

**An assessment of the mechanisms for the transfer of lead and mercury from atmospherically contaminated organic soils to lake sediments with particular reference to Scotland, UK.**

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**Abstract**

While the sediment records of upland lakes are known to be valuable natural archives of depositional changes, recent studies in the U.K. have shown that full basin records of trace metals are not showing the decline expected as a result of the massive reduction in emissions since the 1970s. As trends in metal deposition across Europe are known to be declining, this ‘additional’ trace metal input to upland lakes can only be the result of mobilisation from catchment storage. We undertook a multiple sediment core, multi-pollutant study at nine lakes across Scotland to test hypotheses that this additional input was a result of (i) a simple time-lag; (ii) catchment soil erosion; (iii) leaching with dissolved organic carbon. We constructed decadal resolved full basin inventories for Pb, Hg and spheroidal carbonaceous particles (SCPs), a particulate component of fly-ash, at lakes with thin soils, lakes with eroded soils and lakes with non-eroded soils in their catchments to assess temporal trends. The use of both trace metals and SCPs allowed a comparison between erosive (SCPs and metals) and leaching (metals only) processes. Our results showed that the full basin inventories for Hg, Pb and SCPs for lakes with thin catchment soils had similar temporal trends to those of atmospheric emissions and deposition. For lakes with significantly eroded catchment soils, increasing trends in inventories continued to the most recent decades while those with non-eroded soils showed an intermediate pattern with some similarity to atmospheric deposition patterns, but with a reduced recent decline. We

conclude that catchment soil erosion is the main transfer mechanism for trace metals at these sites and that although the leaching of metals bound to dissolved organic carbon (DOC) may play a role this appears to be less significant. The processes that lead to soil erosion and leaching of DOC from the catchment are exacerbated by increased winter rainfall, prolonged summer drought and increased frequency of high intensity rain events. Hence, predicted climatic changes will increase pollutant transfer from catchment to surface waters. The catchment storage of deposited pollutants is a massive potential reservoir that could keep fluxes of contaminants to surface waters elevated for many decades to come. This would counteract the benefits of reductions in deposition resulting from policy implementations over recent decades and may elevate exposure of aquatic biota to these contaminants.

## 1. INTRODUCTION

Recent studies have shown the sensitivity of remote mountain lakes to atmospherically deposited pollutants. Such lakes have no direct sources of contamination and often small catchments making them ideal natural collectors of deposited pollutants (Battarbee, 2005; Rose, 2007a) while their sediment records additionally provide a valuable natural archive of temporal depositional changes. Since 1970, emissions of trace metals to the atmosphere in the UK have declined dramatically. The UK National Atmospheric Emissions Inventory (<http://www.naei.org.uk/>) shows that emissions of mercury (Hg), lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu) and zinc (Zn) have declined by 89%, 99%, 92%, 91%, 73% and 80%, respectively between 1970 and 2007, principally as a result of declining coal use, reduction in iron and steel production, better controls on incinerators and, for Pb, the introduction of unleaded petrol. It would therefore be expected that the sediment records of upland lakes would similarly show a decline in inputs. However, at Lochnagar, a remote mountain lake in Scotland, UK, whole lake sediment basin fluxes of toxic metals (e.g. Pb and Hg) have not declined as might be expected (Yang et al., 2002a). This suggests that the sediment archive has deviated from a faithful record of atmospheric deposition but also implies that declines in deposition as a result of emissions reductions are being counteracted by additional inputs at this lake and presumably many other waterbodies in the UK and across Europe.

Although it is currently uncertain how widespread this problem is, it seems clear that if depositional fluxes are declining across broad geographical areas, then this 'additional' trace metal must be derived from catchment sources and that this is derived from previously deposited contaminants stored in catchment soils. As catchment areas are generally far bigger than lake surface areas, deposition and thus storage in catchment soils is likely to be significantly higher than that deposited directly to the lake surface. Hence, the store of toxic pollutants (trace metals and persistent organic pollutants; POPs) with potential to be released to freshwaters may be very large. Yang et al. (2002a) proposed that Pb released from this store at Lochnagar is now a significant contributor to the total flux to the loch and showed that the catchment soils, although sparse, contain the equivalent of more than 400 years of Pb deposition at 2000 levels. A similar situation has also been observed for Hg

at Lochnagar (Yang et al., 2002b) although the full basin flux of Hg continued to increase through time, and more importantly across the period of Hg emission reduction, rather than level off in recent decades as observed for Pb.

There are four possible mechanisms by which this lack of decline in sediment metals may be explained. First, a simple time-lag, i.e. it takes decades for metals deposited onto the catchment to pass through to the lake (or stream) water. Second, the increase in dissolved organic carbon (DOC) observed in many waterbodies across Europe over recent decades (including Lochnagar; Monteith et al., 2007a) is bringing in metals and POPs for which it has a high affinity. This increase may be a response to the recovery from acidification (Evans et al., 2005; Monteith et al., 2007b) or a result of increased decomposition of catchment organic matter in warmer summers (Freeman et al., 2001) and elevated leaching in wetter winters. Third, climate change is increasing catchment soil erosion (Helliwell et al., 2007) elevating the input of previously deposited metals bound to soils. Fourth, longer ice-free periods as a result of climate warming allows longer for algae to scavenge metals from the water column as long as sufficient nutrients are present within the water body to permit this increased production (e.g. Outridge et al., 2005; Stern et al., 2009; Carrie et al., 2010). The aim of this study is to assess these mechanisms and determine which, if any, provide the main means by which catchment stored trace metals (and by inference other deposited pollutants such as POPs) are transferred to surface waters and subsequently to the aquatic food chain.

## **2. MATERIALS AND METHODS**

### **2.1. Site selection**

Lakes were sampled in three regions of Scotland, UK. Scotland provides a steep historical pollutant deposition gradient from high deposition in the south to low in the north and a large number of standing waterbodies with a range of catchment types, including many with organic peat soils, from which to select the most appropriate for this study. Three regions within Scotland were selected: the

north-west (low pollutant deposition); the south-west (high pollutant deposition) and the north-east (moderate pollutant deposition).

Within each of these regions, three lakes were selected to represent different catchment soil coverages. First, a lake with thin soils and / or little soil coverage in the catchment. Use of these lakes (hereafter referred to as 'thin soil sites') was to observe historical trends in atmospheric deposition with only minimal influence from catchment soils. Hence, they were selected to act as 'control' sites. Second, a lake with a high proportion of peat soil coverage in the catchment but with little or no evidence of erosion (hereafter known as 'non-eroded sites'). Third, a lake with a high proportion of peat soil coverage in the catchment but where extensive areas of soil erosion were known to be present especially close to the loch shore (hereafter known as 'eroded sites').

These lakes were selected with the aid of colleagues from the Macaulay Land-Use Research Institute (MLURI) in Aberdeen. To select sites, the appropriate 1:250,000 soil coverage maps were used which provide, for each map unit, the dominant soil series. Generally in Scotland, organic soils have >50% organic carbon content, an average pH < 4 and are characterised by mire and blanket bog plant communities. 24% of the land classed as peatlands in Scotland has significant signs of erosion (Helliwell et al., 2007). For some of the 'Organic Soil' map units the dominant soil is classed as 'eroded basin / blanket peat' and lakes were selected from within these map units. To assess the area of eroded soils within each catchment, it was assumed that the whole map unit was covered by the dominant soil-type as map units could not be apportioned spatially. The lake catchment boundary was then overlain on the soil map and the proportion of the catchment that was covered by the units labelled as eroded peat were calculated. In the field, these eroded areas were confirmed visually by the presence of hags and gullies. Where erosion is significant these gullies can be 1 – 2m in depth and several metres wide resulting in a complex topography with considerable variability in depth (Helliwell et al., 2007). The locations of the selected sites are given in Table 1 and morphological data for the lochs and their catchments are given in Table 2.

## **2.2. Sampling strategy and hypotheses**

At each lake multiple sediment cores were taken and analysed for trace metals and spheroidal carbonaceous particles (SCPs) in order to determine the full lake sediment basin fluxes of these atmospherically deposited contaminants. Spheroidal carbonaceous particles are a component of fly-ash, the particulate by-product of high temperature, industrial combustion of fossil-fuels such as coal and oil (Rose, 2001). They are morphologically distinct and have no natural sources and hence provide an unambiguous indication of contamination from these industrial sources. Similarly to trace metals and other deposited contaminants, SCPs may be stored in catchments soils (Yang et al., 2001) but as they are particulate they are only transferred from soils to surface waters by erosive processes and cannot be leached as trace metals can. Hence, by comparing the full sediment basin records of trace metals and SCPs at these different lake types we can establish and test a series of hypotheses:

**Hypothesis 1:** That lakes with only thin soils in their catchments are minimally affected by soil processes and therefore temporal trends in the sedimentary full basin inventories of all pollutants will show the same historical patterns as those shown by atmospheric deposition. *This hypothesis may be tested by assessing the full basin inventories of trace metals and SCPs in lakes with thin soils in their catchments. If the hypothesis is correct then full basin inventories for all deposited pollutants should show atmospheric deposition trends. If the hypothesis is incorrect and the inventory data differs from atmospheric deposition, then enhanced algal scavenging may be the cause.*

**Hypothesis 2:** That catchment soil erosion is the main cause of increased pollutant transfer from catchment soils to lake sediments. *This hypothesis may be tested by comparing the full basin inventories of all pollutants at eroded sites with those at non-eroded sites. If the hypothesis is correct then lakes with non-eroded catchment soils should not show enhanced catchment inputs but lakes with eroded catchment soils will. The full basin inventories of both trace metals and SCPs will be affected. The sediment records of pollutants at lakes with thin catchment soils should be unaffected.*

**Hypothesis 3:** That enhanced leaching from catchment soils, as a result of elevated allochthonous DOC is the cause of increased pollutant transfer from catchment soils to lake sediments. *This hypothesis may be tested by comparing the full basin inventories of trace metals with those of*

*SCPs at both eroded and non-eroded sites. If the hypothesis is correct then all lakes with good soil coverage (eroded and non-eroded) in their catchments should show enhanced inputs. The records of trace metals at these lakes should be enhanced as they bind to DOC. The records of SCPs should not be affected by this mechanism. The sediment records of pollutants at lakes with thin soils should be unaffected.*

### **2.3. Lake bathymetries**

In order to establish the area of each lake basin covered by sedimentation and to assess the area of the basin attributable to each sediment core, a detailed bathymetric survey was undertaken for each lake using a combined echo sounder and global positioning system (GPS). This system was mounted on a small inflatable boat and combined soundings and GPS fixes were taken every second as the boat progressively traversed the lake. This resulted in a large number of readings for each lake basin from which a bathymetry was produced. A geographic information system (GIS) was used to store and manipulate these data, and interpolation used to construct a gridded depth 'surface'. The spatial resolution of this grid was dependant upon the size of the lake but was typically around 10m. The accuracy of depth measurements are to the nearest 1 cm. Bathymetric maps were then used to determine lake basin areas within identified depth boundaries. Coring locations and areas of sediment coverage could also be mapped onto these bathymetries.

### **2.4. Sediment and soil coring**

Sediment and soil coring was undertaken in June 2004. Multiple sediment cores are required to truly assess trends across a sedimenting basin (Engstrom et al., 2007). Short gravity cores (Glew, 1991) were taken from three representative depths within each lake. One core was taken from the deepest area, the second from as shallow an area as possible with reasonable sediment accumulation (see below) and the third, from an area intermediate between these two. This distribution by depth interval

ensured that sampling locations throughout the sedimenting basin were representative (Rippey et al., 2008) while three cores represents the minimum number required to achieve an error of 5% for full basin calculations (Rowan et al., 1995; Rippey et al., 2008).

Prospecting using the sediment corer was used to establish the shallowest limits of sediment accumulation at each lake. At between 3 – 5 locations (depending on lake size) around the perimeter of each lake a transect from the shore towards the lake centre was undertaken sampling at frequent intervals with the sediment corer. The depth at which sediment accumulation began (defined as the depth at which sediment was successfully retrieved in the core tube) was recorded and the mean taken for the lake. The shallow water core was then collected typically 10 – 30m beyond this point (depending on lake size and sediment retrieval).

All sediment cores except those from Loch Coire an Lochain were extruded vertically in the field at 0.5 cm intervals from 0 – 20cm and then at 1 cm intervals from 20 cm to the base of the core. For Loch Coire an Lochain cores, the sediment accumulation rate of this lake was known to be very low (Appleby et al., 1990) and so the core was extruded in 0.25 cm intervals from 0 – 5cm, then 0.5 cm intervals from 5 cm depth to the base of the cores.

A soil core was taken from a representative area of each catchment in order to provide an estimate of the catchment soil inventory of stored contaminants. Selected coring locations in each catchment were in reasonably flat, undisturbed areas in open ground away from large obstructions (e.g. boulders) and in areas of uniform, typical vegetation. Areas close to the lake shore were selected preferentially if possible but areas of severe erosion, where present, were avoided in case enhanced drainage by gullyng affected the accumulated record. Soil cores were taken by pushing an acid-washed plastic tube vertically into the soil and cores were extruded horizontally in the field at 1cm intervals. Each slice was individually weighed before any further treatment or analysis was undertaken.

