of porewater Pb. When comparing distributions between sample sites, GT forest site possesses the greatest proportion (mean: 33%) within the small colloidal fraction, 30–3 kDa. In comparison, this fraction contains a mean of 24% and 15% of Pb at FM and ED respectively. GT forest also shows the lowest proportion of Pb within the large colloidal fraction (mean: 38%). On the whole, <10% of aqueous Pb is within the smallest sub fraction of <3 kDa and classified as ‘dissolved’ with the remaining >90% associated with the highly coloured colloids. There is no consistent change in the fractional distribution with increasing depth.
Figure 5.29  Porewater ultrafiltration for FM, GT and ED showing sub fractions, stacked fraction totals and original concentration totals.
These data imply Pb is preferentially associated with large colloids within peat/soil porewaters with a slant towards association with smaller colloidal species in the forest soil environment. Larger colloids are the least mobile of the colloidal phases due to a combination of physical bulk and low surface area-to-mass ratio. These factors make large colloids the most likely to transition into the generally immobile solid phase. In contrast, smaller colloidal species are more easily transported via diffusion and are capable of passing through smaller soil transmission pores that may be too small to allow passage of larger colloids. The predominant association of Pb with large colloids is in agreement with the literature supposition of immobility in peatland and organic rich systems (e.g. Shotyk, 1997; Farmer et al., 1997a; Shotyk et al., 2002; 2004, Weiss et al., 1999a; 1999b; MacKenzie et al., 1997a; 1998b). However, the greater influence of small colloidal species in the forest environment may explain the trends observed in $^{206}$Pb/$^{207}$Pb ratio at the GT site discussed in Section 5.5.1.3 and Section 5.5.2.2. The conclusion of Bacon et al. (2004) that the petrol Pb-fraction was the most labile in the soils of Glensaugh in combination with the high proportion of Pb associated with small colloids at GT and the comparatively high mobility that the small colloidal fraction possesses may account for the distortion of the petrol $^{206}$Pb/$^{207}$Pb signature at GT.

Lead distribution data alone is not sufficient to completely explain Pb associations in the aqueous phase. Although the colloidal species are visibly highly coloured, it has not yet been established what these colloidal species are, or how they are distributed between these size fractions. Distribution of colloidal species and further
characterisation of this material will be presented in Chapter 7 to allow further interpretation of aqueous Pb phase associations.

### 5.6 Further discussion

In order to draw further conclusions as to Pb’s behaviour and association within the FM, GT, ED and AM environments, a greater understanding of the organic matter in these systems is necessary. The properties of organic matter and specifically humic matter are clearly of great importance as the majority of Pb is associated with these species. The high [Fe] in the GT and AM environments where also cannot be overlooked as the influence of Fe-cycling processes appears to perturb the Pb profile at the AM site. Organic matter characterization its associations with Fe will be addressed in Chapter 7 in order to allow further discussion as to their influence upon Pb in peat/soil systems.

### 5.7 Chapter Conclusions

At the FM and ED sites, historical records of Pb deposition were well-preserved and showed peak Pb flux due to coal burning and petrol consumption within the layers corresponding to 1940-1980, in agreement with the literature (e.g. Farmer et al., 1997; MacKenzie et al., 1997; Cloy et al., 2005). The close agreement between the $^{206}\text{Pb}/^{207}\text{Pb}$ value of 1.145±0.017 reported for 2007 Scottish rainwater (Farmer et al., 2010) and the range of $^{206}\text{Pb}/^{207}\text{Pb}$ values of ~1.125-1.149 for the surface vegetation layers from FM, GT, ED and AM in this study also suggests that the $^{206}\text{Pb}/^{207}\text{Pb}$
signature, and conceivably the sources from which that Pb originated, has not changed significantly in the time period ~2007-2010. Excepting the layers of this study’s cores that have accumulated since the studies of Cloy et al. (2005; 2008) and MacKenzie et al. (1997), Pb deposition chronologies for FM and ED have proven consistent with those recorded approximately a decade previously. The good agreement between chronologies derived from these distinct studies provides strong evidence to support literature assertions that Pb is immobilised following deposition on surface vegetation and subsequent incorporation into the peat in these peatland environments. It is important to emphasise that the surface vegetation at the study sites was up to 15 cm thick and accounted for the most recent ~20-30 years of Pb deposition. These vegetation layers preserved recent trends in $^{206}$Pb/$^{207}$Pb deposition ratio and also comprised the upper sections of $^{210}$Pb-activity profiles where activities were highest. These results highlight the importance of retaining the surface vegetation sections of sampled cores when reconstructing historical records. The 2-4 cm depth offsets in key [Pb] and $^{206}$Pb/$^{207}$Pb features between adjacent Cuttle and Malcolm (1979) and monolith cores due to core compaction by the former sampling methodology highlights the need to consider the impacts of corer-derived physical disturbances when interpreting results. Once the offsets were taken into account, spatial variation in [Pb], $^{206}$Pb/$^{207}$Pb and Pb inventories on an intra-site scale (10s of metres) was found to be somewhat lower (~1.6-fold variation) than variation on inter-site scale (~2.13-fold variation over distances of <100 km). At the AM peatland site $^{210}$Pb-activity profile does not decay exponentially with depth in the near-surface vegetation sections of the core the period of maximum flux at the site appears to correspond to 2002. Furthermore, the AM $^{206}$Pb/$^{207}$Pb aqueous phase profile showed
higher than expected isotope ratios in its near-surface sections when compared with the corresponding layers of the solid phase profile. The abnormal regions in the AM profile all occurred within the 7-15 cm layers, the section of the core that encompasses the vegetation/peat interface, the depth of the water table and the solid phase [Fe] maximum. It is therefore conceivable that the redox cycling of Fe is influencing the perturbation of the $^{210}$Pb profile. This hypothesis will be explored further in Chapter 7. At GT, the $^{206}$Pb/$^{207}$Pb profile was narrow in range and did not show the historical transition in isotopic ratio from typical coal burning/smelting influences to those of Australian-sourced Pb petrol additives. However, the $^{210}$Pb-activity and [Pb] profiles at GT appear unperturbed which suggests that some petrol-sourced Pb alone is being transported within the core, resulting in the mixing of $^{206}$Pb/$^{207}$Pb ratios. The conclusion of Bacon et al. (2004) that petrol-sourced Pb is the most labile Pb sub-fraction in the upland soils of Glensaugh, in conjunction with this study’s findings that there was a higher proportion of porewater [Pb] in the small (3-30 kDa) organic colloidal fraction when compared to FM and ED, suggests that petrol-sourced Pb may be becoming selectively mobilised in the GT porewaters and transported vertically in association with small humic colloids. In the solid phase of each site, Pb is mostly associated with humic matter although the proportion of Pb associated with humic material can vary considerably (~10-99%) within a core. In the aqueous phase, sequential ultrafiltration demonstrated that Pb is primarily associated with large (0.22 µm–100 kDa) brown coloured colloidal species. In the forest environment, a larger proportion of Pb is associated with small (30 kDa–3 kDa) brown colloidal species. The proportion of truly dissolved Pb (<3 kDa) is low in all environments.
Chapter 6  Mercury

6.1 Introduction

Mercury (Hg) is a group 12 metal element of atomic number 80. It has a melting point of -38.83°C, a boiling point of 356.62°C and a density of 13.546 g cm⁻³ (Haynes, 2012). The average atomic weight of Hg is 200.59 and average atomic radius is 150 pm. The metal in its pure form is a silvery grey liquid under standard temperature and pressure conditions, leading to its nickname of ‘quicksilver’. The average crustal concentration of Hg is estimated to be within the region of 0.08-0.09 mg kg⁻¹ (e.g. Rudnick and Gao, 2003). Mercury does not blend well with crustal matter and is often found in concentrated pockets as opposed to even dispersion, resulting in historic underestimation of crustal abundance, e.g. as low as 0.0123 mg kg⁻¹ (Rudnick and Gao, 2003).

6.2 Toxicity and risk to human health

Tragedies such as the Minimata Bay incident in Japan during the 1950s, where several thousands of human and animal deaths resulted from Hg poisoning, are stark reminders of the dangers posed by Hg to life (Ekino et al., 2007). The harmful effects of Hg have been known for over 2000 years as rivers of the metal were reportedly used to defend the tomb of Chinese emperor Qin Shi Huang from intruders (Yong and Tong, 1985). Mercury is a non-essential element and toxic to humans with an LD50 (median lethal dose, 50% lethality) of as little as 1 mg kg⁻¹ for organic Hg species. To the average human (~70 kg; Waloppe et al., 2012), this
translates as a lethal dose of ~100 mg organic Hg, e.g. methylmercury (MeHg), or ~1 g inorganic Hg, e.g. Hg$^{II}$ salts (Bidstrup, 1964). The detrimental consequences of Hg exposure are experienced throughout the entire body and include kidney damage, high blood pressure and attack of the brain, thyroid and the nervous system (Holmes et al., 2009). Toxic effects can be observed when concentrations of ~50 µg l$^{-1}$ in blood or ~100 µg l$^{-1}$ in urine are reached. The result of prolonged exposure to lower concentrations of <10 µg l$^{-1}$ is still the subject of some debate. Some studies cite no abnormal effects due to low concentrations (Dart, 2003) whereas others suggest susceptibility of adult nervous systems (Harada et al., 1994) and the foetus (Snyder, 1971) even at concentrations <10 µg l$^{-1}$ (Zahir et al., 2005). The metal’s toxicity varies greatly with speciation and method of bodily intake. Consumption of fish is the main human ingestion route of organic Hg species. A 1999–2000 study (Vupputuri et al., 2005) highlighted higher blood [Hg] among US women who regularly ate fish (2.3 µg l$^{-1}$) when compared to those who did not (0.5 µg l$^{-1}$). Methylmercury (MeHg) is readily absorbed through the gastrointestinal tract (about 95% absorbed) where it forms a complex (via binding to sulphhydryl groups) with the amino acid, cysteine. This new complex resembles the large neutral amino acid found in the body, methionine, and can more easily gain entry into cells. In particular, it can penetrate the blood-brain barrier causing accumulation in brain tissue (Zahir et al., 2005). The harmful effects of both organic and inorganic Hg are summarised in Table 6.1.
6.3 Speciation, geochemical behaviour, and environmental forms of Hg

The atomic or molecular form of an element and its chemical form can greatly alter the chemical behaviour and environmental fate of that element (Hill, 1997) as previously described in Section 5.3. The speciation of Hg in the environment is of key importance due to the differences in bioavailability and toxicity of its different forms, as described in Section 6.2. This section will discuss the isotopes, chemical compounds, redox species and geochemical behaviour of Hg.
6.3.1 Hg Isotopes

There are seven naturally occurring stable Hg isotopes of which $^{199}$Hg, $^{200}$Hg, $^{201}$Hg and $^{202}$Hg are the most common with 17%, 23%, 13% and 30% relative abundance, respectively (Emsley, 2003). There are over 30 recorded Hg radioisotopes, although the majority are short-lived and exist only for a few hours. $^{203}$Hg and $^{199}$Hg are the longest lived of the radioisotopes with half-lives of ~45 days and ~450 years, respectively.

6.3.2 Hg in the environment

Geologically, Hg is found predominantly as cinnabar, HgS, although some deposits of elemental Hg, Hg$^{0}$, have also been recorded (Gray, 2003). Other Hg minerals are relatively rare and are primarily sulfur- and oxychloride-containing species produced by the weathering of parent cinnabar, e.g. livingstonite (HgSb$_4$S$_8$) and corderoite (Hg$_3$S$_2$Cl$_2$); eglestonite (Hg$_4$Cl$_2$O) and terlinguaite (Hg$_2$ClO) and calomel (Hg$_2$Cl$_2$). These rarer ores comprise ~2% of the geologic Hg reservoir (Laznicka, 2010).

6.3.2.1 Hg in the atmosphere

Mercury is subject to widespread atmospheric cycling as shown in Figure 6.1. Atmospheric Hg exists primarily in three major forms. Elemental Hg, Hg$^{0}$, exists in vapour form, inorganic Hg$^{II}$ dissolves in atmospheric water droplets, and suspended particulate matter may also contain adsorbed Hg$^{II}$ (Lee and Iverfeldt, 1991; Biester et al, 2002). It has been suggested, however, that >95% of atmospheric Hg exists as
elemental Hg\(^0\) (Schroeder and Munthe, 1998), consistent with the form released from major anthropogenic sources and the result of key environmental processes. For example, fossil fuel combustion, ore roasting, temperature-related-evaporation of environmental Hg, or photochemical excitement of Hg in water bodies (Carpi and Lindberg, 1997; Liu et al., 2000., Gustin et al, 2002., Bahlmann et al, 2006) volatise Hg into the atmosphere as elemental Hg vapour, Hg\(^0\). This vapour can be deposited via dry deposition, scavenged from the atmosphere via vegetation (Rea et al, 2002) or can be oxidised to Hg\(^{II}\) (Iverfeldt, 1991; Zhang et al.,, 2012). Wet deposition of dissolved Hg\(^{II}\) or particulate fallout removes adsorbed Hg\(^{II}\) from the atmosphere and facilitates transfer to aqueous and terrestrial systems (Lodenius, 1998; Sakata and Murumoto, 2005). Deposited Hg is not necessarily removed from the global cycle and can be remobilised back into the atmosphere, especially if present in the elemental form. Based upon current understanding and estimates of pre-industrial Hg emissions, approximately 50% of Hg deposited to the environment is re-emitted (Sunderland and Mason, 2007).

Figure 6.1  Environmental cycling and conversion of Hg species (Clarkson et al, 2003).
6.3.2.2 Hg in the aqueous environment

In addition to wet and dry deposition processes, terrestrial runoff can act as an additional source of Hg to the aqueous environment (Louis et al., 1996; Driscoll et al., 1998). As mentioned above, Hg$^{II}$ is significantly more soluble than Hg$^{0}$, e.g. $>100 \text{ g l}^{-1}$ dependent on the specific Hg$^{II}$ salt compared with only $\sim 2.7 \times 10^{-5} \text{ g l}^{-1}$ for its elemental counterpart (Clever et al., 1985). Major fresh water inorganic Hg species include HgSO$_4$, Hg(SO$_4$)$_2^{2-}$, HgNO$_3^+$, Hg(NO$_3$)$_2$, Hg(CN)$_2$, Hg(SO$_3$)$_2^{2-}$, Hg(SH)$_2$, Hg(NH$_3$)$_2^{2+}$, HgCO$_3$, HgHCO$_3^+$, Hg-humus, HgCl$_4^{2-}$, HgCl$_2$ and Hg(OH)$_2$ (Lindqvist et al., 1991; Schuster, 1991). Hydroxide and Cl species dominate Hg in soil solution unless other ligands are in abnormally large concentrations (Schuster, 1991; Renneberg and Dudas, 2001). Major organic Hg species in the neutral fresh water include CH$_3$HgCN, CH$_3$HgSO, CH$_3$HgS$^-$, (CH$_3$Hg)$_2$S, CH$_3$HgNH$_3$, CH$_3$HgNH$_3^+$, CH$_3$HgCl, and CH$_3$HgOH depending on the aqueous medium and pH. Dissolution is not the only means by which Hg enters the aqueous environment; binding of Hg to humic colloids has also been established as a mobilisation route (Benes et al., 1976).

6.3.2.3 Hg in terrestrial systems

6.3.2.3.1 Hg binding to soil organic and mineral matter

The behaviour of Hg in soil systems is complex and not entirely understood. Once in the soil, Hg$^{0}$ will either volatise back into the gaseous phase, or will be adsorbed onto the surface of soil particles (Renneberg and Dudas, 2001). Mercury in soils is
believed to be primarily associated with humic substances (Lindqvist et al., 1991), particularly humic acids, which act as a repository and effectively immobilise Hg on a solid phase medium (Yudovich and Ketris, 1994). The probable mechanisms of Hg binding to humic structures include association with O- or S-containing functional groups. Mercury and S share favourable binding energetics, partially explained via hard-soft ligand theory with Hg$^{2+}$ being a Lewis acid and S ligands comprising the corresponding Lewis bases (Ravichandran, 2004). However, humic matter itself has also been implicated in the reduction of inorganic Hg to its elemental form (Alberts et al., 1974; Rocha et al., 2000; Serudo et al., 2007). Reduction of Hg$^{II}$ bound to solid phase organic matter may subsequently release previously bound Hg to the atmosphere as Hg$^0$ resulting in Hg not becoming immobilised in the solid phase to the same degree as Pb (Section 5.3.3).

In addition to the organic soil components, soil mineral matter has also been implicated in binding Hg. Clay minerals reportedly have an affinity for Hg$^{II}$ with ion exchange processes controlling adsorption and desorption from surfaces and colloidal particles (Kohut et al., 1995; Sarkar et al., 2000). Bridging species with mineral Fe oxy-hydroxides have also been reported (Obukhovskaya, 1993, Forstner et al., 1995) in addition to Hg coordination with phosphate, carbonate and sulphate-containing minerals (Schuster, 1991). Overall, Hg may associate with a wide range of soil components, resulting in its binding preferences and its residence time in the solid phase being open to further debate.
6.3.2.3.2 Peatlands as records of Hg deposition

There is considerable debate within the literature regarding the use of traditional environmental archives of peat (and sediment cores) as a means of accurately reconstructing past Hg fluxes. Whilst peat profiles discussed later in Section 6.3.5 appear to match the chronologies established by ice cores, residence times of Hg within these systems are not entirely established. Biester et al. (2002) suggest that Hg’s affinity for humic matter will cause it to interact strongly with the solid phase, rendering it effectively immobile and susceptible to loss only via erosion and subsequent transportation when adsorbed to suspended particulates in the aqueous phase. However, the widely acknowledged volatility and resultant loss of Hg from soils to the atmosphere does not appear entirely compatible with that assumption. Although Hg loss from peatlands might be predicted, depositional fluxes are in fact larger than expected and this discrepancy has been the subject of research. Biester et al. (2003) suggested that decomposition of the organic matter to which Hg$^{II}$ is bound may drive its reduction to Hg$^{0}$ which is subsequently volatilised and lost from the system. Further work by Biester et al. (2007) also hypothesised that the larger reported Hg depositional fluxes in peatlands, in comparison with sediment archives (e.g. Mast et al., 2010, Thevenon et al., 2011) may be due to a smearing of $^{210}$Pb in the upper layers of peat cores, leading to underestimation of age and overestimation of Hg flux when $^{210}$Pb-dating is employed. Madsen (1981) attempted to reconcile peat archives and reconstructed ice core chronologies and found peatlands to exhibit fluxes between 1 and 2 orders of magnitude greater than ice core records would suggest. However, work by Shotyk et al. (2003) on peat bogs in Greenland and in Denmark found close agreement in mid 1950s fluxes, $\sim$165 µg m$^{-2}$ yr$^{-1}$ and $\sim$185 µg.
m$^{-2}$ yr$^{-1}$, respectively, and also found [Hg] peaks corresponding to the mid 1950s. This peak corresponded to similar deposition maxima for other elements including Pb and As which were derived primarily from coal combustion, showing the potential for similar preservation of Hg pollution trends within the peat matrix. Contrary to the earlier work of Madsen (1981), Shotyk et al. (2003) did find good agreement between 40 year snow records and those of the Greenland peat bog, implying that Hg deposition records may be preserved to similar degrees in varied environmental media. With no clear consensus within the literature, the questions surrounding preservation of chronological Hg deposition in peat, soil, sediments and other environmental media are still unresolved.

### 6.3.2.4 Hg in forest and peatland vegetation

Vegetation is of considerable importance in relation to Hg retention, or re-emission from terrestrial systems. Mercury is transferred to the surface of vegetation via both wet and dry deposition. However, some is re-emitted since there is a continuous exchange of Hg between the atmosphere and vegetation (Lodenius et al., 2003). For the remainder, uptake and retention of Hg by vegetation and the subsequent death, decomposition and incorporation of plant matter into underlying soil and peat is a major route of transfer of Hg to terrestrial systems (Grigal, 2003; Rydberg et al., 2010).

In forest environments, tree canopies (Witt et al., 2009) and underlying vegetation such as ferns (Han et al., 2006) intercept atmospheric Hg to varying degrees.
Additionally, Hg uptake through root systems has been reported. Relationships have been demonstrated between [Hg] in soils and in plant roots (Han et al., 2006). Plant uptake can either increase or decrease the transfer of Hg to soils. For example, litterfall from canopies can provide a 2-3 times greater flux to the underlying soil than wet deposition (St Louis et al., 2001). Conversely, fern cover in boreal forest systems has been observed to increase rates of Hg re-emission to the atmosphere, an effect that was attributed to a combination of (i) variations in soil moisture due to air–H₂O emissions from plants, and (ii) bacterial interactions in the rhizosphere of plants (Han et al., 2006).

Overlying moss is common to each of the sampling sites used in this study and therefore the interactions between Hg and mosses are of particular relevance. Moss possesses no vascular system and so nutrients are taken up from the atmosphere rather than from groundwater, although limited cases of Hg uptake via ion-exchange from solution by some moss species have been reported (Kondoh et al., 1998). The weak or absent moss cuticle in combination with very thin leaves enables exchange of Hg between the atmosphere and cell walls (Lodenius, 2013). As a result of moss’ nutrient source, some studies have demonstrated that mosses uptake a greater quantity of atmospheric Hg than other plant species in close proximity (Huckabee, 1973) although this observation may be due to the ability of mosses to retain a larger proportion of dry deposited Hg⁰ relative to other plant species (Schroder et al., 2010). Even within mosses of the Sphagnum genus, Hg uptake can vary by species. Rydberg et al. (2010) showed that Sphagnum subsecundum accumulated
significantly higher [Hg] when compared to adjacent *Sphagnum centrale* plants (24 ± 3 µg kg\(^{-1}\) and 18 ± 2 µg kg\(^{-1}\), respectively).

