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Lead dynamics in the forest floor and mineral soil in south-central Ontario

SHAUN A. WATMOUGH*, THOMAS C. HUTCHINSON
and PETER J. DILLON
*ERS Department, Trent University, Peterborough, Ont., Canada K9J 7B8; *Author for correspondence (e-mail: swatmough@trentu.ca; phone: +1-705-748-1011 (extn. 1647); fax: +1-705-748-1569)*

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Abstract. Recent studies have suggested that the residence time of Pb in the forest floor may not be as long as previously thought, and there is concern that the large pulse of atmospheric Pb deposited in the 1960s and early 1970s may move rapidly through mineral soils and eventually contaminate groundwater. In order to assess Pb mobility at a woodland (JMOEC) in south-central Ontario, a stable Pb isotope tracer ^{207}Pb ($8\,\mathrm{mg\,m^{-2}}$) was added to the forest floor in white pine (*Pinus strobus*) and sugar maple (*Acer saccharum*) stands, respectively, and monitored over a 2-year period. Excess ^{207}Pb was rapidly lost from the forest floor. Applying first-order rate coefficients (k) of 0.57 (maple) and 0.32 (pine) obtained from the tracer study, and estimates of Pb deposition in the region, current predicted Pb concentrations in the forest floor are 1.5–3.1 and $2.1–5.8\,\mathrm{mg\,kg^{-1}}$ in the maple and pine plots, respectively. These values compare favorably with measured concentrations (corrected for mineral soil contamination) of 3.1–$4.3\,\mathrm{mg\,kg^{-1}}$ in the maple stand and $2.6–3.6\,\mathrm{mg\,kg^{-1}}$ in the pine stand. The response time ($1/k$) of Pb in the forest floor at the sugar maple and white pine plots was estimated to be 1.8 and 3.1 years, respectively. The rapid loss of Pb from the forest floor at the JMOEC is much greater than previously reported, and is probably due to the rapid rate of litter turnover that is characteristic of forests with mull-type forest floors. In a survey of 23 forested sites that border the Precambrian Shield in south-central Ontario, Pb concentrations in the forest floor increased exponentially with decreasing soil pH. Lead concentrations in the forest floor at the most acidic survey sites, which exhibited mor-type forest floors, were approximately 10 times higher ($\sim 80\,\mathrm{mg\,kg^{-1}}$) than at the JMOEC, and pollution Pb burdens were up to 25 times greater. Despite the rapid loss of Pb from the forest floor at the JMOEC, the highest pollution Pb concentrations were found in the upper (0–1 cm) mineral soil horizon. Lead concentrations in the upper 30 cm of mineral soil were strongly correlated with organic matter content, indicating that pollution Pb does not move as a pulse down the soil profile, but instead is linked with organic matter distribution, indicating groundwater contamination is unlikely.

Introduction

Lead deposition in eastern North America increased dramatically during the middle-to-latter half of the 20th century, primarily due to the use of alkyl Pb as an anti-knock agent in gasoline (Nriagu 1990; Miller and Friedland 1994). The release of Pb into the environment has caused the atmospheric concentration, long-range transport and atmospheric deposition of Pb to increase by several orders of magnitude during the 20th century (Nriagu 1990). Lead, emitted as volatile compounds or sorbed on fine aerosols can be circulated into the upper troposphere and transported thousands of kilometers from its point of origin. Elevated Pb concentrations in forest soils have been reported at remote sites in eastern North America and Europe (Johnson et al. 1982; Friedland and Johnson 1985; Billet et al. 1991; Friedland et al. 1992; Miller and Friedland 1994; Bindler et al. 1999; Brannvall et al. 2001; Johansson et al. 2001). Some studies have suggested that Pb concentrations in the forest floor are approaching levels that may cause biological effects, even in these remote areas, far from emission sources (Bringmark and Bringmark 2001).

Despite major reductions in leaded gasoline consumption in North America that began in the 1970s, the environmental impact of Pb remains a major concern (Miller and Friedland 1994; Johnson et al. 1995). Lead is generally considered to be strongly retained in organic soil horizons and early reports suggested that the residence time of Pb in the forest floor could be in the order of several hundred years (Benninger et al. 1975; Tyler 1978; Friedland and Johnson 1985; Turner et al. 1985). If these estimates are correct, Pb concentrations in the forest floor in many areas could continue to increase to potentially toxic levels, despite substantial reductions in Pb deposition. However, more recent reports have suggested that the residence time of Pb in the forest floor may not be as long as previously thought (Friedland et al. 1992; Miller and Friedland 1994). Over the past two decades, for example, Pb burdens in the forest floor at a number of sites in eastern North America have decreased in the order of 20–40% (Friedland et al. 1992; Miller and Friedland 1994). The relatively rapid loss of Pb from the forest floor has lead to concerns that Pb movement down the soil profile may also be rapid. As a consequence, the large pulse of Pb that was released into the atmosphere in the 1960s and 1970s may ultimately result in contamination of groundwater (Miller and Friedland 1994). Transport velocities of Pb in forest soils were reported to be between 0.39 and 0.83 mm year^{-1} at over 40 forested sites in Europe (Dorr and Munnich 1991), 5 mm year^{-1} in Mediterranean soils (Erel et al. 1997; Erel 1998) and between 8.2 and 19.7 mm year^{-1} at different depths in a northern hardwood forest in Vermont, USA (Miller and Friedland 1994). Miller and Friedland (1994) suggested that the large pulse of Pb-deposited after 1960 in eastern North America might begin to be released to upland streams sometime in the middle of the 21st century. As forest soils contain appreciable amounts of pollution Pb even in remote areas, it is clearly important to understand the dynamics of Pb movement in forest soils.