## **2.5. Lithostratigraphy**

Water content and organic matter content (as estimated by loss-on-ignition (LOI) at 550 °C; Boyle, 2004) were measured on every sample of all sediment and soil cores. Wet density measurements were



undertaken on every fifth sample of the sediment cores using standard procedures (Stevenson et al., 1987). Dry bulk density for each sediment and soil sample was calculated from the water content and wet density data for the sediment samples and from the water content, volume and mass of each complete soil slice.

## 2.6. Sediment dating

Radiometric dates were obtained for one sediment core from each lake by measuring  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  by gamma spectrometry using well-type, coaxial, low background, intrinsic germanium detectors fitted with NaI(Tl) escape suppression shields (Appleby et al., 1986) at the Bloomsbury Environmental Isotope Facility (BEIF), UCL. Lead-210 is a naturally occurring radionuclide of half-life 22.26 years and measurements of  $^{210}\text{Pb}$  activity in excess of the supporting  $^{226}\text{Ra}$  are used to determine a chronology for the past 100-150 years. Cesium-137 and  $^{241}\text{Am}$  are artificial radionuclides first introduced into the environment on a global scale in 1954 by the atmospheric testing of thermo-nuclear weapons. Fallout of  $^{137}\text{Cs}$  reached a maximum in 1963 and then declined sharply following the treaty in that year banning further atmospheric tests. Sediment records of this maximum can be used to identify the 1963 level in a core and confirmed using the  $^{241}\text{Am}$  record to distinguish this from a possible 1986 Chernobyl peak ( $^{137}\text{Cs}$  only). There are two principal methods for determining the initial  $^{210}\text{Pb}$  activity of a sediment layer necessary for the calculation of its  $^{210}\text{Pb}$  date. These are the CRS (constant rate of unsupported  $^{210}\text{Pb}$  supply) model (Appleby and Oldfield, 1978) and the CIC (constant initial  $^{210}\text{Pb}$  concentration) model. Factors governing model choice are discussed in (Appleby and Oldfield, 1983; 1992). Sediment depth-age models and accumulation rates for the dated cores were produced from these model outputs.

Chronologies from the radiometrically dated cores were cross-correlated with the undated cores from the same lake by matching the cumulative SCP inventory profiles (Renberg and Wik, 1984; Rose and Appleby, 2005) and by using shared features within the lithostratigraphic profile data. Shared features in the concentration profiles of analysed metals (including Cu, Ni, Zn, Cd) were also used where required to confirm these correlations. In this way chronologies could be ascribed to cores which were not radiometrically dated (Figure 1).

## 2.7. Spheroidal carbonaceous particle (SCP) analysis

SCP analysis followed the procedure described in Rose (1994). Sequential treatments using nitric, hydrofluoric and hydrochloric acids removed organic, siliceous and carbonate fractions respectively resulting in a suspension of mainly carbonaceous material in water. A known fraction of this suspension was then evaporated onto a coverslip and the number of SCPs counted using a light microscope at 400 times magnification. The criteria for SCP identification under the light microscope followed Rose (2008). Sediment and soil SCP concentrations was calculated in units of 'number of particles per gram dry mass of sediment (or soil)' ( $\text{gDM}^{-1}$ ). Analytical blanks and SCP reference material (Rose, 2008) were included in each batch of sample digestions. Reference concentrations agreed with expected values while no SCPs were observed in the blanks. The detection limit for the technique is typically c.  $100 \text{ gDM}^{-1}$  and calculated concentrations typically have an accuracy of c.  $\pm 45 \text{ gDM}^{-1}$ .

## 2.8. Trace metal analyses

Precisely weighed c. 0.3g freeze-dried sediment and soil samples were heated with 10 mL Aristar  $\text{HNO}_3$  in 50 mL Teflon beakers at  $100^\circ\text{C}$  on a hotplate for 1 hour. The resulting solutions were made up to 30 mL using deionised water ( $18.2 \text{ M}\Omega$ ). The final solutions were homogenised, 10 mL used for Pb, Zn, Cu, Cd and Ni analyses, whilst the remaining 20 mL was retained for Hg. Mercury was measured by cold vapour atomic adsorption spectrometry (CV-AAS) following reduction of Hg in the solution to its elemental state by 2 mL fresh  $\text{SnCl}_2$  (10% in 20% v/v HCl; Engstrom and Swain, 1997). The other metals were measured using normal AAS. Certified standard reference material was digested and analysed along with the sample analyses. Measured concentrations of Pb in the standard reference material SRM2704 (Buffalo River sediment) was  $158 \mu\text{g g}^{-1}$  ( $N = 10$ ; Std dev. =  $6.0 \mu\text{g g}^{-1}$ ) while the certified value is  $161 \mu\text{g g}^{-1}$ . For Hg, a standard stream sediment reference material (GBW07305) was used. Measured Hg concentrations were  $93 \text{ ng g}^{-1}$  ( $N = 10$ ; Std dev =  $8.6 \text{ ng g}^{-1}$ ) while the certified value is  $100 \text{ ng g}^{-1}$ . Mean recovery rates for Pb and Hg were therefore 98.1% and

93.0% respectively. Standard solutions and quality control blank digestions were measured every five samples to monitor measurement stability. Calibrations were made using these standard solutions. Analytical detection limits for Pb, Zn, Cu, Cd, Ni and Hg were 2.9, 1.9, 1.1, 0.3 and 2.0  $\mu\text{g g}^{-1}$  and 6.3  $\text{ng g}^{-1}$ , respectively. While other trace metal results were used for chronological cross-correlations (Section 2.6; Figure 1), only Pb and Hg results are discussed in detail here.

## 2.9. Calculating decadal full sediment basin inventories

The analytical work described above resulted in a radiometrically-derived or cross-correlated date and a Pb, Hg and SCP concentration for each analysed sediment sample. The calculation of the decadal full sediment basin inventories was then undertaken in a number of steps.

- i) The proportion of each sediment sample deposited within a given decade was calculated. For example, a sediment slice for which the upper and lower dates were 1954 and 1944 respectively could be allocated 40% to the 1950 – 1960 decade and 60% to the 1940 – 1950 decade. The total amount of trace metal and number of SCPs per unit area for each decade for each core could then be calculated from this proportion, the core slice interval, the contaminant concentration and the dry bulk density and then summing these for each core slice represented in that particular decade. Hence:

$$\text{Total contaminant per decade per core} = \sum_i^j (C_{Mi} \cdot D_i \cdot I_i \cdot P)$$

where  $C_{Mi}$  is the concentration of contaminant M in sediment sample  $i$ ;  $D_i$  is the dry bulk density of sediment sample  $i$ ;  $I_i$  is the sediment interval for sample  $i$ ,  $P$  is the proportion of sample  $i$  allocated to that decade and where sediment samples between  $i$  and  $j$  contribute to the sediment deposited within that decade.

- ii) The area of the sedimenting lake basin represented by each core was calculated digitally from the lake bathymetries. Hence, the area represented by the shallow water core was the area of the lake basin from the shallowest depth of continuous sediment accumulation to the depth

mid-way between the coring depths for the shallow water and mid-depth cores; the area of the lake basin represented by the mid-depth core was the area of the lake basin from mid-way between the coring depths for the shallow water and mid-depth cores to mid-way between the coring depths for the mid-depth and deep water cores; and the area of the lake basin represented by the deep water core was the area of the lake basin below mid-way between the coring depths for the mid-depth and deep water cores. In this way, the whole sedimentating lake basin was allocated to a sediment core on a water depth basis.

- iii) The total of each contaminant in each of these three depth zones for each decade could be calculated from the product of Equation 1 and the areas of each depth zone.
- iv) The total mass of Hg and Pb (or number of SCPs) deposited to the sediment for each decade for the whole sedimenting lake basin could then be calculated by adding together the decadal totals from each of the three lake basin depth zones. These totals could then be converted to a mean full basin contaminant flux for each decade.

## 2.10. Statistical analysis

Additive models were used to estimate trends in the pollutant profiles at individual sites. An additive model is one that incorporates smooth functions of one or more covariates and are thus able to model non-linear relationships between covariate and response. We fitted an interaction model of the form:

$$y_{ij} = \alpha_0 + \alpha_{1j}Site_{ij} + f_j(Time_i) + \varepsilon_i, \quad \varepsilon_i \sim N(0, \sigma^2)$$

where  $\alpha_0$  is the model intercept (the mean value of the response,  $y_{ij}$ , in the reference Site),  $\alpha_{1j}$  is the difference between the mean response for the  $j$ th Site and  $\alpha_0$ ,  $f_j(\cdot)$  are centered, smooth functions of a time variable and represent the trend in the response for the  $j$ th Site, and  $\varepsilon_i$  are the model residuals, assumed Gaussian distributed with mean 0 and variance  $\sigma^2$ . As such this model incorporates a separate trend for each site into a single model of temporal changes in pollutant across the nine sites. Thin-plate regression splines were used to parametrise the  $f_j$  (Wood 2003). The fitted smooth functions,  $f_j$ , were

compared for selected pairs of sites via the use of a prediction matrix  $\mathbf{X}_p$  that is related to the fitted values of the response ( $\hat{y}_p$ ) for a set of new data points  $\mathbf{p}$  via the relationship:

$$\hat{y}_p = \mathbf{X}_p \hat{\boldsymbol{\beta}}$$

where  $\hat{\boldsymbol{\beta}}$  is the vector of fitted coefficients;  $\alpha_0, \alpha_{1j}$ , plus the set of penalised coefficients for the basis functions representing the fitted smooths  $f_j$  (Wood, 2006). For pairs of sites ( $a, b$ ), the rows of  $\mathbf{X}_p$  corresponding to these sites are subtracted from one another and the columns of the resulting matrix  $\mathbf{X}_{p(a,b)}$  not associated with the  $f_j$  for this pair of sites are set to 0.  $d_{p(a,b)} = \mathbf{X}_{p(a,b)} \hat{\boldsymbol{\beta}}$  is then the difference in the two smooths for the pair of sites. The standard errors for this difference are given by the diagonal elements of:

$$\mathbf{X}_{p(a,b)} \hat{\mathbf{V}}_{\boldsymbol{\beta}} \mathbf{X}_{p(a,b)}^T$$

where  $\hat{\mathbf{V}}_{\boldsymbol{\beta}}$  is the variance covariance matrix of the estimated model coefficients and  $^T$  represents the matrix transpose. These standard errors were used to generate approximate, 95% pointwise confidence intervals on the difference between pairs of smooths (trends).

Least squares regression was used to investigate the relationship between sediment TOC and pollutant concentrations. All statistical analyses were performed with the R statistical software, version 2.11.1 (R Core Development Team, 2010) and the mgcv package, version 1.6-2 (Wood 2004, 2006).

### 3. RESULTS AND DISCUSSION

#### 3.1. Sediment core chronologies

The cores selected from each lake for radiometric dating all produced reliable chronologies. A full discussion of the dating of each core is beyond the scope of this paper, but briefly, the cores from Dow Loch (DOW), Loch Mhic Ghille-chaoile (MHGC), Loch Cnapan (CNAP) and Loch Coire an Lochain (COR) dated well with the CRS model dates from the  $^{210}\text{Pb}$  in good agreement with the  $^{137}\text{Cs}$  record

for both 1963 and 1986 atmospheric weapons and Chernobyl peaks respectively. By contrast, the least satisfactory chronology was produced from Loch Tanna (TAN) where the CRS and CIC models gave good agreement, but uncertainty over the  $^{137}\text{Cs}$  record meant that there was no independent check on this chronology. Similarly, for Loch a' Chnapaich (CHNA) dates from the CRS and CIC  $^{210}\text{Pb}$  models were in good agreement but high  $^{241}\text{Am}$  in the upper parts of the core made it difficult to resolve the  $^{210}\text{Pb}$  record with the weapons testing data and hence only the CRS modelled dates were used for this core. For the Loch na Gabhalach Nodha (NODH) and Round Loch of the Dungeon (RLDN) cores, use of the CIC model was precluded due to the non-monotonic variation in unsupported  $^{210}\text{Pb}$ . However, for both cores the CRS model gave good agreement with the  $^{137}\text{Cs}$  data, especially at NODH where there were well-resolved  $^{137}\text{Cs}$  peaks for both 1963 and 1986. For Loch Coire Fionnaraich (FION) there was a slight discrepancy between the dates produced by the CRS and CIC models and hence the  $^{210}\text{Pb}$  chronology was corrected using the  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  records.

The resulting chronologies showed a large variation in sediment accumulation over the last 100 – 150 years. The dated cores from COR and TANN had very slow accumulation rates ( $0.0021 - 0.005 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) while those from NODH and MHGC were typically an order of magnitude higher. The period of time covered by the derived chronologies varied from c. 100 years at Loch Tanna to c. 180 years for Dow Loch. In order to derive a 150 year chronology for each core, dating covering a shorter period of time was cautiously extrapolated using basal accumulation rates, although it should be stressed that this increases the potential error of the dating cross-correlation and the full basin profiles.