### 6.3.3 Methylmercury in the terrestrial and aquatic environment

Methylmercury (MeHg) species are of particular interest due to the very high toxicity of this chemical species. This toxicity is attributable to the greater propensity with which it crosses the blood-brain barrier in comparison with inorganic mercury (Section 6.2). Methylmercury has been reported in a variety of environmental media including sediments (e.g. Jiang *et al*., 2011), wetlands (e.g. King *et al*., 2002), salt marshes (e.g. Kongchum *et al*., 2006), soils (e.g. Rieder *et al*., 2011) and peatlands (e.g. Mitchell *et al*., 2008). Although atmospheric MeHg has been reported (Lee and Iverfeldt, 1991; Lamborg *et al*., 1995, St. Louis *et al*, 1995), its concentration is negligible and thus MeHg is predominantly encountered in terrestrial and aquatic environments.

Within the terrestrial and aquatic environment, inorganic and organic Hg species can be readily inter-converted by bacterial processes (Merritt and Amirbahman, 2009). Successive studies by Benoit *et al*. (1998; 1999a; 1999b; 2001a; 2001b) and some by other authors (e.g. Compeau and Bartha, 1985) have implicated sulphur-reducing bacteria as being primarily responsible for formation of MeHg under anoxic conditions although the exact mechanism by which the bacteria accomplish this conversion remains ambiguous. Methylation of Hg often coincides with conditions that favour sulphate reduction, including high concentrations of organic matter (Choi
and Bartha, 1994; Pak and Bartha, 1998), reducing conditions (Korthals and Winfrey, 1987; Regnell et al., 1996), and the presence of sufficient sulphate concentration (Gilmour et al., 1992; Brandfireun et al., 1999). Sulphate-reducing biotia that specifically rely upon vegetation to thrive have also been shown to possess the capacity to alter Hg speciation; Yu (2010) demonstrated methylation of Hg via *Sphagnum*-associated biota.

Chemical conversion of Hg via alternative abiotic aqueous oxidation mechanisms involving ozone (Munthe, 1992) and bromine species (Wang and Pehkonen, 2004), among others (e.g. Falter and Wilken, 1998) have been reported. Reaction with acetate (Bloom et al., 1997; Gardfeldt et al., 2003; Hammerschmidt et al., 2007), organic acids with a reactive methyl group (Falter, 1999), other methylated metals (Cerrati et al., 1992; Weber, 1993), and humic matter (Weber, 1993) have been also been implicated as viable methylation pathways. An example of methylation via acetate is shown in Equations 5.1 and 5.2 where n = 1-4 (Gardfeldt et al., 2003).

\[
\text{Hg}^{2+} + (\text{CH}_3\text{COO})_n \rightleftharpoons [\text{Hg(\text{CH}_3\text{COO})}_n]^{2-n} \quad \text{Equation 5.1}
\]

\[
[\text{Hg(\text{CH}_3\text{COO})}_n]^{2-n} \rightarrow \text{CH}_3\text{Hg}^+ + \text{CO}_2 + (n-1)[\text{CH}_3\text{COO}]^- \quad \text{Equation 5.2}
\]

Aquatic plants have also been shown to facilitate the abiotic conversion of inorganic Hg to MeHg via generation of reactive methyltin (Weber, 1993). It is however widely accepted that biotic processes account for the production of the majority, if not all, environmental MeHg (Celo et al., 2006).
Whatever the mechanism of formation, MeHg can be demethylated in the environment under strongly oxidising conditions (Phillips et al., 1987). Exchange of MeHg between different sulfhydryl groups at solid/aqueous phase interfaces, turbidity caused by high flow rates or other disturbances, and low pHs can cause release of MeHg to the aqueous environment where demethylation is more likely to occur (Phillips et al., 1987). Association with solid phase and suspended aqueous particulate matter hinders demethylation and thus prevents re-emission to the atmosphere by subsequent conversion to Hg_0. The degree to which organic and inorganic Hg species are converted and how these processes influence retention of Hg by plant species and the underlying soils and peats is not entirely clear and further research into this area is warranted.

6.3.4 Mercury emissions to the environment

6.3.4.1 Natural sources of Hg

Some of the natural emission sources and transportation routes of Hg to the environment are similar to those of Pb. It is estimated that approximately 60% of contemporary Hg emissions are from natural emission sources and remobilisation of previously emitted Hg, although exact proportions vary over time and with region (Pirrone et al., 1996; Pacyna et al., 2006). In some regions, anthropogenic emissions have been so prevalent that natural sources only account for 10–40% of regional atmospheric Hg (Lindqvist and Rhode, 1985., Nriagu, 1989). Volcanic eruptions (~90 Mg yr\(^{-1}\)), evaporation from ocean surfaces (~2800 Mg yr\(^{-1}\)), release from soils and plant matter (~1650 Mg yr\(^{-1}\)) and forest fires or other natural combustion
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processes are the major contributors into the environment (~675 Mg yr\(^{-1}\)). Other less predominant sources include the weathering of rocks, windblown, transport of windblown dust, and transpiration/decay of vegetation (Fantozzi et al., 2013). Current total natural atmospheric emissions of Hg are estimated to be approximately 5500 Mg yr\(^{-1}\) (Mason, 2008). This is an increase from estimates of pre-industrial emissions of ~1360 Mg yr\(^{-1}\) from oceans and ~8 Mg yr\(^{-1}\) from terrestrial sources (Sunderland and Mason, 2007). Overall, natural Hg emissions are likely to be underestimated due to incomplete knowledge regarding all sources and recognition that emissions from some pools, such as coal-bed fires and forest fires, are currently inexact (Pirrone et al., 2009). Only within the past decade have early emissions estimates (Lindqvist et al., 1991) been superseded by more comprehensive models (Gustin, 2003). Estimated natural emissions totals for 2008 are presented in Table 6.2.

Table 6.2 Hg emissions from natural sources during 2008 (Pirrone et al., 2009)

<table>
<thead>
<tr>
<th>Source</th>
<th>Mercury (Mg yr(^{-1}))</th>
<th>Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceans</td>
<td>2682</td>
<td>52</td>
</tr>
<tr>
<td>Lakes</td>
<td>96</td>
<td>2</td>
</tr>
<tr>
<td>Forests</td>
<td>342</td>
<td>7</td>
</tr>
<tr>
<td>Tundra/Grassland/Savannah</td>
<td>448</td>
<td>9</td>
</tr>
<tr>
<td>Prairie/Chaparral</td>
<td>546</td>
<td>10</td>
</tr>
<tr>
<td>Desert/Metaliferous/Non-vegetated Zones</td>
<td>128</td>
<td>2</td>
</tr>
<tr>
<td>Agricultural areas</td>
<td>200</td>
<td>4</td>
</tr>
<tr>
<td>Evasion after mercury depletion events</td>
<td>675</td>
<td>13</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>Volcanoes and geothermal areas</td>
<td>5207</td>
<td>100</td>
</tr>
<tr>
<td>TOTAL</td>
<td>5207</td>
<td>100</td>
</tr>
</tbody>
</table>

Mercury 274
Anthropogenic 

Anthropogenic Hg release to the atmosphere on a large scale is a relatively recent phenomenon. Ice core studies from North American glaciers (USGS, 2002) demonstrate an approximately constant flux of Hg until ~1850 when gold (Au) mining surged for several decades leading to considerable elevation of Hg above the background. As industry developed new and increased methods of utilising Hg (such as Hg-cells in the chlor-alkali process; e.g. Ferrara et al., 1992), and as fossil fuel consumption increased, the anthropogenic output of Hg increased gradually from ~1900 until 1980 (Sunderland and Mason, 2007) from when a rapid decline in deposition over the next two decades can be attributed to the phasing out of the chlor-alkali process (EC, 1997; UNEP 2012) and widespread adoption of green technology, such as exhaust gas scrubbing (USEPA, 2005), across the developed world (Pacyna and Pacyna, 2002; Pacyna et al., 2006). Recently, anthropogenic Hg emissions to the atmosphere have begun to increase again due to the demands especially within Asia for fossil fuels (Pottinger et al., 2004). China, India and the USA are currently the greatest emitters of Hg on a per-country basis (Pirrone et al., 2009).

The predominant contemporary anthropogenic sources of Hg are industry-related and are estimated to emit approximately 2320 Mg yr\(^{-1}\) Hg (Pirrone et al., 2009). The main contributors are fossil-fuel power stations (~810 Mg yr\(^{-1}\)), small scale gold mining operations (~400 Mg yr\(^{-1}\)), non-ferrous metallurgy (~310 Mg yr\(^{-1}\)), production of cement (~236 Mg yr\(^{-1}\)), waste disposal (~187 Mg yr\(^{-1}\)), and caustic
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soda production (~163 Mg yr\(^{-1}\)). Coals and oils typically contain <0.01–55 mg kg\(^{-1}\) (Wilhelm, 2001; Yudovich and Ketris, 2005; Mukherjee et al., 2009) and their combustion alongside other fossil fuels releases this Hg to the atmosphere. Artisanal mining operations, primarily of Au, utilise a Hg-amalgam extraction approach and create Hg waste as a byproduct. In addition to these major sources, China’s production of PVC from coal, which adopts Hg as a catalyst, is estimated to release ~450 Mg yr\(^{-1}\) although precise emissions data is not openly available (Tsinghua University, 2006). Sources and their contemporary emissions estimate are provided in Table 6.3.

<table>
<thead>
<tr>
<th>Source</th>
<th>SC</th>
<th>NFMP</th>
<th>PISP</th>
<th>CP</th>
<th>CSP</th>
<th>MP</th>
<th>GP</th>
<th>WD</th>
<th>O</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Africa</td>
<td>32.6</td>
<td>0.3</td>
<td>1.3</td>
<td>2.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
<td>0.6</td>
<td>1.3</td>
<td>40.2</td>
</tr>
<tr>
<td>China</td>
<td>268.0</td>
<td>203.3</td>
<td>8.9</td>
<td>35.0</td>
<td>0.0</td>
<td>27.5</td>
<td>44.7</td>
<td>14.1</td>
<td>7.6</td>
<td>609.1</td>
</tr>
<tr>
<td>India</td>
<td>124.6</td>
<td>15.5</td>
<td>4.6</td>
<td>4.7</td>
<td>6.2</td>
<td>0.0</td>
<td>0.5</td>
<td>77.4</td>
<td>7.5</td>
<td>240.9</td>
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<tr>
<td>Australia</td>
<td>2.2</td>
<td>11.6</td>
<td>0.8</td>
<td>0.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
<td>0.2</td>
<td>0.6</td>
<td>16.6</td>
</tr>
<tr>
<td>Europe</td>
<td>76.6</td>
<td>18.7</td>
<td>0.0</td>
<td>18.8</td>
<td>6.3</td>
<td>0.0</td>
<td>0.0</td>
<td>10.1</td>
<td>14.7</td>
<td>145.2</td>
</tr>
<tr>
<td>Russia</td>
<td>46.0</td>
<td>5.2</td>
<td>2.6</td>
<td>3.9</td>
<td>2.8</td>
<td>0.0</td>
<td>4.3</td>
<td>3.5</td>
<td>1.5</td>
<td>69.8</td>
</tr>
<tr>
<td>N. America</td>
<td>65.2</td>
<td>34.7</td>
<td>12.8</td>
<td>15.1</td>
<td>10.3</td>
<td>0.0</td>
<td>0.0</td>
<td>13.0</td>
<td>1.7</td>
<td>122.8</td>
</tr>
<tr>
<td>S. America</td>
<td>8.0</td>
<td>13.6</td>
<td>1.8</td>
<td>6.4</td>
<td>2.2</td>
<td>0.0</td>
<td>16.2</td>
<td>0.0</td>
<td>1.5</td>
<td>49.7</td>
</tr>
<tr>
<td>Total</td>
<td>623.2</td>
<td>302.9</td>
<td>32.8</td>
<td>88.6</td>
<td>27.8</td>
<td>27.5</td>
<td>65.3</td>
<td>118.9</td>
<td>36.4</td>
<td>1324.3</td>
</tr>
<tr>
<td>Rest of the world</td>
<td>186.8</td>
<td>7.1</td>
<td>10.4</td>
<td>147.1</td>
<td>135.1</td>
<td>22.5</td>
<td>333.7</td>
<td>68.5</td>
<td>28.2</td>
<td>939.4</td>
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<tr>
<td>Total</td>
<td>810.0</td>
<td>310.0</td>
<td>43.2</td>
<td>235.7</td>
<td>162.9</td>
<td>50.0</td>
<td>400.4</td>
<td>187.4</td>
<td>64.6</td>
<td>2319.7</td>
</tr>
</tbody>
</table>

*SC: Stationary combustion; NFMP: Non-ferrous metal production; PISP: Pig iron and steel production; CP: Cement production; CSP: Caustic soda production; MP: Mercury production; GP: Gold production; WD: Waste disposal; O: Other; T: Total.

6.3.5 Environmental Hg research in Scotland

Relatively little data exists regarding Hg deposition and Hg in environmental media in Scotland. The DEFRA monitoring network has recorded Hg deposition across the UK although very limited data exists. Figure 6.2 shows wet Hg deposition in mg ha\(^{-1}\)
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Mercury  for the UK during 2007 (DEFRA, 2010). Dry deposition is presumed to be comparatively negligible (DEFRA, 2010). Typical contemporary UK deposition is approximately 30-100 mg ha\(^{-1}\) yr\(^{-1}\), lower than the 150-250 mg ha\(^{-1}\) yr\(^{-1}\) experienced by mainland Europe (EMEP, 2012). The regions of the UK which experience the greatest annual precipitation, i.e. western Scotland and Wales (Met Office, 2010), also experience the greatest levels of Hg deposition. These regions also generally contain the greatest density of UK peatlands (Billett, 2010). Although deposition maps provide no measure as to what degree Hg is remobilised back into the atmosphere, the study of peatlands allows the determination of the quantities of deposited Hg being stored by terrestrial systems.

Figure 6.2  Wet deposition of Hg across the UK for 2007 (DEFRA, 2010).
The most detailed Scottish peatland study available was performed by Farmer et al. (2009) on four Scottish peat bogs: Flanders Moss (central; near Stirling), the Red Moss of Balerno (east; near Edinburgh), Turclossie Moss (north east) and Carsegowan Moss (south west). Mercury concentrations peaked a few cm below the surface before dropping to near constant values at greater depth. Maximum concentrations were 515-663 µg kg\(^{-1}\) with the most contemporary near-surface layer concentrations dropping to 100-180 µg kg\(^{-1}\). The [Hg] profiles for Flanders Moss are shown in Figure 6.3.

Figure 6.3  Concentration profiles of Hg for two Flanders Moss cores (Farmer et al., 2009). Dashed line represents vegetation-peat interface.
Pre-1800 Scottish Hg fluxes of 3.7-4.5 µg m\(^{-2}\) yr\(^{-1}\) were reported, increasing to a maximum flux of 51-85 µg m\(^{-2}\) yr\(^{-1}\) in 1935-1970 depending on the site. In agreement with ice core trends discussed in Section 6.3.4.2, Hg fluxes decreased over the past two decades to a mean value of 27 ± 15 µg m\(^{-2}\) yr\(^{-1}\) in the early 2000s. These deposition values are greater than would be predicted from DEFRA (2010) and EMEP (2012) deposition maps, although it should be noted that such maps do not take into account Hg from dry deposition. The results of Farmer et al. (2009) are in agreement with those obtained by Yang et al. (2002) who profiled sediment cores at Lochnagar, Cairngorms, Scotland. Yang reported that the flux to the sediments increased from the ~1880 until ~1970 and remained approximately constant until the present day where the Hg flux is approximately 36 µg m\(^{-2}\) yr\(^{-1}\), twice that of the 1880 natural background. Another study by Yang and Rose (2003) demonstrated similar sediment profiles for cores taken from Loch Chon, NW Scotland. More recently, Rose et al. (2013) demonstrated seasonal peaks in wet deposition of 1.2 ng l\(^{-1}\) MeHg during Scottish winters (Rose et al., 2013). Farmer et al. (2009) noted that in addition to local and regional influences, Hg accumulation rates in Scottish bogs could only be completely explained if long-range atmospheric transport and global distribution was taken into account. It was also proposed by Farmer et al. (2009) that further investigation of deposition, uptake and retention of Hg by the living plants at the surface of peatlands and the biogeochemical processes potentially responsible for retention and loss of Hg in the peat layers themselves was required to unambiguously establish whether peat bogs can provide a true historical record of atmospheric Hg deposition. None of the published Scottish studies have tackled analysis of the peat aqueous phase, although this is unsurprising based on the overall lack of peat
aquous phase studies in worldwide literature and the analytical difficulties that arise from the very low [Hg] concentrations involved.

### 6.4 Current Hg research needs

Three current priorities in peat bog Hg research include speciation, aqueous phase behaviour and archival integrity. The speciation and associations of Hg within soil and peat systems are still not entirely understood. The majority of speciation studies have focused on simulated idealised laboratory environments (e.g. Song and Heyst, 2005; Yang et al., 2007; Obrist et al., 2010) or have adopted sequential extraction techniques that broadly categorise Hg into reactive groupings rather than the assessing the specific species present (e.g. Liu et al, 2006; Zheng et al, 2008; Issaro et al, 2009., etc). Further investigation and application of alternative techniques are warranted to better understand Hg speciation and how it changes within different compartments of soil and peat systems. The aqueous phase associations and behaviour of Hg in peat and soil systems remains broadly unknown. Despite a wealth of research focused upon Hg in lakes (e.g. Nguyen et al., 2005), rivers (e.g. Heaven et al., 2000) and oceans (e.g. Andersson et al., 2008), groundwaters and porewaters in terrestrial systems have not been characterised in sufficient detail. Furthermore, as discussed in Section 6.3.2.3.2, the validity of Hg solid phase peat and soil profiles as records of historical deposition remains subject to debate. Additional research is required to address the concerns surrounding terrestrial Hg records. To address these deficiencies in the current understanding of Hg, this chapter will address Hg speciation, aqueous phase behaviour and the possibility of peatlands acting as historical archives of Hg deposition.
6.5 Results and discussion

6.5.1 Solid phase [Hg] at Flanders Moss (FM), Glentress Forest (GT), Easter Deans (ED) Peat Bog and Auchencorth Moss (AM)

The solid phase [Hg] profiles for the four sampling sites adopted in this study (FM, GT, ED and AM) are provided below in Figure 6.4. Concentration data was acquired via acid digestion and ICP-MS analysis as described in Section 2.3.17. Dates were established via $^{210}$Pb-dating using the CRS model as demonstrated in Appendix 7. The dates for core layers from FM and AM were extrapolated from those obtained for sister cores taken directly adjacent to the primary analysis cores. Core Hg inventories and key features are summarised in Table 6.4 and discussed in Section 6.5.2.

The [Hg] profile for FM is shown in Figure 6.4. There was a near-surface [Hg] peak in the vegetation layer (0-15 cm) of $0.17 \pm 0.001$ mg kg$^{-1}$ at 3-4 cm followed by a steady decrease to a minimum of $0.063 \pm 0.001$ mg kg$^{-1}$ at 11-12 cm. Below the vegetation layer, the [Hg] increased to a maximum of $0.22 \pm 0.001$ mg kg$^{-1}$ at 20-21 cm ($1923 \pm 20$). Below this depth, the [Hg] again decreased, this time to a minimum of $0.044 \pm 0.016$ mg kg$^{-1}$ at 27.5 cm. The peak [Hg] reported by Farmer et al. (2009) of $0.523$ mg kg$^{-1}$ and $0.625$ mg kg$^{-1}$ are more than a factor of 2 greater than the maximum value of $0.22 \pm 0.001$ mg kg$^{-1}$ reported within this study, although the overall shape of these profiles are generally similar. Additionally, Farmer et al. (2009) and this study both showed broad sub-surface [Hg] peaks corresponding to a
span of ~23 years (this study: ~1923-1947; Farmer et al., 2009: ~1937-1960) with some chronological overlap, although there is some discrepancy in the dates at which the largest absolute [Hg] is recorded (this study: ~1923-1949; Farmer et al., 2009: 1955 ± 3 and 1960 ± 9). However, the concentration peaks reported by Farmer et al. (2009) for the Red Moss and Carsegowan Moss showed concentration peaks in layers dated at ~1935 and ~1937, respectively, which are in closer agreement to the ~1923-1949 peak shown here.

The [Hg] profile for GT Forest shown in Figure 6.4 exhibits a maximum [Hg] of 0.56 ± 0.030 mg kg\(^{-1}\) in its uppermost layer which comprises the surface vegetation (0–1 cm). There was a general decrease in [Hg] with increasing depth to a minimum concentration of 0.11 ± 0.031 mg kg\(^{-1}\) at 15-16 cm but at 9-11 cm the concentrations rose to 0.41-0.42 mg kg\(^{-1}\) corresponding to layer ages of ~1955, in agreement with the peaks reported for the FM cores in Farmer et al. (2009).

The ED [Hg] profile (Figure 6.4) was broadly similar to that of GT. Overall, [Hg] decreased from a surface maximum of 1.35 ± 0.062 mg kg\(^{-1}\) within the vegetation layer (0-10 cm) to a minimum of 0.036 ± 0.047 mg kg\(^{-1}\) at 25-26 cm depth. At a depth of 19-20 cm, the slight maximum of 0.51 ± 0.046 mg kg\(^{-1}\) corresponded to ~1947 ± 30. This was in broad agreement with the maximum concentration of 0.523 mg kg\(^{-1}\) in peat sections from FM dated at ~1955 reported by Farmer et al. (2009).
Mercury concentration generally decreased with increasing depth in the AM core. The [Hg] maximum of 0.79 ± 0.003 mg kg⁻¹ occurred at 1-2 cm within the vegetation layer of the core (0-11 cm) with the minimum concentration of 0.013 ± 0.001 mg kg⁻¹ towards the base of the core at 45 cm. Between the depths of 10 cm and 40 cm, [Hg] was highly variable in the range 0.334-0.028 mg kg⁻¹. However, a near surface [Hg] peak of 0.51 ± 0.010 mg kg⁻¹ was evident at 8-9 cm, a layer dated to the year
1999 ± 1.3. In contrast with the other sampling locations, there was no sub-surface [Hg] peak evident at AM.

