Biogeochemistry (2006) 78: 31–49
DOI 10.1007/s10533-005-2230-y

Estimating the mean residence time of lead in the organic horizon of boreal forest soils using 210-lead, stable lead and a soil chronosequence

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Received 11 June 2004; accepted in revised form 16 August 2005

Key words: Chronosequence, Forest soil, Mor layer, Pb isotopes, Residence time

Abstract. Knowledge about the residence time of lead in the organic horizon (mor layer; O-horizon) overlaying forest mineral soils is important for the prediction of past and future lead levels in the boreal environment. To estimate the mean residence time (MRT) of lead in the mor layer, we use in this study from Northern Sweden three different approaches: (1) lead-210 is applied as a tracer of lead migration; (2) estimations of loss rates of stable lead (concentrations and ^{206}Pb/^{207}Pb ratios) from the mor layer at an undisturbed forest setting, and (3) a study of lead in a soil series with sites of different age (a chronosequence of 20–220 years). In the last two approaches we compared measured inventories in the soil with estimated inventories derived using analyses of lake sediments. The results suggested a MRT of about 250 years in the mor layer in the mature forest and in the older parts of the chronosequence it was at least >170 years. The agreement between the three different approaches gives good credibility to this estimate. It is also supported by a modeling of trends in the ^{206}Pb/^{207}Pb ratio both between single cores and with depth in the mor layer. Our results suggest that it will take centuries for the deeper parts of the mor layer of undisturbed boreal forest soils to fully respond to decreased atmospheric lead pollution. However, data from the chronosequence indicate that the response could be much faster (MRT< 50 years) in the mor layer at early stages of forest succession where graminoid and broadleaved litter fall dominates over conifer litter.

Introduction

The atmospheric deposition of lead (Pb) has declined markedly in Europe during the last three decades (Rühling and Tyler 2001), mainly as a result of the phasing out of Pb in gasoline. However, arge amounts of this toxic metal have accumulated in the errestrial environment as a consequence of more than three millennia of atmospheric pollution (Patterson 1972; Renberg et al. 1994; Brännvall et al. 1999; Brännvall et al. 2001a). This long-term pollution has resulted in pollution Pb inventories of 0.5 to above 3 g Pb m^{-2} in Swedish boreal forest soils (Bindler et al. 1999; Brännvall et al. 2001b; Klaminder et al. 2004). Currently, the concentration of Pb in the organic horizon overlying forest mineral soils of podzol type has concentration values commonly between 50 and 100 mg kg^{-1}, which we previously suggested to be up to 1000 times higher than natural background levels (Bindler et al. 1999). High Pb levels, in comparison with levels in the pristine, pre-pollution environments, are of concern since Pb has a negative effect on microbial respiration and the vitality of soil organisms in forest soils (Bringmark and Bringmark 2001; Laskowski et al. 2003). The fate of the pool of Pb pollution in the organic horizon is not well known and it is of great importance to determine to what extent decreasing atmospheric Pb deposition rates will drive Pb levels in this layer towards values similar to those in pristine environments.

The mean residence time (MRT) of Pb in the organic horizon, i.e. the time it takes for the pool of deposited Pb to decrease to the 1/e (ca. 37%) of its original amount due to chemical, physical and biological soil processes, has been estimated to be about 50–150 years in forest soils in North America (Miller and Friedland 1994; Johnson et al. 1995a; Wang and Benoit 1997; Kaste et al. 2003). In the boreal forest of Sweden the cool climate and the coniferous tree species favors the development of an O-horizon with an acid humus form classified as mor (Klinka 1997), which is characterized by low biological activity and slow mineralization rates (from here on to emphasize these properties the O-horizon is referred specifically as the mor layer). The MRT of Pb in the mor layer has been estimated to be in the range of 450–1000 years (Tyler 1978, 1981; Bergkvist 2001). These estimates for the mor layer originate from *in situ* measurements of soil water fluxes of Pb using lysimeters for soil solution sampling and estimations involving simple steady state assumptions. However, several studies have argued that large fluctuations in atmospheric Pb deposition do not justify calculations including assumptions of steady-state conditions between the soil and the atmosphere, and that soil lysimeters might fail to sample Pb-containing particles moving within the soil matrix (Miller and Friedland 1994; Wang and Benoit 1997). This criticism has indirectly questioned the relevance of previous estimates of the MRT of Pb in the mor layer of boreal soils.

The objective of our present paper is to provide a robust estimate of the MRT of Pb in the mor layer of forest soils in northern Sweden using three different approaches. The first approach uses ^{210}Pb, a radionuclide commonly used for dating peat and lake sediments (Appleby and Oldfield 1978; Appleby et al. 1986), as a tracer. Unlike the atmospheric deposition of stable Pb pollution, the atmospheric input of unsupported ^{210}Pb, (in contrast to the supported ^{210}Pb from *in situ* production from the radioactive decay of radon) to forest soils is considered to be constant over time-scales longer than a year. The distribution of unsupported ^{210}Pb in the soil matrix is, therefore, solely a function of the radioactive decay rate and the downward migration rate of Pb (Dörr and Münnich 1991; Dörr 1995). Assuming that ^{210}Pb and stable Pb have the same behavior in soils, the distribution of ^{210}Pb in the soil might reveal long-term information about Pb mobility that could not be achieved by short-term field studies.

In our second approach we model a residence time of Pb in the mor layer using reconstructed atmospheric inputs during the last 1000 years, by calculating a loss rate that explains the measured inventories of Pb. The ^{206}Pb/^{207}Pb ratio of the atmospheric Pb preserved in Swedish peat bogs and herbarium collections is used for calculating the ^{206}Pb/^{207}Pb ratio of the lead remaining in the mor to evaluate the relevance of the estimated residence time, i.e. by comparing modeled values with measured.