The non-radiometrically dated cores from each lake were cross-correlated with the dated cores to provide a chronology for each as shown in Figure 1. In some cases (NODH, CNAP, COR) these other cores cross-correlated well with the cumulative SCP profiles (Renberg and Wik, 1984). In all lakes at least one undated core was cross-correlatable in this way. Where there were discrepancies, additional correlation was sought using the concentration profiles of trace metals and also from lithostratigraphic data (Figure 1). The dating of shallow water sediment cores can be very difficult in some lakes as accumulation may be transitory as sediments move from shallow to deeper waters (e.g. Håkanson, 1977) and in some cases producing a reliable chronology for shallow water cores can prove

to be very problematic (e.g. Anderson and Odgaard, 1994). However, using this multi-parameter approach to cross-correlation has allowed a reasonably reliable chronology to be obtained for all cores in each lake. These data provide the basis for the chronologies used throughout this paper and those shown on all Figures.

### **3.2 Contaminant concentration data**

The Hg, Pb and SCP concentration data for each sediment core are provided as Supplementary Figures 1 – 3 respectively. Except for the cores from NODH and the mid-depth core from RLDN, the length of all sediment cores exceeded that of the chronologies and hence the sediment records extend beyond 1850. Hence, in some cases, these records can be assumed to extend back some hundreds of years. The more rapid accumulation at NODH is probably at least partly due to the eroded nature of its catchment.

For all determinands, concentrations in cores from the south-west region were considerably higher than those in either of the other regions especially for SCPs where peak concentrations were elevated by approximately an order of magnitude. It is interesting to note that with the exception of NODH, presumably due to its shorter record, the basal Hg and Pb concentrations for cores within each lake were reasonably consistent. In the context of this current study, this suggests that although the full anthropogenic signal may be observable over many hundreds and possibly thousands of years in Scotland (Yang and Rose, 2003) the vast majority of metal concentration enhancement and certainly the recent industrial inputs are fully captured by these sediment records. This is supported by the SCP data where all core concentrations fall to  $0 \text{ gDM}^{-1}$ , again with the exception of the cores from NODH. With the exception of COR the concentration profiles within a lake varied considerably with depth in agreement with previous studies (e.g. Yang et al., 2002b; Rose, 2007b; Rippey et al., 2008) showing the necessity of multiple cores in estimating full basin inventories (Engstrom et al., 2007).

### **3.3. The full basin record for lakes with thin catchment soils**

The decadal full basin inventories for Hg, Pb and SCPs are shown for the lakes with thin catchment soils in Figure 2a – 2c respectively. Each data ‘point’ on these Figures represents a decadal mean. The fitted trends for these data are also shown in Figures 3, 4 and 5 respectively (bottom row in each) and these allow a better comparison between sites and determinands.

For Hg and Pb, the trends are similar for each site. At CHNA there is an increasing trend from the start of the record through to the 1960s and 1970s followed by a marked decline through to most recent times. For, DOW a similar temporal pattern is observed although the period prior to 1940 shows only a moderate increase while that for the period 1940 – 1970 is much greater. Again, the post-1970 period is represented by a marked decline through to the present. For COR, while the ‘raw’ inventory data for Hg and Pb indicate a similar temporal pattern to those of CHNA and DOW (Figure 2a, b) the spread of the data points relative to the length of the record means we are unable to distinguish a trend over the period from random variation (Figure 3 and 4). Hence, while there is some indication that the historical patterns of Hg and Pb at all ‘thin soil’ sites are similar, statistically these data are consistent with a model of no change at COR. For SCPs the inventory data (Figure 2c) shows similar patterns for all sites, confirmed for COR and DOW in the fitted trends (Figure 5) while the low SCP concentrations for CHNA in the north-west of Scotland suggest an increase over the period, although this is not significant. The historical SCP trends for COR and DOW are in good agreement with those for Pb and Hg with a slow increase from the start of the record through to c. 1940 followed by a rapid increase to the 1970s and 1980s and a subsequent decline. These historical trends are very similar to the temporal pattern usually observed for SCP concentration profiles in the UK (Rose and Appleby, 2005) and therefore faithfully reflect the historical record of fossil-fuel combustion and emission.

UK fossil-fuel consumption has been dominated by coal combustion since the mid-19<sup>th</sup> century and these patterns therefore confirm coal combustion, particularly from the electricity generation industry, as the dominant source historically not only of SCPs but also for Hg and Pb (e.g. Farmer, 1999) for these lakes. The rapid increase in the mid-20<sup>th</sup> century reflects the massive increase in demand for electricity following the Second World War while the peak and decline towards the end of the 20<sup>th</sup> century is indicative of emissions reductions policies, the decline of heavy industry and the introduction of particle arrestor technology at electricity generating stations from the 1970s onwards.



The additional and significant role of Pb from vehicular sources also made a considerable contribution during the second half of the 20<sup>th</sup> century through to its ban in 2000 (Cloy et al. 2005).

In summary, the historical records for Hg, Pb and SCP inputs to lakes with thin catchment soils, as represented by their decadal sediment inventories, appear to reflect the temporal pattern of emissions to the atmosphere (Pacyna, 1988; Pacyna et al 2009; UK National Atmospheric Emissions Inventory website) thereby supporting Hypothesis 1.

### **3.4. The full basin record for lakes with eroded catchment soils**

The decadal full basin inventories for Hg, Pb and SCPs are shown for the lakes with eroded catchment soils in Figure 6a – 6c respectively. The fitted trends for these data are also shown in Figures 3, 4 and 5 respectively (top row). It is immediately apparent that the historical records for these lakes are quite different from those lakes with thin catchment soils indicating a different source of contaminant input.

For all pollutants, the temporal patterns show increases from the start of the record through to the most recent decade indicating continued increasing inputs in contrast to the historical pattern of atmospheric emission (e.g. Pacyna et al 2009; UK National Atmospheric Emissions Inventory website). The only exceptions to this are for Hg and Pb at TAN where the fitted trends (Figures 3 and 4) indicate that this is not a significant increase. For NODH, the only exception to the continuous increase throughout the record is a peak in inputs in the decade 1960 – 1970 (Figure 6), although this only appears to be the case for Hg (Figure 3). This may be due to elevated organic matter input at this time (see Section 3.6) and may also explain the peak at the end of the 19<sup>th</sup> century in the Pb and Hg curves (Figure 6a and b). For Pb at NODH and for SCPs at NODH and TAN, the fitted trends indicate a significant and continuous increase throughout the period. At CNAP, all pollutants show a marked increase in input from the 1960s through to the present in contrast to the historical trends observed for the sites with thin catchment soils.

In summary, the historical records for inputs of both trace metal (Pb, Hg) and particulate (SCP) contaminants to lakes with eroded catchment soils, as represented by their decadal sediment inventories, provide evidence for increases from the mid-19<sup>th</sup> century to most recent decades thereby

showing no response to the recent declines in atmospheric emission (Pacyna et al 2009) or deposition (Baker et al. 2001) of these contaminants and supporting Hypothesis 2.

### **3.5. The full basin record for lakes with non-eroded catchment soils**

The decadal full basin inventories for Hg, Pb and SCPs in the lakes with non-eroded catchment soils are shown in Figure 7a – 7c respectively. The fitted trends for these data are also shown in Figures 3, 4 and 5 respectively (middle row). For these lakes the temporal patterns appear to be more complicated with a variety of trends in both the ‘raw’ inventory data and the fitted trends. Hg (and to a lesser extent Pb) in FION and Pb and SCPs in RLDN show similar patterns to those of the sites with thin catchment soils i.e. a rapid increase in inputs from the mid-20<sup>th</sup> century to the 1970s and a subsequent decline to most recent times. Conversely, Hg at RLDN and SCPs at FION and MHGC show continuous and significant linear increases in the fitted data despite small-scale declines in most recent decades in the ‘raw’ inventory data. Here, the model is unable to detect these slight declines sufficiently to affect the fitted trend. Indeed, all pollutants for all lakes show declines in the ‘raw’ decadal full basin inventory data in the decades following the peaks and hence could be said to show some similarities with the lakes with thin catchment soils. However, these reductions are not always large enough to be significant. For Hg and Pb at MHGC the temporal changes in the full-basin inventories are small and broad (Figure 7a and b) and hence the fitted trends indicate no significant change through the period.

In summary, the lakes with non-eroded catchment soils seem to be intermediate with respect to the other site-types. Some show temporal patterns close to those of the lakes with thin catchment soils and all show some measure of recent decline. While this pattern is in contrast to the lakes with eroded catchment soils these declines are sometimes small and lack statistical significance. Hence, although there is certainly some deviation from the expected historical atmospheric emission pattern, support for Hypothesis 3 is equivocal.

### **3.6. Mechanisms of transfer from catchment soils**

A comparison of the decadal full basin inventories for Hg, Pb and SCPs for lakes with thin catchment soils, with eroded soils and with non-eroded soils allows the three proposed hypotheses to be tested. The first hypothesis stated that at the lakes with thin catchment soils the full basin inventories for all pollutants (trace metals and SCPs representing leachable and non-leachable contaminants) should show the same temporal trends as those of atmospheric emissions. The assumption is that these simple sites have negligible catchment influences and that their sediment records are acting as archives of atmospheric deposition and therefore should follow the same historical patterns. Any deviation from this expected trend therefore cannot be due to soil erosion or leaching. An hypothesis that may explain an observed deviation could be that algal scavenging of metals from the water column is enhanced during an extended growing season as a result of warmer lake water temperatures (Outridge et al., 2005), although this is also potentially limited by nutrient availability (Rose and Battarbee, 2007; Stern et al., 2009). Our data show that where the full basin inventories for Pb, Hg and SCPs at lakes with thin catchment soils do show significant temporal trends these are similar to those posited for emissions to the atmosphere. At sites where contamination is low, the trends in the raw inventory data appear to follow the same patterns, but there is no statistical significance to their fitted trends.

The implication of this result is that sediment cores from lakes unaffected by external processes continue to faithfully reflect atmospheric emission trends, thereby supporting a major assumption in the use of the lake sediment record in contamination studies. Furthermore, the reduction in Hg and Pb full basin inventories in these ‘thin soil’ lakes between the observed peak and the values for the most recent decades are between 60 – 80% for all lakes except for Hg at DOW for which the reduction is only 35% (Figure 8). While direct comparisons should be drawn with caution, it might be expected that for lakes acting simply as deposition collectors (in contaminant terms) a reduction in the sediment basin inventory might be of the same order as that observed for deposition measurements. Reductions in deposition of over 90% since the 1970s have been reported for Pb in the UK (National Atmospheric Emissions Inventory; Baker et al., 2001) and across Europe (Pacyna et al., 2009). Long-term deposition data for Hg are more scarce but reductions in emissions of Hg to the atmosphere since 1970 are reported as 70 - 80% for the UK (National Atmospheric Emissions Inventory) and also for Europe (Pacyna et al., 2009) and hence are of a similar scale of reduction to that observed in these

sediment records (Figure 8). Our data therefore indicate that Hypothesis 1 is correct and that upland lakes with thin catchment soils continue to faithfully record atmospheric emission trends.

The second hypothesis stated that if catchment soil erosion enhances the transfer of pollutants from soils to lake sediments then lakes with eroded catchment soils will show little or no decline in recent decades in response to emissions reductions and that the temporal records of both trace metals and SCPs would be affected. This is in contrast with the third ‘leaching’ hypothesis whereby SCPs would not be affected as, being particulates, they cannot be leached by being bound to, and transported with, DOC. The second hypothesis also indicates that if erosion is the major mechanism then lakes with good catchment soil cover and no erosion should show a response that resembles those of the lakes with thin catchment soils i.e. atmospheric emission trends.

We can test the difference between the historical patterns of metal inputs for the various lake types by determining the difference between the fitted trends (shown in Figures 3-5) for Hg and Pb within each region. Figure 9 shows the difference between the fitted trends for Hg for each region (NW, NE and SW top-to-bottom respectively) for each lake-type. The comparison between sites with thin catchment soils and those with eroded soils are shown in the first column and the comparison between sites with thin catchment soils and those with non-eroded soils are shown in the second column. Figure 10 shows the same comparisons for Pb. If we first consider the comparison between the sites with thin catchment soils and those with eroded soils then the differences between the historical patterns are apparent. In the NW and NE regions, there is little difference between the sites (difference is close to zero; note scale on y-axes) until around the 1960s when there is a change in slope to a steeper, more positive gradient. This indicates that from this point on, the eroded sites are receiving greater Hg and Pb inputs than the sites with thin catchment soils. For the NW, this is shown by a slight decline followed by a steep increase from around 1960 and this is due to a difference in timing of trace metal inputs. In the early decades of the 20<sup>th</sup> century Pb and Hg inputs at CHNA is increasing slightly more rapidly than at NODH and hence the difference in trend declines slightly. In the mid-20<sup>th</sup> century the direction in slope changes to an increase representing the period where CHNA peaks and then declines, while inputs at NODH continue to increase (Figure 4). The same shape is observed for both Hg and Pb in the SW region. There is little difference between the fitted trends for

DOW and TAN up to 1930s as both are increasing at approximately the same rate. From the 1940s to the 1960s inputs at DOW for both metals are higher than for TAN but from 1960 the slope reverses and inputs at the eroded site (TAN) continue to increase while those at DOW peak and decline.