In this study, we used a stable isotope tracer technique to monitor the rate of loss of ^{207}Pb from the forest floor and its movement through the underlying mineral soil. The study was conducted at a woodland located in a rural area of south-central Ontario. Previous work, using natural variations in Pb isotope composition, demonstrated that less than 2% of the pollution Pb-deposited at the site is present in the mull-type forest floor implying that Pb is rapidly transferred downward to the mineral soil (Watmough and Hutchinson 2003). Results from the stable isotope tracer experiment described herein were used to reconstruct changes in forest floor Pb in response to changing Pb deposition over the past 100 years and to monitor the movement of pollution Pb through the mineral soil.

Materials and methods

Study site

The study was conducted at the newly established James McLean Oliver Ecological Centre (JMOEC) located approximately 40 km north of Peterborough and 150 km northeast of Toronto in south-central Ontario (44°57′N;78°50′W). The ~30 ha forest has an average basal area of $18.7\,\mathrm{m}^{-2}\,\mathrm{ha}^{-1}$ and a stem density (<10 cm dbh) of 565 stems/ha, although there is considerable variation in forest basal area resulting from past logging activities. The forest is dominated by sugar maple (*Acer saccharum* Marsh), which comprises 48% of the basal area. Other notable tree species include white ash (*Fraxinus americana* L.), white birch (*Betula papyrifera* Marsh.), basswood (*Tilia americana* L.), white cedar (*Thuja occidentalis* L.), black cherry (*Prunus serotina* Ehrh.), American elm (*Ulnus americana* L.), ironwood (*Ostrya virginiana* [Mill] K. Koch). White pine (*Pinus strobus* L.) is also present, and occurs primarily in two dense stands at the southwest and northwest sections of the woodland.

Soil plots and tracer application

Soil plots (0.5 m × 0.5 m) were established in undisturbed areas of the woodland dominated by mature white pine at the southern part of the woodland (basal area $28.8\,\mathrm{m}^{-2}\,\mathrm{ha}^{-1}$) and at a site dominated by mature sugar maple (basal area $25.7\,\mathrm{m}^{-2}\,\mathrm{ha}^{-1}$), approximately 200 m north of the white pine stand. Three replicate treatment plots and three reference (untreated) plots were established at each site. Soils, which overlay dolomite limestone, were classified as orthic melanic brunisols according to the Canadian System of Soil Classification (1998) and are characterized by high soil pH, a mull forest floor and a deep (>10 cm) Ah horizon. The soil type was very similar beneath the maple and pine plots at the JMOEC. The forest floor is very shallow (1.5–2 cm) and there is no pronounced H horizon. The forest floor bulk density was $0.02\text{–}0.04\,\mathrm{g\,cm}^{-2}$. In this study we are defining a mull forest floor as a shallow forest floor that undergoes rapid decomposition without a pronounced humus (H) layer. By contrast, we consider a mor forest floor found in the regional survey to be generally deeper and contains a distinct H layer. As Federer (1982) points out, there can be considerable variation in how the forest floor is identified and defined in the field. In this study, all mineral soil samples had %LOI (loss on ignition at 400 °C for 8 h) values less than 40%, whereas %LOI values for the forest floor were between 65 and 71%. Results from this study should be compared to others with consideration of the difficulties in separating and identifying organic horizons in the forest floor, the different soil type and working definition we use. Mineral soil pH (dd H_2O; 1:5 soil:water ratio) at the JMOEC was relatively uniform with depth (up to 30 cm), averaging 6.4 in the pine stand and 5.9 in the maple stand.

Stable metal isotope tracers offer a novel approach for investigating trace metal cycling in forest ecosystems (Watmough et al. 1999). Unlike radio-isotopes, stable isotopes do not decay over time and several elements have multiple stable isotopes that can be measured simultaneously. In addition, the development of sophisticated inductively coupled plasma mass spectrometers (ICP-MS) with extremely high sensitivity and resolution capacities has enabled isotopes of trace metals to be measured at sub part per billion levels. Combined, these characteristics mean that stable metal isotopes can be applied to different forest compartments at trace levels, and changes in isotope distribution may be measured over time. Lead has four naturally occurring stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) and in this study ^{207}Pb (22.6% relative abundance) was chosen as the Pb isotope tracer. Stable isotope stock solutions were prepared by dissolving 75 mg ^{207}Pb (92.85% enrichment; ^{206}Pb/^{207}Pb 0.027) standards obtained from TRACE Sciences International (Mississauga, Ont.) in 25 ml 10% trace grade HNO_3. The application solution was prepared immediately before application of the solution to the forest floor. Application solutions were prepared by diluting the stock solution ($\sim 3\,mg\,ml^{-1}$ Pb) in 250 ml of simulated rainfall adjusted to pH 4.5 (using a 2:1 molar ratio of H_2SO_4 and HNO_3), to obtain application concentrations of approximately $0.008\,mg\,ml^{-1}$ Pb. Solutions were prepared in acid-washed glass conical flasks, sealed with Parafilm^{TM}. Solutions (250 ml; equivalent to a 1 mm rainfall event) were sprinkled onto the forest floor in each of the 0.5 m × 0.5 m permanent plots in July 2000 after making small punctures in the Parafilm^{TM} seal. The solution volume was sufficient to obtain a relatively even distribution of the isotope tracer over the forest floor, but was insufficient to cause significant percolation through the soil profile.