In the third approach, we utilize the difference in ^{206}Pb/^{207}Pb ratio between lead derived from soil minerals, having a ^{206}Pb/^{207}Pb ratio above 1.3, and atmospheric Pb having a ratio around 1.15 (Bindler et al. 1999; Brännvall et al. 2001b). By applying a mixing model between these two sources we calculate the inventory of Pb derived from atmospheric deposition in the organic layer along a chronosequence, which consists of a series of soil samples with ages ranging from 20 to 220 years. This chronosequence is the product of the continued isostatic rebound in the region surrounding the Gulf of Bothnia, and its vegetation succession has been studied in detail by Svensson and Jeglum (2003b). Loss rates of Pb along the chronosequence are estimated by comparing measured inventories of pollution Pb with the modeled atmospheric deposition over time.

Methods

Sampling and analysis

We collected soil samples from two forested sites in north Sweden (Figure 1). The first site was a *Pinus sylvestris* and *Picea abies* old-growth forest, undisturbed by forest fire and extensive logging since 1696 (Tirén 1923), located within the Kulbäcksliden experimental forest (64°10′ N, 19°35′ E, 275 m.a.s.l.). The O-horizon at the site, consisting of Oi, Oe and Oe sub-layers, had a humus

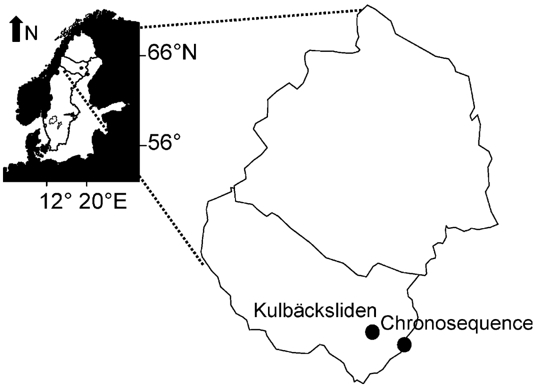

Figure 1. Map over the study sites in northern Sweden.

form mainly of humimor type according to the taxonomic classification by Klinka (Klinka 1997).The second site was a 60-m long transect going from the present-day coastline of the Gulf of Bothnia into a dense *Picea abies* forest (63°51′ N, 20°43′ E). The site corresponds to transect 5a, previously described in detail by Svensson and Jeglum (Svensson and Jeglum 2003b). The topography was measured with a theodolite and due to the on-going land-uplift of 8.4 mm yr^{-1}, the topographic sequence is equivalent to a chronosequence of soils between 20 and 220 years old. The O-horizon in the chronosequence site had a humus form that changed gradually from a fibrimor via a lignomor to a humimor within about 200 years.

The upper 10–40 cm of the soil from Kulbäcksliden (n = 11) and the chronosequence (n = 19) was sampled with a steel auger containing a removable plastic liner (diameter 42 mm), making intact soil coring possible. At Kulbäcksliden, deeper soil samples of one master core were collected from a pit dug by spade, from which the bulk density of the mineral soil was measured with steel cylinders (volume of 204 cm^3) applied horizontally. Soil samples were transported and stored at 4 °C in plastic bags until preparation. The distinction between the mor layer and the underlying mineral soil was made visually in the field and tested in the laboratory by burning dried high-resolution samples (4 mm) at 550 °C for 4 h to confirm that the definition of the mor layer in our study followed the recommended criteria of more than 40% loss-on-ignition (Federer 1982). Slices of mor samples representing the whole organic layer were lumped as single samples, with the exception of the master core and one additional layer. Samples were dried at 50 °C until constant weight and organic samples were homogenized using a mill with agate balls.

^{210}Pb and ^{137}Cs were measured through non-destructive direct gamma counting at the University of Liverpool. Unsupported ^{210}Pb, i.e. ^{210}Pb derived from atmospheric deposition, was determined by subtracting ^{210}Pb derived from *in situ* decay of ^{226}Ra from the total activity. Detailed description of the technique can be found elsewhere (Appleby et al. 1986). Stable Pb concentrations and isotopic composition (^{206}Pb and ^{207}Pb) of samples were determined using ICP-MS (Perkin-Elmer model ELAN 6100) following digestion of ~0.2 g dried soil using strong acids (conc. HNO_3 + $HClO_4$, 10:1). Concentrations of Pb were verified against the certified multi-element standard, SPEX ICPMS-2 (SPEX CertiPrep Certified Reference materials) having a ten-point calibration range within 0.5–75 ppb. Analyses of Pb nuclide masses 206 and 207 were made using dwell times of 50 ms and were corrected empirically by repeated analysis of the NIST SRM 981 reference material (fractionation constant 0.1–0.4% per a.m.u.). The Pb analyses were validated by including two certified reference materials (NIST 1571 and IAEA SL-1) and an internal reference material (lake sediment) that we have analyzed repeatedly over an 8-year period; analytical error is estimated as $<10\%$ for Pb concentration and $<0.5\%$ for the ^{206}Pb/^{207}Pb ratio. Total carbon and nitrogen contents were determined using a Perkin-Elmer CHNS/O analyzer model 2400.

Mean residence time (MRT) modeling

The equation we used to describe the migration of stable Pb and ^{210}Pb within an organic layer was

$$Q_t = Q_{t-1} + P_t - \lambda Q_{t-1} - KQ_{t-1} \tag{1}$$

where: Q_t is the inventory of ^{210}Pb or stable Pb in a soil horizon at time t; P_t is the amount of ^{210}Pb or stable Pb entering the horizon each year, i.e. from the atmosphere or a overlying horizon; λ is the radioactive decay constant, i.e. λ is equal to 0.03114 for ^{210}Pb and 0 for stable Pb; and K is a first-order rate constant describing losses by all mechanisms combined. Most studies accept that the atmospheric deposition of ^{210}Pb at a site is reasonably constant when averaged over several years and the ^{210}Pb soil profile were considered to be in equilibrium with the atmosphere ($\partial Q/\partial t = 0$). We solved K in the ^{210}Pb-model using the equation

$$K = \frac{P - \lambda Q_t}{Q_t} \tag{2}$$

where the input of ^{210}Pb (P), to the uppermost soil horizons equaled

$$P = \lambda Q_{\mathrm{tot}} \tag{3}$$

and where Q_{tot} is the total inventory of ^{210}Pb found in the soil profile. We defined the MRT of lead in each soil compartment as $1/K$.