6.5.2 Discussion of solid phase Hg profiles

6.5.2.1 Inter-site comparison

Mercury concentration profiles from FM, GT and ED were broadly similar in terms of general trend and profile shape, although the magnitudes, depths and corresponding dates of Hg maxima were variable. The AM profile was unique in shape among the four sites due to its lack of an evident sub-surface [Hg] peak. Key features for each location are presented in Table 6.4.

All four sites showed a [Hg] peak in the near-surface vegetation section of the core, and FM, GT and ED each showed a sub-surface concentration peak in the peat/soil below the vegetation layer. Absolute [Hg] maxima occurred within the top 0-3cm of each core with the exception of FM where a broad peak is apparent in the 18-21 cm sections. However, a near-surface [Hg] peak of lesser magnitude (0.17 ± 0.001 mg kg⁻¹) is still present in FM’s near-surface vegetation at 3.5 cm. ED showed the largest [Hg] maximum of any site in this study. The near-surface ED peak of 1.35 ± 0.062 mg kg⁻¹ is ~8-fold greater than the equivalent maximum at FM (0.017 ± 0.001 mg kg⁻¹).
<table>
<thead>
<tr>
<th>Core</th>
<th>Depth of near-surface vegetation [Hg] maximum (cm)</th>
<th>Near-surface vegetation [Hg] maximum (mg kg(^{-1}))</th>
<th>Near-surface vegetation [Hg] maximum layer date</th>
<th>Depth of sub-surface peat/soil [Hg] maximum (cm)</th>
<th>Sub-surface peat/soil [Hg] maximum (mg kg(^{-1}))</th>
<th>Sub-surface peat/soil [Hg] maximum layer date</th>
<th>[Hg] minimum (mg kg(^{-1}))</th>
<th>Hg-inventory; 1950 (mg m(^{-2}))</th>
<th>Hg-inventory; vegetation (mg m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM</td>
<td>3.5</td>
<td>0.17±0.001</td>
<td>1996±0.8</td>
<td>20.5</td>
<td>0.22±0.001</td>
<td>1923±20</td>
<td>0.04±0.016</td>
<td>2.82</td>
<td>0.78</td>
</tr>
<tr>
<td>GT</td>
<td>1.0</td>
<td>0.56±0.030</td>
<td>2003±1.0</td>
<td>9-11</td>
<td>0.42±0.021</td>
<td>1934-1959</td>
<td>0.11±0.031</td>
<td>4.60</td>
<td>0.25</td>
</tr>
<tr>
<td>ED</td>
<td>1.5</td>
<td>1.35±0.062</td>
<td>2007±0.7</td>
<td>19.5</td>
<td>0.51±0.046</td>
<td>1947±30</td>
<td>0.04±0.047</td>
<td>3.23</td>
<td>2.00</td>
</tr>
<tr>
<td>AM</td>
<td>1.5</td>
<td>0.79±0.003</td>
<td>2007±0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01±0.001</td>
<td>2.20</td>
<td>0.13</td>
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</tbody>
</table>
The ~8-fold inter-site variation is considerably greater than the ~2-fold variation observed for [Pb] maxima across these sites (Section 5.5.2). Variation in the sub-surface peat [Hg] peaks was far less pronounced. The largest sub-surface [Hg] maximum (ED: 0.51 ± 0.046 mg kg\(^{-1}\)) was only ~2.5 times greater than the smallest (FM: 0.22 ± 0.001 mg kg\(^{-1}\)). This degree of variation is more in line with the ~2-fold inter-site Pb variation reported in Section 5.5.2. The dates of the layers in which the sub-surface [Hg] occurs are broadly in agreement between ED and GT at ~1950. The peak at FM occurred somewhat earlier (1923 ± 20) and although this discrepancy may be due to the extrapolation of layer dates from an adjacent sister core (Section 4.6), although it should be noted that such an effect was not apparent in relation to Pb-deposition chronologies (Section 5.5.1). The depths of sub-surface [Hg] peaks at FM, GT and ED (20.5 cm, 9-11 cm and 19.5 cm, respectively) are in good agreement with [Pb] peaks reported in Section 5.5.1 (19.5 cm, 9 cm and 19.5 cm, respectively). These [Pb] peaks correspond to the period of maximum emission from coal burning (Section 5.3.4) and it should be noted that coal combustion is also a significant source of Hg (Pacyna et al., 2006). The co-occurrence of these peaks provides evidence to suggest that Hg deposition is retained to some degree within these peat/soil systems (Farmer et al., 2009).

Mercury inventories were calculated for each site to 1950 as layers dated to this period are shared by all four cores and are located beneath the vegetation interface. With the exception of GT, the post-1950 inventories are remarkably similar at 2.82 mg m\(^{-2}\), 3.23 mg m\(^{-2}\) and 2.20 mg m\(^{-2}\) for FM, ED and AM, respectively. The larger inventory at GT, 4.60 mg m\(^{-2}\), is likely a result of increased Hg interception by the
forest canopy which has been shown to increase total Hg deposition to underlying soils by about a factor of 2 (e.g. St Louis et al., 2001; Witt et al., 2009), in agreement with the inventory differences reported here. Rydberg et al. (2010) also reported ~2 fold greater Hg inventories in peat and surface mosses underlying pine forests when compared to the open moss due to the influence of the canopy. Inventories reported by Farmer et al. (2009) for the 1900-2000 period in four Scottish bogs were in the range 3.53-7.46 mg m\(^{-2}\), in good agreement with the 3.80 mg m\(^{-2}\) 1900-2000 FM inventory recorded by this study. The 1900-2000 Hg inventory from AM is only a little lower than these values at 2.90 mg m\(^{-2}\). The DEFRA Hg deposition map (Figure 6.2; DEFRA, 2010) shows that Hg is deposited to similar degrees across inland areas of Scotland. As 1950 inventories, and the 1990-2000 inventories where available, are in good agreement between peatland sites, any long-term Hg loss must either be approximately equivalent, or negligible from site-to-site. However, the proportion of post-1950 Hg deposition represented by the vegetation layers varied considerably from site-to-site. Vegetation inventories varied by more than a factor of 10 from the lowest vegetation inventory of 0.13 mg m\(^{-2}\) at AM to 2.00 mg m\(^{-2}\) at ED. Whilst long-term Hg inventories appear to be in broad agreement, attempts to reconstruct shorter term deposition records from vegetation layers of a core must be approached with some caution. The influence of vegetation layers upon Hg profiles will be discussed in more detail in Section 6.5.2.2.

#### 6.5.2.2 Influence of vegetation upon Hg profiles

The [Hg] peaks visible in the top 0-3 cm in the vegetation layers of each site have not been widely reported within the literature (Benoit et al., 1998; Shotyk et al., 2003) and
Mercury are only apparent in a small sample of studies (e.g. Farmer et al., 2009). The possibility of a recent increase in Hg deposition due to a localised emission source can be discounted as all four sites exhibit this vegetation peak. A wider scale increase in atmospheric [Hg] and subsequent deposition is also unlikely and has not been reported in the literature or by atmospheric monitoring stations (Fowler et al., 2006; DEFRA, 2010) for the dates that correspond to the surface layers of FM, GT and ED, i.e. 2003-2007. As discussed in Section 5.5.2.1.1, differences in coring practices have been shown to affect the shape of elemental concentration profiles in peat bogs. Until recently, the surface vegetation on cores was simply discarded and so information relating to recent elemental deposition was lost (Farmer et al., 2006, 2009, etc). In addition, traditional corers such as the Cuttle and Malcolm (1979) corer compacts surface vegetation into a plug usually of <2 cm thickness that was either discarded or greatly distorted in relation to its original structure. Where cores are sectioned at 2 cm depth intervals, the vegetation plug becomes the top section of the core and digestion analysis of this material would provide a mean [Hg] for the entire depth of vegetation. As Farmer et al. (2006, 2007) pointed out, the vegetation can correspond to ~2 decades and so resolution over the contemporary period is lost. In contrast, a monolith core enables collection and sectioning of the vegetation layer and should therefore enable changes in [Hg] in recent deposition to be examined. However, two of the cores studied by Farmer et al. (2009) adopted the monolith tin coring approach and yet did not observe near-surface vegetation [Hg] peaks of this nature. Since the cores taken by Farmer et al. (2009) were collected in the months of September-November (2001-2004), the same time of year that this study’s GT and ED cores were sampled, the influence of seasonality can be discounted. Experimental error
also appears unlikely as (i) uncertainties in [Hg] in the core top sections were much smaller than the changes in concentration between consecutive layers; and (ii) the results obtained for the peat reference material NIMT/UoE/FM/001 digested using the optimised method described in Chapter 3 were in good agreement with certified values. With respect to ICP-MS analysis, Hg carry-over from standards was minimised as outlined in Chapter 3 and so higher values for the near-surface sections were not due to instrumental artefacts. On the basis that [Hg] peaks were observed within the living vegetation of each of the four cores, it is likely that biotic processes are responsible.

Section 6.3.2.4 established that plants can scavenge atmospheric Hg (e.g. Schroeder and Munthe, 1998) and accumulation of Hg within mosses is well documented (Matilainen et al., 2001; Lodenius et al., 2003; Nasr and Arp, 2011). Surface vegetation at all sites investigated in this study were dominated by Sphagnum mosses which can bioaccumulate Hg in their leaves through direct atmospheric uptake due to their thin cuticle and narrow cell walls (Lodenius et al., 2003). As discussed above, the Hg inventories in each core’s vegetation layers (Table 6.4) encompassed a wide range of values. ED had the greatest vegetation inventory of 2.00 g m\(^{-2}\) with FM, GT and AM possessing inventories of 0.78 g m\(^{-2}\), 0.25 g m\(^{-2}\) and 0.13 g m\(^{-2}\), respectively. While it could be assumed that the differences in vegetation inventories were due to different rates of uptake and scavenging as described by Grigal (2003) and Huckabee (1973), the broadly equivalent Hg inventories to 1950 in addition to the similarities between respective inventories to 1900-2000, that all incorporate the underlying peat/soil layers, show that similar quantities of Hg have been sequestered by each
system over longer timescales. The considerably smaller vegetation inventory at FM (0.78 mg m$^{-2}$) in comparison with ED (2.00 mg m$^{-2}$), despite the additional ~10 year period embodied by the FM vegetation, provides further evidence that differences in plant-related processes are determining the distribution of Hg within the uppermost sections of these cores.

The greater presence of non-moss, especially heather, species at AM (Section 4.7.14) may account for the very different solid phase profile recorded at the site although it is also possible that the Fe redox-cycling process at AM discussed in Chapter 5 are perturbing both the Pb and Hg profiles. Apparent agreement between the post-1950 Hg inventories between sites in this study, alongside the broad agreement between the 1900-2000 Hg inventory at AM and FM, implies that approximately equivalent quantities of Hg have been incorporated into AM’s solid phase over time. Uptake of Hg through root systems may be occurring from the deeper peat layers into the vegetation layers through vascular stems, resulting in vertical transportation of Hg. Such an effect is well-documented (e.g. USEPA, 1997; Ellis and Eslic, 1997; Han et al., 2006). If uptake rate is proportional to concentration, as suggested by Han et al. (2006), then a continual smearing and averaging of the Hg profile would be expected to occur. Greater quantities of Hg are removed from layers with high concentrations resulting in a narrowing of concentration ranges down the profile. However, additional study of the surface plant species AM is required to confirm this hypothesis. It is presumed that this effect does not occur at FM, GT and ED due to the abundance of Sphagnum mosses, which lack a vascular system, at these sites.

Possible perturbation effects including plant-related and Fe redox-cycling will be
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explored in more detail via examination of aqueous phase [Hg] profiles in the following section.

6.5.3 Aqueous phase [Hg] at FM, GT, ED and AM

Mercury concentration profiles for 0.2 µm-filtered porewaters extracted from each peat section of the cores taken from FM, GT, ED and AM are provided below in Figure 6.5. Concentration data was obtained via ICP-MS analysis as described in Section 2.3.17.

The [Hg] in the porewaters from the FM core were typically in the range 0.047-0.59 µg l⁻¹ but there were several narrow bands (0-1 cm, 14-18 cm, 25-27 cm) of high concentration. The maximum concentrations within each of these bands were 2.58 ± 0.029 µg l⁻¹ at 0-1 cm, 1.84 ± 0.019 µg l⁻¹ at 14-15 cm, 4.40 ± 0.051 µg l⁻¹ at 25-26 cm, and 1.04 ± 0.012 µg l⁻¹ at 41-42 cm. The minimum [Hg] of 0.047 ± 0.001 µg l⁻¹ occurred at a depth of 7-8 cm. For the GT core, the porewater [Hg] profile showed a decrease in concentration from a surface maximum of 2.03 ± 0.061 µg l⁻¹ to 0.03 ± 0.001 µg l⁻¹ at a depth of 4-6 cm. Below this, [Hg] increased again to a maximum value of 1.31 ± 0.008 µg l⁻¹ at 8-10 cm before decreasing to concentrations of 0.01-0.06 µg l⁻¹ from 11-20 cm.
Figure 6.5  Porewater (<0.2 µm) [Hg] profiles for FM, GT, ED and AM. Note the different scale for the AM core. Dashed line represents vegetation interface.

The range in porewater [Hg] for the ED core was 0.81-1.55 µg l⁻¹. Mercury concentrations decreased from 1.38 ± 0.051 µg l⁻¹ at 4-5 cm to 0.09 ± 0.040 µg l⁻¹ at a depth of 10-11 cm. At 13-14 cm, the [Hg] increased to the core maximum of 1.55 ± 0.053 µg l⁻¹ before decreasing gradually with depth to a minimum of 0.81 ± 0.051 µg l⁻¹ at the base of the core at 28-29 cm. No concentration data is available for the surface layer of the core as this layer comprised vegetation which did not yield
sufficient porewater following extraction. The porewater concentrations for the AM core were typically low (0.01-0.13 µg l⁻¹) but with a few concentration peaks outwith this range: 0.23 ± 0.023 µg l⁻¹ in the surface layer, 0.63 ± 0.065 µg l⁻¹ at a depth of 10-11 cm, and 0.27 ± 0.028 µg l⁻¹ at 13-14 cm.

It is difficult to compare these porewater profiles with the literature as very little vertical porewater profile data appears to exist. Mean Hg porewater (<0.45 µm, [Hg] determined via CVAAS) concentrations of 5 ng l⁻¹ (USGS 2002, Bergman et al., 2012) have been reported for peatlands, values that are considerably lower than those within this study. The possibility of Hg contamination from the filtration methodology (Section 2.3.1) inflating the results of this study can be ruled out as blank deionised water samples included alongside each sample set typically demonstrated [Hg] below the detection limit of the ICP-MS system of 0.001 µg l⁻¹, i.e. 1 ng l⁻¹ (Section 2.3.16.3).

### 6.5.3.1 Aqueous Hg profile discussion and comparison with solid phase profiles

Comparing the four sampling sites, each had a similar shaped porewater [Hg] profile although the depths and magnitudes of concentration maxima varied from site-to-site. The highest porewater concentration, 4.40 ± 0.051 µg l⁻¹, occurred in the FM core whilst the lowest maximum value of 0.634 ± 0.065 µg l⁻¹ was recorded for the porewaters from the AM core. More generally, the lowest porewater [Hg] was determined for the AM core. Each of the four sites showed a surface peak in
porewater [Hg] and at least one sub-surface Hg maximum. The peatland sites FM, ED and AM each had a porewater [Hg] maximum at or one layer above the vegetation/peat interface.

Solid and aqueous phase [Hg] profiles are compared in Figure 6.6. Aqueous phase concentrations were of the order of only a few µg l\(^{-1}\). Since both the solid phase and porewater profile at FM showed a near-surface enhancement in [Hg] the higher [Hg] concentrations in the surface layers of the solid phase were clearly not an artefact of the analytical procedures involved. Deeper in the core, the aqueous phase [Hg] peak at ~14 cm occurred above its closest solid phase counterpart (~18-19 cm), these layers representing the vegetation/peat transition region. The porewater [Hg] maximum at ~25 cm does not have a corresponding solid phase [Hg] maximum.

Similar solid/aqueous phase comparisons can be made for the GT and ED cores. GT showed a near-surface maximum in its vegetation layer in both solid phase and porewater profiles with a sub-surface porewater [Hg] maximum just above a corresponding solid phase peak (~10 cm). At ED, the same is true, although the sub-surface porewater and solid-phase peaks both occur at the same depth (~13.5 cm). The AM solid and aqueous phase profiles were generally similar although there were a number of solid phase [Hg] peaks that were not shared by the aqueous phase (e.g. at 4.5 cm). The most notable feature of both profiles is the large [Hg] peak in close proximity to the vegetation/peat interface.
Comparison of Hg porewater profiles with pH, conductivity and DOC profiles presented in Section 4.7.1 revealed no apparent links to the Hg porewater concentration at any site. Likewise, the broadly featureless moisture content, organic content and solid phase pH profiles contained no profile features at depths corresponding to the Hg porewater concentration peaks. However, porewater [Hg]
peaks did generally occur in layers where the solid phase peat/soil density increased (Section 4.7.1). The vegetation-peat interface layers at FM (~15 cm), ED (~10 cm) and AM (~11 cm) all had a porewater Hg maximum within one core layer of this point. At the vegetation interface, layer densities increased considerably (FM: $0.58 \rightarrow 1.01$ g cm$^{-3}$; ED: $0.70 \rightarrow 1.07$ g cm$^{-3}$; AM: $0.98 \rightarrow 1.84$ g cm$^{-3}$) due to decomposition of plant matter and formation of a cohesive peat substrate. At GT, where the vegetation layer was only 1 cm thick, no density increase was observed at the interface point. However, the transition from dead and partially decomposed litter into the peat itself occurred at ~6 cm depth and this was accompanied by an increase in soil density of $0.25 \rightarrow 0.41$ g cm$^{-3}$. A broad density peak spanned the depth range of 6-11 cm, the midpoint of which corresponded to the sub-surface porewater [Hg] maximum at ~9 cm. The large sub-surface porewater [Hg] peak at FM at 25.5 cm also correlated with a broad density peak (24.5-26.5 cm) and an increase in layer density of $0.99 \rightarrow 1.55$ g cm$^{-3}$ was recorded. Bulk density is generally accepted to be a measure of the degree of decomposition of peatland organic matter (e.g. Givelet, 2004; Franzen, 2006) with regions of high density typically containing more decomposed matter. Decomposition of peatland organic matter may result in the breakdown and depletion of the organic functionalities that bind Hg (e.g Wieringa, 1964; Section 1.3.2.2; etc) and it is conceivable that these processes may be causing limited release of Hg from the solid phase into the aqueous phase, accounting for peaks in porewater [Hg] in layers of high density. Importantly, such releases may have implications regarding the integrity of peatlands as records of historical Hg deposition. Thus, further characterisation of the solid phase OM, especially involving comparison of OM composition in high and lower density peat, in addition to
more detailed elucidation of the forms and associations of Hg in the porewaters, is required to assess this hypothesis.

### 6.5.4 Archival records of Hg deposition

As outlined in Section 6.4 it is unclear whether solid phase [Hg] profiles represent historical deposition trends. The main concerns surrounding the integrity of peat as an Hg record are: (i) vertical migration of Hg within the peat/soil porewaters; (ii) near-surface accumulation by plants; and (iii) losses of Hg\(^0\) to the atmosphere (Tipping et al., 2011).

**Mercury migration within the soil/peat porewaters**

At all four locations, porewater [Hg] is a small fraction of [Hg] in the solid phase (porewater [Hg] typically <5 µg l\(^{-1}\); solid phase [Hg] typically >0.1 mg kg\(^{-1}\)). Furthermore, the sub-surface solid phase [Hg] concentration peaks do not consistently show a corresponding porewater [Hg] peak at equivalent depth, implying that vertical migration of Hg through the aqueous phase may be occurring. For example at FM, there was a large porewater [Hg] maximum (4.4 µg l\(^{-1}\)) at 25.5 cm without a corresponding solid phase maximum and low porewater [Hg] in the layers immediately above and below this peak (<1 µg l\(^{-1}\)). Although porewater [Hg] peaks apparently correlate with regions of increasing peat density (Section 6.5.2.1), the porewater [Hg] peaks occurring in close proximity to the vegetation/peak interface also generally correspond to peaks in solid phase [Fe] (Section 4.7). The vegetation/peat interface solid phase [Hg] peak, corresponding porewater [Hg]
maximum, a region of density increase (Section 6.5.2.1) and the solid phase [Fe] maximum were present at depth ranges of 7-13 cm at GT, 10.5-13.5 cm at ED and 10-12 cm at AM. Although this study did not record an [Fe] profile for FM, Cloy et al. (2009) reported an [Fe] maximum and region of density increase at the vegetation/peat interface of FM, the position where porewater and solid phase [Hg] peaks were found in this study. These depths are just below the vegetation/peat interface in the region of the water table at each site (Section 4.7.1). It must therefore be considered that the redox cycling of Fe (Section 4.5.7) is influencing the solid and aqueous [Hg] profiles. Although the vegetation/peat interface represents a change in density within the profile, the position of the water table marks the boundary between oxic and sub-oxic conditions, consistent with the presence of a solid phase [Fe] maximum. Without detailed aqueous phase [Fe] profiles it is impossible to adequately explore this theory and additional study is required. If Fe cycling does indeed influence Hg in the aqueous phase, a degree of perturbation of the solid phase Hg profile relative to historical deposition would be expected.

**Near-surface accumulation of Hg by plants**

It is possible that the [Hg] maxima within the vegetation layers of each of the cores may be representative of increased recent Hg deposition but this explanation runs contrary to recent literature (e.g. Farmer et al., 1999) and monitoring data (DEFRA, 2010; EMEP, 2012) which demonstrated that peak deposition occurred in the mid 1950s and that Hg deposition has continued to decrease to the current time. At the FM, GT and ED sites where moss species dominate at the core surface, both solid and aqueous phase [Hg] profiles showed similar trends. At AM, where some vascular
plants including heather species were growing at the surface of the core, the Hg profile showed no near-surface maximum, perhaps more in line with recent deposition. The lack of uptake of Hg by these vascular plants appears to yield a different Hg profile with diminished [Hg] maxima near the vegetation/peat interface when compared to sites with abundant mosses. It would appear that sites where surface vegetation is entirely mosses distort Hg deposition records relative to recent deposition. However, it is notable that despite the apparent differences in plant uptake processes between AM and FM, post-1950 inventories are in good agreement (AM: 2.20 mg m\(^{-2}\); FM: 2.82 mg m\(^{-2}\)), particularly when the vegetation component is subtracted yielding inventories of 2.07 mg m\(^{-2}\) at AM and 2.04 mg m\(^{-2}\) at FM.