The distribution of the ^{207}Pb-spike was determined 3 days after the application and in this study it is assumed that ^{207}Pb distributed within the forest floor and mineral soil at this point behaves in an identical way to pollution Pb that is input to the forest floor in throughfall. After 3 days, the forest floor was sampled from one corner of each 0.5 m × 0.5 m plot and soil pits were dug at the outer edge of the plots to a depth of $\sim$50 cm. Soil was sampled from the pit face located within the plot using a stainless steel spatula at 1 cm intervals (0–5 cm), 2.5 cm intervals (5–10 cm) and 10 cm intervals (10–20 cm) and at 30 cm depth. Soil samples were placed in sealed Zip Lock bags for transport to the laboratory. Samples for bulk density estimates were obtained using soil cores extracted at 5 cm intervals. Sampling of the forest floor (using different portions of the plots) was repeated after 1 and 2 years, whereas mineral soil was re-sampled only after 1-year. Samples from violet (*Viola pensylvanica*) leaves were also collected from each plot after 1 and 2 years.

Regional survey

The JMOEC lies in a region just south of the limit of the Precambrian Shield. As a result, soil chemistry can vary tremendously over a short distance from the JMOEC. In order to evaluate how representative the JMOEC is of forested sites in the region, forest floor and foliage from 23 sites (11 sugar maple, 12 white pine) were sampled in August 2002. It has previously been shown that elevation (and precipitation) and age of the forest floor can affect Pb concentrations in the forest floor (Johnson et al. 1982). In order to minimize these effects, all sites were located within a narrow elevation range (280–420 m), and within a 40 km radius of one another to minimize climatic effects. In addition, only mature (basal area $>23\,\mathrm{m}^{-2}\,\mathrm{ha}^{-1}$) forest plots dominated by either sugar maple or white pine were sampled, and all plots were at least 500 m (and usually >1 km) from the nearest paved road. Forest floor samples were collected from within a 25 cm × 25 cm area at three locations within each plot. Care was taken to minimize contamination with upper mineral soil, although some contamination is inevitable. Loss on ignition values in forest floor samples were on average 68%, but ranged between 59 and 79%. Foliar samples (maple leaves and 1 and 2 years composite pine needles) were collected from the mid-canopy of three mature trees of each species using 10 m telescopic aluminum pruners. Each forest floor sample and foliar sample (3 per site) was placed in a sealed Zip Lock bag for transport to the laboratory.

Sample preparation and analysis

Soil and forest floor samples were oven dried (65 °C) for at least 72 h, sieved (2 mm mesh) and ground in a Wiley Mill prior to analysis. Vegetation samples were washed in de-ionized water, oven dried (65 °C) for at least 72 h and ground prior to analysis. Soil, vegetation and forest floor samples (0.2 g) were cold digested in 2.5 ml trace grade HNO_3 overnight and then digested under reflux at 100 °C for 8 h. Samples were diluted to 25 ml and filtered through Whatman No. 42 filter paper prior to analysis by ICP-MS.

The major lead isotopes (*m/z* 208, 207 and 206) and Pb concentrations were measured on a SCIEX (71 Four Valley Drive, Concord, Ont, Canada) Elan 5000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) utilizing solution nebulization. Dwell times employed were 200 ms for ^{208}Pb, and 400 ms each for ^{206}Pb and ^{207}Pb, in order to collect approximately equal numbers of ions for each isotope. Eight measurements were recorded to produce one replicate, and eight replicates were collected for a total analysis time of approximately 2 min. Longer analysis times did not yield significant improvement in the measured standard deviations. Accuracy of measurements was checked by comparison to NIST 981 Common Lead Isotopic Standard. Standard solutions were measured throughout the course of the analysis, with NIST 981 concentrations of 25, 50 and 100 ppb (ng ml^{-1}). The average ^{206}Pb/^{207}Pb ratio measured was 1.093 ± 004 ($N = 8$) with a relative standard deviation (RSD) of 0.4% (certified ^{206}Pb/^{207}Pb ratio is 1.093 ± 0.001).

Excess ^{207}Pb was calculated as

$$\mathrm{Excess}^{207}\mathrm{Pb} = \mathrm{Sample}^{207}\mathrm{Pb} - \mathrm{Background}^{207}\mathrm{Pb}, \qquad (1)$$

where

$$\mathrm{Background}^{207}\mathrm{Pb} = \mathrm{Background}\frac{^{207}\mathrm{Pb}}{^{206}\mathrm{Pb}} \times \mathrm{Sample}^{206}\mathrm{Pb}. \qquad (2)$$

In all the calculations, correction was made for the small amount of ^{206}Pb that was contained in the tracer (Hintelmann and Nives 2003) and which was added to the treated plots (<0.2 mg m^{-2}) and which would slightly increase the ^{206}Pb concentration in treated samples. Background ^{206}Pb/^{207}Pb ratios were determined in soil and forest floor from the three untreated soil pits at the maple and pine stands, respectively.

Precision and accuracy were confirmed by repeated analysis of reference sugar maple leaf material (NIST 1515) and San Joaquin soils (NIST 2709). Recovery was greater than 96% for leaf material, but only 75–85% for reference mineral soil samples. Digestion in HNO_3 does not obtain 100% Pb recovery from mineral soil samples, although this method is suitable for extracting anthropogenic Pb (and thus ^{207}Pb tracer) from soils (Erel et al. 1997). Changes in ^{207}Pb concentration and ^{206}Pb/^{207}Pb ratios in the forest floor over time were assessed using repeated measures ANOVA on log-transformed data (Zar 1984).