In contrast to the ^{210}Pb model, the driving variable P_t for the stable Pb model (Eq. (1)) was a non-steady state function, due to the significant historical variations in deposition (Shotyk et al. 1998; Bindler et al. 1999; Klaminder et al. 2003). The basis for the reconstruction of the temporal variations of P_t was published pollution records from varved lake sediments in Kassjön, Koltjärn and Nylandsjön (Brännvall et al. 1999), and modern atmospheric Pb wet deposition rates calculated from Pb concentrations in forest mosses using the transfer functions established by Berg and Steinnes (1998). These mosses, *Hylocomium splendens* and *Pleurozium schreberi*, were collected every fifth year since 1975 within 20 km of Kulbäcksliden as a part of a national survey (Rühling and Tyler 2001) and provided a possibility to assess the temporal variation in wet Pb deposition at a local scale. The temporal variations of pollution Pb in the sediment record were normalized to the estimated Pb wet deposition rates at Kulbäcksliden ($\mathrm{Pb_{wet}}$) according to a polynomial regression (Figure 2), to cope with additional pollution Pb inputs originating from the catchment and sediment focusing. The resulting mean wet Pb deposition model is shown in Figure 3a. To cope with the higher atmospheric inputs of Pb at the coast, as seen during the last three decades (Rühling and Tyler 2001), the atmospheric wet input ($\mathrm{Pb_{wet}}$) at the chronosequence was increased by a factor of 2.2 in comparison to the site at Kulbäcksliden before solving K from Eq. (1). These numbers originate from analyses of mosses collected at the site in 2001, having Pb concentrations of

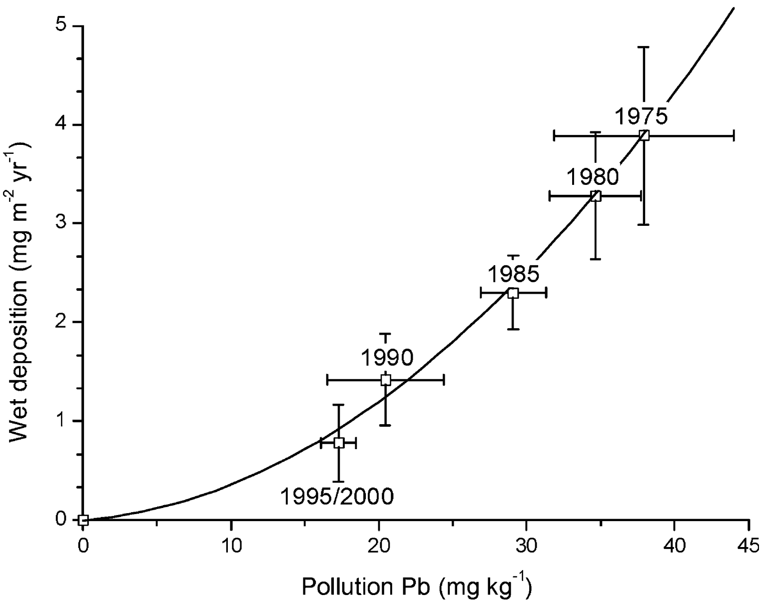

Figure 2. The polynomial calibration regression (σ^2 = 0.995) between atmospheric wet deposition compiled from the Swedish National Survey (Rühling and Tyler 2001) and the pollution Pb record found in varved lake sediments of Nylandsjön, Koltjärn and Kassjön by Brännvall et al. (1999). Error bars indicate one standard deviation.

11.2–12.6 mg kg^{-1}, indicating a 2.2 times higher wet deposition when using the transfer function established by Berg and Steinnes (1997).

The total atmospheric deposition of stable Pb(P_t) at Kulbäcksliden, including the inputs from dry Pb deposition was calculated using the equation:

$$P_t = P_{\text{wet}} + \text{Pb}_{\text{wet}} \times \frac{\text{Pb}_{\text{dry}}}{100} \tag{4}$$

where Pb$_{dry}$ is the percentage of the total Pb deposition contributed by dry Pb deposition. We used Pb$_{dry}$ values found in the literature for remote boreal forests (mean 38, $1\sigma = \pm 26$), to describe P_t at Kulbäcksliden (Bergkvist et al. 1989; Fowler et al. 1998; Ukonmaanaho et al. 2001). The total atmospheric deposition models for the two sites are shown in Figure 3b. Using the uncertainties of the transfer function between pollution Pb and wet deposition and the literature value of α in a Monte Carlo simulation, the estimated uncertainty of the deposition model is 32% (1σ). The MRT of stable Pb in the mor layer was solved by applying the estimated temporal variations of P_t (Figure 3b) to Eq. (1), and an iterative search for a K-value that reproduces the measured inventories by minimizing the sums of the squares of the deviation between modeled and measured inventories in the different soil compartments.