**Losses of Hg\(^0\) to the atmosphere**

Dated peatlands across Europe all demonstrate similar Hg chronologies (Shotyk et al., 2003; Bindler, 2006; Farmer et al, 2009; etc) with peak Hg deposition occurring around 1950 ± 20. Moreover, the good agreement between peat and ice core records in terms of dates (Schuster et al., 2002; USGS, 2002) increases the apparent integrity of the peat records. The core inventories presented within this project provide additional evidence for the retention of Hg within peatlands. Peatlands as archival records of Pb deposition are well established (Section 5.3.5) and yet the Pb inventories to 1980 across FM, ED and AM show a larger factor of difference (3.07) than the 1950 inventories for Hg (2.09). GT is omitted from this comparison due to enhanced Hg capture by the forest canopy, discussed in Section 6.5.2.1. The good agreement between inventories at the sites in this study and those in literature, in combination with the typically even distribution of inland wet Hg deposition
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(DEFRA, 2010), implies that any vapour loss of Hg\(^0\) from these terrestrial systems is either equivalent at each site, or negligible. Furthermore, considering only the most recent 10 years of Hg accumulation, each site in this study has accumulated more Hg (FM: \(~400\) mg ha\(^{-1}\) yr\(^{-1}\); GT: \(~200\) mg ha\(^{-1}\) yr\(^{-1}\); ED: \(~700\) mg ha\(^{-1}\) yr\(^{-1}\)) or about the same amount of Hg (AM: \(~100\) mg ha\(^{-1}\) yr\(^{-1}\)) as would be expected from the 2007 wet deposition figures alone (\(~100\) mg ha\(^{-1}\) yr\(^{-1}\); DEFRA, 2010). The sites where Hg accumulation greatly exceeds wet deposition are all abundant in surface mosses which are known to scavenge atmospheric Hg (Huckabee, 1973) to a greater extent than other plant species. This may account for the larger than expected inventories commonly reported in the literature (e.g. Biester et al., 2007). Losses of Hg\(^0\) to the atmosphere are evidently not resulting in a shortfall in Hg inventories. Despite the available evidence that suggests historical Hg deposition trends are partially preserved, in order to assess the degree to which peat records reflect Hg deposition, it is necessary to compare detailed wet and dry deposition records with high resolution core profiles and associated inventories. Unfortunately, lack of detailed deposition and emission data prevents this comparison from being fully realised. As existing deposition records (e.g. Fowler et al., 2006; DEFRA, 2010) become more comprehensive, these comparisons may be possible in the future. Taking an alternative approach, assessment of the speciation of Hg in peatlands may provide an indication of the likelihood of Hg loss to the atmosphere. For example, the presence of large quantities of Hg\(^0\) would represent the potential for considerable loss from a system, whereas Hg\(^{2+}\) species should be bound to the solid phase and thus immobilised (Section 6.3.2.3.1). Mercury speciation is therefore discussed in more detail in Section 6.5.4.
6.5.5 Hg speciation and fractionation

6.5.5.1 Solid phase Hg speciation

The majority of literature approaching the topic of Hg speciation has focused on simulated laboratory environments (Song and Heyst, 2005; Liu et al., 2006; Yang et al., 2007; Zheng et al., 2008; Issaro et al., 2009; Obrist et al., 2010). Where speciation studies have been attempted on real environmental samples, harsh extraction conditions call into question whether true environmental Hg speciation is being maintained post-extraction (e.g. Guedron et al., 2009). In order to further investigate the role of vegetation and peat/soil in retaining Hg, the speciation of solid phase Hg at FM, GT and ED was assessed via 2-mercaptoethanol extraction (Section 2.3.14.3) followed by HPLC-ICP-MS analysis as per the method developed in Section 3.3. Due to time constraints, solid phase samples from AM were not subjected to this method. The proportions of $\text{Hg}^{2+}$ (inorganic), $\text{MeHg}^+$ and $\text{EtHg}^+$ (organo-Hg) relative to solid phase concentration totals for selected depth sections from the FM, GT and ED cores are presented in Figure 6.7. As the proportion of $\text{Hg}^0$ cannot be directly measured via HPLC-ICP-MS, the mass balance deficit may be assumed to approximate $\text{Hg}^0$. 
High proportions of organo-Hg were found in the 0-1 cm, 4-5 cm, and 9-10 cm layers of the FM core. These forms constituted 86%, 69% and 93% of total Hg in each of these respective layers. Below this, the proportion of organo-Hg decreased to
30% of total Hg at 12-13 cm depth and to only 2% of total Hg at 19-20 cm. Recovery rates from combined fraction totals relative to total [Hg] were 98%, 92%, 98%, 72% and 97% for 0-1 cm, 4-5 cm, 9-10 cm, 12-13 cm and 19-20 cm layers, respectively.

At GT, inorganic Hg\(^{2+}\) dominated the speciation for the majority of layers. At 0-1 cm, inorganic Hg constituted 62% of total Hg, 79% at 1-2 cm depth, 45% at 2-3 cm, and 83% at 3-4 cm. By comparing the combined Hg fractions with the total [Hg] for each layer, the calculated mean recovery was 83%.

Organo-Hg constituted 85% and 80% of total Hg in the extracts from the 0-3 cm and 6-9 cm layers at ED, respectively. At 12-15 cm, the proportion of organo-Hg decreased to 25% of the total. Below this, the percentage of organo-Hg was slightly higher, i.e. 37% at 18-21 cm and 45% at 24-27 cm. Recovery rates relative to total Hg at ED were in excess of 89% for all layers and increased with increasing depth. It is conceivable that this trend represents surface Hg\(^0\) being lost from the surface vegetation resulting in smaller amounts of Hg\(^0\) being retained in the deeper core sections.

Mercury speciation at the FM and ED sites was broadly similar. Within the vegetation sections of each core, i.e. 0-15 cm for FM and 0-10 cm for ED, organo-Hg dominated, with >85% of Hg in the form of Me- and Et-Hg. Within the FM and ED peat layers, there was a major change in solid phase Hg speciation, with 54–98%
now in the form of Hg$^{2+}$. The highest proportion of Hg$^{2+}$ was determined for the deepest sections of both cores. The trends observed in the peatland sites are similar to those reported by Selvendrian et al. (2008) who observed higher concentrations of MeHg in near-surface layers of wetland sites and considerably lower concentrations with increasing depth. However, the MeHg concentrations for upper core sections reported by Selvendrian et al. (2008) of 6-7 µg kg$^{-1}$ are considerably lower than those of this study (~0.04-2.06 mg kg$^{-1}$). This difference may be attributed to inherent differences between the wetland site studied by Selvendrian et al. (2008) and the peat environments used in this study. It should also be noted that good agreement between combined sub-fraction [Hg] and total layer concentrations, in addition to the good certified reference material results, imply that the values reported in this study are not excessively high.

The near-surface layer of peatlands where organo-Hg species were dominant is not apparent at in the GT soil where Hg$^{2+}$ dominated (50-80%) at all depths. The predominance of inorganic Hg$^{2+}$ in soils and in the deeper sections of FM and ED, in conjunction with Hg$^{2+}$'s strong associations with the sulfur groups inherent in humic matter (Biester et al., 2003) are a further indication that Hg is generally immobile in peat/soil systems.

Only a small fraction of total Hg was present in the form of EtHg with the exception of the 4-5 cm layer of FM and the 9-10 cm layer of ED which showed 56% and 93% EtHg, respectively, relative to total Hg. For all of the other selected layers from each
of the three sites, EtHg does not exceed 7% of total Hg. In the absence of application
of EtHg-containing pesticides, the presence of EtHg has not been widely reported in
literature. This is believed to be partly due to the tailoring of extraction and analysis
techniques specifically for MeHg (Holmes and Lean, 2006). Environmental EtHg has
been reported in wetlands, mining soils and the Florida Everglades. (Hintlemann et
al., 1995; Cai et al., 1997; Siciliano et al., 2003; Holmes and Lean, 2006) and so its
occurrence in soils and peatlands is not without precedent. Mao et al. (2010)
explored the possibility of CH$_3$SHg and EtHg being confused via chromatographic
analysis techniques and successfully demonstrated that EtHg was indeed present in
the Florida Everglades and not merely a procedural artefact.

Alkylation of environmental Hg by sulfur-reducing bacteria was discussed in Section
6.3.3. However, vegetation processes are also reportedly responsible for alkylation of
Hg. Species of mosses including $H$. splendens and $P$. schreberi are known to
methylate inorganic Hg to a greater degree than shrub and tree leaves/needles
(Moore et al., 1995), providing an explanation for the larger contribution of inorganic
Hg in the surface layers of the forest environment relative to the vegetation layers of
the two peatland sites. It is further possible that vegetation merely acts as the host for
Hg-alkylating bacteria. To explore this concept, and to better understand the
processes driving the abundance of organo-Hg in the vegetation layers of FM and
ED, Chapter 7 will assess the activity of (poly)phenol oxidase in peat, a measure that
has previously been adopted as an approximation of overall microorganism activity
in peat/soil systems.
6.5.5.2 Speciation and associations of Hg in porewaters

6.5.5.2.1 Aqueous Hg speciation

At the FM, ED and GT sites, only inorganic Hg$^{2+}$ was detected within porewaters (<0.22 µm) via HPLC-ICP-MS analysis. Organo-Hg species were either not present, or were present in insufficient quantity to be detectable. This result is in agreement with published work (Zhang et al., 2004; Holmes and Lean, 2006; Goulet et al., 2007) which reported that inorganic Hg$^{2+}$ species were the predominant form of Hg in wetland porewaters. This finding is significant as it provides further evidence of that Hg will be retained within the peat system as Hg$^{2+}$ is likely to readily associate with solid phase organic material (e.g. Benes et al., 1976; Biester et al., 2003) or ultimately precipitate out of solution if in the form of HgS (Zhang et al., 2004).

6.5.5.2.2 Aqueous Phase Hg characterisation via sequential ultrafiltration

Following characterisation of the associations of Pb in peat and soil porewaters (Section 5.5.4.2), similar procedures were applied to investigate the associations of Hg. To these ends, porewaters from FM, GT and ED were subject to sequential ultrafiltration as outlined in Section 2.3.2 and their [Hg] analysed via ICP-MS. As a result of the low concentrations of total Hg in porewaters, [Hg] in many of the ultrafilter fractions was below the limit of detection. The only data obtained was for the ED porewaters and this is shown in Figure 6.8.
Figure 6.8 Concentration of colloidal and dissolved fractions following sequential ultrafiltration of ED porewaters.

At the ED site, all layers for which data ultrafiltration data exists showed the largest proportion of Hg in the >100 kDa colloidal size fraction. In this fraction, 47%, 38% and 32% of detected Hg was present at 3-6 cm, 6-9 cm and 27-30 cm, respectively. Mercury was evenly distributed across the remaining size fractions in all core sections with distribution ranging from 15-25%. These results were similar to those for Pb distribution where the >100 kDa size fraction was also most important. These results suggest that large colloids present favourable binding environments for porewater Hg$^{2+}$. Ultrafiltration experiments performed by Graham et al. (2011) also demonstrated the importance of the large colloid fraction for the mobility of U in porewaters from a contaminated soil system.

The recovery rates from the ultrafiltration experiment were, however, poor with ~45% recoveries relative to total Hg. The Hg loss may be due to adsorption onto the internal surface and membrane component of the PET ultrafiltration vials. In future,
this effect could be explored by attempting to extract any membrane-bound Hg using mercaptoethanol to determine the amount lost to the membrane or simply by repeating the procedure with a chemically different membrane. For example, high recoveries for MeHg and total [Hg] have been reported in the literature (Babiarz et al., 2003) using regenerated cellulose membranes. Additionally, standard solutions of known [Hg] could be subjected to ultrafiltration and their concentration measured before and after filtration to confirm that loss is occurring during the ultrafiltration process. For the purposes of this study, it will be assumed that Hg distribution among fractions is preserved despite loss and will be compared to distributions of DOC in Chapter 7 to allow further interpretation of aqueous phase characterisation results.

6.6 Chapter Conclusions

The profile layers in which maximum [Hg] were recorded were similar to those in which the [Pb] maximum due to coal burning and petrol emissions was observed. As coal represents a significant source of both Hg and Pb, the co-occurrence of these peaks provides strong indication that the period of maximum flux of both elements was similar and that this feature of Hg deposition has been preserved within these profiles. Post-1950 Hg inventories from FM, ED and AM peatlands were broadly similar at 2.82 mg m\(^{-2}\), 3.23 mg m\(^{-2}\) and 2.20 mg m\(^{-2}\), respectively; in addition, the 1900-2000 inventories from FM and AM were in agreement with those reported in literature (Farmer et al., 2009). Since these similarities imply that Hg has been sequestered to a similar degree, this study appears to provide supporting evidence that peatlands can act as an archival record of Hg deposition. At 4.60 mg m\(^{-2}\), the Hg inventory to 1950 for GT was 1.5-2.0 times larger than those at the three peatland
sites, attributable to the increased interception of atmospheric Hg by the forest canopy. Across the sampling sites in this study, three categories of aqueous phase $[\text{Hg}]$ maxima were recorded: (i) Surface $[\text{Hg}]$ maximums in the vegetation layer controlled by processes dependent upon the types and species of plants and mosses present; (ii) Peaks occurring around the core vegetation/peat interface as a result of Fe redox-cycling induced mobilisation into the aqueous phase; and (iii) $[\text{Hg}]$ peaks occurring in the deeper peat layers of the core corresponding to layers where density increases and consequently organic matter is in a state of more advanced decomposition. Organo-Hg species are more abundant than inorganic Hg$^{2+}$ species in the solid phase near-surface vegetation of peatland sites due to alkylation by plant species or the biota associated therein, although the processes responsible for such alkylation are reportedly species dependent. At depths below the vegetation/peat interface where living plant matter is absent, this relationship is reversed as Hg$^{2+}$ consistently comprises >50% of total $[\text{Hg}]$. In the GT forest environment, inorganic Hg$^{2+}$ is the dominant species across the entire core profile due to the thinner surface moss layer (~1 cm thick) than those at the peatland sites (~10-15 cm thick) combined with reportedly lesser capability of tree leaves/needles to alkylate Hg. In the aqueous phase, only inorganic Hg$^{2+}$ is detectable across all sampling sites suggesting that mobility in the aqueous phase is limited due to the propensity for Hg$^{2+}$ species to associate with solid phase organic matter or to precipitate out of solution via formation of HgS. The large (>100 kDa) brown colloidal porewater fraction contained a greater proportion of Hg than any other size sub-fraction suggesting that these colloids present a move favourable binding environment than the smaller
alternatives. However, this result must be considered in context as recovery rates from porewater fractionation studies were low at ~45%
Chapter 7: Properties of peat and soil organic matter

7.1 Introduction

In the previous chapters the associations and speciation of Pb and Hg have been explored in peatlands and forest soil systems in Scotland. The key to better understanding why these associations occur lies in an improved characterisation of the composition of the organic matter present within these terrestrial systems. Organic matter in peatlands has previously been characterised via a wide variety of techniques. Approaches include: determination of elemental composition analysis via CHNO analysis (e.g. Silamikele et al., 2010; Heim et al., 2012); analysis of hydrocarbon and oxygen-containing functional groups via FT-IR spectroscopy (e.g. Stevenson, 1994; Cocozza et al., 2003) and quantitative wet chemical methods (e.g. Schnitzer and Gupta, 1965; Stevenson, 1994); free-radical and aromatic functional group analysis via fluorescence spectroscopy (e.g. Miano and Senesi, 1992; Miano and Alberts, 1999); and structural assessment via NMR spectroscopy (e.g. Preston et al., 1987). The abundance of humic substances in peatlands has resulted in many researchers extracting and specifically characterising this material. The degree of humification is widely considered to indicate the level of decomposition of peatland organic matter. The techniques listed above have also been applied to characterise humic extracts although additional approaches such as measurement of supramolecular size can also be employed (e.g. Silamikele et al., 2010).

Organic matter constituted the majority of the solid phase material at all three of the peat bog sampling locations in this study with >80% of solid phase material in FM,
ED and AM comprising organic matter. In the top sections of GT >90% of solid phase matter is in the organic fraction, decreasing to 30-50% in the lower core sections (Section 4.7.1). This chapter discusses functional group distribution in solid phase organic matter in order to explain variations in the humic association of Pb within the peat/soil profiles (Section 5.5.5.1) and the mobility of Hg near the vegetation/peat interface (Section 6.5.2.1 and Section 6.5.3) the enzymatic activity of microorganisms to further investigate trends in Hg speciation (Section 6.5.4.1), and the distribution of DOC between the various colloidal size fractions to improve understanding of Pb and Hg porewater associations (Section 5.5.5.2 and Section 6.5.3.2.2).

7.2 Functional group chemistry and links to metal binding in peat systems

7.2.1 Carboxyl, carbonyl and hydroxyl functionality of peat

Oxygen groups are frequently implicated in the binding of metals to SOM, particularly deprotonated -OH groups. Multi-dentate interactions involving carboxyl, carbonyl and phenolic groups are the route through which most metal-HA binding is believed to occur (e.g. Davies et al., 1997; Xia et al., 1997). To further investigate the relationship between functional group and metal distribution, the molar equivalents of carboxyl, carbonyl and hydroxyl groups were measured for humic extracts (Section 2.3.12) from FM and AM core layers via the methods presented in Section 2.3.6. Functional group profiles are shown in Figure 7.1. It should be noted that there will be overlap between the functional groups detected by these techniques.
Figure 7.1  FM (top) and AM (bottom) depth profiles for carboxyl, carbonyl, and hydroxyl functional group molar cmol, kg$^{-1}$ humic matter. Dashed line represents vegetation-peat interface.
The carboxyl content at AM increased from 0.48 cmol$_c$ kg$^{-1}$ in the surface vegetation layer to 0.77 cmol$_c$ kg$^{-1}$ directly above the vegetation/peat interface. Within the peat proper, the carboxyl content again increased with increasing depth to a maximum value of 0.89 cmol$_c$ kg$^{-1}$ at 33.5 cm depth. Below 33.5 cm, the sharp decrease in carboxyl functionality coincides with the rapid drop in organic matter content (Section 4.7.1) as the core transitions into underlying clay. The carbonyl content profile for AM closely follows the carboxyl functionality trends. The concentration increases from 0.54 cmol$_c$ kg$^{-1}$ in the uppermost vegetation layer to 0.87 cmol$_c$ kg$^{-1}$ above the vegetation interface. Below the interface, the concentration drops to 0.76 cmol$_c$ kg$^{-1}$ before increasing to 1.18 cmol$_c$ kg$^{-1}$ at 33.5 cm. Carbonyl concentration also decreased rapidly as the core material transitioned into a clay-rich substrate. The hydroxyl functionality profile differed from those of the carboxyl and carbonyl groups in that it had a single peak of 12.6 cmol$_c$ kg$^{-1}$ at 21.5 cm depth and an approximately constant concentration of ~8-10 cmol$_c$ kg$^{-1}$ across the remainder of the core.

Both sites showed an increase in carboxyl functionality with depth in both the vegetation and peat layers, with a small decrease in concentration immediately below the vegetation/peat interface. The overall increase in carboxyl functionality at FM was greater than that at AM. Carbonyl concentration profiles differed between the two sites in both profile trend and concentration ranges. In contrast with the FM results, the AM carbonyl profile largely followed that for carboxyl. The AM carbonyl concentrations were also significantly lower than those at FM. Hydroxyl concentration profile trends were almost identical at FM and AM although the depths
at which the single peak occurred was different (7.5 cm for FM and at 21.5 cm for AM); the FM hydroxyl peak occurred in the vegetation layers whereas the AM hydroxyl concentration peak corresponded to peat material. The hydroxyl functionality at AM was consistently a factor of ~2 greater than at FM.

The range of carboxyl group concentrations for peat/soil humic extracts in the literature is varied, with values of 2.8-3.6 cmol c kg\(^{-1}\) (Portal et al., 1986), 2.3-3.1 cmol c kg\(^{-1}\) (Bonnet and Cousins, 1987), 0.8 cmol c kg\(^{-1}\) (Karlsson et al., 2007) and 0.3-4.9 cmol c kg\(^{-1}\) (Brunetti et al., 2007) having been reported. Publications reporting carbonyl concentrations are less commonplace with values of 3.0-5.4 cmol c kg\(^{-1}\) (Portal et al., 1986) recorded. Hydroxyl functionality in literature includes ranges of 3.1-5.9 cmol c kg\(^{-1}\) (Portal et al., 1986) and 3.71-8.55 cmol c kg\(^{-1}\) (Brunetti et al., 2007). The published carboxyl functionality concentrations are greater in magnitude than those reported at FM and AM. In contrast, those relating to hydroxyl concentrations were lower than observed in this study. Carbonyl functionality concentration at FM was comparable to the literature values although the concentrations at AM were somewhat lower than those reported by Portal et al. (1986). The differences between functional group concentrations reported in literature may be the an effect of the NaOH treatment used to extract the humic matter or, alternatively, may reflect small, site-specific variations in the composition of organic matter.
Since most of these studies involved the use of humic substances extracted from homogenised, bulk peat samples, the extent of vertical variations at any individual location have been lost. This study has shown clear trends in functionality with increasing depth, and evidence of changing composition around the transition from vegetation to peat. Although there are some similarities between the vertical profiles, there are also clear differences in composition between the humic material from FM and that from AM.