Modeling Pb losses from the forest floor at the JMOEC

In order to model temporal changes in Pb concentration in the forest floor, we assumed that the dynamics of Pb can be described by a linear first-order rate process with a single reservoir (Martin and Coughtrey 1987; Miller and Friedland 1994).

$$\frac{\mathrm{d}A}{\mathrm{dt}} - F_{\mathrm{in}} - \mathrm{kA}, \tag{3}$$

where A is the Pb content of the forest floor (mg m^{-2}), F_{in} is the atmospheric input of Pb (mg m^{-2} year^{-1}), and k (year^{-1}) is a first-order rate constant representing the fraction of A transported out of the forest floor per unit time. Lead deposition in eastern North America increased dramatically during the middle to latter half of the 20th century and then decreased rapidly from the early 1970s (Evans and Dillon 1982; Miller and Friedland 1994; Graney et al. 1995). In this study we only consider Pb changes after 1900, and assume that Pb deposition prior to 1900 was 1 mg m^{-2} year^{-1}. Deposition data for Pb were obtained from estimates using lake sediment cores and published and unpublished bulk deposition data for the region (Jeffries and Snyder 1981; Evans and Dillon 1982). The first-order rate constant k was obtained from changes in excess ^{207}Pb in the forest floor measured over the 2-year monitoring period. The solution to equation (3) is

$$A(t) = \frac{F_{\mathrm{in}}}{k} - \left[\left(\frac{F_{\mathrm{in}}}{k}\right) - A_0\right] e^{-kt}, \tag{4}$$

where A_0 is the Pb content at $t = 0$. We present changes in forest floor concentration rather than content, assuming that the mass of the forest floor has remained constant. The Pb concentration at time 0 (1900) was estimated using the first-order rate constant, k, and a background Pb deposition of 1 mg m^{-2} year^{-1}. The response time (t_{resp}) for this system is defined as

$$t_{\mathrm{resp}} = \frac{1}{k}. \tag{5}$$

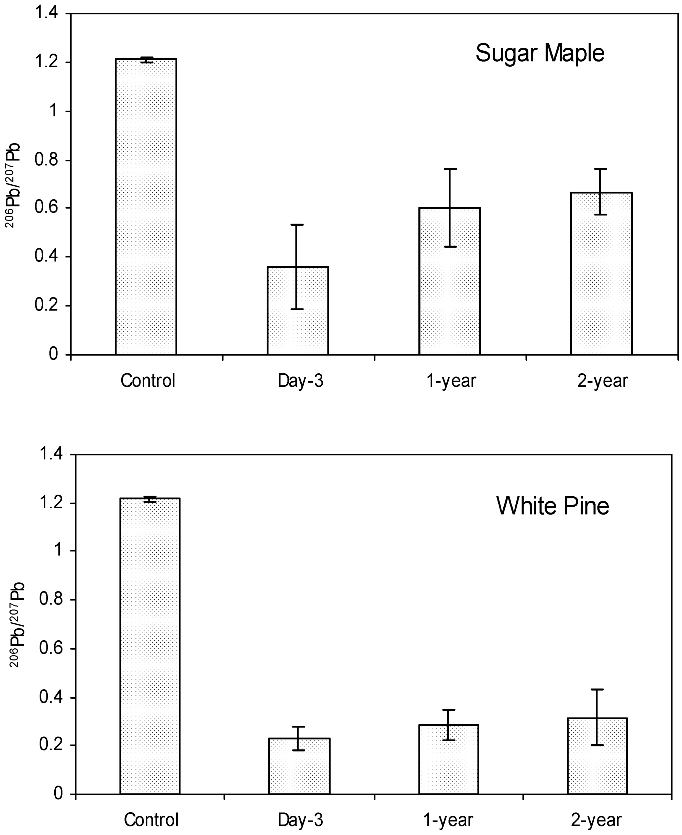


Figure 1. ^{206}Pb/^{207}Pb ratios in forest floor samples from ^{207}Pb treated plots located in sugar maple (upper) and white pine (lower) plots at the JMOEC. The forest floor samples were taken 3 days, 1 year and 2 years after the tracer application ($n = 3$). ^{206}Pb/^{207}Pb ratios in the forest floor of control (untreated) plots are also shown. All values are means ± S.D.

Results and discussion

Movement of ^{207}Pb from the forest floor

Three days following application of ^{207}Pb to treatment plots, the ^{206}Pb/^{207}Pb ratio in the forest floor was substantially lower than the ^{206}Pb/^{207}Pb ratio in untreated plots (Figure 1). Untreated forest floor had a ^{206}Pb/^{207}Pb value around 1.2, whereas ^{206}Pb/^{207}Pb ratios were ~ 0.4 and ~ 0.25 in the treated sugar maple and white pine plots, respectively. Over the 2-year period, ^{206}Pb/^{207}Pb ratios in the forest floor increased, although this increase was only statistically significant ($p < 0.05$) in the sugar maple plots (Figure 1). The increase in ^{206}Pb/^{207}Pb ratios over time is due to a gradual loss of the ^{207}Pb spike from the forest floor.

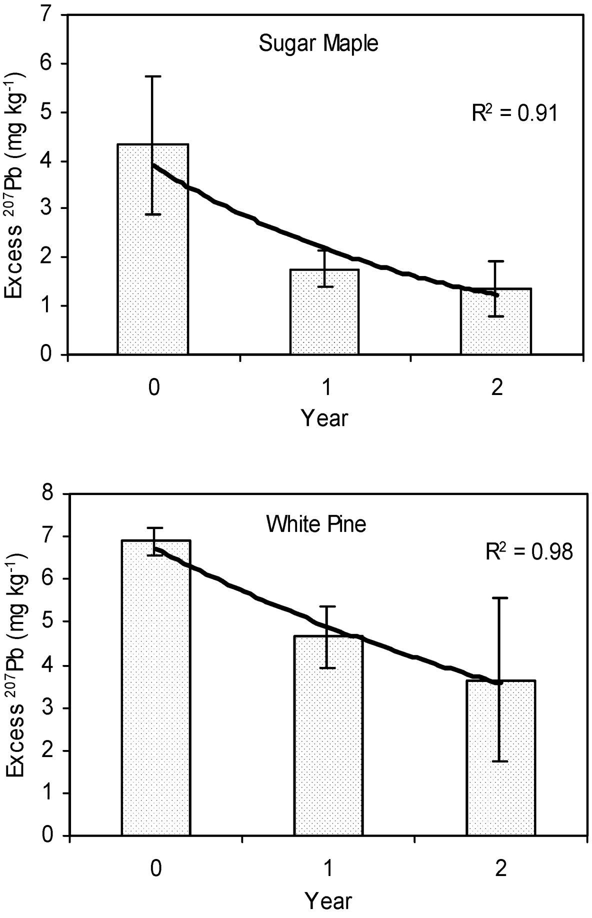


Figure 2. Excess ^{207}Pb (mg kg^{-1}) in forest floor samples from ^{207}Pb treated plots located in sugar maple (upper) and white pine (lower) plots at the JMOEC. The forest floor samples were taken 3 days, 1 year and 2 years after the tracer application ($n = 3$). All values are means ± S.D.