Considering the comparison between the sites with thin catchment soils and those with non-eroded soils (second columns in Figures 9 and 10) then it is clear that in most cases the differences are low in all regions for Pb while for Hg significant changes only occur in the NW and SW after the 1960s. For the SW, this is because the RLDN Hg fitted trend, although significantly increasing, is linear and hence the profile of the difference between this and DOW is the inverse of the DOW profile. Hence, while the difference between the fitted trends for the lakes with thin catchment soils and those with eroded soils appear to be significantly different for both Hg and Pb and show elevated inputs in both metals at the eroded sites from the 1960s, a similar comparison with sites with non-eroded catchment soils suggests far less difference over the last 150 years. This indicates that erosion is the major mechanism for Hg and Pb transport from catchment soils to these lakes. Leaching from soils may play an additional role (note the difference between non-eroded sites and sites with thin catchment soils in Figure 8) but our data indicate that this role is minor with respect to inputs from catchment soil erosion.

If erosion is an important process in the transfer of pollutants from catchment soils to lake sediments then we might expect that for lakes where the main catchment soils are peats the full basin inventory of organic matter would increase along with the metal and SCP signal. The lakes with eroded and non-eroded catchment soils were selected to have mainly peat soils and Figures 11a – c show the decadal full basin inventories for total organic carbon (TOC) for the lakes with eroded catchment soils, non-eroded soils and thin soils respectively. These decadal inventories were calculated as for the trace metal and SCP data, except that the TOC input was estimated from the loss-on-ignition (LOI) profiles. Meyers and Teranes (2001), in their review on sediment organic matter, state that typical organic matter contains approximately 50% carbon so LOI data are double TOC values. Rippey et al (2008) suggest a similar figure. We therefore used the LOI data from each sediment core to estimate the decadal TOC basin inventories for the nine study lakes in the same way as those for Pb, Hg and SCP.

Figure 11a shows the decadal full basin TOC inventories for the lakes with eroded catchment soils. Records show little change, or slight increases up to 1950s and 1960s after which there is an accelerated input through to the present, similar to the Hg, Pb and SCP profiles. The exception is NODH, which shows a peak in TOC in the 1970s while more recent data appear to continue the previous trend. This suggests that organic matter input increased dramatically at NODH in the 1970s and may have been a result of accelerated catchment erosion at that time. Increased erosion of surface peats would have imported considerably more trace metals and SCPs and would explain the unusual temporal profiles for the full basin inventories for all pollutants in NODH seen in Figure 6. Furthermore, this would explain the unusual position of NODH in Figure 8 and accounting for this would move it to the bottom left quadrant along with the other lakes with eroded catchment soils (arrow in Figure 8). Normalising the TOC data to the mid-19<sup>th</sup> century 'baseline' for these eroded sites shows an increase by a factor of 2 - 4.5 (Figure 12a) while recent decadal inventories for the organic matter input at these lakes are considerably higher than for the other site types (i.e. note y-axis values in Figure 11). Least squares regression of TOC inventories with those of Hg, Pb and SCP reveal highly significant relationships for all pollutants at all eroded sites except for SCP at TAN (Table 3) highlighting the importance of eroded peat soils to pollutant inputs at these sites.

Absolute and normalised decadal TOC full basin inventories for the lakes with non-eroded catchment soils are shown in Figures 11b and 12b respectively. Data for RLDN and MHGC show little temporal trend with normalised data around 1.0 indicating little change in organic matter input since the mid-19<sup>th</sup> century. A small peak in the 1950s at MHGC may explain the similar peaks in Hg and Pb shown in Figure 7 and both Hg and Pb are significantly correlated with TOC at this site (Table 3). TOC at FION is also highly correlated with Hg, Pb and, uniquely for the non-eroded sites, SCP suggesting that at this lake too, the trace metals may be driven by organic matter inputs. However, this cannot be derived from catchment soil erosion and in contrast to the lakes with eroded catchment soils, TOC at FION only doubles before declining in recent decades (Figure 12b). For the lakes with thin catchment soils (Figure 11c and 12c) TOC enhancement is again less than two-fold for DOW while CHNA in the north-west shows a decline since the 1960s. COR shows a major TOC peak in the early decades of the 20<sup>th</sup> century considerably higher than at any other point in its record. The cause of this

feature is currently unclear as possibilities for allochthonous inputs are limited (15% catchment soil cover; <1% peat) and although this feature coincides with peaks in the profiles for Hg and Pb (Figure 2a and b) correlation of TOC with these metals and SCP are low (Table 3).

It would appear that for lakes with eroded catchment soils there is a record of increasing trace metals and SCP input from the mid-19<sup>th</sup> century through to the present. The initial increase from the mid-19<sup>th</sup> century was due to elevated emissions of atmospheric pollutants during a period of industrial development and is also observed in lakes with thin catchment soils and those with non-eroded catchments. However, when emission reductions, from the 1970s, caused a decline in metals inputs at these latter lake-types, inputs of pollutants at the lakes with eroded catchment soils continued to increase due to erosive processes. This erosion is also marked by a concomitant increase in organic matter input and correlations between organic matter and all measured pollutants are highly significant as a result. At lakes with thin and non-eroded catchment soils this pattern in TOC is not observed, the scale of organic matter input is lower and correlations with trace metals are less- or not significant.

Although these data indicate that catchment soil erosion is an important mechanism in the transfer of pollutants from catchment soils to lake sediments, this may not be the only transfer process. Our third hypothesis states that enhanced leaching of metals, bound to elevated inputs of allochthonous DOC, could also cause an increase in pollutant transfer. In this case, all lakes with good catchment soil coverage should show enhanced inputs for those pollutants that bind to DOC and so the SCP record should remain unaffected. Similarly, this mechanism would leave the records for trace metals and SCPs at the lakes with thin catchment soils unaffected, as has been observed. Our data show that the decadal full basin inventories for both trace metals and SCPs for the lakes with non-eroded catchment soils do show some similarities to those observed for the lakes with thin catchment soils and all show a surface decline in 'raw' inventory profiles in contrast to those with eroded soils. As a result, on Figure 8, these lakes plot close together but the declines for Pb and Hg are 30 – 50% and 20 - 30% respectively, less than those observed for lakes with thin catchment soils. This implies that there may be some external influence on metal input to these lakes and this may be due to leaching from the catchment. If so, then this transfer mechanism would appear to be making a

contribution to trace metal transfer for these catchments as observed in other studies (e.g. Tipping et al., 2010; Demers et al 2010) but this is less significant than erosive processes.

The decadal full basin inventories of TOC at the non-eroded sites RLDN and MHGC generally show little trend except for a peak at MHGC in the 1950s while at FION there is a significant increase from 1930s to 1970 and a decline to the present. These profiles do not represent any reported temporal pattern for DOC concentrations in upland lakes which have been generally increasing over the last 20 years (e.g. Monteith et al., 2007b). Therefore it is unlikely that DOC input is driving the observed organic matter trends at these lakes. However, while these TOC trends are not due to catchment soil erosion or DOC inputs, they may be due to changes in autochthonous organic matter production resulting from an increase in algal productivity. In these instances, elevated metal inputs to the sediment may be a result of enhanced scavenging of metals from the water column by algae and may explain the significant correlations for Hg and Pb at some of these sites as shown in Table 3.

### **3.7 Implications of climate change**

Our data have shown that the erosion of organic-rich catchment soils is a major mechanism for the transfer of trace metals from catchment storage to lake sediment, although leaching via adsorption to DOC may also play a role. Both of these mechanisms have previously been identified as being important in this transfer process although no similar comparative studies have been undertaken. Although no other mechanisms were tested, Rothwell et al. (2007a) showed how the erosion of peat soils was important for Pb input into fluvial systems in the Pennines, UK and how storm events led to increased erosion of peat gully walls. Elevated inputs of even uncontaminated ‘pre-industrial’ material may enhance the flux of ‘legacy’ pollutants into surface waters when significant inputs of low concentration material are eroded (Engstrom et al., 2007). As a consequence terrestrial soils have become a significant contributor to surface water contamination. Gabriel and Williamson (2004) suggest that up to 60% of Hg entering surface waters does so via the catchment and that in boreal drainage lakes up to 75% total Hg and more than 50% methyl Hg enters via soil erosion. Similarly,



Yang et al. (2002a) showed how catchment derived inputs of Hg and Pb at Lochnagar in Scotland were significantly higher than direct inputs via atmospheric deposition. As regards leaching, DOC forms strong complexes with trace metals including Hg (Schuster, 1991) and Pb (Rothwell, 2007b) such that DOC influences the mobility of heavy metals in soil (Qureshi et al., 2003) and the bioavailability of Hg(II) by inhibiting its availability to methylating bacteria (Barkay et al., 1997). Tipping et al (2010) showed that metal transport associated with dissolved organic matter was more important for weakly-sorbed metals such as Ni, Zn and Cd than for strongly-sorbed metals such as Pb suggesting that this mechanism accounts for up to 30% of Pb transport within an upland catchment although they neglected to consider erosion as an alternative mechanism. The flushing of DOC from catchment soils after heavy rainfall, in particular, has been shown to increase metal transfer from soils to surface waters and stormflow may play a major role in the release of dissolved Pb from peatlands (Graham et al., 2006). In upland catchments snowmelt may also cause seasonal maxima in flow hydrographs (Jenkins et al. 2007) and such events may also play an important role in metal transport with DOC even though DOC concentrations themselves may be low at these times (Demers et al., 2010).

Any process that exacerbates catchment soil erosion or DOC export from catchments to surface waters will therefore also enhance the export of stored pollutants and predicted climatic changes will do both. Increased winter rainfall and more frequent and intense rain events will increase soil erosion and surface water contamination has been shown to be enhanced in stormwater runoff as a result. By contrast, predicted prolonged drier periods in summer will lead to greater 'oxygenation' of peatlands and DOC production (Rothwell et al., 2007b) which can then be flushed out in wetter winter periods leading to elevated DOC in stormwaters (Wallage et al., 2006). Such processes are thought to control dissolved Pb export (Rothwell et al., 2007b) and increase the upward mobility of metals in saturated soils (Qureshi et al., 2003). Elevated winter rainfall, increased summer drought and increased frequency of storm events will therefore all exacerbate the transfer of pollutants from storage in catchment soils to surface waters and this increased input from catchments may result in a continued lack of response to emissions reductions and possibly even an increase in pollutant fluxes to waters and their sediments despite significant emission reductions since the 1970s. This is in contrast to the

aims of the Water Framework Daughter Directive (2008/105/EC; Commission of the European Communities, 2008) which states that for a few pollutants, including Hg, “Member States should ...ensure that existing levels of contamination in biota and sediments will not increase”.

These continued inputs from the catchment depend on the levels of storage in the catchment soils. Table 4 shows our estimates of soil storage for each of the lakes for the three contaminants and shows that considerable quantities of pollutants remain in the soils especially those where the catchments are large such as FION and TAN. This indicates a massive reservoir of potential contamination that could be subject to leaching and erosion for many years (Meili et al., 1991) and Yang et al. (2002a) have shown that the Hg and Pb stored in the soils at Lochnagar are equivalent to 400 years of deposition at 2000 levels. This legacy of previously deposited pollutants could therefore be a major, continuing and widespread source of contamination to upland lakes in northern Europe for many decades to come (Tipping et al 2010). While this paper has focussed on Hg, Pb and SCPs a similar legacy exists for other trace metals and for persistent organic pollutants (POPs) which also bind to particulate and dissolved organic matter. Therefore, they are subject to the same transfer mechanisms although many POPs will have a far shorter depositional record than trace metals and hence, by comparison, a reduced depositional legacy. While SCPs are not themselves harmful to biota, both metals (e.g. Petersen et al., 1995; Seigneur et al., 2005) and POPs (e.g. Ohsaki et al., 1995; Wey et al., 1998; Ghosh et al., 2000; Persson et al., 2005) are known to bind to their surfaces and hence the erosive transfer of these particulate contaminants may further enhance metal and POPs inputs from soils to surface waters.

The impact of this continued elevated pollutant input on aquatic biota in upland lakes is currently unknown although the role of climate on enhanced uptake of both Hg and POPs into the Arctic food-chain has been reported (Carrie et al 2010) indicating elevated contaminant storage in predator fish muscle and liver. Trace metals and POPs are known to have a detrimental effect on growth, deformity, egg development and embryonic abnormalities, hatching success, transgenerational effects and they also cause endocrine disruption at very low concentrations (Garcia-Reyero et al., 2005). These impacts will transfer both up the food chain and to water supplies downstream where they may impact on piscivorous raptors and mammals and human health.