### 7.2.2 Functional group chemistry and Pb-humic associations

Comparison of functional group profiles with the total [Pb] concentration profiles (Section 5.5.1 and Section 5.5.3) showed no apparent correlation between the functional groups investigated and [Pb] although it should be noted that these functional groups do not only bind Pb and are involved in binding to many other species, including other metals (e.g. Tsidris et al., 2006; Pettit, 2010). The key features in the metal profiles are not matched by apparent features in functional group profiles. The possible exception to this was the presence of a hydroxyl concentration peak ~20 cm at AM, the depth of peak solid phase [Pb]. Lack of correlation between metals and functional groups suggests that none of the functional groups analysed here are uniquely responsible for the binding of Pb. However, the functional group distribution in the humic material may still explain how the Pb-humic associations change with depth. The association of Pb with humic substances was presented previously in Section 5.5.5.1. Composite graphs of functional group concentration and Pb-humic association are shown below in Figure 7.2.
Carboxyl functionality and the degree of Pb-humic association both increased with depth. The carbonyl functionality profile showed its maximum of 6.6 cmol$_c$ kg$^{-1}$ at 7.5-10 cm depths, the same depth at which a minimum in Pb-humic association of ~20% is observed. A peak in the hydroxyl concentration of solid phase humic matter also occurred at 7.5 cm depth but does not continue into the 10 cm layer. Overall, there is a general trend of increasing Pb binding with increasing carboxyl content although the sections in which the humic substances were rich in carbonyl and hydroxyl functionality appear to discourage Pb-humic association. Phenolic and carbonyl compounds are reportedly generated in the early steps of diagenesis and are transient (Baldock et al., 1997; Barkovskii et al., 2009) which would imply that this region of the FM core corresponds to early-stage humification. The implication that these functional groups are not retained in the later stages of decomposition also accounts for the decreases in their concentration at depth where decomposition has progressed further. It is apparent that the 7-10 cm layers are unique in terms of organic matter composition and functionality and further study is required to
determine in what way the Pb-humic associations differ at this depth. Pb-humic associations are investigated in further detail via gel electrophoresis in Section 7.3.

### 7.2.3 Functional group chemistry and Hg mobility near the vegetation/peat interface

The small decrease in carboxyl functionality that occurred close to the vegetation/peat interface (Section 7.2.1) in each of FM (15.5 cm) and AM (12.5-16.5 cm transition) also occurred within one layer of the porewater [Hg] maximum (FM: 14.5 cm; AM: 11.5 cm) in these cores. As discussed previously in Section 6.5.3.1, these layers correspond to regions of density increases and to the depths at which solid phase [Fe] peaks are observed. The reduction of Fe\textsuperscript{III} (a terminal electron acceptor) is known to fuel microbial decomposition of OM in soils and peats (Weber \textit{et al.}, 2006; DeAngelis \textit{et al.}, 2013). It is known that certain acidic functional groups are preferentially utilised during microbial breakdown processes (e.g. Volk \textit{et al.}, 1997). Thus microbial alteration of the OM during Fe reduction at these depths, resulting in partial depletion of carboxyl functionality, may be responsible for the release of Hg into the porewater at depths of 15.5 cm and 10 cm at FM and AM, respectively. However, as highlighted previously in Section 6.5.3 further study is required to confirm this hypothesis.
7.3 Fractionation of humic matter by gel electrophoresis

Section 5.5.5.1 established that the majority of Pb was associated with humic substances. In order to investigate these associations further, solid phase humic substances from selected depths in each of FM, GT and ED were fractionated via gel electrophoresis using the methodology outlined in Section 2.3.13 and the concentration of Pb within the successive 1-cm gel strips was measured by ICP-MS. The distribution of Hg could not be measured due to fractional concentrations falling below detection limits. The distribution of Pb is shown in Figure 7.3 for 9 selected layers from each of the three sites. Layers were chosen to span the near-surface of each core, representing both vegetation and peat/soil sections with high [Pb] to aid detection following fractionation. To these ends, layers at 0-1 cm, 1-2 cm, 6-7 cm, 7-8 cm, 9-10 cm, 13-14 cm, 15-16 cm, 17-18 cm and 19-20 cm were selected at FM; layers corresponding to depths of 0-3 cm, 3-6 cm, 6-9 cm, 9-12 cm, 12-15 cm, 15-18 cm, 18-21 cm, 21-24 cm and 24-27 cm were selected from GT; and layers from 0-2 cm, 2-4 cm, 4-6 cm, 6-8 cm, 8-10 cm, 10-12 cm, 12-14 cm, 14-16 cm and 17-19 cm were chosen at ED.

As discussed previously in Section 2.3.13, humic molecules of smaller sizes are transported further across the gel plate than larger molecules of equivalent charge density. If two molecules are identical in size, the one possessing a greater charge density may also be transported a greater distance from the well. Gel strips, sliced at 1-cm intervals, were numbered from 1-10 with strip #1 located nearest the well, and strip 10 the further distance from the well in the direction of the positive electrode. The residual humic material remaining in the gel well was also analysed for [Pb].
Figure 7.3  Gel fraction [Pb] distribution across plates with migration from left to right along the horizontal axis for (A) FM, (B) ED and (C) GT.
7.3.1 Gel electrophoresis Pb results

Flanders Moss (FM) Pb gel distribution

In terms of a mass balance, the combined fractions including the gel well material for each FM layer accounted for a mean of 80% of the Pb concentration of the original humic extract, calculated by comparing total Pb of combined gel fractions to the total Pb in 0.2 ml sub samples of humic extract, determined via ICP-MS analysis (Appendix 10).

Comparison of the Pb distributions amongst the gel fractions obtained for humic substances isolated from the peat at selected depths from the FM core revealed significant differences. For the three layers within the top 0-6 cm, the greatest [Pb] was obtained for gel fraction #1. Pb was present at lower and relatively uniform concentrations in gel fractions #2→8 and almost no Pb was present in fractions #9 and #10. For the humic substances extracted from the 7-8 cm FM layer, there was a broad [Pb] peak in fractions #1-2 but the maximum concentrations were obtained for fractions #7-8. At 9.5 cm, [Pb] peaks were in fractions #2 and #5, with much lower [Pb] across fractions #6-10. At the 13.5 cm depth, there was a broad [Pb] peak spanning fractions #3-4 and a further peak at #6. The [Pb] for fractions #7-10 remained consistently lower than those for the less mobile fractions. In the deepest layers investigated, i.e. those within the 15-20 cm layers, Pb was broadly confined to fractions #2 and #3, with very low concentrations in fractions #6-10. Overall, the majority of Pb migrated to #1 for the humic substances from the uppermost 0-6 cm of FM. Peak [Pb] of ~0.3-0.65 µg fraction⁻¹ for #1 were almost twice the [Pb] of ~0.2
µg fraction\(^{-1}\) within the other gel fractions at these depths. The prevalence of Pb in the low-numbered fractions is indicative of association with large, bulky and/or low-charged humic molecules. Progressing to the mid-depths (7-14 cm), the Pb distribution was much broader with concentrations of 0.08-0.28 µg fraction\(^{-1}\) extending into the fractions containing smaller and/or higher-charged humic molecules (e.g. fractions #7-8 for humics from the 7-8 cm section). There was then a dramatic shift in the distribution at greater depths, 15-20 cm, where the Pb was focused within #2-#3, indicative of a uniform association with large/low-charged humic molecules. At all depths the amount of Pb residual in the gel well was small at <0.25 µg fraction\(^{-1}\).

**Glentress (GT) Pb gel distribution**

The mass balance for humic substances extracted from the GT soils was extremely good; combined gel fractions from GT samples yielded a mean Pb recovery of 94% relative to equivalent volumes of humic extracts. The gel fractions from the GT site showed similar Pb distributions to FM from the surface to 12.0 cm depth. For the humic material from each of the six layers contained therein, the highest [Pb] were obtained for fractions #1 and #3-4 and values decreased towards fractions #6-10. In the deeper layers of GT, 12-18 cm, there was a pronounced Pb peak centred on fraction #3. In these deeper layers, fractions #6-10 again contained low [Pb]. Although the Pb distributions for humic substances from the GT core exhibited less pronounced peaks than FM, the overarching trends were similar. At all depths, with the exception of 7 cm, the majority of humic bound Pb is associated with the humic
material in gel fractions #1-4, indicating a preference for bulky to medium sized humic matter. At depths of 7-9 cm, the distribution of Pb between gel fractions was more even but, at depths below 12 cm, there was a change to focused concentration peaks within fractions #2-4. At all depths the amount of Pb residual in the gel well was small at <0.35 µg fraction$^{-1}$.

**Easter Deans (ED) Pb gel distribution**

A total Pb recovery from combined fractions yields a mean recovery of 103% relative to Pb concentration in the humic extract, again indicating excellent mass balances for the electrophoretic fractionation process. There were [Pb] peaks in fractions #1 and #3 for humic substances from the uppermost layer at ED. The remaining Pb was distributed evenly across the other gel fractions. All gel fractions obtained for humic material extracted from the 4.5 cm and 7.5 cm layers showed broadly consistent Pb concentrations of 0.20-0.25 µg fraction$^{-1}$ and there were no pronounced concentration peaks. In contrast, there was a prominent peak in fraction #5 for the humic substances from the 10.5 cm layer. The humic substances from next layer, 13.5 cm, yielded a similar Pb distribution to the 10.5 cm layer although the large [Pb] peak at fraction #5 was absent and there were two peaks centred in fractions #3 and #8. The distribution pattern for humics from the 16.5 cm layer was similar to the layer above in that the peak at fraction #3 was again present. There was, however, no peak at fraction ‘8. The fractionated humic substances from the deepest core layers investigated, 19.5-25.5 cm, all showed peak [Pb] in fraction #3. The results for the ED core show similar trends in the uppermost layers to those at
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FM and GT. Below 10 cm depth, the ED’s mid-layers, 10-14 cm, show high [Pb] peaks of 0.28-0.43 µg fraction⁻¹ within the larger humic size fractions #1, #3 and #4 indicating strong association with larger humic molecules within this mid-depth region. Again, as for the FM and GT sites, there was a shift towards Pb association with larger/low-charged humic molecules towards the bottom of the core. For the four deepest core layers, 11-19 cm, the shift in [Pb] distribution to 0.24-0.58 µg fraction⁻¹ centred on fraction #3. At all depths the amount of Pb residual in the gel well was generally the lowest among the three sites at <0.1 µg fraction⁻¹.

7.3.2 Discussion of gel electrophoresis Pb distribution

During the electrophoretic process, all humic molecules passing through the gel structure must be <200 nm in size (Narayanan et al., 2006) as this is the reported maximum pore size for a 1% w/v agarose gel. As a result, any humic molecules remaining in the electrophoretic gel well should therefore be >200 nm in size or possess negligible net charge. The largest humic molecules residual in the electrophoresis well did not show [Pb] peaks for any of the layers analysed and therefore molecular size is evidently not the sole controlling factor that determines Pb association. However, molecular size does appear to be important in the associations of Pb as the highest [Pb] was typically found in the large humic molecules of fractions #1-4. For all humic extracts from each site, fractions #1-4 corresponded to a visible brown humic band. This implies that the majority of humic matter in the original extract consists of these large molecules. Within the three near-surface layers and in the deepest three layers of each core assessed, fraction #3 is
most often the fraction with highest [Pb] across the gel plates. Based on the proposed binding mechanisms by Wang and Benoit (1996), this phenomenon likely arises from there being an optimal size range that facilitates multi-dentate ligand binding around the Pb$^{2+}$ ions. This process is energetically favourable at acidic pH values because it helps to balance the overarching negative point charges on molecules. It should be noted, however, that no analysis of the humic molecular size within each fraction has been performed in this study. Research by Graham et al. (2008; 2011), however, demonstrated that distance travelled through the gel towards the positive electrode was primarily related to the size of humic molecules. More specifically, Graham et al. (2011) showed that, during gel electrophoresis, humic colloids in the size range 100 kDa-0.2 µm kDa were commonly transported to the near-well fractions #1-4 and were visible to the eye as a brown band in the gel. In contrast, those within the range 3-30 kDa were transported predominantly to fractions #4-6, corresponding to a secondary brown band of material with a front of fluorescent material within the gel. Applying these molecular size ranges to this study, it appears that Pb is predominantly associated with humic substances within the 100 kDa-0.2 µm size range within the upper vegetation sections and in the deeper peat/soil. However, for the uppermost vegetation sections, some Pb is, associated with 3-30 kDa humic substances in faint brown bands in fractions #5-6 and with even smaller size fractions represented by the bands of fluorescent matter (detected via UV light) in fractions #6-8 of some gels.

For the mid-depths at FM (7.5-13.5 cm) and ED (10.5-16.5 cm), Pb was distributed more sporadically across the gel. In agreement with the results for the bulk humic
extracts, there was less humic-associated Pb in the fractions from these FM layers. Section 7.2.2 hypothesized that the low Pb-humic association observed in the 7.5-10.5 cm layers of FM was related to the extent of decomposition of the organic material in these layers. The humic substances had much higher hydroxyl and carbonyl concentrations than in those layers immediately above or below (Section 7.2) and this has been linked with a transitional stage in the humification process (Baldock et al., 1997; Barkovskii et al., 2009). From the gel electrophoretic results in this study, it appears that the decomposition of organic matter in the mid-depth layers typically results in a decrease in the molecular size of the humics and to which Pb is bound. This decrease in size is consistent with the results presented in Chung et al. (2005). The results of this transitional stage in terms of the effect on Pb associations is specific to each location but the longer term picture is remarkably similar, i.e. once within the peat, Pb is predominantly bound to humic molecules within the same narrow size range.

7.3.3 Distribution of Fe in gel electrophoretic fractions of humic substances

Iron (Fe) has been implicated as a potential controlling factor in the behaviour of Pb (Schroth et al. (2008); Section 5.4; Section 5.5.3.5) and in the mobilisation of Hg into the aqueous phase in peat/soil systems (Section 6.5.3 and Section 7.3.2). Fe distribution across the humic fractions obtained by gel electrophoresis was also assessed to investigate potential links to Pb and Hg distribution. As discussed in the preceding Section, the concentration of Hg in gel sub-fractions was below detection
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There was a general trend of increasing concentration of humic-associated Fe with increasing depth. The vertical trends in the distribution of Fe across the gel fractions, however, were similar to those for Pb. At 0-1 cm depth, Fe was concentrated within the fractions #1-3 and fractions #7-8. From 3-4 cm to 5-6 cm, [Fe] was at its peak (2.76-3.37 µg fraction\(^{-1}\)) in the near-well fraction #1 but decreased to ~0.75 µg fraction\(^{-1}\) across fractions #5-8. There were only small amounts of Fe in fractions #9-10 in these near-surface layers. The 7-8 cm layer showed Fe peaks in gel fractions #1, #7 and #8 with comparatively low [Fe] in all other fractions. Deeper down the core at 9-10 cm, fractions #1-4 showed [Fe] of 2.56-3.18 µg fraction\(^{-1}\) dropping to 0.05-1.6 µg fraction\(^{-1}\) in fractions #5-10. The 13-14 cm layer at FM showed a large Fe peak of 13.91 µg fraction\(^{-1}\) centred on fraction #3 with concentrations dropping to 0.68-1.16 µg fraction\(^{-1}\) in fractions #6-10. Depths of 15-20 cm all showed [Fe] peaks of 7.6-15.1 µg fraction\(^{-1}\) across gel fractions #1-4. In these deeper layers only 0.8-1.2 µg Fe fraction\(^{-1}\) are apparent in gel fractions #5-10.

Flanders Moss (FM) gel electrophoretic distribution of Fe
Figure 7.4  Gel fraction [Fe] distribution across plates with migration from left to right along the lower axis for (A) FM, (B) ED and (C) GT.
Glentress (GT) gel electrophoretic distribution of Fe

In comparison with FM, the concentrations of humic-associated Fe at GT were typically a factor of ~2 higher but the general trend of increased humic association with increasing depth was again evident. The Fe distribution at GT for the uppermost core layers, 1-5 cm, showed peak concentrations of 1.5-6.36 µg fraction\(^{-1}\) within gel fractions #1-4. In each case, the [Fe] peak was centred on fractions #2 and #3. For fractions #5-#10, [Fe] were <1 µg fraction\(^{-1}\). The humic substances from the layer corresponding to ~7 cm depth had [Fe] peaks of ~6 µg fraction\(^{-1}\) in fractions #1-#2 and #6 with a larger peak concentration of 14.4 µg fraction\(^{-1}\) in fraction #4. Towards the base of the GT core (8.0-18.5 cm), Fe was concentrated (8-26 µg fraction\(^{-1}\)) in fractions #1 and #2 with all remaining fractions possessing 0-3 µg Fe fraction\(^{-1}\). In contrast with all other humic extracts, those from the layer at ~13 cm yielded a high concentration of 25.4 µg Fe fraction\(^{-1}\) in the gel well.

Easter Deans (ED) gel electrophoretic distribution of Fe

The concentrations of humic-associated Fe in the fractionated humics from ED were very similar to those for the GT humics and again there was a clear trend of increased association with increasing depth. The distribution of Fe across humic fractions from three layers within the top 0-9 cm of the ED core was broadly similar. [Fe] increased with distance from the well until peaks of 4.8-7.0 in fractions #3 and #4. From these peak values, concentrations decreased to ~1 µg fraction\(^{-1}\) in fractions #6-10. The 3-6 cm layer exhibited an exception to this trend with an additional [Fe] peak of 2.8 µg fraction\(^{-1}\) in fraction #7. Towards the base of the ED core, the layers
corresponding to ~9-12 cm to 25-27 cm each exhibited [Fe] peaks clustered around fractions #2-4. The [Fe] were in the range of 8-23 µg fraction⁻¹.

**Discussion of gel electrophoretic patterns for Fe**

The Fe distribution at FM, GT and ED was in good agreement with the Pb distribution trends in the top and bottom regions of each core but much less agreement was observed in the middle sections where peak [Pb] and [Fe] were sometimes associated with different fractions. Both Pb and Fe were predominantly associated with the brown humic bands in fractions #1-4, the near-well fractions that correspond to large molecules of 100 kDa-0.2 µm (Graham *et al*., 2011). This trend adds weight to the literature implication (Dong *et al*., 2000; Schroth *et al*., 2008) that Fe oxides and Pb generally bind to similar humic matter binding sites. When assessing the differences in Pb and Fe distribution in the 13.5-18.0 cm GT profiles, it is important to remember the relative [Fe] present in the forest soil system (~1.38% w/w Fe at 13 cm) compared to FM (0.2-0.3% w/w Fe; Farmer *et al*., 2005) and ED (~0.3% w/w Fe) (Section 4.7.1). The respective Fe fraction⁻¹ in the distributions above suggests that similar amounts of humic-bound Fe are present at both GT and ED despite the total [Fe] at ED being considerably lower. The differences in distribution of Pb and Fe across sites and with depth may arise from the number of ways in which Fe may become associated with humic matter including direct interaction of Fe ions or interactions of Fe-oxides or similar species. Where Pb and Fe demonstrate co-occurrence in the electrophoretic results, it is possible that Pb is becoming associated with Fe phases or Pb-Fe oxide-humic via ternary interactions.
with aluminium oxides, as discussed previously in Section 5.3.3 (Bargar et al., 1996., Bargar and Brown, 1998). This hypothesis however is not supported by the gel distributions in the mid core regions in particular where some fractions showed high [Pb] but very little discernible Fe. Additional evidence is required before Fe can be confirmed as implicit in Pb-humic matter association in the solid phase.

### 7.4 SEM-EDX analysis of solid phase Pb associations

In order to further investigate solid phase Pb associations and potential links with Fe, soil and peat samples and humic extracts obtained as per Section 2.3.12 from FM, GT and ED were subjected to SEM-EDX analysis as outlined in Section 2.3.14. Again, Hg was present at concentrations which were too low to be detected via SEM-EDX analysis. Figure 7.5 shows representative SEM images for FM, GT and ED, respectively.

The peat/soil images showed that at the 100-200 µm scale, the composition of each site is somewhat different. These images, however, provide little information and direct analysis of elemental composition on a smaller scale is required. It should be noted that SEM-EDX only detects the presence of elements within a small circular radius on the surface of a sample.
Figure 7.5 Peat/soil samples (left) and corresponding humic extracts (right) images for FM 19.5 cm (top), GT 9 cm (mid) and ED 22.5 cm (bottom).

While detector response and the resulting spectral peaks will increase in intensity with increasing concentrations of a given element, interference, signal noise and lack of true homogeneity all prevent this methodology from providing quantitative concentration measurements. If an element peak does not appear on an SEM-EDX spectrum, it does not necessarily mean that the element is not present; it may be
present in insufficient quantity to generate a response above background noise. Detection limits of $<10 \text{ mg kg}^{-1}$ have been reported for Al, Mg, Fe and Ca whereas the limit of detection for Pb can be as low as $2 \text{ mg kg}^{-1}$ (Kuisma-Kursula, 2000).

### 7.4.1 SEM-EDX results and discussion

Table 7.1 shows the elemental environments in which Pb was detected, including the number of spots in which a specific elemental signature was found. Pb was, however, not found in detectable quantities in all spots for all samples. Initial spot selection rationale was to examine ‘white’ areas on surface images. These lighter areas were presumed to contain Pb as they correspond to denser material although, in practice, Pb was not regularly detected in these light image regions. Shifting analysis to the darker areas which correspond to organic and humic material increased the detection rate of Pb. The results in Table 7.1 represent spots sampled only from organic and humic material where Pb was detected. Due to the high abundance of residual NaOH utilised in the humic extraction process, sodium (Na) was detected within every humic sub-sample. As a result, Na is not recorded in table 7.1. Furthermore, zinc (Zn) cannot easily be examined within the humic sub-samples as the most prominent Zn peaks shoulder those of Na and are overwhelmed by the large Na peaks in humic samples.
### Table 7.1

Chemical environments detected in bulk peat/soil and humic extracts from SEM-EDX analysis. *n* represents the number of occurrences of a specific combination of elements within the qualitative output.