Both the excess ^{207}Pb spike and the 'background' Pb concentration in the sample influence ratios of ^{206}Pb/^{207}Pb in the forest floor; the higher the background Pb concentration in a sample, the greater the amount of ^{207}Pb spike that is necessary to alter the ^{206}Pb/^{207}Pb ratio. In order to monitor the rate of loss of the ^{207}Pb spike from the forest floor, ^{206}Pb/^{207}Pb ratios were calculated as excess ^{207}Pb concentrations (mg kg^{-1}), which standardizes against changes in the 'background' Pb concentration in the samples. Excess ^{207}Pb concentrations in the forest floor decreased over time at both the sugar maple and white pine plots (Figure 2). Three days following application, excess ^{207}Pb concentrations in the forest floor were ~4.3 mg kg^{-1} in the sugar maple plots and ~6.8 mg kg^{-1} in the white pine plots (Figure 2). After 1 year, the excess ^{207}Pb concentration had decreased to ~1.8 mg kg^{-1} in the sugar maple plots and $\sim 4.6\,\mathrm{mg\,kg^{-1}}$ in the white pine plots. Several studies have shown that high metal levels can impair biological activity and alter rates of litter decomposition, thus affecting the rate of transport of metals from the forest floor to the underlying mineral soil (Friedland et al. 1986; Berg et al. 1991; Cotrufo et al. 1995). However, the small amount of excess ^{207}Pb measured immediately following application ($\sim$4–6 $\mathrm{mg\,kg^{-1}}$), and very low background Pb concentrations in the forest floor at the JMOEC ($\sim 10\,\mathrm{mg\,kg^{-1}}$) are substantially less than concentrations expected to affect biological functioning (Friedland et al., 1986). We used the change in excess ^{207}Pb concentration over the 2-year period to obtain an estimate of the first-order rate coefficients (k) by fitting exponential curves to the data (Figure 2). The first-order rate coefficients were 0.57 ($\pm$0.08) and 0.32 ($\pm$0.06) for the sugar maple and white pine plots, respectively, and these values were used to model temporal changes in Pb concentration in the forest floor at the JMOEC.

This difference in k values between the two sites is likely due to the more rapid turnover of litter at the sugar maple site versus the white pine site. For example, Watmough and Hutchinson (2003) reported that the mass of sugar maple in litter bags placed in the forest floor close to the sugar maple plots had decreased by $46.3 \pm 5.4\%$ over an $\sim$180-day period between May and November, 2001. The rate of maple leaf decomposition was significantly ($p < 0.01$) higher than that of white pine needles ($30.1 \pm 6.7\%$) measured in litter bags placed in the forest floor close to the white pine plots over the same time period. The more rapid loss of ^{207}Pb from the forest floor at sugar maple plots is unlikely due to pH-related leaching, because the pH of litter at the maple plots (5.7 ± 0.2) was significantly ($p < 0.01$) higher than at the white pine plots (5.1 ± 0.3).

Movement of ^{207}Pb in the mineral soil

Three days after the application of ^{207}Pb, excess ^{207}Pb was measured in the forest floor and the upper (0–1 cm) soil horizon at both the sugar maple and white pine plots (Figures 3 and 4). As the surface (0–1 cm) soil horizon contains much more ‘background’ Pb (higher mass and Pb concentration) than the forest floor, a large amount of excess ^{207}Pb was required to alter the ^{206}Pb/^{207}Pb ratio by even a small amount. Therefore, even though ^{206}Pb/^{207}Pb ratios in the spiked plots are only slightly lower than background ^{206}Pb/^{207}Pb ratios ($\sim$1.16 (spiked) v.s. 1.22 (background)), this represents an appreciable amount of ^{207}Pb tracer in the mineral soil (Table 1). Three days after application, $\sim 4.3\,\mathrm{mg\,m^{-2}}$ of excess ^{207}Pb was found in the forest floor, $\sim 2.0\,\mathrm{mg\,m^{-2}}$ was in the 0–1 cm soil layer and $\sim 0.5\,\mathrm{mg\,m^{-2}}$ was present in the 1–2 cm layer in the sugar maple plots (Table 1). Similarly, $\sim 6.8\,\mathrm{mg\,m^{-2}}$ of excess ^{207}Pb was found in the forest floor and $\sim 1.7\,\mathrm{mg\,m^{-2}}$ was in the 0–1 cm soil layer at the white pine plots. The relatively high amount of excess ^{207}Pb found in the upper mineral soil is due to the rapid movement of the application tracer solution through the very shallow forest floor at the JMOEC. In total, $\sim 6.8\,\mathrm{mg\,m^{-2}}$ was recovered in the sugar maple plots and $8.5\,\mathrm{mg\,m^{-2}}$ was recovered in the white pine plots, which represents approximately