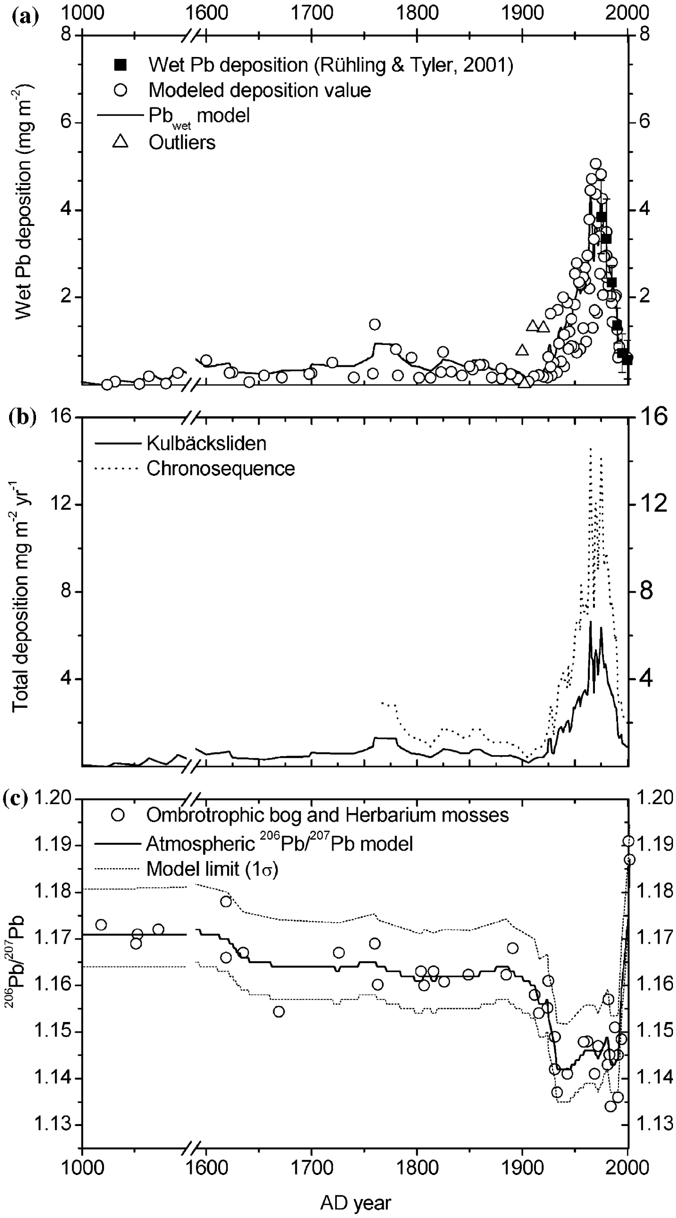

Figure 3. (a) The atmospheric wet deposition Pb flux, (b) the total atmospheric Pb deposition, and (c) the $^{206}Pb/^{207}Pb$ ratio of the atmospheric Pb pollution as a function of time, calculated from varved lake sediments (Brännvall et al. 1999), herbarium moss samples (Klaminder et al. 2004), and peat from ombrotrophic bogs (Bindler et al. 2003). The models are expressed as a running mean of individual values. The divergence between individual sample and running means has been used to remove 4 outliers (plotted as open triangles) from the original datasets of Brännvall et al. 1999.

The temporal variation in the ^{206}Pb/^{207}Pb ratio of atmospheric Pb (Figure 3c), determined using ombrotrophic bogs and herbarium collections of forest mosses (Brännvall et al. 1997; Bindler et al. 1999; Klaminder et al. 2003), was used to simulate the isotopic composition of the Pb entering the mor layer over time for an independent validation of the estimated MRT values. The equation used was:

$$^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{mor}} = \frac{P_{\mathrm{tot}}}{P_{\mathrm{tot}} + Q_{t-1}} \times {}^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{t} + \frac{Q_{t-1}}{P_{\mathrm{tot}} + Q_{t-1}} \times {}^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{mor}(t-1)} \tag{5}$$

where ^{206}Pb/^{207}Pb$_{mor}$ is the ^{206}Pb/^{207}Pb ratio of the Pb fraction remaining in the mor layer at a certain period of time; ^{206}Pb/^{207}Pb$_t$ is the ^{206}Pb/^{207}Pb ratio of the atmospheric Pb entering the mor layer (Figure 3c); and ^{206}Pb/^{207}Pb$_{\mathrm{mor}(t-1)}$ is the ^{206}Pb/^{207}Pb ratio of the Pb fractions remaining in the mor layer from previously deposited atmospheric Pb. The uncertainty of the calculated ^{206}Pb/^{207}Pb ratio was estimated through 500 trials of a Monte Carlo simulation of the model letting all variables vary around their mean values assuming a normal frequency distribution (3σ).

The amount of Pb originating from atmospheric pollution (Pb$_{\mathrm{pollution}}$) in an organic horizon at the chronosequence was calculated using a simple mixing model.

$$\mathrm{Pb}_{\mathrm{population}} = \frac{^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{organic}} - {}^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{geogenic}}}{^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{pollution}} - {}^{206}\mathrm{Pb}/^{207}\mathrm{Pb}_{\mathrm{geogenic}}} \times \mathrm{Pb}_{\mathrm{tot}} \tag{6}$$

where ^{206}Pb/^{207}Pb$_{\mathrm{organic}}$ is the ^{206}Pb/^{207}Pb ratio of the organic horizon; ^{206}Pb/^{207}Pb$_{\mathrm{pollution}}$ is the time-weighted mean ratio of atmospheric Pb pollution according to Figure 3c; ^{206}Pb/^{207}Pb$_{\mathrm{geogenic}}$ is the ratio of the local geogenic Pb (the Pb found at 20–60 cm depth); and Pb$_{\mathrm{tot}}$ is the amount of Pb in a soil sample (dry mass multiplied with the Pb concentration).

Results

Stable lead, ^{210}Pb, and ^{137}C analyses

The concentration of stable Pb in the soil at Kulbäcksliden follows the distribution of carbon, i.e. the highest concentrations of about 40 mg kg^{-1} are found in the carbon rich mor layer and decreases along with decreasing carbon levels in the mineral soil to values around 3 mg Pb kg^{-1} (Figure 4). The ^{206}Pb/^{207}Pb ratio of the Pb in the mor layer varies from 1.14 to 1.17 and increases to values as high as 2.0 in the C-horizon. Despite the higher concentrations in the mor layer the Pb inventory found there, typically around 270 mg Pb m^{-2}, is small compared to the inventory of Pb in the mineral soil

(Figure 5a–b). Unsupported ^{210}Pb, i.e. ^{210}Pb not derived from *in situ* decay of ^{226}Ra, is almost exclusively found in the mor layer; only minor detectable amounts of unsupported ^{210}Pb are found in the Ah horizon of the underlying mineral soil (Figures 4 and 5a–b). In contrast to ^{210}Pb, ^{137}Cs is detected in all analyzed horizons (Figure 5a) with the main inventory found in the mor and Ah horizon (Figure 5b).