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Total: 9 11 12 16 15 22
Due to this effect, Zn is tentatively listed for samples in which the Zn peaks appear to be visible as a shoulder of the Na peak. Listings for Zn should, however, be treated with some caution.

At FM, only 1 out of 9 spots from peat samples where Pb was detected also exhibited detectable Fe; this increased to 2 out of 11 for the corresponding humic extract sample. Co-occurrence of Pb and Fe appears more prevalent for ED where 6 out of 12 of the peat samples and 10 out of 16 of the Pb-bearing humic extract sample spots show presence of Fe. The proportion of Pb-bearing sample spots in which Fe is also detectable within GT is 13 out of 15 in the soil sample and 19 out of 22 spots for the humic extract sample, respectively.

Section 5.5.4.1 has already demonstrated that across each core, Pb is primarily associated with the humic matter fraction in peats and forest soils, making characterisation of the humic matter extracts more important to this study than the soil and peat materials themselves. Across the three sites assessed, the proportion of sample spots containing both Pb and Fe is greater in the humic extract samples than in the peat or soil themselves. The proportion of sample spots in which Pb and Fe occur together further increases alongside increasing mineral matter content of the sample sites, FM<ED<GT, as established in Section 4.7.1. This information, alongside the gel electrophoresis results in Section 7.3, appears to support the implications by Schroth et al., (2008) that Fe plays a more controlling role in the
binding and associations of Pb within forest ecosystems. Aside from Al and Si, Fe occurs alongside Pb more often than any other element across all sites.

The abundance of Al and/or Si in 84 out of the 85 Pb containing sample spots is notable and must be addressed. Detection of Si occurs increasingly within the forest environment which would be expected due to the higher proportion of mineral matter at the site. The occurrences of Al and Si may indicate the presence of aluminosilicates in the humic extract samples. It is conceivable that aluminosilicate mineral material, which often contains hydroxyl functionality (Wada, 1967), has been extracted alongside the humic matter which may account for the high hydroxyl group concentrations recorded for humic extracts in Section 7.2. For aluminosilicates to be present in the extract they would have to be bound directly to the humic material itself or small enough in molecular size to be able to be suspended in the NaOH extractant solution. Whilst the regularity with which Pb, Al, and Si co-occur in SEM-EDX analysis may be indicative of association between Pb and aluminosilicate structures, the lack of detectable Pb in the high density mineral spots on the image surfaces would imply that this is not the case. The gel electrophoresis study in Section 7.3 further rules out Pb-aluminosilicate association as the predominant Pb binding method: (i) gel electrophoresis demonstrated Pb occurring alongside brown bands of humic matter and not predominantly in gel sections where humic matter was not clearly visible; and more importantly, (ii) analysis of the gel electrophoresis fractions for Al distribution (Appendix 10) did not show an evident relationship between Pb and Al in the fractionated humic extract. Aluminium was
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

generally distributed evenly across all gel fractions whereas Pb demonstrated distinct concentration peaks as discussed previously.

7.5 Peatland enzyme activity and phenolic functionality

7.5.1 The role of (poly)phenol oxidases (PO) in peatlands

Section 4.2.1.2 and 6.3.3 discussed the role of soil bacteria and micro-organisms and their roles in the decomposition of soil organic matter and the alkylation of Hg. Peatland environments can denature many soil enzymes excreted by these micro-organisms that would otherwise be active in aerated soils and or neutral pH conditions (Okolo et al., 2007). (Poly)phenol oxidases (PO) are one enzyme classification that reportedly retain some activity within peat systems (e.g. Freeman et al., 2004). (Poly)phenol oxidases (Figure 7.6) are copper-based enzymes produced by plants and micro-organisms (Sinsabaugh, 2010). PO enzymes are known to catalyse the oxidation of phenol groups in fruits and controlled laboratory environments while consuming oxygen [EC 1.10.3.1, EC 1.14.18.1] and are found both intra-cellularly and excreted extra-cellularly by fungi species including basidiomycetes (Bollag and Leonowicz, 1984) and ascomycetes (Dekker and Barbosa, 2001) among others (Fortina et al., 1996). Organisms typically deploy PO for synthesis of nutrients, for pigment formation, to facilitate the degradation of lignin (Solomon et al., 1996) or as a defence against toxic metal and toxic organic species (Mayer, 2006).
Within soils, the activity of these enzymes can be measured as an indicator of soil quality (Dick, 1994) but have recently been a source of interest in peatlands specifically due to their perceived role in the decomposition of recalcitrant organic matter, specifically aromatic phenolic compounds (Cullen and Kersten, 1996) derived from lignins and plant cellulose (Haslam, 1989). The decomposition of phenolic functional groups and similar recalcitrant organics has the potential to liberate some of the terrestrial carbon store and potentially, previously sequestered metal contaminants such as Pb and Hg. Depolymerisation of large humic and lignin molecules (Baldrian, 2006) generates smaller organic radicals that can then either be repolymerised into humic material (Fakoussa and Frost, 1999; Dec et al., 2003; Zavarzina et al., 2004) or transported via the peat/soil aqueous phase.
The importance of the organic matter decomposition pathways enabled by PO had previously been overlooked within soil systems as the number of competing reaction processes can both mask and complicate its effect. PO requires oxygen to function which would imply that its activity at depth in peatlands could be assumed to be minimal in all but the uppermost layers. The transport of oxygen to deeper peat layers decreases with depth because the diffusion coefficient and hydraulic conductivities of the peat decrease with increasing water saturation and compaction (e.g. Limpens et al., 2008). Freeman et al., (2004) demonstrated that PO activity increases dramatically with increasingly oxic conditions, leading potentially to phenolic depletion and acceleration of organic matter decomposition when peat becomes exposed to air due to erosion-related exposure or lowering of the water table. Published studies have previously measured the activity of PO as an approximation of overall microorganism activity in soil and peat systems (e.g. Giai and Boerner, 2007; Hamman et al., 2008) and therefore measurement of PO will be adopted by this study as an indicator of overall microorganism activity.

### 7.5.2 Enzyme analysis and phenolic concentration results

The activity of PO at AM was determined via the methodology outlined in Section 2.3.7. The PO activity profile and high resolution phenolic equivalent concentration profile are presented in Figure 7.7 below. Phenolic functionality concentration was also assessed via the L-DOPA assay for selected sections of AM as per the methodology outlined in Section 2.3.6.1. PO activity must be measured on fresh samples in order to obtain realistic results. As a result, enzyme activity data is not
The activity of PO decreases overall with depth although there is considerable fluctuation in activity down the core. Activity peaks at ~590 nmol DICQ min$^{-1}$ g$^{-1}$ in the vegetation layer (0-11 cm) and decreases to a value of ~130 nmol DICQ min$^{-1}$ g$^{-1}$ towards the deepest layers of the core. Some layers had almost no detectable activity and these occurred throughout the profile, e.g. at 5.5 cm, 12.5 cm, etc. A broad region of minimal activity was recorded in the 30-35 cm region. The range of values obtained in this study were consistent with with those reported for soils and peatlands in literature with values of 0-566 DICQ min$^{-1}$ g$^{-1}$ reported for the L-DOPA assay (Sinsabaugh et al, 2008; Sinsabaugh, 2010). The high activity in the surface layers
reflects the penetration of oxygen into the system, with the high activity range of 
~550-590 continuing until 14 cm, below the onset of the water table at ~10 cm.

The concentration of phenolic equivalents decreased from 6.2 cmol\textsubscript{e} kg\textsuperscript{-1} in the 2.5 cm layer to a value of 2.7 cmol\textsubscript{e} kg\textsuperscript{-1} at 12.5 cm. Below this point, the concentration increased to a maximum phenolic equivalent concentration of 12.18 cmol\textsubscript{e} kg\textsuperscript{-1} at 38.5 cm depth. Published phenolic functionality ranges are narrower than those presented here, including reports of 2.4-3.8 cmol\textsubscript{e} kg\textsuperscript{-1} (Bonnet and Cousins, 1987) and 1.54-3.95 cmol\textsubscript{e} kg\textsuperscript{-1} (Brunetti \textit{et al.}, 2007). The concentration of phenolic functional group profile was similar to the other assessed in Section 7.2 but showed greater variation with depth. Notably, the 16.5 cm layer where minima in carbonyl and carboxyl functionality were observed also showed a minimum in phenolic group concentration. Furthermore, the 38.5 cm layer immediately above AM’s clay layers exhibits peaks in phenolic, carbonyl and carboxyl functionalities. The low phenol concentration of ~3-6 cmol\textsubscript{e} kg\textsuperscript{-1} coincided with the depth interval over which the highest PO activities were obtained. In deeper layers, the phenolic functionality concentration then increased gradually where PO activity is low. Overall there is a broadly inverse relationship between PO activity and phenolic functionality in the AM profile.

It has already been established that the PO assay can act as an indicator of overall microbial activity (e.g. Giai and Boerner, 2007; Hamman \textit{et al.}, 2008) and many studies have implicated micro-organisms in altering speciation of Hg in peat/soil.
Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems (Compeau and Bartha, 1985; Benoit *et al.*, 1998; 1999a; 1999b; 2001a; 2001b; Merritt and Amirbahman, 2009). Speciation analysis of Hg in peatlands in Section 6.5.4.1 revealed high proportions (~70-90%) of organo-Hg in the uppermost 10 cm layers of the peatland sites in this study. These layers of high organo-Hg concentration occur within the same depth range as the regions of high PO activity. While there is no evidence to suggest that PO itself is directly alkylating Hg species, its use as a proxy for microorganism activity may indicate the influence of microorganisms in the abundance of MeHg and EtHg in near-surface peat layers. The proportions of organo-Hg decreased considerably at greater depths where layers are below the water table (~10 cm), becoming increasingly anoxic (e.g. Limpens *et al.*, 2008), possess lower PO and therefore lower microorganism activity. The relationship between microorganism activity and Hg speciation requires further investigation and future study and additional data is required to better explore this apparent link.

### 7.6 Key outcomes of solid phase characterisation

The combination of humic association analysis, gel electrophoresis and SEM-EDX analysis imply that solid phase Pb was primarily associated with large humic molecules (0.2µm – 100kDa) in the near surface sections of FM, ED and GT. Gel electrophoresis also demonstrated regular co-occurrence of Pb and Fe within the near-surface and deeper solid phase humic matter with the size fractions containing the greatest concentration of Pb also containing the greatest concentration of Fe. However, co-occurrence of Pb and Fe was not observed in the mid depths of these
cores where distributions of Pb and Fe were in poor agreement. SEM-EDX analysis showed that Pb-Fe mineral particles were largely absent from the bulk solid peat samples (FM and ED). For the solid phase bulk material, only GT showed regular co-occurrence of Pb and Fe via SEM-EDX analysis. There was even more regular co-occurrence of Pb and Fe for the humic extracts from this material. Although further work is required to establish whether Pb is bound directly to humic substances or via Fe oxides which are also bound to humic substances, there is some evidence from the gel electrophoretic distributions that Pb does form direct associations with the former. In addition, there appeared to be a strong relationship between the extent of Pb-humic binding and the carboxyl functionality of the humic substances at FM. The deprotonated acidic OH (carboxyl and phenolic) groups are most often implicated in Pb binding to organic matter (e.g. Davies et al., 1997; Xia et al., 1997). The solid phase characterisation also demonstrated a link between functionality and microbial activity. For example, the ~15 cm layer of AM contained humic substances with low carboxyl functionality, low phenolic functionality but it had high microorganism activity. The minimum in carboxyl functionality was also the region of lowest Pb-humic interaction at FM, perhaps demonstrating a link between microorganism activity, the stage of organic matter humification and the capacity for humic matter to bind Pb. The situation may, however, be even more complex due to the consideration that this layer (i) is below the water table; (ii) exhibits high microbial activity; (iii) is the region in which Fe reduction occurs; (iv) demonstrates loss of phenolic and carboxyl functionality. The combination of these features with the porewater [Hg] at this depth may indicate that the reduction of Fe is
fuelling microbial decomposition of the organic matter culminating in release of Hg to the aqueous phase.

7.7 *Aqueous phase DOC distribution and comparison with metal fractionation*

7.7.1 **Sub-fractionation of porewater DOC via sequential ultrafiltration**

The distribution of Pb and Hg in porewater colloidal size fractions was presented previously in Section 5.5.4.2 and Section 6.5.3.2.2. Although the distribution of metals between porewater fractions is important, without specific knowledge of the distribution of the colloidal and dissolved organic species themselves it is difficult to fully interpret the metal distribution results. To investigate porewater DOC the distribution relative to total DOC between the >100 kDa, 100-30 kDa, 30-3 kDa and <3 kDa ultrafiltration fractions was measured for FM, GT and ED porewaters via UV/Visible spectroscopy as outlined in Section 2.3.11. Due to the brown colour observed in porewater sub-fractions, it was hypothesised that these brown species were humic colloids. Humic matter standards were used to determine the concentration of DOC in sub-fractions as humic colloids are known to absorb at 254 nm. The detection of absorption bands in sub-fractions at 254 nm is indicative that the colloidal DOC material is these samples is indeed humic in nature. Humic matter colloidal distribution data are shown alongside corresponding metal distributions in Tables 7.2 to 7.4.
### Table 7.2 Distribution of DOC and Pb among colloidal size fractions at FM

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<th>Depth (cm)</th>
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### Table 7.3 Distribution of DOC, Pb among colloidal size fractions at GT

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<td>DOC (%)</td>
<td>34</td>
<td>18</td>
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<td></td>
<td>Pb (%)</td>
<td>59</td>
<td>11</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>3.5</td>
<td>DOC (%)</td>
<td>39</td>
<td>21</td>
<td>32</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Pb (%)</td>
<td>31</td>
<td>15</td>
<td>41</td>
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</table>

### Table 7.4 Distribution of DOC and Pb and Hg among colloidal size fractions at ED

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Fraction distribution:</th>
<th>&gt;100 kDa-0.2 µm</th>
<th>30-100 kDa</th>
<th>3-30 kDa</th>
<th>&lt;3 kDa</th>
</tr>
</thead>
<tbody>
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<td>4.5</td>
<td>DOC (%)</td>
<td>35</td>
<td>21</td>
<td>27</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>Pb (%)</td>
<td>46</td>
<td>25</td>
<td>20</td>
<td>9</td>
</tr>
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<td></td>
<td>Hg (%)</td>
<td>46</td>
<td>22</td>
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<td>16</td>
</tr>
<tr>
<td>7.5</td>
<td>DOC (%)</td>
<td>40</td>
<td>17</td>
<td>35</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Pb (%)</td>
<td>53</td>
<td>15</td>
<td>26</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Hg (%)</td>
<td>38</td>
<td>21</td>
<td>23</td>
<td>18</td>
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<tr>
<td>13.5</td>
<td>DOC (%)</td>
<td>45</td>
<td>25</td>
<td>23</td>
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<td></td>
<td>Pb (%)</td>
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<td>22</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Hg (%)</td>
<td>38</td>
<td>25</td>
<td>18</td>
<td>19</td>
</tr>
<tr>
<td>16.5</td>
<td>DOC (%)</td>
<td>41</td>
<td>21</td>
<td>31</td>
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<td>Pb (%)</td>
<td>76</td>
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<td>3</td>
</tr>
<tr>
<td></td>
<td>Hg (%)</td>
<td>43</td>
<td>24</td>
<td>20</td>
<td>12</td>
</tr>
<tr>
<td>19.5</td>
<td>DOC (%)</td>
<td>43</td>
<td>24</td>
<td>26</td>
<td>7</td>
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<tr>
<td></td>
<td>Pb (%)</td>
<td>76</td>
<td>11</td>
<td>8</td>
<td>5</td>
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<tr>
<td></td>
<td>Hg (%)</td>
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<td>18</td>
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<td>DOC (%)</td>
<td>45</td>
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<td></td>
<td>Pb (%)</td>
<td>70</td>
<td>11</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hg (%)</td>
<td>32</td>
<td>25</td>
<td>20</td>
<td>23</td>
</tr>
</tbody>
</table>
Across all three sites assessed, the majority of the humic material is contained within the large colloidal >100 kDa and the small colloidal 30-3 kDa fractions. The porewaters from FM had most DOC (26-45%) in the >100 kDa fraction, <10% of total DOC in the 100-30 kDa fraction, 23-35% in the 30-3 kDa, and 18-32% in the dissolved <3 kDa fraction. GT porewaters had 30-39% of total humic colloids in the >100 kDa fraction, 18-25% in the 100-30 kDa fraction, the highest proportion of DOC (32-39%) in the 30-3 kDa fraction, with 6-12% DOC in the <3 kDa (truly dissolved) fraction. The humic colloid distribution at ED showed that the >100 kDa fraction contains 35-45% of total DOC, the 100-30 kDa fraction contains 17-25% of DOC, 23-35% is present in the 30-3 kDa fraction, whilst the remaining 7-17% DOC was contained in the <3 kDa (truly dissolved) fraction. Notable features of these humic colloid distributions are that FM porewaters had almost no colloidal humic material in the 100-30 kDa size fraction whereas GT and ED both showed low proportions of truly dissolved DOC. In contrast with FM and ED porewaters which had the greatest proportion of DOC in the 100 kDa-0.2 µm fraction, GT was the only site to exhibit approximately even distribution of DOC between the 100 kDa-0.2 µm and 3-30 kDa fractions.

### 7.7.2 Humic colloid distribution and Pb associations

The distribution of metals among the colloidal and truly dissolved size fractions was broadly similar to the distributions of humic material itself although there were a number of key differences between the percentage values. In both FM and ED peatland sites, there was a greater percentage of the total porewater Pb present in the...
>100 kDa fraction than the percentage of total humic matter contained in the same fraction. For example, the 28.5 cm ED layer contains 45% of humic colloids in the 100 kDa-0.2 µm fraction but contains 70% of the total porewater Pb. The other size fractions did not show a consistent excess or deficiency of Pb relative to humic matter at these sites. However, for GT, the relationship observed for the 100 kDa-0.2 µm fraction was not repeated, as metal distribution trends generally followed the distribution of humic material, with no layer consistently possessing a greater or lower percentage of Pb than humic colloids across the core.

If it is assumed that each unit mass of humic material possesses an equal number of metal binding sites then it is evident that the >100 kDa colloidal humic size fraction in the peatlands sites are binding a greater proportion of Pb than would be expected. It could be considered, however, that larger colloidal size fractions will present fewer metal binding sites due to their exposed surface area to volume ratio being lower. This relationship is apparent if colloids are treated as idealised spheres as presented in Figure 7.8. As the specific organic functional groups of each colloidal sub-fraction have not been assessed in this study then it is assumed that colloidal sub-fractions contain similar functional group composition.
Fig. 7.8 Idealised spherical colloidal species showing approximate surface area to volume ratio.

The ‘Pb-rich’ status of the 100 kDa-0.2 μm fraction is observable to varying extents across all investigated FM and ED layers and therefore this fraction can be assumed to favourably bind Pb in these peat environments. The observed relationship between Pb and Fe discussed in Section 7.3 and Section 7.4 may also be the key to explaining the preference of Pb for large colloids. The colloidal fractionation study by Graham et al. (2008) demonstrated that close to 100% of porewater Fe was associated with the large >100 kDa colloids in a soil environment. The Fe in the >100 kDa fractions was not present as discrete phases but was associated with the humic substances in a similar manner to the solid phase results of this study reported above. However, it was still not clear whether or not the Pb was binding to the Fe or to the humic material. It is probable that the organic matter present in the forest environment from coniferous plants in addition to the different moss species differs from that of peatlands resulting in differences in the functional group composition of OM when
the forest and peatlands are compared (Sections 7.2, 7.3 and 7.4). Such differences are likely to, in turn, impact Pb binding mechanisms.

### 7.7.3 Humic colloid distribution and Hg associations

As discussed in Section 6.5.3.2.2, ultrafiltration data only exists for porewater Hg at the ED site due to detection limit issues for the other sites. The proportion of Hg and humic colloids present in the larger colloidal size fractions, 100 kDa-0.2 µm and 30-100 kDa, where almost identical for all layers with neither of these size fractions being consistently Hg-rich or Hg-deficient. The 3-30 kDa size fraction is consistently Hg-deficient as each layer had 5-12% less Hg than the fraction’s percentage share of total humic material. With the exception of the 4.5 cm layer, the truly dissolved (<3 kDa) size fraction was Hg-rich with the 7.5 cm layer exhibiting 8% of total DOC and 18% of the total porewater Hg, and the 28.5 cm layer demonstrating 8% of total DOC and 23% of total porewater Hg.

It should be highlighted that the <3 kDa ultrafiltration fraction does contain humic species as absorbance at 254 nm is detected above samples blanks. This means that Hg species present in this ultrafiltration fraction may be associated with very small, truly dissolved humic molecules and not simply dissolved as metal ions. However, it is impossible to determine the proportions that are associated with <3 kDa organic matter relative to the proportion present as free ions or inorganic complexes in solution. Nevertheless, Hg appears to preferentially bind to large colloidal species.
with an even distribution between medium colloids, small colloids and truly dissolved species.