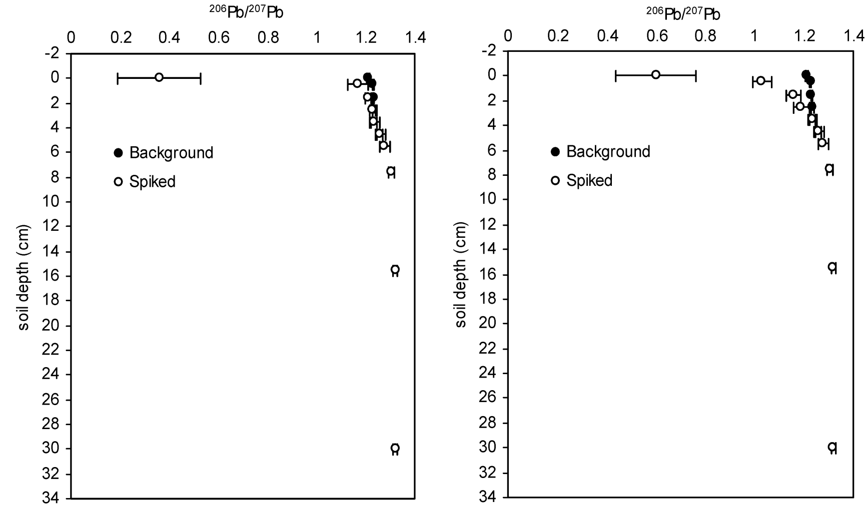


Figure 3. $^{206}Pb/^{207}Pb$ ratios in forest floor and mineral soil samples from ^{207}Pb treated plots located in sugar maple plots at the JMOEC. Samples were taken 3 days (left) and 1 year (right) after the tracer application ($n = 3$). Points are located at the mid point each sampling layer (1 cm layers 0–5 cm; 2.5 cm layers 5–10 cm; 10 cm layer 10–20 cm) and at 30 cm depth. All values are means ± S.D.

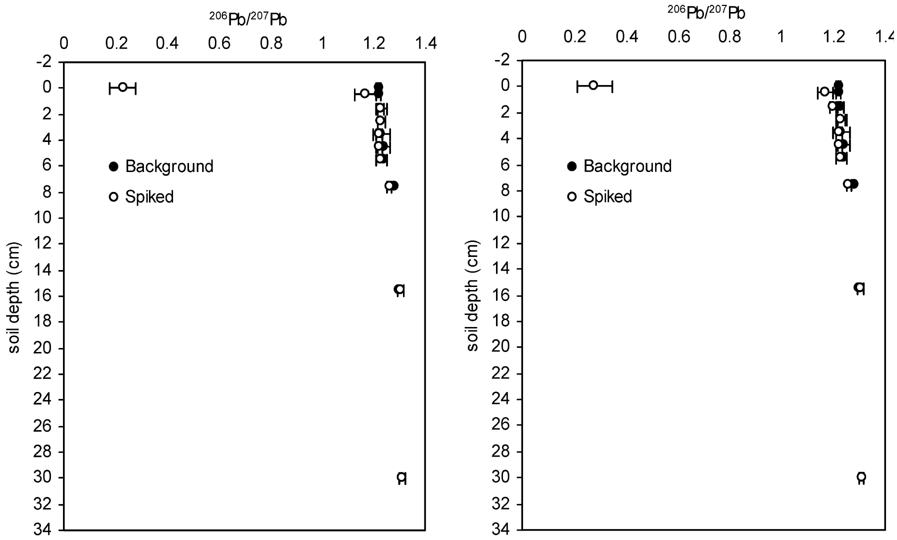


Figure 4. $^{206}Pb/^{207}Pb$ ratios in forest floor and mineral soil samples from ^{207}Pb treated plots located in white pine plots at the JMOEC. Samples were taken 3 days (left) and 1 year (right) after the tracer application ($n = 3$). Points are located at the mid point each sampling layer (1 cm layers 0–5 cm; 2.5 cm layers 5–10 cm; 10 cm layer 10–20 cm) and at 30 cm depth. All values are means ±S.D.

Table 1. Distribution of excess (spike) ^{207}Pb applied to sugar maple and white pine soil plots at the JMOEC: nominal application (8 mg m^{-2}).

	Excess ^{207}Pb in maple plots (mg m^{-2})		Excess ^{207}Pb in pine plots (mg m^{-2})	
	3 days	1 year	3 days	1 year
Forest floor	4.3	1.8	6.8	4.6
0–1 cm	2.0	4.2	1.7	2.2
1–2 cm	0.5	1.6	0	0.1
2–3 cm	0	0.7	0	0
3–4 cm	0	0	0	0
4–5 cm	0	0	0	0

No excess ^{207}Pb was detected below 5 cm depth.

85–106% of the total ^{207}Pb tracer which was applied (Table 1). The small discrepancy between recovered and applied ^{207}Pb may be due to heterogeneous distribution of excess ^{207}Pb within the plots, slight errors in mass calculation (bulk density) of the various soil horizons or retention of ^{207}Pb to the walls of the conical flask applicators.