In the chronosequence, the ^{206}Pb/^{207}Pb ratio of the mor is as high as 1.29 and decreases with increasing ground age and LOI (Table 1). The Pb in the mineral soil (10–60 cm depth), i.e. the geogenic Pb fraction, has ^{206}Pb/^{207}Pb ratios ranging between 2.28 and 3.37 (n = 8). The Pb concentrations and the total Pb inventories in the mor layer vary from 12 to 45 mg kg^{-1} and 15 to 750 mg m^{-2}, respectively, and show a positive trend with increasing ground age, even though the highest inventory is found of 167 years (Table 1). The calculated pollution Pb inventories for the chronosequence (Eq. (6)) vary from 15 to 740 mg Pb m^{-2}.

Mean residence time modeling

For all cores analyzed for ^{210}Pb from Kulbäcksliden we calculated *K*-values lower than 0.005 yr^{-1} when using ^{210}Pb as a tracer, which corresponds to a MRT longer than 200 years (Table 2). Lower reliable values of *K* cannot be

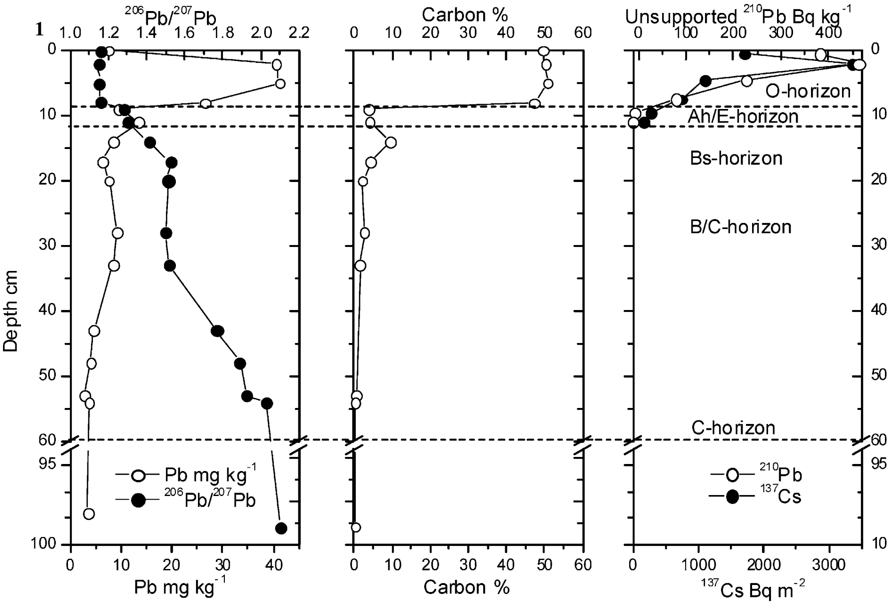

Figure 4. Stable Pb concentration, ^{206}Pb/^{207}Pb ratio, carbon content, unsupported ^{210}Pb, and ^{137}Cs for the master soil profile at Kulbäcksliden.

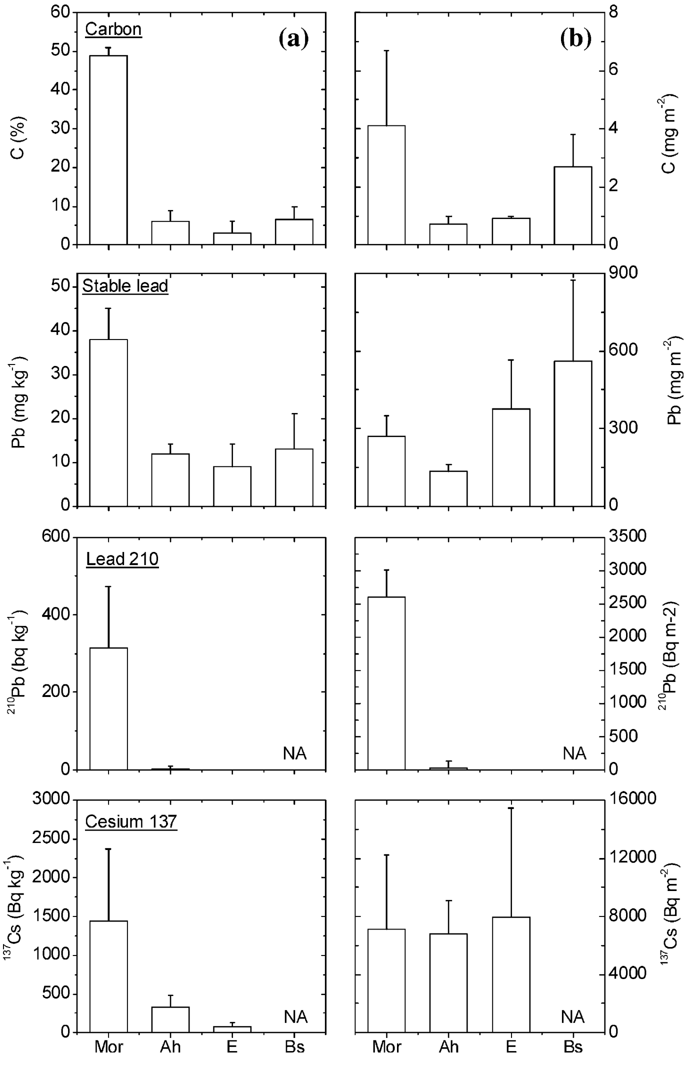

Figure 5. Element concentration (a) and inventories (b) of carbon, stable Pb, unsupported ^{210}Pb and ^{137}Cs in soil layers from Kulbäcksliden. Average values are calculated from 5 individual cores with the exception of values of carbon and stable Pb in the mor layer, which are derived from 11 different cores. Error bars represent one standard deviation. Note that the mor layer and E-horizon are of different thickness between cores and that the Bs-horizon represents the upper 4 cm of the B-horizon. Samples not analyzed for ^{210}Pb and ^{127}Cs are marked with NA.