7.8 Chapter conclusions

Increasing humic matter carboxyl functional group concentrations at FM correlated with increasing levels of Pb-humic association except in layers where the onset of decomposition and humification result in high concentrations of carbonyl and hydroxyl functionalities. Depletion of binding carboxyl functional groups due to microbial activity fuelled by Fe-reduction processes may be responsible for liberation of Hg into the aqueous phase at depths of 15.5 cm at FM and 10 cm at AM. Based upon gel electrophoresis studies, the majority of solid phase Pb is associated with large molecular size (0.22 µm – 100 kDa) humic material in the near-surface, and deeper sections of FM, GT and ED. In the mid sections of the core, Pb is distributed more sporadically between humic molecular size fractions. Approximation of microorganism activity at AM via analysis of (poly)phenol oxidase activity demonstrated 3-fold higher microorganism activity in the vegetation section of the core when compared to the underlying peat and thus supporting the hypothesis that alkylation by microorganisms is responsible for the high proportions (up to 98%) or organo-Hg in the vegetation layers of peatlands. In the aqueous phase, large humic colloids (>100 kDa) are preferentially binding Pb in peatland sites as these colloids are sequestering a greater proportion of Pb than their proportion of total humic colloidal material. Porewater Hg is mostly contained within the large (>100 kDa) colloidal humic species and is distributed evenly amongst the other colloidal sub-fractions. The small colloidal (30-3 kDa) and ‘dissolved’ (<3 kDa)
fractions are Hg-rich as they showed greater proportions of total Hg than their proportion of total colloidal humic material
Chapter 8 Conclusions

8.1 Project conclusions

8.1.1 Behaviour of Pb in near-surface sections of peatlands and forest soils

At the FM and ED sites, historical records of Pb deposition were well-preserved and showed peak Pb flux due to coal burning and petrol consumption within the layers corresponding to 1940-1980, in agreement with the literature (e.g. Farmer et al., 1997; MacKenzie et al., 1997; Cloy et al., 2005). The close agreement between the $^{206}$Pb/$^{207}$Pb value of 1.145±0.017 reported for 2007 Scottish rainwater (Farmer et al., 2010) and the range of $^{206}$Pb/$^{207}$Pb values of ~1.125-1.149 for the surface vegetation layers from FM, GT, ED and AM in this study also suggests that the $^{206}$Pb/$^{207}$Pb signature, and conceivably the sources from which that Pb originated, has not changed significantly in the time period ~2007-2010. Excepting the layers of this study’s cores that have accumulated since the studies of Cloy et al. (2005; 2008) and MacKenzie et al., (1997), Pb deposition chronologies for FM and ED have proven consistent with those recorded approximately a decade previously. The good agreement between chronologies derived from these distinct studies provides strong evidence to support literature assertions that Pb is immobilised following deposition on surface vegetation and subsequent incorporation into the peat in these peatland environments. It is important to emphasise that the surface vegetation at the study sites was up to 15 cm thick and accounted for the most recent ~20-30 years of Pb deposition. These vegetation layers preserved recent trends in $^{206}$Pb/$^{207}$Pb deposition ratio and also comprised the upper sections of $^{210}$Pb-activity profiles where activities were highest. These results highlight the importance of retaining the surface
vegetation sections of sampled cores when reconstructing historical records. Furthermore, the 2-4 cm depth offsets in key [Pb] and $^{206}\text{Pb}/^{207}\text{Pb}$ features between adjacent Cuttle and Malcolm (1979) and monolith cores due to core compaction by the former sampling methodology highlights the need to consider the impacts of corer-derived physical disturbances when interpreting results. Once the offsets were taken into account, spatial variation in [Pb], $^{206}\text{Pb}/^{207}\text{Pb}$ and Pb inventories on an intra-site scale (10s of metres) was found to be somewhat lower (~1.6-fold variation) than variation on inter-site scale (~2.13-fold variation over distances of <100 km).

At the AM peatland site and in the GT forest soil Pb profiles showed evidence of perturbation as some Pb has been mobilised and transported vertically within the cores. The manifestations of these perturbations and their respective causes appear to be different between sites. At AM, the $^{210}\text{Pb}$-activity profile does not decay exponentially with depth in the near-surface vegetation sections of the core and without appropriate context, the period of maximum flux at the site appears to correspond to 2002. Furthermore, the AM $^{206}\text{Pb}/^{207}\text{Pb}$ aqueous phase profile showed higher than expected isotope ratios in its near-surface sections when compared with the corresponding layers of the solid phase profile. The abnormal regions in the AM profile all occurred within the 7-15 cm layers, the section of the core that encompasses the vegetation/peat interface, the depth of the water table and the solid phase [Fe] maximum. It is therefore conceivable that the redox-cycling of Fe is contributing to the perturbation of the Pb profile. Whilst further work would be required in order to explore this hypothesis, one explanation may be as follows. On the basis that Pb in the peatland environment is predominantly associated with Fe-
bearing humic material, the reduction and subsequent transfer of this Fe into solution at depth may result in the loss of favourable binding sites for Pb in the humic structure. This could conceivably be due to (i) the direct loss of Fe from the humic structure into the aqueous phase and the physical changes to binding sites that this causes, or more plausibly, (ii) the enhanced localised decomposition of the humic structure by microbial processes that require Fe as an electron acceptor (e.g. Weber et al., 2006). The Pb released into solution is then transported via diffusion (e.g. Manassero and Shackelford, 1994) and becomes reassociated with the solid phase further up the profile.

At GT, the \(^{206}\text{Pb}/^{207}\text{Pb}\) profile was narrow in range and did not show the historical transition in isotopic ratio from typical coal burning/smelting influences to those of Australian-sourced Pb petrol additives. However, the \(^{210}\text{Pb}\)-activity and \([\text{Pb}]\) profiles at GT appear unperturbed which suggests that some petrol-sourced Pb alone is being transported within the core, resulting in the mixing of \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios. The conclusion of Bacon et al. (2004) that petrol-sourced Pb is the most labile Pb sub-fraction in the upland soils of Glensaugh, in conjunction with this study’s findings that there was a higher proportion of DOC and porewater \([\text{Pb}]\) in the small (3-30 kDa) humic colloidal fraction when compared to FM and ED, suggests that petrol-sourced Pb may be becoming selectively mobilised in the GT porewaters and transported vertically in association with small humic colloids. It is notable that the soil from the GT and peat from the AM site both contained high concentrations of Fe (0.16-1.60% w/w and 0.11-2.02% w/w, respectively) relative to the typical peatland sites such as ED (0.19-0.34% w/w).
Based on the observations of Schroth et al. (2008), who suggested that Fe may play a controlling role in forest environments, this study investigated the relationship between Pb and Fe in two peat (FM, ED) and one forest soil (GT) core. Although perturbations of historical records of atmospheric Pb deposition were not observed for these peatlands, this study revealed some correlations between Pb and Fe associations with extracted humic substances and it was hypothesised that that in terrestrial systems where [Fe] were high, the Fe exerted more control over Pb binding/associations than at sites where [Fe] was low. This hypothesis was supported by the increasing co-occurrence of Pb and Fe in the order FM<ED<GT identified via SEM-EDX analysis of solid phase peat/soil (FM: 1 of 9; ED: 6 of 12; GT: 13 of 15) and corresponding humic extracts (FM: 2 of 11; ED: 10 of 16; GT: 19 of 22). Even at the FM and ED sites where Fe is not present at high concentrations, fractionation via gel electrophoresis still suggested that both Fe and Pb are associated with similar sub-fractions of humic substances which had been isolated from the solid phase. However, at depths of ~7-10 cm in FM, a decrease in Pb-humic association alongside scattered distribution of Pb and Fe among gel electrophoresis sub-fractions shows that associations of Pb change with depth in a manner which is not necessarily related to the behaviour of Fe, providing evidence for at least partial direct association of Pb with the humic material. This region of comparatively low Pb-humic association corresponded to peaks in the concentrations of hydroxyl and carbonyl functionality which were related to humification processes occurring at these depths.
More generally, within the peat layers of FM, ED and GT large proportions (~40-99%) of total [Pb] were found to be associated with humic substances. Furthermore, gel electrophoresis demonstrated that at FM, ED and to a lesser extent, GT, the highest [Pb] among sub-fractionated humic extracts were in the large molecular species held in the gel strips near to the gel well. A study by Graham et al. (2011) previously reported that humic matter in these gel fractions represented large colloidal species (100-30 kDa), the size fraction of porewater-based humic colloids found to contain a high proportion (up to 70%) of total porewater Pb. Overall, this study has demonstrated that in both the solid and aqueous phase, Pb preferentially associates with large, low-mobility colloidal species, especially at FM and ED where the historical records of Pb deposition were found to be preserved. In contrast, at GT where a larger proportion of Pb was associated with small, mobile humic colloids, perturbation of the $^{206}$Pb/$^{207}$Pb ratio profile, specifically the downwards movement of petrol-derived Pb, was observed. The role of small humic colloids in vertical migration of metals in soil systems was also identified by Graham et al. (2011).

8.1.2 Behaviour of Hg in near-surface sections of peatlands and forest soils

There is some evidence to suggest that the peatlands in this study act as long-term records of Hg deposition. The profile layers in which maximum [Hg] were recorded were similar to those in which the [Pb] maximum due to coal burning and petrol emissions was observed. As coal represents a significant source of both Hg and Pb,
the co-occurrence of these peaks provides strong indication that the period of maximum flux of both elements was similar and that this feature of Hg deposition has been preserved within these profiles. Post-1950 Hg inventories from FM, ED and AM peatlands were also broadly similar at 2.82 mg m$^{-2}$, 3.23 mg m$^{-2}$ and 2.20 mg m$^{-2}$, respectively; in addition, the 1900-2000 inventories from FM and AM were in agreement with those reported in literature (Farmer et al., 2009). The Hg inventory to 1950 for GT was 1.5-2.0 times larger than those at the three peatland sites, attributable to the increased interception of atmospheric Hg by the forest canopy. The integrity of these archives and the effect of losses of Hg$^{0}$ to the atmosphere cannot be satisfactorily assessed without comparing detailed deposition data with core inventories. However, speciation analysis suggests that typically <10% of Hg in the near-surface layers of FM, GT and ED is in the form of Hg$^{0}$. Furthermore, the predominance of inorganic Hg$^{2+}$ species in the peat/soil layers below the vegetation/peat interface (>50% total [Hg]) alongside the lack of any other detectable Hg species in porewaters would indicate that Hg losses from such layers is limited due to the propensity for Hg$^{2+}$ to bind strongly to organic matter. The near-surface vegetation layers of peatlands showed a different speciation distribution of Hg relative to the forest environment with high proportions (up to ~98%) of organo-Hg species (MeHg and EtHg). This observation is attributed to the alkylation of Hg by plant species and specifically the microorganisms associated with those plants. Approximation of microorganism activity at AM via analysis of (poly)phenol oxidase activity demonstrated 3-fold higher microorganism activity in the vegetation section of the core when compared to the underlying peat and thus supporting this hypothesis.
Whereas solid phase Hg profiles appeared to represent historical Hg deposition, certain features in the aqueous phase profiles suggested that there was some post-depositional mobility. There were three specific regions of concern and the observed high [Hg] at each were attributed to a different process: (i) surface porewater [Hg] maxima in the vegetation layer were controlled by Hg uptake processes dependent upon the types and species of plants and mosses present; (ii) porewater [Hg] peaks occurred around the core vegetation/peat interface as a result of Fe redox-cycling induced mobilisation into the aqueous phase, similar to those reported for Pb; and (iii) deeper porewater [Hg] peaks occurred in peat layers of the core where density increased and organic matter was presumed to be in a state of more advanced decomposition. The large (100 kDa-0.2 µm) brown colloidal porewater fraction contained a greater proportion of Hg than any other size sub-fraction suggesting that these colloids presented a more favourable binding environment than the smaller alternatives. It should be noted that Hg is distributed more evenly across colloidal sub-fractions than Pb when the proportion of DOC in each fraction is taken into account.

8.1.3 General conclusions

Consideration of both the Pb and Hg research in this study demonstrates two key shared outcomes. The first of these is the clear importance of Fe and large humic species in the associations, distribution and potential for mobilisation of both Pb and Hg in terrestrial systems. In light of these findings, not only is further research into the specific binding interactions between Fe/Pb/Hg/other metals and humic...
substances required, but it must be considered that large humic molecules and Fe may play influential roles in the distribution of trace metal contaminants in some peatland and forest environments.

Secondly, the importance of vegetation in the uptake, speciation and retention of atmospherically deposited metal contaminants is clear. The peatland sites in this study have shown that the most recent decades of deposition of Pb are stored within moss layers, whereas Hg speciation studies highlighted the way in which different plant types and species can change the way in which Hg is incorporated into the peat system and even alter the speciation of that Hg. These results emphasise the need to consider the vegetation and underlying peat/soil as one dynamic system and cross-disciplinary studies that combine geochemical expertise with plant- and microbiology are required to obtain a clearer picture of the exact processes at work in the vegetation sections of these terrestrial systems.

8.2 Further research directions and challenges

There are a number of routes through which this study could be expanded and developed. In regard to deposition records, this study has not addressed the composition of sources that make up contemporary Pb deposition and its $^{206}\text{Pb}/^{207}\text{Pb}$ ratio. Further studies in addition to careful review and monitoring of forthcoming publications will be required to obtain a clearer understanding of the origins of current atmospheric Pb. In the case of Hg, comparison of long-term atmospheric
deposition records with terrestrial inventories is essential in order to assess the integrity of peat/soil archives.

Improved characterisation of humic matter and the molecular-sub units that comprise it is an essential next step in determining the specific chemical associations of Pb. Such a study would most likely require considerable fractionation and purification of humic extracts to provide uniform sub-fractions that could be analysed via powerful spectroscopic and spectrometric techniques (e.g. NMR spectroscopy, Fourier Transform-Ion Cyclotron Resonance-Mass Spectrometry). Continued advances in both physical (e.g. ultrafiltration, field-flow fractionation, etc) and chemical (e.g. chromatographic techniques) separation methodologies will ultimately facilitate such fractionation.

Refinement of the Pb-humic association and gel electrophoresis studies in order to allow similar analysis of Hg associations would provide an improved understanding of the behaviour of Hg in peat/soil systems. The absence of such information from this study was due to detection limit problems following sub-fractionation and so Hg pre-concentration techniques either prior to or during the ICP-MS analysis process could be employed to alleviate these issues.
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Appendix 1 Determination of the percentage recovery of porewater DOC following sub-fractionation

The relevant methodologies to this appendix are outlined in Section 2.3.2 and Section 2.3.11.

**Example: ED layer 3 (7.5 cm)**

Calculation of mass of DOC in bulk porewater sample.

\[
[\text{DOC}]_{\text{TOT}} \text{ (mg l}^{-1}\text{)} = \text{absorbance} \times \text{gradient of standard plot} \quad \text{Equation A1}
\]

\[
=> \quad 1.5929 \times 46.851 = 74.63 \text{ mg l}^{-1}
\]

\[
\text{DOC (mg)} = [\text{DOC}]_{\text{TOT}} \text{ (mg l}^{-1}\text{)} \times \text{volume (l)} \quad \text{Equation A2}
\]

\[
=> \quad 74.63 \times 0.0075 = 0.560 \text{ mg}
\]

Application of Equation A1 and Equation A2 to 0.0005 l volumes of porewater following sequential ultrafiltration (Section 2.3.2) yields the following masses of DOC.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>DOC (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;100 kDa</td>
<td>0.186</td>
</tr>
<tr>
<td>100-30 kDa</td>
<td>0.080</td>
</tr>
<tr>
<td>30-3 kDa</td>
<td>0.166</td>
</tr>
<tr>
<td>3 kDa</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Table A1 Masses of DOC in ED 7.5 cm layer calculated via Equations A1 and A2
Calculation of percentage recovery from addition of sub fractions.

\[
\text{Recovery (\%)} = \frac{\text{Frac}_1 + \text{Frac}_2 + \text{Frac}_3 + \text{Frac}_4}{[\text{DOC}]_{\text{TOT}}} \times 100 \quad \text{Equation A3}
\]

\[
=> \quad = \frac{0.186 + 0.080 + 0.166 + 0.037}{0.560} \times 100
\]

\[
=> \quad = 83.75\%
\]
Appendix 2 Creation of solutions from solid phase precursors and dilution of existing solutions

The relevant methodologies to this appendix are numerous and include those in Sections 2.3.6-2.3.8, 2.3.12-2.3.14 and 2.3.16-2.3.17.

Example: Preparation of 500 ml of 1.89M sodium carbonate solution

Molar mass Na$_2$CO$_3$ = 106 g mol$^{-1}$

Moles = Concentration (M) x volume (l) \hspace{1cm} \text{Equation A4}

=> = 1.89 x 0.5

=> = 0.945 moles

Mass Na$_2$CO$_3$ = Moles x Molar Mass (g) \hspace{1cm} \text{Equation A5}

=> = 0.945 x 106

=> = 100.17 g

Therefore, dissolving 100.17 g Na$_2$CO$_3$ in 500 ml deionised water will yield the desired solution.
**Example: Creation of 20 ml of 100 mg l\(^{-1}\) Pb standard via dilution of 1000 mg l\(^{-1}\) stock solution**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation A6</td>
<td>Dilution factor $= \frac{\text{Initial concentration}}{\text{Final concentration}}$</td>
</tr>
<tr>
<td>=&gt;</td>
<td>$= \frac{1000}{100}$</td>
</tr>
<tr>
<td>=&gt;</td>
<td>$= 10$</td>
</tr>
</tbody>
</table>

| Equation A7 | Volume\(_{\text{STOCK}}\) $= \frac{\text{Total volume (ml)}}{\text{Dilution factor}}$ |
| => | $= \frac{20}{10}$ |
| => | $= 2$ ml |

Therefore, mixing 2 ml of 1000 mg l\(^{-1}\) stock Pb solution with 18 ml deionised water will yield 20 ml of 100 mg l\(^{-1}\) Pb solution.
Appendix 3 Calculation of solid phase concentrations from aqueous ICP-OES/MS concentration measurements

The relevant methodologies to this appendix are those involved in the preparation and execution of ICP-OES/MS analysis. These methods are described in Sections 2.3.14, 2.3.16 and 2.3.17.

Example: Calculation of solid phase Hg concentration for ED layer 1 (1.5 cm)

Mass Hg (25 ml digest) = Analytic concentration (mg l\(^{-1}\)) x digest volume (l) \(\frac{1000}{1000}\)

\[
\text{Mass Hg} = 0.0135 \times \frac{25}{1000}
\]

\[
\Rightarrow 3.375 \times 10^{-4} \text{ mg}
\]

Therefore, there is \(3.375 \times 10^{-4}\) mg Hg in the 0.25 g digested solid phase sample.

\[
[Hg]_{\text{SOLID}} = \frac{\text{Mass in sub sample(mg)} \times 1000}{\text{Sub-sample mass (g)}}\]

\[
\Rightarrow 3.375 \times 10^{-4} \times \frac{1000}{0.25}
\]

\[
\Rightarrow 1.35 \text{ mg kg}^{-1}
\]
Appendix 4 Hg methodology development data

This table provides more detail regarding results presented in Section 3.2.3.2 and expands upon Table 3.2 and Table 3.3. As method I represented oven heating only, no concentration analysis was carried out in direct relation to this methodology.

Table A2 Replicate data for NIMT/UEO/FM/001 Hg methodology development recoveries

<table>
<thead>
<tr>
<th>Method</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>Replicate 3</th>
<th>Mean</th>
<th>s.d.</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>0.002</td>
<td>0.004</td>
<td>0.003</td>
<td>0.004</td>
<td>0.001</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>0.125</td>
<td>0.148</td>
<td>0.063</td>
<td>0.112</td>
<td>0.044</td>
<td>66</td>
</tr>
<tr>
<td>IV</td>
<td>0.094</td>
<td>0.078</td>
<td>0.074</td>
<td>0.082</td>
<td>0.011</td>
<td>48</td>
</tr>
<tr>
<td>V</td>
<td>0.157</td>
<td>0.153</td>
<td>0.146</td>
<td>0.152</td>
<td>0.006</td>
<td>90</td>
</tr>
<tr>
<td>VI</td>
<td>0.151</td>
<td>0.155</td>
<td>0.159</td>
<td>0.155</td>
<td>0.004</td>
<td>92</td>
</tr>
<tr>
<td>VII</td>
<td>0.164</td>
<td>0.159</td>
<td>0.172</td>
<td>0.165</td>
<td>0.007</td>
<td>98</td>
</tr>
<tr>
<td>Certified values</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.169</td>
<td>0.007</td>
<td>-</td>
</tr>
</tbody>
</table>

Table A3 Replicate data for CRM 7002 Hg methodology development recoveries

<table>
<thead>
<tr>
<th>Method</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>Replicate 3</th>
<th>Mean</th>
<th>s.d.</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>0.009</td>
<td>0.004</td>
<td>0.005</td>
<td>0.006</td>
<td>0.003</td>
<td>7</td>
</tr>
<tr>
<td>III</td>
<td>0.049</td>
<td>0.069</td>
<td>0.053</td>
<td>0.057</td>
<td>0.011</td>
<td>63</td>
</tr>
<tr>
<td>IV</td>
<td>0.091</td>
<td>0.069</td>
<td>0.047</td>
<td>0.069</td>
<td>0.022</td>
<td>77</td>
</tr>
<tr>
<td>V</td>
<td>0.093</td>
<td>0.075</td>
<td>0.096</td>
<td>0.088</td>
<td>0.011</td>
<td>97</td>
</tr>
<tr>
<td>VI</td>
<td>0.072</td>
<td>0.081</td>
<td>0.072</td>
<td>0.075</td>
<td>0.005</td>
<td>83</td>
</tr>
<tr>
<td>VII</td>
<td>0.075</td>
<td>0.088</td>
<td>0.083</td>
<td>0.082</td>
<td>0.007</td>
<td>91</td>
</tr>
<tr>
<td>Certified values</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.090</td>
<td>0.012</td>
<td>-</td>
</tr>
</tbody>
</table>
Table A4  
RePLICATE DATA FOR CRM 7004 Hg METHODOLOGY DEVELOPMENT RECOVERIES

<table>
<thead>
<tr>
<th>Method</th>
<th>Replicate 1</th>
<th>Replicate 2</th>
<th>Replicate 3</th>
<th>Mean</th>
<th>s.d.</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>0.004</td>
<td>0.039</td>
<td>0.020</td>
<td>0.021</td>
<td>0.018</td>
<td>9</td>
</tr>
<tr>
<td>III</td>
<td>0.178</td>
<td>0.239</td>
<td>0.198</td>
<td>0.205</td>
<td>0.031</td>
<td>91</td>
</tr>
<tr>
<td>IV</td>
<td>0.122</td>
<td>0.103</td>
<td>0.183</td>
<td>0.136</td>
<td>0.042</td>
<td>61</td>
</tr>
<tr>
<td>V</td>
<td>0.187</td>
<td>0.194</td>
<td>0.177</td>
<td>0.186</td>
<td>0.009</td>
<td>83</td>
</tr>
<tr>
<td>VI</td>
<td>0.194</td>
<td>0.189</td>
<td>0.187</td>
<td>0.190</td>
<td>0.004</td>
<td>85</td>
</tr>
<tr>
<td>VII</td>
<td>0.219</td>
<td>0.168</td>
<td>0.189</td>
<td>0.192</td>
<td>0.026</td>
<td>86</td>
</tr>
<tr>
<td>Certified values</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.223</td>
<td>0.016</td>
<td>-</td>
</tr>
</tbody>
</table>

Table A5  
P-VALUES FROM NIMT T-TEST COMPARISONS OF [Hg] ANALYSIS METHODS.