#### 4. CONCLUSIONS

This multiple lake, multiple core and multi-pollutant study has tested hypotheses relating to the transfer of previously deposited pollutants, stored in catchment soils, to upland lakes in Scotland. We conclude that:

- Temporal patterns at the nine lakes indicate that this is not a simple time-lag effect and that additional processes are involved in the transfer.
- The main transfer mechanism is catchment soil erosion, whereby Hg and Pb bound to organic particles are in-washed to surface waters. Particulate pollutants are also affected by this mechanism.
- The leaching of metals bound to dissolved organic carbon (DOC) may also play a role in this transfer, although this appears minor in these systems compared to erosive processes.
- Upland lakes with thin soils act as simple atmospheric deposition collectors and the temporal records of their full basin inventories show similar patterns to those expected from atmospheric emissions.
- The processes that lead to soil erosion and leaching of DOC from the catchment are exacerbated by increased winter rainfall, decreased summer rainfall and increased frequency of high intensity rain events. Hence, predicted climatic changes will elevate pollutant transfer from catchment to surface waters.
- The catchment storage of deposited pollutants is very large indicating a massive potential reservoir of contamination that may keep contaminant fluxes elevated for many decades to come. This counteracts the positive effects of emission reductions policies, and would make the aims of the EU Water Framework Directive significantly more difficult to achieve. Furthermore, exposure of aquatic biota to these contaminants will also remain at an elevated level.

- It is expected that the transfer mechanisms identified here, the role of climate change and the impacts on aquatic biota are similar for other atmospherically deposited pollutants such as persistent organic pollutants.

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**Table 1.** Locational data for study sites

Site-type	Name	Site code	Latitude	Longitude	Altitude (m a.s.l.)
<b>North-west Scotland</b>					
Non-eroded	Loch Coire Fionnaraich	FION	57° 29' 30" N	05° 25' 48" W	236
Eroded	Loch na Gabhalach Nodha	NODH	57° 49' 57" N	04° 45' 49" W	570
Thin soil	Loch a'Chnapaich	CHNA	57° 48' 35" N	04° 56' 07" W	680
<b>South-west Scotland</b>					
Non-eroded	Round Loch of the Dungeon	RLDN	55° 08' 01" N	04° 24' 28" W	280
Eroded	Loch Tanna	TAN	55° 38' 12" N	05° 18' 24" W	322
Thin soil	Dow Loch	DOW	55° 05' 48" N	04° 25' 11" W	475
<b>North-east Scotland</b>					
Non-eroded	Loch Mhic Ghille-chaoile	MHGC	57° 06' 09" N	03° 46' 46" W	500
Eroded	Loch nan Cnapan	CNAP	57° 02' 35" N	03° 47' 11" W	870
Thin soil	Loch Coire an Lochain	COR	57° 06' 21" N	03° 41' 02" W	920

**Table 2.** Lake and catchment data

	Surface area (ha)	Maximum depth (m)	Catchment: Lake ratio	Catchment soil cover (ha)
<b>North-west</b>				
FION	9.3	14.5	60.16	447
NODH	7.3	3.7	19.37	134
CHNA	5.4	8.1	19.73	53
<b>South-west</b>				
RLDN	4.8	10.4	20.38	83
TAN	34.3	3.5	9.83	303
DOW	0.6	3.3	18.49	7
<b>North-east</b>				
MHGC	10.2	8.1	5.82	56
CNAP	2.4	4.2	32.09	73
COR	9.7	32.1	9.94	14

**Table 3.** Significance of relationships between total organic carbon (TOC) with Hg, Pb and SCPs for the nine studied lakes determined by least squares regression.

Site-type	Region	Lake	Hg	Pb	SCP
Eroded	NW	NODH	$F_{1,12} = 422; p < 0.001$	$F_{1,12} = 262; p < 0.001$	$F_{1,12} = 50.8; p < 0.001$
	NE	CNAP	$F_{1,12} = 599; p < 0.001$	$F_{1,12} = 505; p < 0.001$	$F_{1,12} = 31.8; p < 0.001$
	SW	TAN	$F_{1,11} = 288; p < 0.001$	$F_{1,11} = 117; p < 0.001$	$F_{1,11} = 4.3; p < 0.1$
Non-eroded	NW	FION	$F_{1,13} = 1162; p < 0.001$	$F_{1,13} = 469; p < 0.001$	$F_{1,13} = 18.9; p < 0.001$
	NE	MHGC	$F_{1,13} = 11.5; p < 0.01$	$F_{1,13} = 62.9; p < 0.001$	$F_{1,13} = 1.5; p = 0.25$
	SW	RLDN	$F_{1,12} = 0.14; p = 0.72$	$F_{1,12} = 0.03; p = 0.86$	$F_{1,12} = 0.33; p = 0.56$
Thin soil	NW	CHNA	$F_{1,13} = 15.9; p < 0.01$	$F_{1,13} = 1.98; p = 0.18$	$F_{1,13} = 4.1; p < 0.1$
	NE	COR	$F_{1,13} = 1.43; p = 0.25$	$F_{1,13} = 1.37; p = 0.26$	$F_{1,13} = 0.15; p = 0.71$
	SW	DOW	$F_{1,13} = 207; p < 0.001$	$F_{1,13} = 44.5; p < 0.001$	$F_{1,13} = 14.1; p < 0.01$

**Table 4.** Estimated catchment soil storage of anthropogenically derived pollutants. SCP mass is estimated based on the assumed particle mass of a SCP of  $4.2 \times 10^{-9}$  g (Rose 2001).

	Hg (kg ha <sup>-1</sup> )	Pb (kg ha <sup>-1</sup> )	SCPs (kg ha <sup>-1</sup> )
<b>North-west</b>			
FION	0.12	26.9	0.19
NODH	0.08	16.6	0.15
CHNA	0.04	22.3	0.09
<b>South-west</b>			
RLDN	0.08	41.6	0.90
TAN	0.17	79.4	2.88
DOW	0.06	43.4	0.61
<b>North-east</b>			
MHGC	0.09	44.0	0.61
CNAP	0.01	6.0	0.08
COR	0.02	22.5	0.07

Figure 1. Cross-correlation curves for the dating of sediment cores within this study. Lakes from the north-west, south-west and north-east of Scotland are on the top, middle and bottom rows respectively. Sites with non-eroded soils, eroded soils and with thin soils (see text for explanation) are in the first, second and third columns respectively. Thick lines in each panel represent the radiometrically dated cores. Differing line types within each panel relate to the different determinands used for cross-correlation purposes. Site codes are given in Table 1. Cores codes for Loch Coire Fionnaraich are denoted LCFR and those Loch a' Chnapaich are CZNH28.

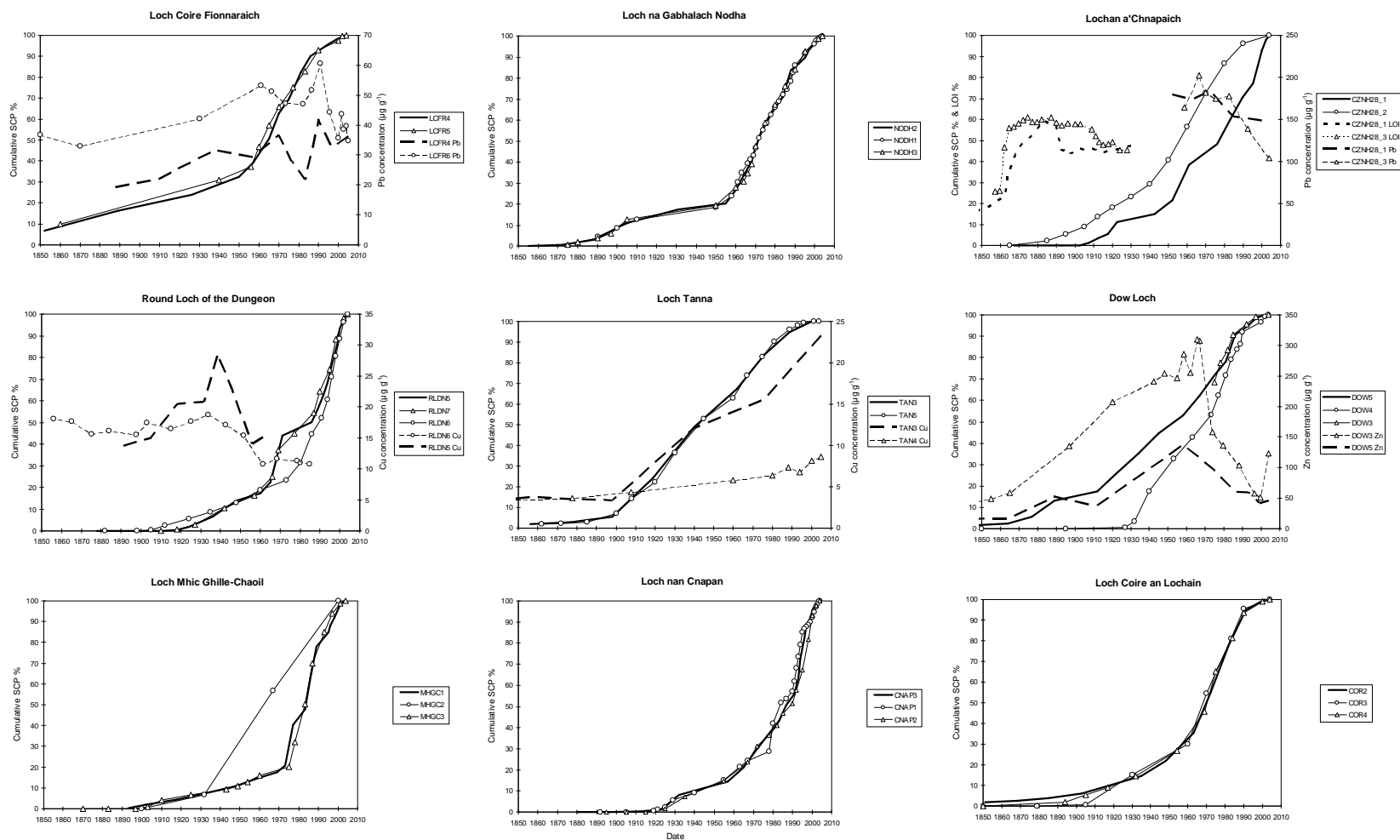
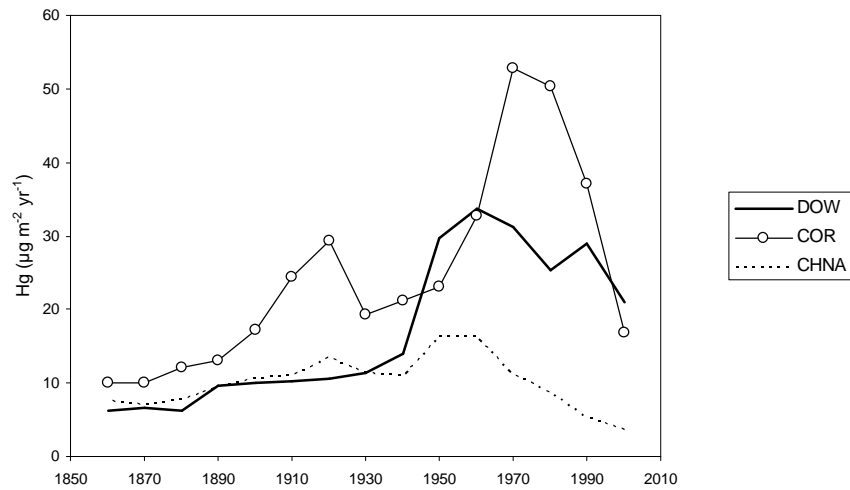
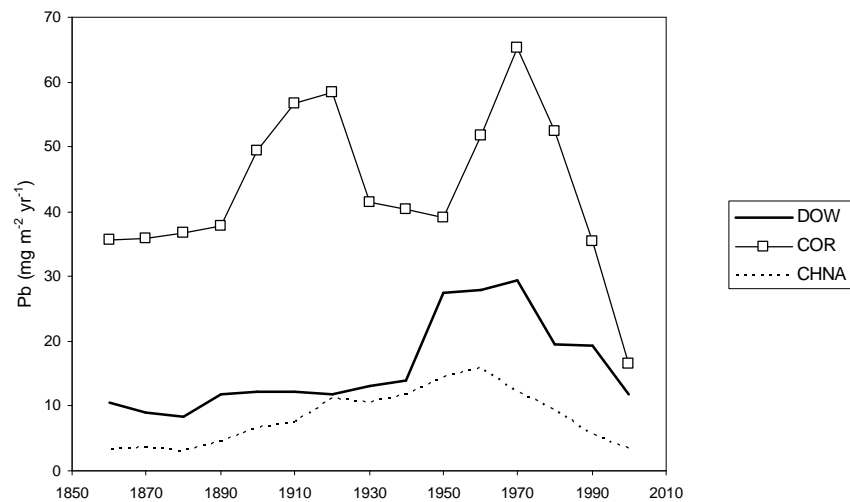