calculated using ^{210}Pb due to the short half-life of the ^{210}Pb nuclide. However, since small fractions of unsupported Pb are detected below the mor layer in two cores (Figure 5b), this indicates that the MRT of Pb is close to 200 years for these cores. In the core where the mor was sectioned into compartments, the ^{210}Pb model suggests a decreasing downward migration rate of Pb

Table 1. Loss-on-ignition, soil carbon (C%), soil dry mass, carbon mass, stable Pb concentration, $^{206}Pb/^{207}Pb$ ratio, total Pb inventory and calculated pollution Pb inventory in the mor layer in relation to ground age at the chronosequence.

Ground age yr	Number of samples	LOI%	C%	Dry mass kg m^{-2}	Carbon mass kg m^{-2}	Pb mg kg^{-1}	$^{206}Pb/^{207}Pb$	Total Pb mg m^{-2}	Pollution Pb mg m^{-2}
13	1	69	27	4	1	12	1.271	49	45
41	3	68–69	31–34	1–2	0–1	13–15	1.254–1.288	15–30	15–25
66	3	60–66	31–36	4–11	1–4	26–45	1.208–1.274	185–300	180–280
102	3	68–88	33–45	4–10	2–5	23–31	1.158–1.178	100–320	100–315
167	2	87–95	44–48	15–21	7–10	36–38	1.160–1.174	585–750	575–740
208	3	96–97	47–50	14–16	6–8	28–31	1.150–1.164	415–460	405–465
220	2	95–96	48–49	16–18	8–9	32–38	1.157–1.179	530–680	525–665
234	3	95–96	48–49	13–15	6–7	27–34	1.150–1.167	390–520	385–510

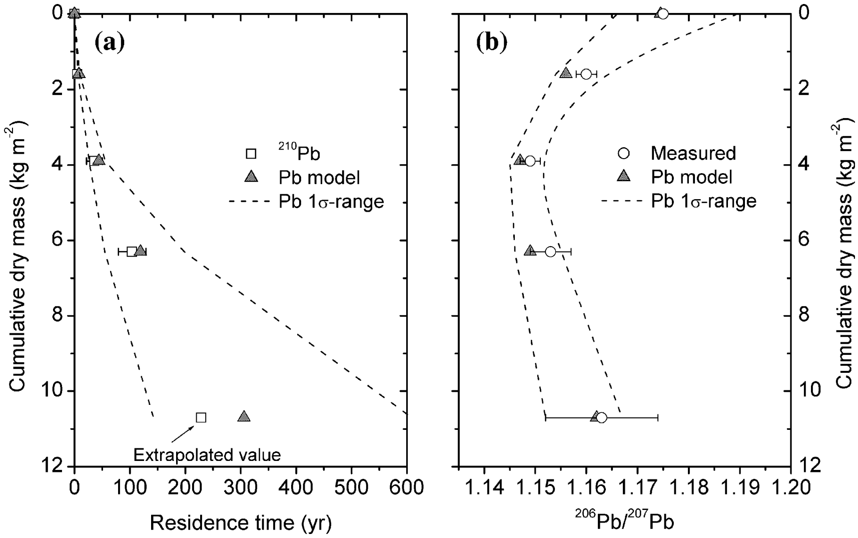

Figure 6. (a) Mean residence time of Pb at different depths of the master core from Kulbäcksliden as estimated by the ^{210}Pb and stable Pb models. Arrow indicates that the estimate is derived from linear extrapolation (see text for explanation). (b) Modeled ^{206}Pb/^{207}Pb ratios at different depths of the mor layer from master core in comparison with the measured. Error bars indicate the analytical standard deviation.

(Figure 6a). Linear extrapolation of the migration rate of ^{210}Pb gives a MRT of about 250 years for the whole layer.

Applying the stable Pb model in the mor layer at Kulbäcksliden (Q_t = 270 mg Pb m^{-2}), we estimate an MRT of Pb around 250 years for the site (Table 2). In the master core, the stable Pb model suggests a similar downward migration rate of Pb throughout the organic layer as the ^{210}Pb model (Figure 6a). Despite a large uncertainty of the estimates from the stable Pb model, the main ^{206}Pb/^{207}Pb ratio trend simulated for each mor compartment using Eq. (5), agrees with the trend measured at depth in the mor (Figure 6b) and between individual cores (Figure 7a). The model predicted an exponential decrease in the loss rate (K) of Pb from the organic horizon with increased amount of accumulated carbon at the Kulbäcksliden site (Figure 7b).

Similar with the results from Kulbäcksliden, our stable Pb model suggested a MRT around 250 years for Pb in the mor layer in the mature conifer forest at the chronosequence, i.e. 167–220 years old (Table 2), and an exponential decrease in the loss rate of Pb from the mor with increased amount of accumulated carbon (Figure 7c). The best proximate value of K in each mor layer sample, estimated using a second-order exponential regression (σ^2 = 0.94) fit to the data (Figure 7c), suggests a sigmoid-shaped trend in the MRT of Pb in the mor layer over time with the highest values found at a ground age around 170 years (Figure 8).