<table>
<thead>
<tr>
<th>Comparison of method ↓</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>/</td>
<td>0.001</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>III</td>
<td>0.001</td>
<td>/</td>
<td>0.316</td>
<td>0.194</td>
<td>0.167</td>
<td>0.108</td>
<td>0.091</td>
</tr>
<tr>
<td>IV</td>
<td>0.003</td>
<td>0.316</td>
<td>/</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>V</td>
<td>0.001</td>
<td>0.194</td>
<td>0.001</td>
<td>/</td>
<td>0.511</td>
<td>0.071</td>
<td>0.033</td>
</tr>
<tr>
<td>VI</td>
<td>0.001</td>
<td>0.167</td>
<td>0.001</td>
<td>0.511</td>
<td>/</td>
<td>0.098</td>
<td>0.039</td>
</tr>
<tr>
<td>VII</td>
<td>0.001</td>
<td>0.108</td>
<td>0.001</td>
<td>0.071</td>
<td>0.098</td>
<td>/</td>
<td>0.523</td>
</tr>
<tr>
<td>Certified value</td>
<td>0.001</td>
<td>0.091</td>
<td>0.001</td>
<td>0.033</td>
<td>0.039</td>
<td>0.523</td>
<td>/</td>
</tr>
</tbody>
</table>
Table A6  
*P*-values from CRM7002 t-test comparisons of [Hg] analysis methods.

<table>
<thead>
<tr>
<th>Comparison of method ↓ with →</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>/</td>
<td>0.002</td>
<td>0.008</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>III</td>
<td>0.002</td>
<td>/</td>
<td>0.446</td>
<td>0.026</td>
<td>0.061</td>
<td>0.029</td>
<td>0.025</td>
</tr>
<tr>
<td>IV</td>
<td>0.008</td>
<td>0.446</td>
<td>/</td>
<td>0.252</td>
<td>0.670</td>
<td>0.385</td>
<td>0.220</td>
</tr>
<tr>
<td>V</td>
<td>0.001</td>
<td>0.026</td>
<td>0.252</td>
<td>/</td>
<td>0.136</td>
<td>0.470</td>
<td>0.842</td>
</tr>
<tr>
<td>VI</td>
<td>0.001</td>
<td>0.061</td>
<td>0.670</td>
<td>0.136</td>
<td>/</td>
<td>0.232</td>
<td>0.116</td>
</tr>
<tr>
<td>VII</td>
<td>0.001</td>
<td>0.029</td>
<td>0.385</td>
<td>0.470</td>
<td>0.232</td>
<td>/</td>
<td>0.375</td>
</tr>
<tr>
<td>Cert. value</td>
<td>0.001</td>
<td>0.025</td>
<td>0.220</td>
<td>0.842</td>
<td>0.116</td>
<td>0.375</td>
<td>/</td>
</tr>
</tbody>
</table>

Table A7  
*P*-values from CRM7004 t-test comparisons of [Hg] analysis methods.

<table>
<thead>
<tr>
<th>Comparison of method ↓ with →</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>/</td>
<td>0.001</td>
<td>0.012</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>III</td>
<td>0.001</td>
<td>/</td>
<td>0.084</td>
<td>0.366</td>
<td>0.453</td>
<td>0.608</td>
<td>0.422</td>
</tr>
<tr>
<td>IV</td>
<td>0.012</td>
<td>0.084</td>
<td>/</td>
<td>0.114</td>
<td>0.091</td>
<td>0.121</td>
<td>0.029</td>
</tr>
<tr>
<td>V</td>
<td>0.001</td>
<td>0.366</td>
<td>0.114</td>
<td>/</td>
<td>0.521</td>
<td>0.725</td>
<td>0.025</td>
</tr>
<tr>
<td>VI</td>
<td>0.001</td>
<td>0.453</td>
<td>0.091</td>
<td>0.521</td>
<td>/</td>
<td>0.902</td>
<td>0.026</td>
</tr>
<tr>
<td>VII</td>
<td>0.001</td>
<td>0.608</td>
<td>0.121</td>
<td>0.725</td>
<td>0.902</td>
<td>/</td>
<td>0.153</td>
</tr>
<tr>
<td>Cert. value</td>
<td>0.001</td>
<td>0.422</td>
<td>0.029</td>
<td>0.025</td>
<td>0.026</td>
<td>0.153</td>
<td>/</td>
</tr>
</tbody>
</table>
Appendix 5 Creation of Hg speciation standards

Mercury speciation standards (100 µg l\(^{-1}\)) were prepared from single species stock chemicals as described in Section 3.3.3.3. Solid phase stock chemicals were first converted into 1000 ml of 0.1 g Hg l\(^{-1}\) solutions and then diluted with 2% v/v HNO\(_3\) (Aristar). Pertinent information is included in Table A8 for reference. These data can be substituted into the examples in Appendix 3.

Table A8 Information on Hg speciation standard stock chemicals

<table>
<thead>
<tr>
<th>Standard</th>
<th>Supplier information</th>
<th>Type</th>
<th>Concentration or molecular weight</th>
<th>Mass required for 1 l of 0.1 g l(^{-1}) Hg solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeHgCl</td>
<td>Alfa Aesar,</td>
<td>Solution</td>
<td>1000 mg l(^{-1})</td>
<td>-</td>
</tr>
<tr>
<td>EtHgCl</td>
<td>Alfa Aesar, &gt;99% purity</td>
<td>Solid</td>
<td>265.10 g</td>
<td>0.132 g</td>
</tr>
<tr>
<td>Hg(I)Cl</td>
<td>Acros Organics, &gt;99% purity</td>
<td>Solid</td>
<td>472.09 g</td>
<td>0.117 g</td>
</tr>
<tr>
<td>Hg(II)Cl</td>
<td>Acros Organics, 99.5% purity</td>
<td>Solid</td>
<td>236.05 g</td>
<td>0.135 g</td>
</tr>
</tbody>
</table>
Appendix 6 Preparation of buffer solutions

Universal buffers employed in Section 3.4.2.4 were created by mixing 0.1 M citric acid and 0.2 M dibasic potassium phosphate in the proportions outlined in Table A9. pH values were adjusted to 0.5 unit increments by dropwise addition of citric acid or potassium phosphate as required.

Table A9 Universal buffer mixtures and corresponding pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>0.2 M Na₂HPO₄ (ml)</th>
<th>0.1 M citrate (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>5.4</td>
<td>44.6</td>
</tr>
<tr>
<td>2.8</td>
<td>7.8</td>
<td>42.2</td>
</tr>
<tr>
<td>3.0</td>
<td>10.2</td>
<td>39.8</td>
</tr>
<tr>
<td>3.2</td>
<td>12.3</td>
<td>37.7</td>
</tr>
<tr>
<td>3.4</td>
<td>14.1</td>
<td>35.9</td>
</tr>
<tr>
<td>3.6</td>
<td>16.1</td>
<td>33.9</td>
</tr>
<tr>
<td>3.8</td>
<td>17.7</td>
<td>32.3</td>
</tr>
<tr>
<td>4.0</td>
<td>19.3</td>
<td>30.7</td>
</tr>
<tr>
<td>4.2</td>
<td>20.6</td>
<td>29.4</td>
</tr>
<tr>
<td>4.4</td>
<td>22.2</td>
<td>27.8</td>
</tr>
<tr>
<td>4.6</td>
<td>23.3</td>
<td>26.7</td>
</tr>
<tr>
<td>4.8</td>
<td>24.8</td>
<td>25.2</td>
</tr>
<tr>
<td>5.0</td>
<td>25.7</td>
<td>24.3</td>
</tr>
<tr>
<td>5.2</td>
<td>26.7</td>
<td>23.3</td>
</tr>
<tr>
<td>5.4</td>
<td>27.8</td>
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<td>21.0</td>
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<td>5.8</td>
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<td>19.7</td>
</tr>
<tr>
<td>6.0</td>
<td>32.1</td>
<td>17.9</td>
</tr>
<tr>
<td>6.2</td>
<td>33.1</td>
<td>16.9</td>
</tr>
<tr>
<td>6.4</td>
<td>34.6</td>
<td>15.4</td>
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<tr>
<td>6.6</td>
<td>36.4</td>
<td>13.6</td>
</tr>
<tr>
<td>6.8</td>
<td>40.9</td>
<td>9.1</td>
</tr>
<tr>
<td>7.0</td>
<td>43.6</td>
<td>6.5</td>
</tr>
</tbody>
</table>
Appendix 7 Calculation of layer age from unsupported $^{210}\text{Pb}$

This appendix demonstrates the calculation of $^{210}\text{Pb}$ activity and layer age in support of the methodology outlined in Section 2.3.18. In Equation A12 and A16 ‘$\lambda$’ represents the decay constant.

Example: Calculation of age of ED layer 1 (1.5 cm)

Calculation of total $^{210}\text{Pb}$ activity

Activity
\[
\text{Activity} = \text{counts per second} \times 100 \times \frac{\text{detector efficiency}}{0.56} \Rightarrow \text{Activity} = 1.11 \text{ Bq}
\]

Specific activity
\[
\text{Specific activity} = \text{activity} \times \frac{1000}{\text{weight (g)}} \Rightarrow \text{Specific activity} = 1.11 \times \frac{1000}{5.05} \Rightarrow \text{Specific activity} = 219.2 \text{ Bq kg}^{-1}
\]

Decay corr
\[
\text{Decay corr} = \text{specific activity} \times \exp(-\lambda \times (\text{year collected} - \text{year run})) \Rightarrow \text{Decay corr} = 219.2 \times \exp(-0.031083 \times (2010.5-2010.92)) \Rightarrow \text{Decay corr} = 222.09 \text{ Bq kg}^{-1}
\]
Calculation of supported $^{210}\text{Pb}$ activity

$^{214}\text{Pb}$ and $^{214}\text{Bi}$ are adopted as proxies for supported $^{210}\text{Pb}$ activity. To these ends, the specific activity of $^{214}\text{Pb}$ at 295 keV and 352 keV and $^{214}\text{Bi}$ at 609 keV, respectively, are calculated using Equations A10-A12 shown above.

\[
\text{Supported } ^{210}\text{Pb activity} = \frac{( ^{214}\text{Pb activity (295 keV)} + ^{214}\text{Pb activity (352 keV)} + ^{214}\text{Bi activity (609 keV)})}{3}
\]

\[
=> \quad = \frac{(0.00 + 0.40 + 0.00)}{2}
\]

\[
=> \quad = 0.20 \text{ Bq kg}^{-1}
\]

*When corrected $^{214}\text{Pb}$ activity at 295 keV is 0 then it is omitted from the mean calculation and the total is instead divided by 2.

Calculation of unsupported $^{210}\text{Pb}$ activity

Unsupported $^{210}\text{Pb}$ activity = total $^{210}\text{Pb}$ activity – unsupported $^{210}\text{Pb}$

\[
=> \quad = 222.1 - 0.2
\]

\[
=> \quad = 221.9 \text{ Bq kg}^{-1}
\]

Calculation of layer inventory

Layer unsupp $^{210}\text{Pb}_{\text{INV}} = \frac{(\text{unsupported } ^{210}\text{Pb activity x layer mass})}{\text{core surface area}}$

\[
=> \quad = \frac{(221.9 \times 0.1403)}{0.014}
\]

\[
=> \quad = 2306 \text{ Bq m}^{-2}
\]
Calculation of layer age

Layer age \( = \lambda^{-1} \times \ln \left( \frac{\text{total unsupported } ^{210}\text{Pb inventory}}{\text{total unsupported } ^{210}\text{Pb inventory below this layer}} \right) \) \hspace{1cm} \text{Equation A16}

\[ \Rightarrow \quad = 0.031083^{-1} \times \ln(20343/18037) \]
\[ \Rightarrow \quad = 3.87 \text{ years} \]
Appendix 8 Core data tables for FM, GT, ED and AM

Tables A7-A10 below show profile data for layers of FM, GT, ED and AM used in the graphs presented in Chapter 5 and Chapter 6.

Table A10 Tabulated profile data for FM

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Year</th>
<th>s.d</th>
<th>[Pb] (mg kg(^{-1}))</th>
<th>s.d</th>
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Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

| Temperature | pH  | Temperature | pH  | Temperature | pH  | Temperature | pH  | Temperature | pH  | Temperature | pH  | Temperature | pH  |
|-------------|-----|-------------|-----|-------------|-----|-------------|-----|-------------|-----|-------------|-----|-------------|-----|-------------|
| 30.5        | 1887| 105.7       | 55.9| 4.76        | 0.317| 0.006       | 1.175| 0.003       | 2.1 | 1.2         | 0.107| 0.011       | 1.165| 0.001       |
| 31.5        | -   | -           | 41.4| 5.03        | 0.206| 0.003       | 1.177| 0.002       | 0.7 | 1.3         | 0.029| 0.003       | 1.176| 0.003       |
| 32.5        | 1849| 197.6       | 45.5| 5.52        | 0.249| 0.004       | 1.172| 0.005       | 2.2 | 1.2         | 0.029| 0.003       | 1.176| 0.006       |
| 33.5        | -   | -           | 36.5| 5.50        | 0.114| 0.000       | 1.176| 0.003       | 4.3 | 1.3         | 0.026| 0.003       | 1.174| 0.007       |
| 34.5        | -   | -           | 35.5| 5.91        | 0.107| 0.002       | 1.180| 0.003       | 1.5 | 1.4         | 0.028| 0.003       | 1.146| 0.029       |
| 35.5        | -   | -           | 52.8| 7.39        | 0.232| 0.005       | 1.186| 0.003       | 4.1 | 1.3         | 0.045| 0.005       | 1.169| 0.004       |
| 36.5        | -   | -           | 33.7| 6.21        | 0.096| 0.002       | 1.188| 0.003       | 0.0 | 1.3         | 0.051| 0.005       | 1.174| 0.024       |
| 37.5        | -   | -           | 34.1| 6.25        | 0.131| 0.003       | 1.193| 0.002       | 0.0 | 1.4         | 0.040| 0.004       | 1.174| 0.011       |
| 38.5        | -   | -           | 33.8| 6.84        | 0.070| 0.001       | 1.185| 0.005       | 4.3 | 1.4         | 0.026| 0.003       | 1.177| 0.010       |
| 39.5        | -   | -           | 35.2| 8.03        | 0.198| 0.003       | 1.184| 0.004       | 0.0 | 1.1         | 0.099| 0.010       | 1.166| 0.006       |
| 40.5        | -   | -           | 37.2| 9.28        | 0.121| 0.003       | 1.182| 0.006       | 3.7 | 1.5         | 0.108| 0.011       | 1.165| 0.006       |
| 41.5        | -   | -           | 31.2| 8.15        | 0.061| 0.002       | 1.191| 0.001       | 4.3 | 1.1         | 0.096| 0.010       | 1.164| 0.006       |
| 43          | -   | -           | 39.1| 10.33       | 0.049| 0.001       | 1.193| 0.005       | 6.4 | 1.5         | 0.097| 0.010       | 1.171| 0.008       |
| 45          | -   | -           | 26.5| 8.33        | 0.013| 0.000       | 1.203| 0.005       | 1.9 | 1.3         | 0.087| 0.009       | 1.173| 0.007       |
Appendix 9 Calculation of metal inventories and fluxes

Inventory and flux data are presented for Pb and Hg in Chapters 5 and 6. The calculations used to derive these values are outlined below.

Example: Calculation of Pb inventory for ED layer 3 (7.5 cm)

\[
Pb_{\text{INV}} = \frac{[Pb] \text{ (mg kg}^{-1}) \times \text{layer dry mass (g)} \times \text{(surface area (m}^2\text{))}^{-1}}{1000 \text{ g}}
\]

\[
=> = 42.23 \times 42.76 \times 0.0135 \times \frac{1}{1000}
\]

\[
=> = 140.1 \text{ mg m}^{-2}
\]

Example: Calculation of Pb flux for ED layer 1 (1.5 cm)

\[
Pb_{\text{FLUX}} = \frac{Pb_{\text{INV}}}{\text{Year span of layer}}
\]

\[
=> = \frac{46.9}{6.3}
\]

\[
=> = 7.44 \text{ mg m}^{-2} \text{ yr}^{-1}
\]
Appendix 10  Gel electrophoresis Pb and Fe data and Al gel distribution

This appendix presents Pb and Fe gel electrophoresis data utilised in graphs presented in Section 7.3 in addition to Al data mentioned in Section 7.4.

Table A11  Pb (µg) per gel fraction for selected FM layers

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Carbon and contaminant trace metal biogeochemistry in surficial organic-rich terrestrial systems

Table A12  
Pb (µg) per gel fraction for selected GT layers

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Table A13  
Pb (µg) per gel fraction for selected ED layers

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Appendices  406
### Table A14  Fe (µg) per gel fraction for selected FM layers

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Table A18  
Al (µg) per gel fraction for selected GT layers

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<td>0.0001</td>
<td>0.0001</td>
<td>0.0007</td>
<td>0.0002</td>
<td>0.0008</td>
<td>0.0004</td>
</tr>
</tbody>
</table>

Table A19  
Al (µg) per gel fraction for selected ED layers

<table>
<thead>
<tr>
<th>Well</th>
<th>1.5 cm</th>
<th>4.5 cm</th>
<th>7.5 cm</th>
<th>10.5 cm</th>
<th>13.5 cm</th>
<th>16.5 cm</th>
<th>19.5 cm</th>
<th>22.5 cm</th>
<th>25.5 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.0024</td>
<td>0.0008</td>
<td>0.0015</td>
<td>0.0010</td>
<td>0.0005</td>
<td>0.0007</td>
<td>0.0010</td>
<td>0.0020</td>
<td>0.0006</td>
</tr>
<tr>
<td>F2</td>
<td>0.0009</td>
<td>0.0011</td>
<td>0.0027</td>
<td>0.0008</td>
<td>0.0011</td>
<td>0.0012</td>
<td>0.0020</td>
<td>0.0082</td>
<td>0.0017</td>
</tr>
<tr>
<td>F3</td>
<td>0.0015</td>
<td>0.0017</td>
<td>0.0037</td>
<td>0.0025</td>
<td>0.0040</td>
<td>0.0051</td>
<td>0.0065</td>
<td>0.0082</td>
<td>0.0051</td>
</tr>
<tr>
<td>F4</td>
<td>0.0012</td>
<td>0.0018</td>
<td>0.0029</td>
<td>0.0011</td>
<td>0.0025</td>
<td>0.0028</td>
<td>0.0032</td>
<td>0.0025</td>
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</tr>
<tr>
<td>F5</td>
<td>0.0008</td>
<td>0.0013</td>
<td>0.0015</td>
<td>0.0006</td>
<td>0.0010</td>
<td>0.0009</td>
<td>0.0007</td>
<td>0.0006</td>
<td>0.0008</td>
</tr>
<tr>
<td>F6</td>
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<td>0.0010</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.0006</td>
<td>0.0002</td>
<td>0.0013</td>
<td>0.0003</td>
</tr>
<tr>
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<td>0.0007</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.0003</td>
<td>0.0002</td>
<td>0.0000</td>
<td>0.0002</td>
</tr>
<tr>
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<td>0.0007</td>
<td>0.0008</td>
<td>0.0019</td>
<td>0.0004</td>
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<td>0.0001</td>
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<td>0.0002</td>
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</tr>
<tr>
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<td>0.0006</td>
<td>0.0006</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0001</td>
<td>0.0003</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
Appendix 11 \[ ^{206}\text{Pb}/^{207}\text{Pb} \] source apportionment calculations

This appendix presents the source apportionment calculation used in Section 5.5.2.1.2 to determine the quantity of petrol-sourced Pb required to be mobilised to shift isotope ratios at GT from 1.18-1.14. The source apportionment calculation is adapted from Farmer et al. (2006). \( ^{206}\text{Pb}/^{207}\text{Pb}_\text{layer} \) represents the isotope ratio of the layer under investigation, \( ^{206}\text{Pb}/^{207}\text{Pb}_\text{anthrop} \) represents the isotopic signature of anthropogenic Pb (1.133) and \( ^{206}\text{Pb}/^{207}\text{Pb}_\text{petrol} \) is the isotopic signature of petrol-sourced Pb (1.076).

**Example: Calculation of % petrol Pb flux for \( ^{206}\text{Pb}/^{207}\text{Pb} \) of 1.18**

\[
Pb_{\text{petrol}} \% = \frac{\left( ^{206}\text{Pb}/^{207}\text{Pb}_\text{layer} - ^{206}\text{Pb}/^{207}\text{Pb}_\text{anthrop} \right)}{\left( ^{206}\text{Pb}/^{207}\text{Pb}_\text{layer} - ^{206}\text{Pb}/^{207}\text{Pb}_\text{petrol} \right)} \times 100 \quad \text{Equation A1}
\]

\[
=> \quad \left( 1.18 - 1.133 \right) \times 100 \\
\quad \left( 1.18 - 1.076 \right)
\]

\[
=> \quad = 45\%
\]

**Example: Petrol Pb mobilisation required for 1.18-1.14 \( ^{206}\text{Pb}/^{207}\text{Pb} \) shift**

\[
Pb_{\text{petrol}} \% \text{ in 1.18 layer} = 45\%
\]

\[
Pb_{\text{petrol}} \% \text{ in 1.14 layer} = 11\%
\]

\[
\text{Required petrol-Pb loss} = (1.18 \text{ percentage}) - (1.14 \text{ percentage}) \quad \text{Equation A20}
\]

\[
=> \quad = 45 - 11
\]

\[
=> \quad = 34\%
\]