Figure 2. Mean decadal full basin inventories for (a) Hg, (b) Pb and (c) SCPs for lakes with thin catchment soils. Solid line represents Dow Loch (DOW; south-west); open symbols represent Loch Coire an Lochain (COR; north-east) and dotted line represents Loch a'Chnapaich (CHNA; north-west). All data for COR and SCP data for CHNA are x10 in order to show all sites on a single scale.

a)



b)



c)

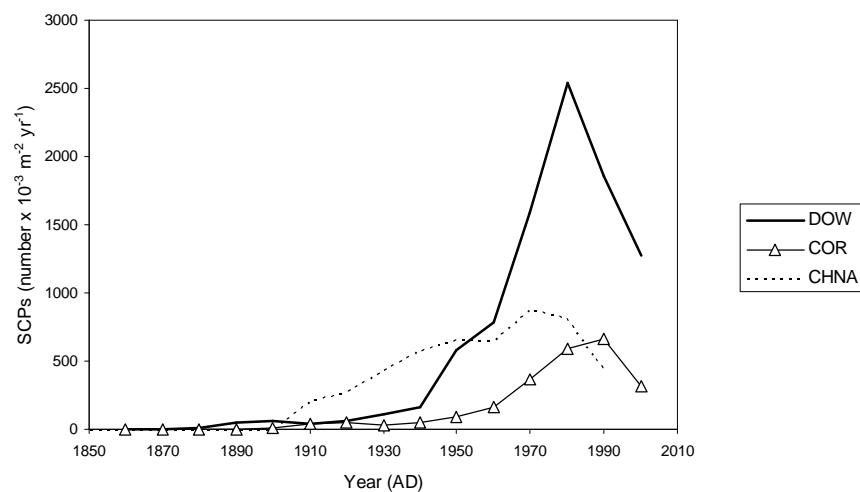


Figure 3. Fitted smooth functions of time (trends; solid lines) and approximate, 95% pointwise confidence intervals (shaded region) for the Hg profiles of the nine study sites arranged by soil type and region. Eroded, non-eroded and thin soil sites are in top, middle and bottom rows respectively. NW, NE and SW regions are in first, second and third columns respectively.

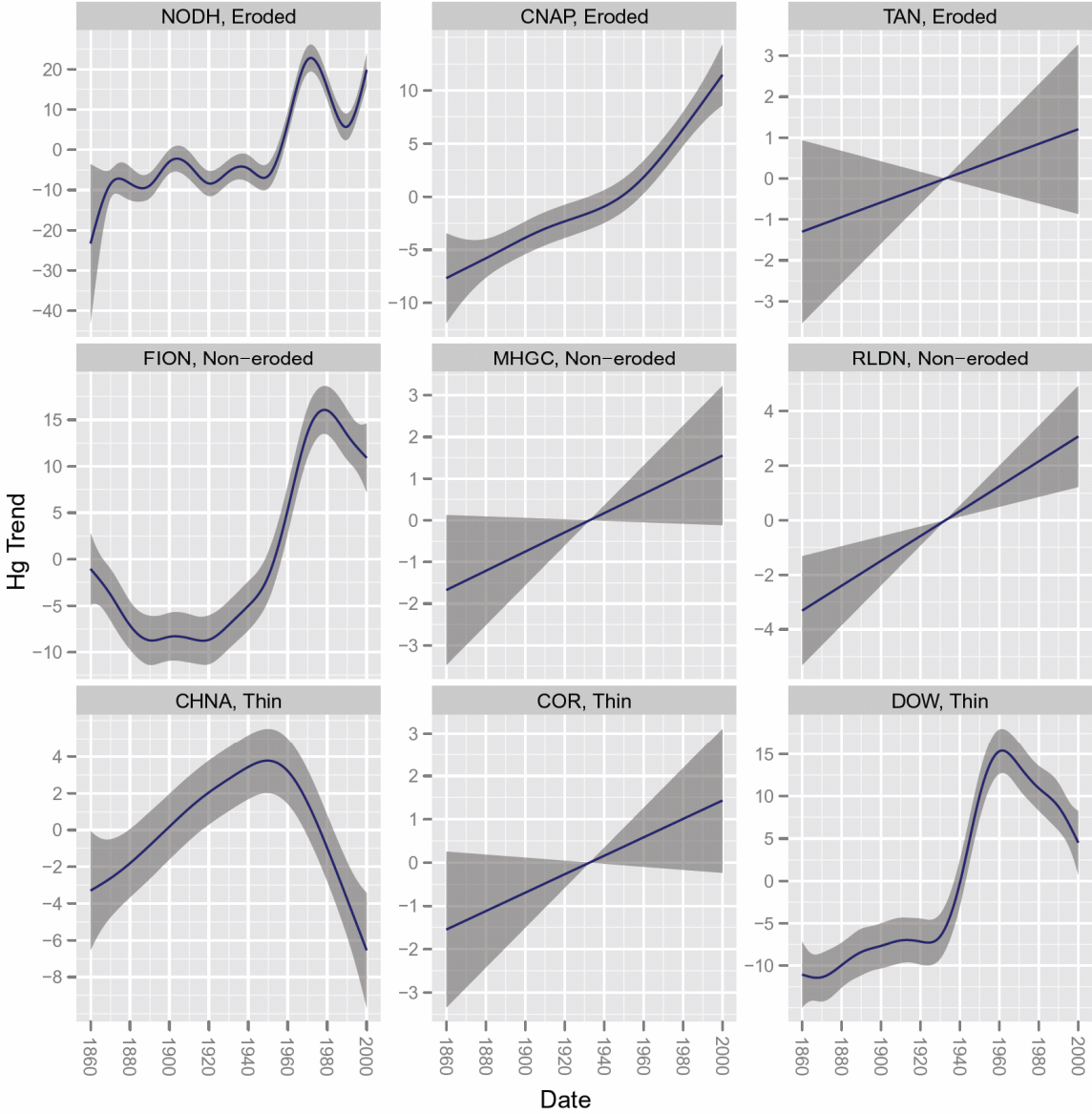


Figure 4. Fitted smooth functions of time (trends; solid lines) and approximate, 95% pointwise confidence intervals (shaded region) for the Pb profiles of the nine study sites arranged by soil type and region. Eroded, non-eroded and thin soil sites are in top, middle and bottom rows respectively. NW, NE and SW regions are in first, second and third columns respectively.

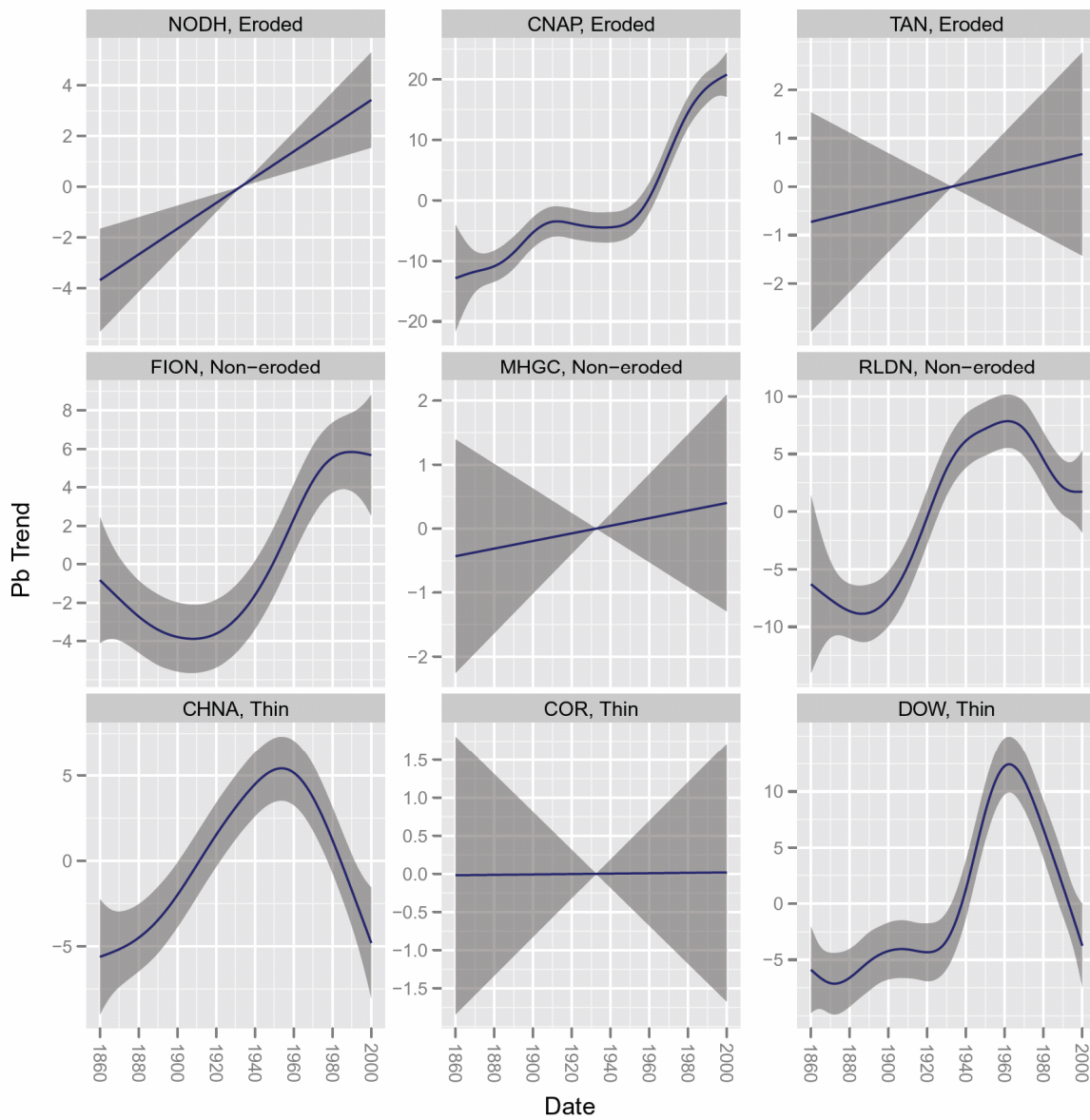




Figure 5. Fitted smooth functions of time (trends; solid lines) and approximate, 95% pointwise confidence intervals (shaded region) for the SCP profiles of the nine study sites arranged by soil type and region. Eroded, non-eroded and thin soil sites are in top, middle and bottom rows respectively. NW, NE and SW regions are in first, second and third columns respectively.

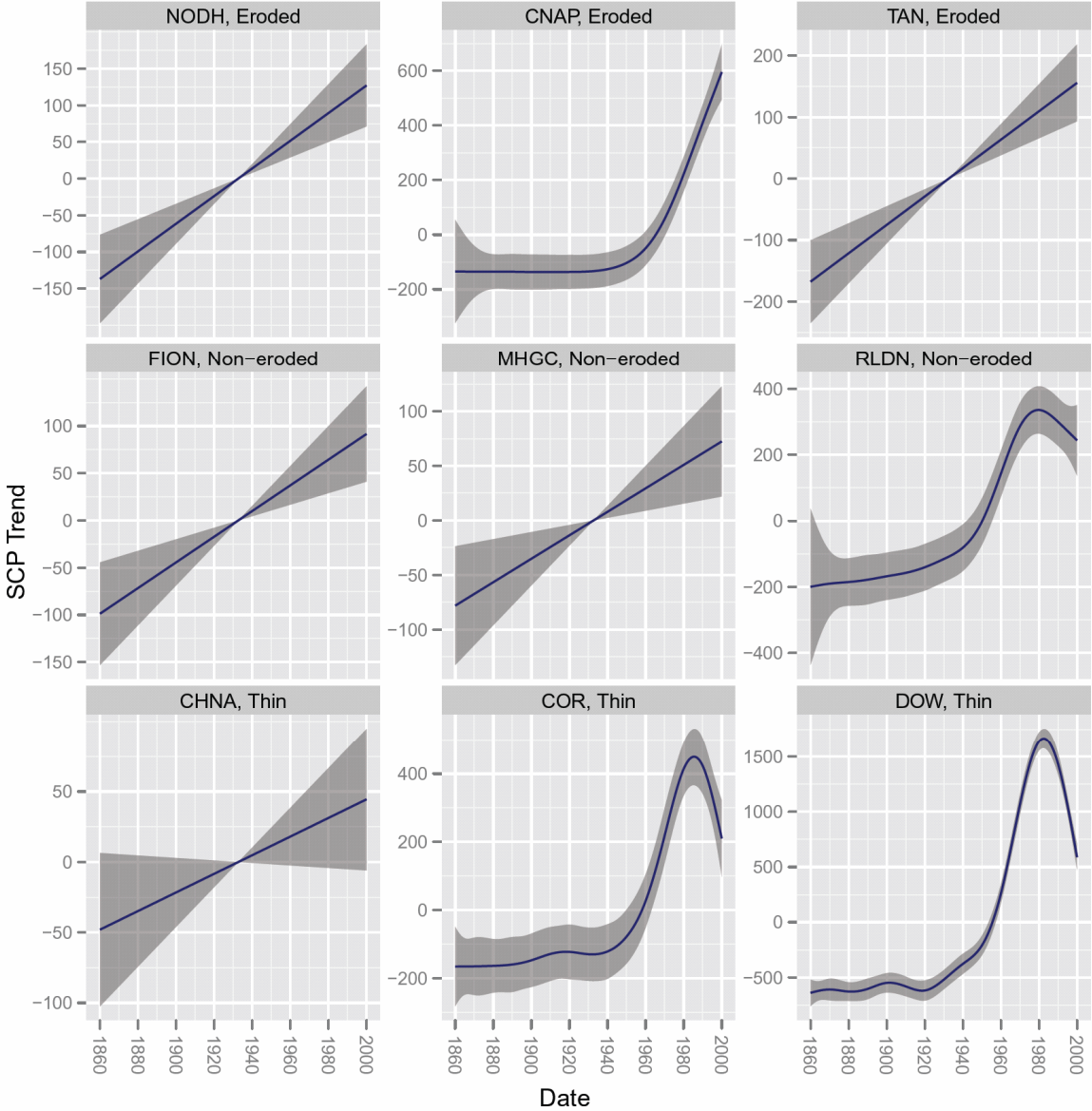


Figure 6. Mean decadal full basin inventories for (a) Hg, (b) Pb and (c) SCPs for lakes with eroded catchment soils. Solid line represents Loch Tanna (TANN; south-west); solid symbols represent Loch nan Cnapan (CNAP; north-east) and dotted line represents Loch na Gabhalach Nodha (NODH; north-west). Hg and Pb data for TANN are x10 in order to show all sites on a single scale.