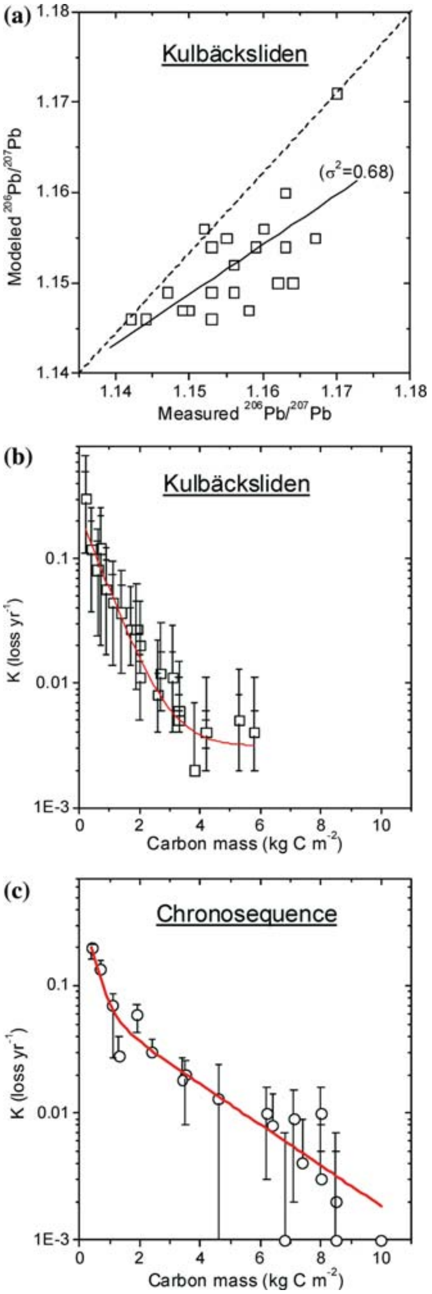

Figure 7. (a) Calculated ^{206}Pb/^{207}Pb ratios for different mor layer compartments in relation to the measured. (b) Calculated loss constants (*K*) for each mor compartment in relation to the accumulated mass of carbon in Kulbäcksliden. (c) Similar figure for the mor layer at the chronosequence.

Discussion

Migration of stable lead, ^{210}Pb and ^{137}Cs in mature undisturbed forest

The low ^{206}Pb/^{207}Pb ratio found in the mor layer in the mature forest at Kulbäcksliden (Figure 4) is similar to that found for atmospheric Pb (Figure 3c) and clearly separated from the ratio found in the mineral soil (Figure 4). This shows that the Pb in the mor is mainly derived from atmospheric pollution and not from local soil minerals. The general tendency of higher measured ^{206}Pb/^{207}Pb ratios than predicted by the stable Pb model (Figure 7a) is a combined effect of the uncertainty of the model and a possible minute influence of local geogenic Pb resulting from upward transport from the mineral soil to the mor by biota or in-mixing of mineral grains in the mor. That only a very small fraction of Pb is derived from the underlying mineral soil is in line with our previous findings suggesting a minute upward transfer of Pb from the mineral soil (Bindler et al. 1999, 2003; Klaminder et al. 2003). Higher ^{206}Pb/^{207}Pb ratios in the mor layer at the chronosequence are likely a cause of more in-mixing of mineral grains in these less well-developed layers, since high ^{206}Pb/^{207}Pb ratios co-occur with low loss-on-ignition values and low levels of carbon (Table 1).

The observed similarities in the vertical accumulation patterns between Pb and carbon in the mineral soil (Figure 4) stress the importance of particulate and colloidal carbon for the downward transport of Pb within the soil matrix, which is consistent with the current understanding of Pb transport in forest soils (Tyler 1981; Dörr and Münnich 1991; Wang and Benoit 1997). This transport causes a downward mixing of pollution Pb with a ^{206}Pb/^{207}Pb ratio around 1.15 into the pool of naturally occurring geogenic Pb with higher ^{206}Pb/^{207}Pb ratios resulting in a gradual increase in ^{206}Pb/^{207}Pb ratio with depth in the mineral soil (Figure 4). Natural variations in the mineralogical composition of the till can also cause variations in the ^{206}Pb/^{207}Pb ratio with depth (Klaminder et al. 2005), but similar trends observed for different European soils (Erel et al. 1997; Bindler et al. 1999; Brännvall et al. 2001b; Brännvall et al. 2001c; Semlali et al. 2001), suggest that diminishing influence of downward migrated atmospheric pollution is the main cause to increasing ^{206}Pb/^{207}Pb ratios in deeper soil layers.

In relation to Pb, the distribution of ^{137}Cs in the soil is much weaker correlated to the accumulation pattern of carbon (Figure 5b). This is a reasonable result since Cs is not strongly adsorbed to humic substances (Kruyts and Delvaux 2000). Cs is also much more mobile than Pb in the studied soil as seen by the more extensive distribution of ^{137}Cs in comparison with ^{210}Pb (Figure 5b). The migration rate of Cs must be at least an order of a magnitude higher than for Pb since the distribution of unsupported ^{210}Pb represents the migration of Pb during more than 200 years, while ^{137}Cs originates from relatively recent inputs, i.e. from nuclear weapon testing during the 1960s and the Chernobyl accident in 1986 (Figure 5b). Higher mobility for Cs than for Pb in

Table 2. Annual loss and mean residence time (MRT) of Pb in a mature mor layer at Kulbäcksliden and at the chornosequence (more than 160 years old) according to the ^{210}Pb model and the stable Pb model.

	210-Pb model		Stable Pb model		1σ-range (yr)
	K (loss yr^{-1})	MRT (1/K)	K (loss yr^{-1})	MRT (yr)	
Kulbäcksliden	≤ 0.005	≥200	0.004	250	150–650
Chronosequence	ND	ND	0.004	250	100–∞

ND = not determined.

soils has also been indicated by previous studies (Dörr and Münnich 1991; He and Walling 1997).

Migration rates of lead from the organic horizon in mature undisturbed forest

Despite a large uncertainty involved in the calculations, all three of our approaches indicate that the mean residence time (MRT) of Pb in the mature organic horizons at Kulbäcksliden and the chronosequence is around 250 years (i.e. between 200 to 250 years, Table 2). This agreement between the different methods, together with the reproducibility of the measured ^{206}Pb/^{207}Pb trends at Kulbäcksliden by the stable Pb model, gives credibility to these estimates.