In this study, we consider the distribution of excess ^{207}Pb after 3 days as the initial pollution Pb distribution and assume that ^{207}Pb movement in the forest floor and mineral soil behaves in an identical manner to pollution Pb thereafter. The soil tracer experiment was designed to last for 10 years and therefore the mineral soil was only sampled after 1 year (the next sampling date will be at 5 years). After 1 year, the ^{206}Pb/^{207}Pb ratio in the 0–1 cm soil horizon in the sugar maple plots had decreased from ~ 1.16 to ~ 1.02 due to the increase in excess ^{207}Pb released from the forest floor (Figure 3). ^{206}Pb/^{207}Pb ratios at 1–2 and 2–3 cm depth had also decreased after 1 year, demonstrating that excess ^{207}Pb had penetrated to at least the 2–3 cm depth after just 1 year. After 1 year, ~ 1.8 mg m^{-2} of excess ^{207}Pb was found in the forest floor, ~ 4.2 mg m^{-2} was in the 0–1 cm soil layer and ~ 1.6 mg m^{-2} was present in the 1–2 cm layer and 0.7 mg m^{-2} was present in the 2–3 cm soil layer at the sugar maple plots (Table 1). In total, 8.3 mg m^{-2} was recovered from the maple plots after 1 year. Much smaller changes in the distribution of excess ^{207}Pb occurred in the mineral soil of the white pine plots after 1-year (Figure 4). There was very little change in the ^{206}Pb/^{207}Pb ratios in the mineral soil, although the ^{206}Pb/^{207}Pb ratio at 1–2 cm depth had decreased slightly (~ 1.20 (1-year) v.s. ~ 1.22 (initial or control)). After 1 year, ~ 4.6 mg m^{-2} of excess ^{207}Pb was found in the forest floor, ~ 2.2 mg m^{-2} was in the 0–1 cm soil layer and ~ 0.1 mg m^{-2} was present in the 1–2 cm layer. In total, ~ 6.9 mg m^{-2} of excess ^{207}Pb was recovered after 1 year at the pine plots.

Uptake of excess ^{207}Pb by vegetation

As there is no well-defined humus layer in the forest floor at the JMOEC, plants roots are primarily located in the surface mineral soil horizon (Ah). In order to

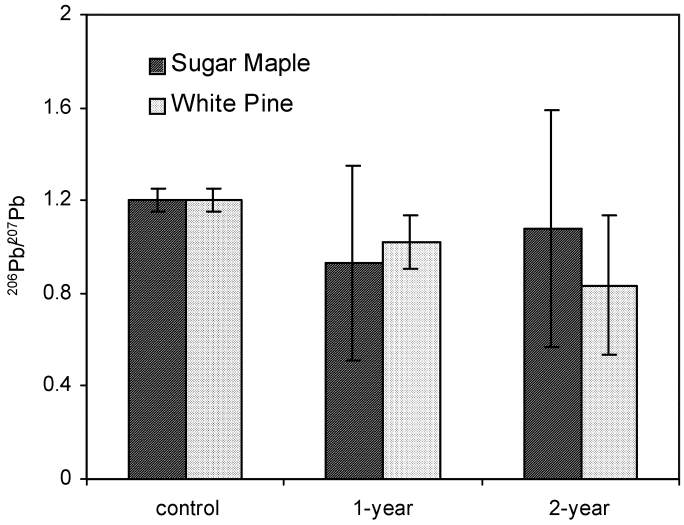


Figure 5. ^{206}Pb/^{207}Pb ratios in *V. pensylvanica* leaves sampled from ^{207}Pb treated plots located in sugar maple and white pine plots at the JMOEC. Leaves were sampled 1 year and 2 years after the tracer application ($n = 3$). ^{206}Pb/^{207}Pb ratios of leaves from control plots are also shown. All values are means ±S.D.

assess whether excess ^{207}Pb could be taken up by vegetation from mineral soil and returned to the forest floor in litter fall, violet leaf samples were collected from plants growing within the plots, 1 and 2 years following tracer application, respectively. Background ^{206}Pb/^{207}Pb ratios in violet leaves from untreated plots were consistently around 1.19 (±0.01), whereas ^{206}Pb/^{207}Pb ratios in leaf samples from treated plots were extremely variable and on average, were lower than background ^{206}Pb/^{207}Pb ratios (Figure 5). These results demonstrate that some of the excess ^{207}Pb spike has entered vegetation, although uptake of excess ^{207}Pb varied considerably between plants. For example ^{206}Pb/^{207}Pb ratios in violets collected from the maple plots after 1 year varied between 0.44 and 1.18. Similarly, ^{206}Pb/^{207}Pb ratios in plants collected from pine plots after 1 year were between 0.89 and 1.12. This variation may be due to variation in excess ^{207}Pb distribution in soil relative to the rooting zone of the plants, or reflect variations among individual plants. Even though excess ^{207}Pb was detected in violet leaves, only a small amount of excess ^{207}Pb was required to alter their ^{206}Pb/^{207}Pb ratio because of the low background Pb concentration in violets. Background Pb concentrations in violets from untreated sugar maple plots were 0.30 ± 0.11 mg kg^{-1} and were 0.41 ± 0.13 mg kg^{-1} in white pine plots. Average excess ^{207}Pb concentrations in violets in the sugar maple plots were 0.023 mg kg^{-1} (range 0.007–0.044 mg kg^{-1}) after 1 year and 0.011 mg kg^{-1} (range 0.002–0.024 mg kg^{-1}) after 2 years. Similarly, excess ^{207}Pb concentrations in violets in white pine plots were 0.008 mg kg^{-1} (range 0.002–0.017 mg kg^{-1}) after 1 year and 0.029 mg kg^{-1} (range 0.001–0.078 mg kg^{-1}) after 2 years.

A crude calculation, assuming a litter fall of $0.4\,\mathrm{kg\,m^{-2}\,year^{-1}}$, which is reasonable for northern hardwood forests (Duchesne et al. 2001), and assuming that ^{207}Pb uptake by violets is representative of uptake by maple and pine (dominant vegetation), suggests that $<0.01\,\mathrm{mg\,m^{-2}}$ of excess ^{207}Pb would be returned to the forest floor annually via litter fall. It appears therefore that the redistribution of pollution Pb by vegetation is unlikely to play a significant role in Pb dynamics of the forest floor at the JMOEC. Previous studies have similarly reported that forest vegetation is not a major component of the anthropogenic Pb budget (Friedland and Johnson 1985; Watmough and Hutchinson 2003).