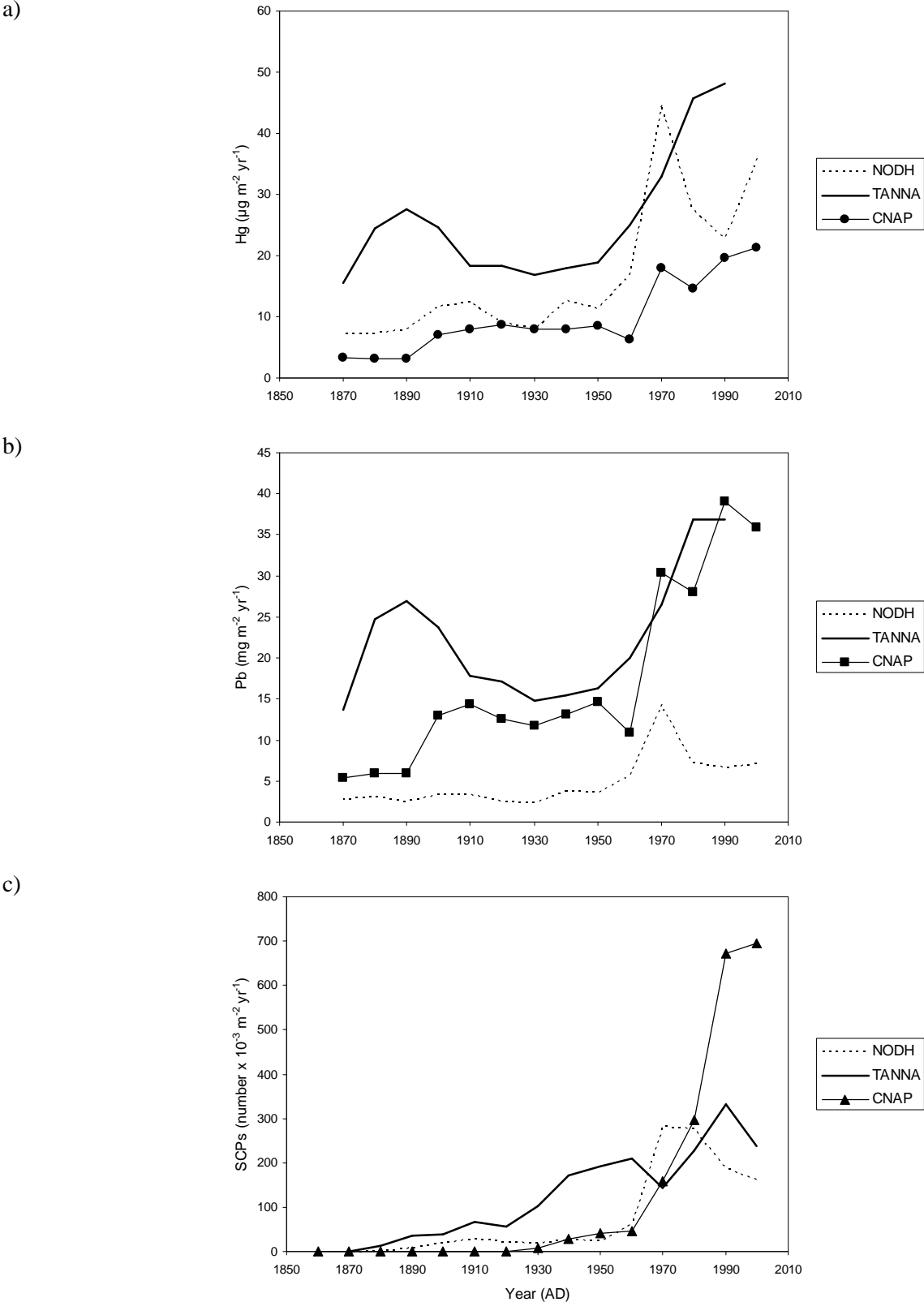
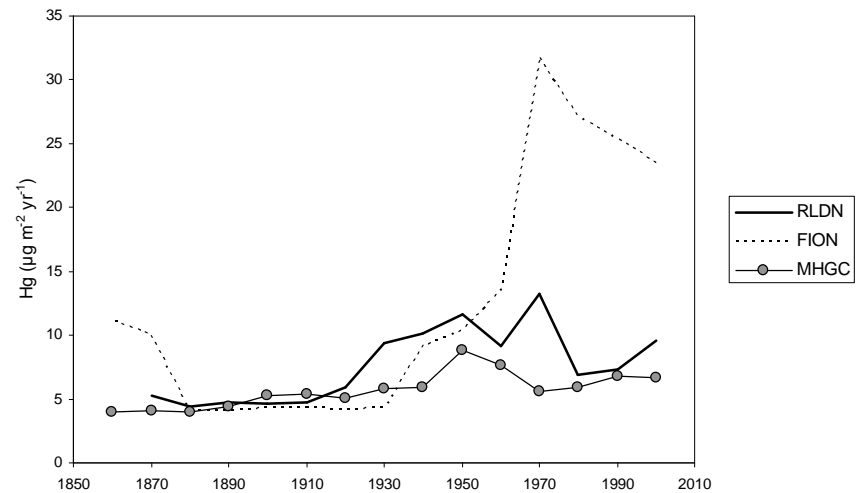
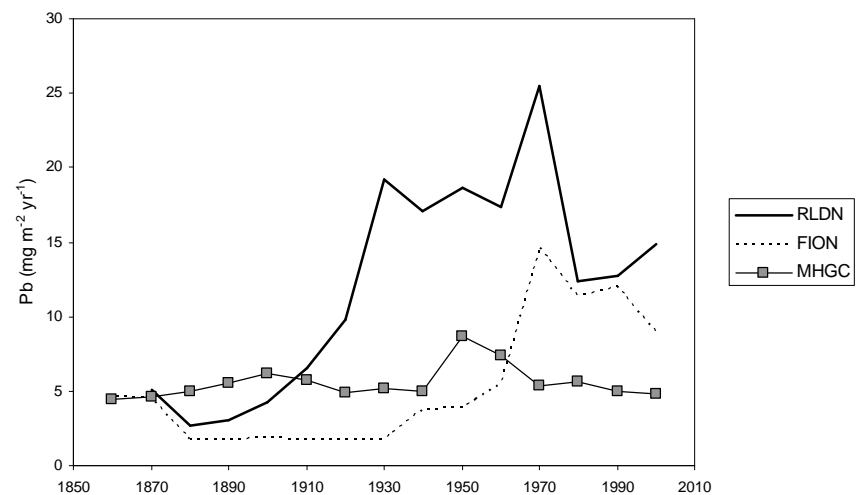


Figure 7. Mean decadal full basin inventories for (a) Hg, (b) Pb and (c) SCPs for sites with non-eroded catchment soils. Solid line represents Round Loch of the Dungeon (RLDN; south-west); shaded symbols represent Loch Mhic Ghille-chaoile (MHGC; north-east) and dotted line represents Loch Coire Fionnaraich (FION; north-west).

a)



b)



c)

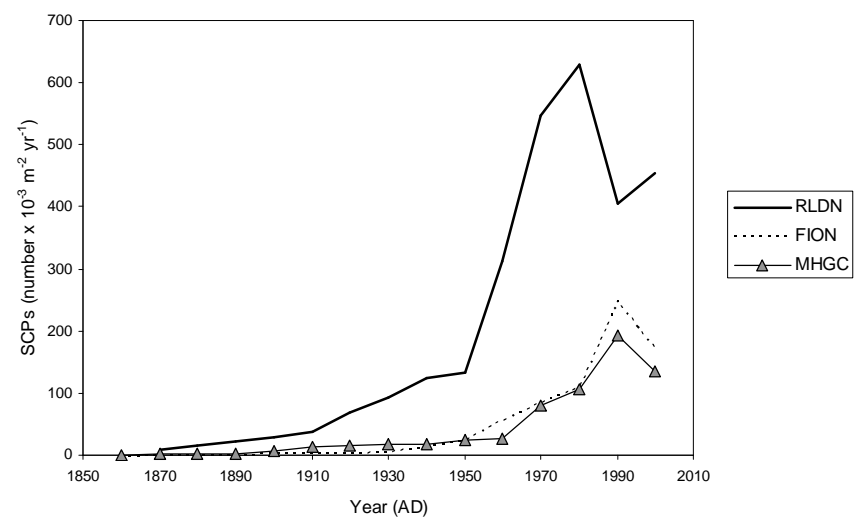


Figure 8. Percentage reduction in decadal full basin inventory for Pb and Hg. ◆ represents eroded sites in the three regions; ◇ represents sites with thin soils; while ◆ represents non-eroded sites. Arrow represents the different position for NODH if the 1970 peak is corrected for enhanced organic matter input as a result of accelerated catchment erosion (see text).

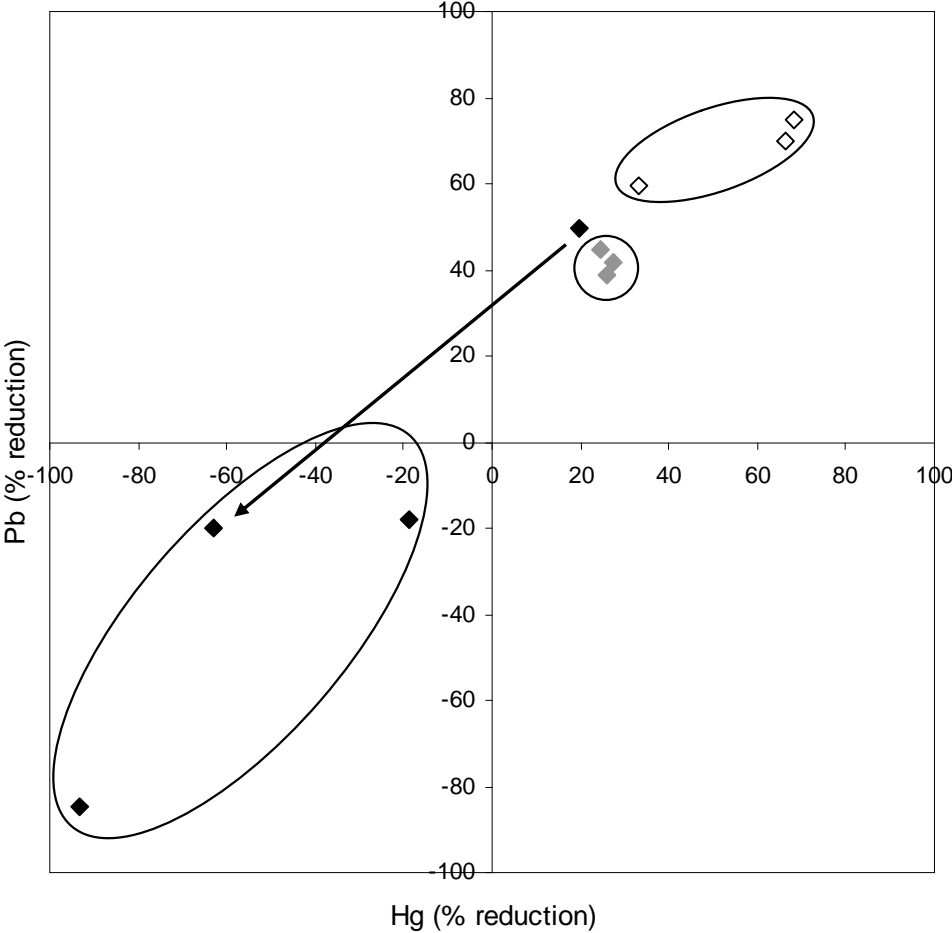


Figure 9. Differences between fitted smooth functions (difference in trends; solid lines) and approximate, 95% pointwise confidence intervals on this difference for Hg profiles in pairs of sites. Lakes with thin catchment soils and those with eroded catchment soils are compared in the first column; lakes with thin catchment soils and those with non-eroded catchment soils are compared in the second column. NW, NE and SW regions are in top, middle and bottom rows respectively.