Our MRT estimates are shorter than previous estimates from the boreal forest, which suggest a MRT of 450–1000 years (Tyler 1978, 1981; Bergkvist 2001), which is expected given the steady-state assumptions involved in these studies. However, they are longer than similar estimates of 3–150 years from different organic horizons in North America (Dörr and Münnich 1991; Miller and Friedland 1994; Johnson et al. 1995b; Wang and Benoit 1997; Kaste et al. 2003). Since the residence time of Pb in an organic horizon is affected by the decomposition rate of carbon (Dörr and Münnich 1991), the turn-over rate of Pb in organic horizons should vary with organic matter quality and climate; hence, our migration rates should not be viewed as a contradiction to previous studies, but rather as a reflection of the biogechemical condition in northern boreal forest soils.

The stable Pb model indicates that the MRT of Pb in the mor layer is positively related to the accumulated amount of carbon in the horizon (Figure 7b–c). High amounts of accumulated carbon in boreal forest soils is mainly an indication of low decomposition rates and high age (Liski et al. 1998). It is, therefore, not surprising to find a negative relationship between the mass of accumulated carbon and the migration rate of Pb (Figure 7b–c), since low decomposition rates result in slow downward migration velocities of Pb (Dörr and Münnich 1991). Increased amounts of carbon also result in increased thickness of the organic layer, which further increases the MRT of Pb in the horizon due to longer downward migration routes of particulate and

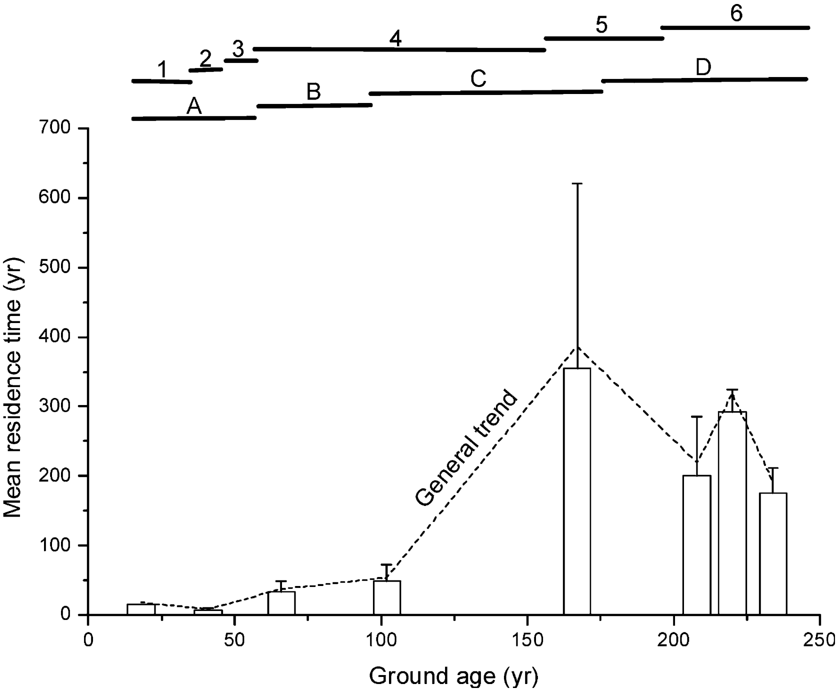

Figure 8. Calculated mean residence time for the different succession stages at the chronosequence. The different tree vegetation stages are classified according to studies by Svensson and Jeglum (2003b): (1) alder, 20–40 years, (2) alder, spruce, 40–50 years; (3) alder, spruce and juniper, 50–60 years; (4) alder, spruce, juniper and rowan, 60–160 years; (5) spruce, juniper and rowan, 160–200 years; (6) spruce from 200 years of ground age and onwards. Field vegetation stages are from Svensson and Jeglum (Svensson and Jeglum 2003a): (a) graminoids without conifer litter; (b) graminoids with low cover of conifer litter; (c) conifer litter with low shrubs; (d) conifer litter without low shrub. Arrows indicate high densities of dead spruce (>10%) (Svensson and Jeglum 2003a).

dissolved Pb (Kaste et al. 2003). Increased inputs of spruce litter and woody debris with slower decomposition rates in relation to graminoid remains or alder leaves (Berg and Meentemeyer 2002), and thicker organic layers are, therefore, the main cause of the increased MRT of Pb in the organic layer at the chronosequence with time (Figure 8).

The results from the chronosequence clearly suggest that the MRT of Pb in an organic horizon is not static over time. Variable Pb turn-over times have previously been suggested by Johnson et al. (1995), who claimed that the processes regulating Pb losses from the organic horizon of a site in the Hubbard Brook Experimental Forest (HBEF) were not consistent throughout the 20th century. They explained a more rapid decline in the organic horizon Pb pool after 1970 than predicted, with a fundamental change in the biogeochemistry of Pb favoring downward migration losses, i.e. suggesting decreased atmospheric inputs of strong acids as a possible explanation. The result from our chronosequence suggests that the MRT of Pb in an organic horizon can change naturally along with forest succession where litter quality and thickness of the organic horizon change significantly. This result constitutes an example that it is not always necessary to involve external stimulus when explaining changing loss rates of Pb from an organic horizon over time.

Implications of the estimated MRT of Pb in the mor layer

The MRT of about 250 years for Pb in mature forest mor suggests that deposited atmospheric Pb pollution is stored there for a long time. As a consequence, a fraction of the inventory of Pb that we find today in the mor is partly derived from centuries-old atmospheric pollution. Furthermore, the response to the recent decrease in atmospheric pollution will be a more prolonged process in the boreal zone than previously predicted when using MRT values of 25–75 years originating from estimates for North American soils (Bindler et al. 1999). However, even though the mor layer as a whole will respond slowly to decreased atmospheric Pb deposition, it is important to underline that the organic matter in the upper parts of the organic horizon will be replaced by fresh litterfall and the MRT of Pb in this part of the layer is only a few years. We can speculate that concentrations of other metals strongly bound to organic matter, such as mercury, will also generally respond over similar timescales as that we have estimated for Pb.

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