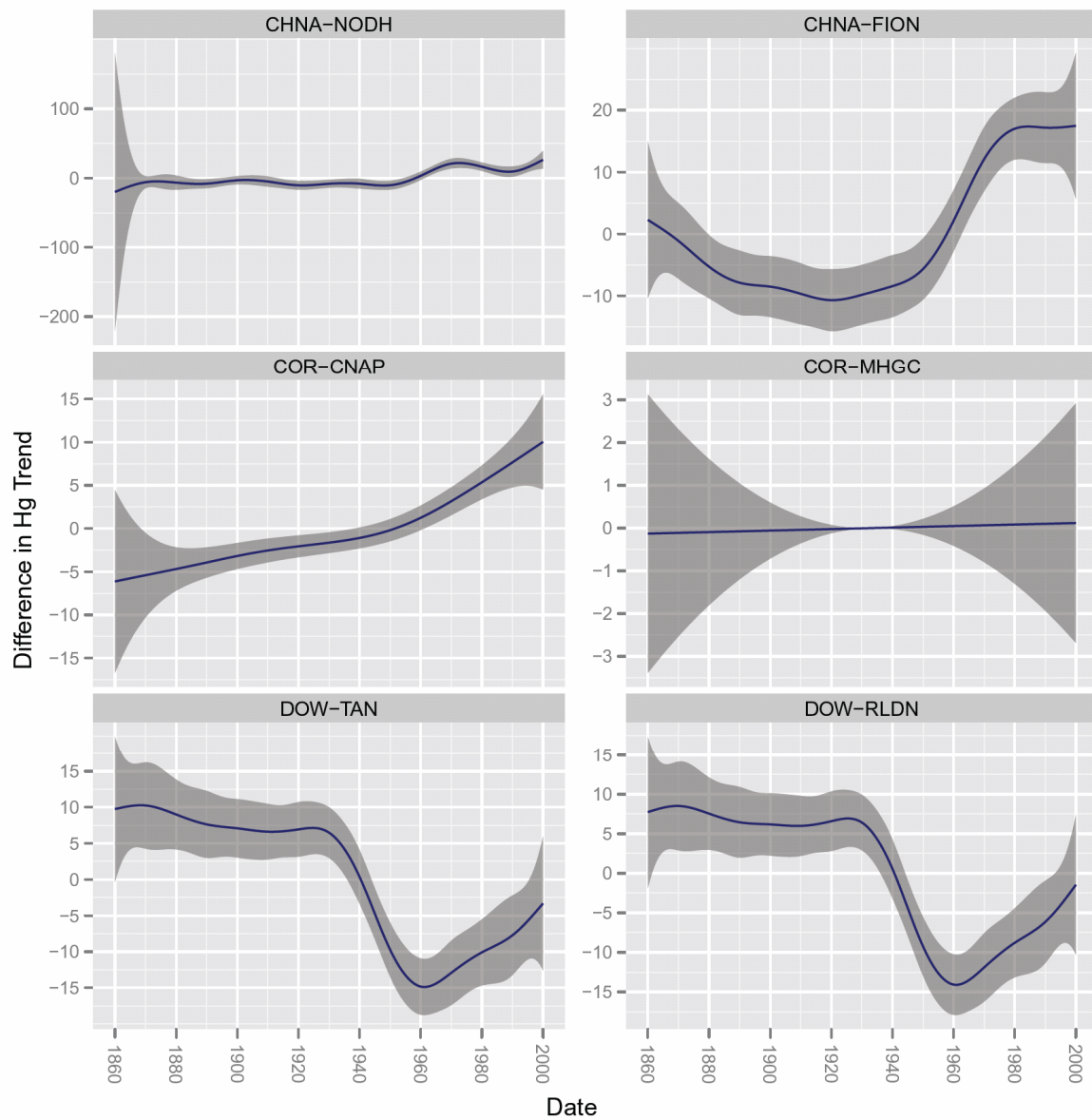


Figure 10. Differences between fitted smooth functions (difference in trends; solid lines) and approximate, 95% pointwise confidence intervals on this difference for Pb profiles in pairs of sites. Lakes with thin catchment soils and those with eroded catchment soils are compared in the first column; lakes with thin catchment soils and those with non-eroded catchment soils are compared in the second column. NW, NE and SW regions are in top, middle and bottom rows respectively.

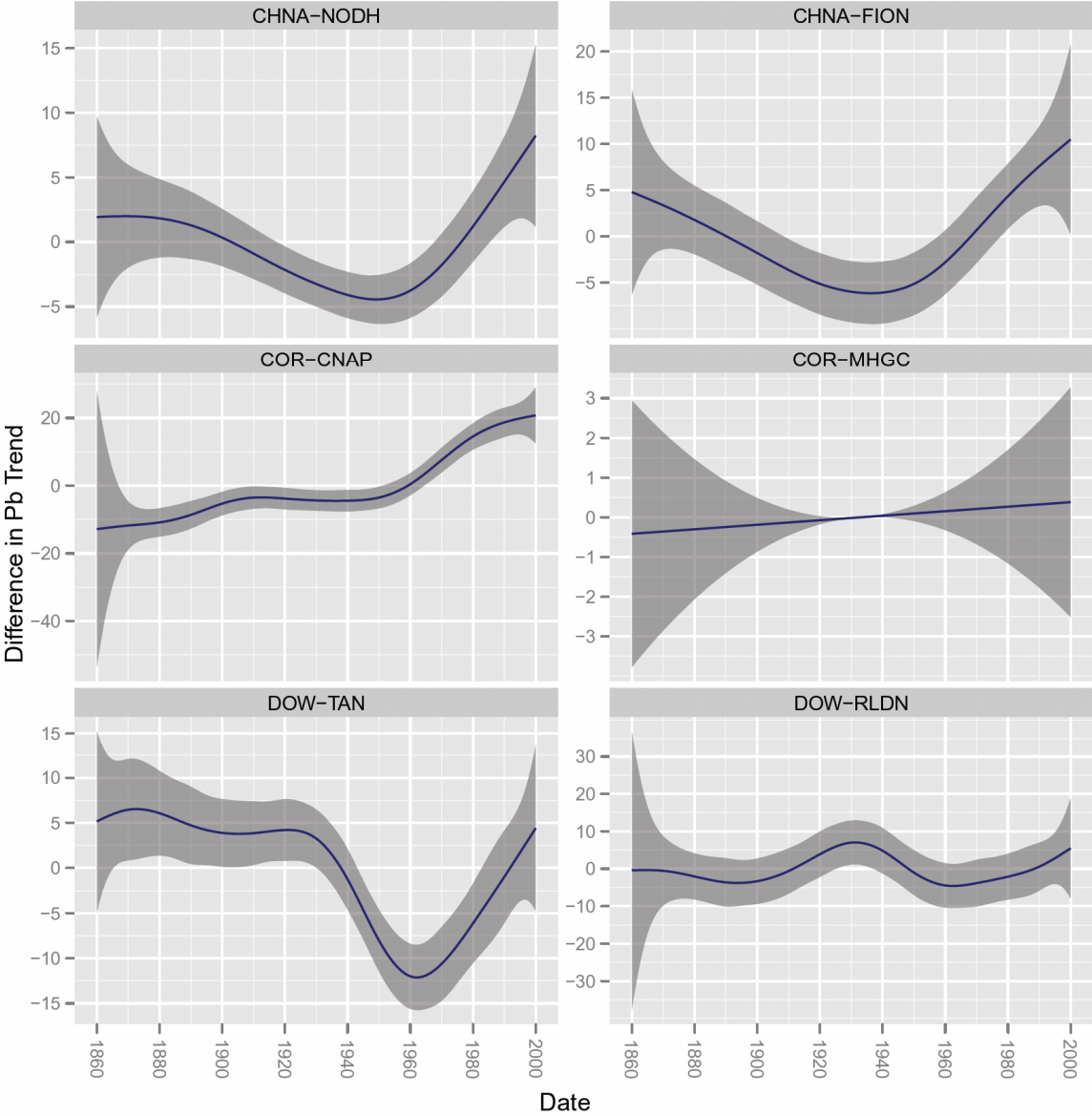


Figure 11. Mean decadal full basin inventories of TOC for lakes with (a) eroded catchment soils (b) non-eroded catchment soils and (c) thin catchment soils. Solid lines represent lakes in the south-west region; symbols represent lakes in the north-east and dotted lines represent sites in the north-west.

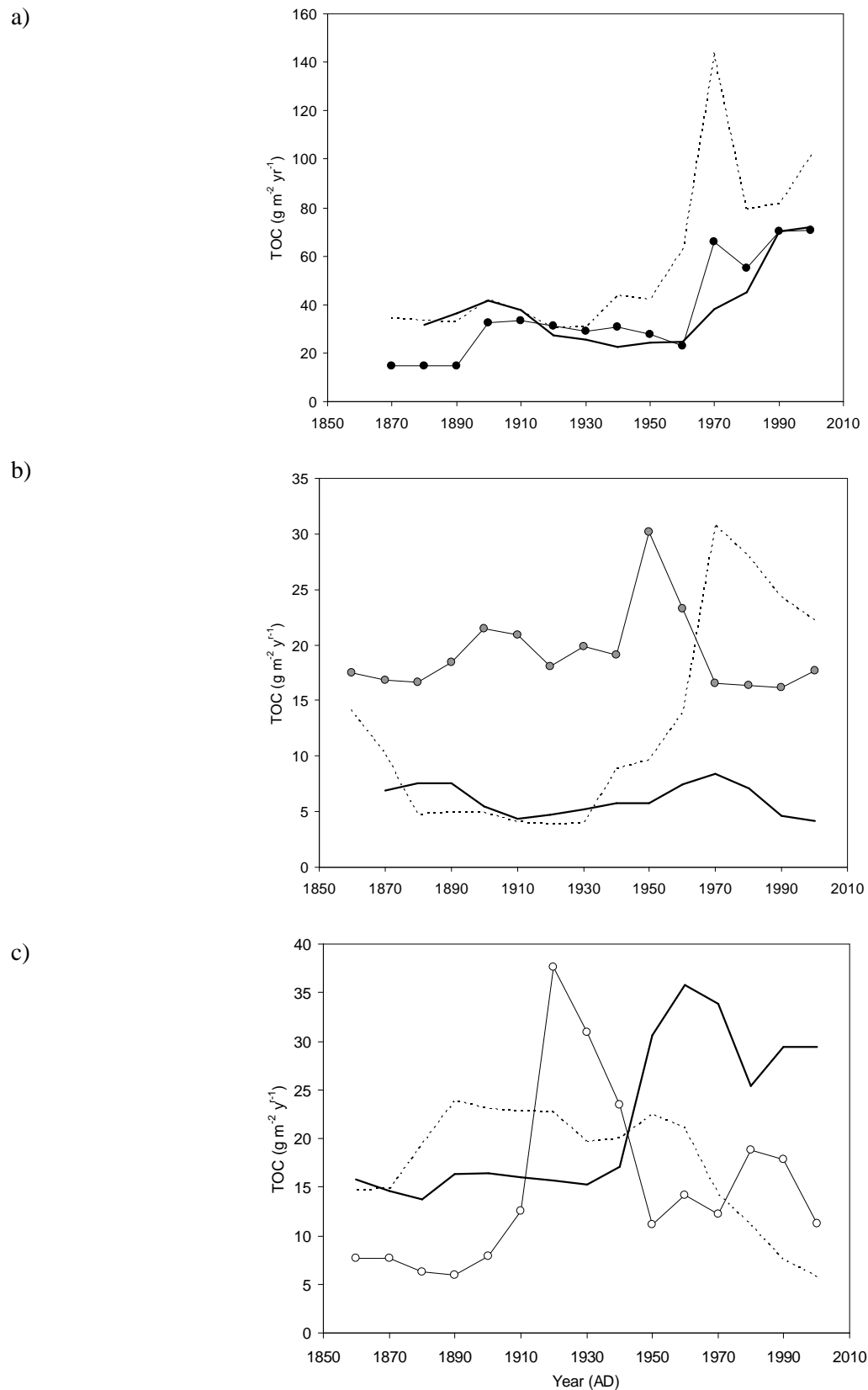


Figure 12. Normalised mean decadal full basin inventories of TOC for (a) eroded catchment soils (b) non-eroded catchment soils and (c) thin catchment soils. Solid lines represent lakes in the south-west region; symbols represent lakes in the north-east and dotted lines represent sites in the north-west.