Overall, results from the tracer experiment can be summarized as follows:

(a) Excess ^{207}Pb was lost rapidly from the forest floor at both sites, although excess ^{207}Pb was lost more rapidly from the forest floor at the sugar maple plots compared with the white pine plots.
(b) The majority of the excess ^{207}Pb lost from the forest floor accumulated in the upper 0–1 cm soil horizon at both sites after 1 year, although excess ^{207}Pb was detected at 2–3 cm depth in the sugar maple plots.
(c) A small amount of the tracer was taken up by vegetation, and because plant roots at the JMOEC are located primarily in the upper mineral soil horizons, some excess ^{207}Pb that is lost from the forest floor may be returned to the forest floor in litter fall. However, the redistribution of Pb by vegetation is unlikely to significantly impact Pb dynamics in this forest system.

Modeling changes in Pb dynamics at the JMOEC over the past 100 years

Pb deposition

In order to evaluate whether results from the isotope tracer experiment are reflective of Pb dynamics in the forest floor and mineral soil, data from the tracer experiment were used to model and predict Pb concentrations in the forest floor over the past 100 years.

However, in order to model temporal changes in Pb concentration in the forest floor (and mineral soil) an estimate of Pb deposition at the JMOEC over the 100-year period is required. In Europe it was reported that Pb pollution could be detected in sediment cores dating back several thousand years (Renberg et al. 2002). In eastern North America, however, Pb concentrations in lake sediment cores show little variation prior to ~1900 (Evans and Dillon 1982; Graney et al. 1995). While it is probable that some Pb pollution in the region occurred prior to this date, Pb deposition would have been low pre-1900, and would therefore have a minimal effect on our calculations. Nevertheless, in order to account for any Pb pollution occurring prior to 1900 we assumed a pre-industrial Pb deposition level of $1\,\mathrm{mg\,m^{-2}\,year^{-1}}$. Changes in Pb deposition (and emissions) in eastern North America over the past 100 years are well-described, with peak Pb deposition values

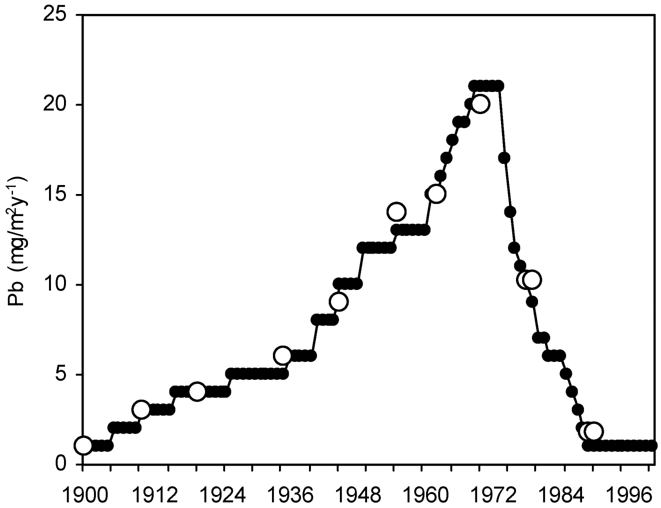


Figure 6. Estimated Pb deposition (mg m^{-2} yr^{-1}) over the past 100 years at the JMOEC. Open circles represent data used to calibrate the Pb deposition history. Lead deposition prior to 1970 was estimated from lake sediment cores in the region (Evans and Dillon 1982), and values after 1970 were obtained from published (Jeffries and Snyder 1981) and unpublished bulk deposition data.

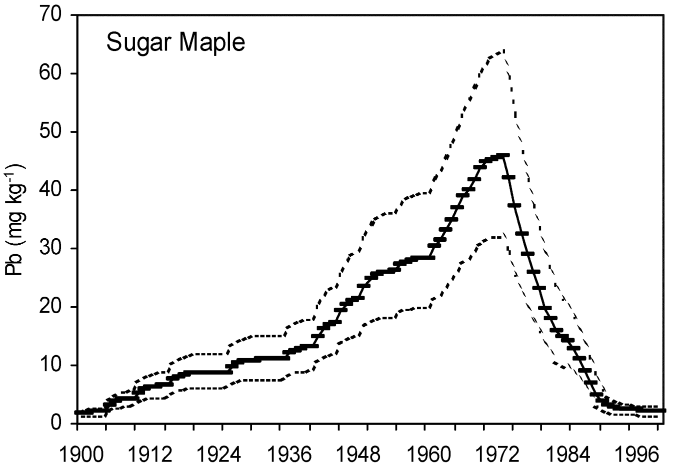
occurring in the late 1960s and early 1970s, and a sharp decline in Pb deposition thereafter (Nriagu 1990; Miller and Friedland 1994; Graney et al. 1995). Lead deposition data prior to 1980 were obtained from lake-sediment core data (Evans and Dillon 1982) and deposition data after 1980 were obtained from published (Jeffries and Snyder 1981) and unpublished bulk Pb deposition data reported for the Muskoka-Haliburton region of Ontario (Figure 6). Anthropogenic Pb burdens for lakes in Muskoka-Haliburton (610–820 mg m^{-2}; Evans and Rigler 1980; Dillon and Evans 1982) were comparable to pollution Pb burdens at the JMOEC (750–860 mg m^{-2}) estimated from changes in Pb concentration and ^{206}Pb/^{207}Pb measurements in soil and vegetation (Watmough and Hutchinson 2003). The agreement between the studies is even better when one considers that Pb deposition estimates from lake sediment are only until 1980 and based on Figure 6, approximately 60 mg m^{-2} Pb has been deposited in the region since this time. Even though the sampled lakes in Muskoka-Haliburton are ~50–70 km north of the JMOEC, close agreement in Pb burdens for the two areas was expected because 24–43% of the pollution Pb burden at Muskoka-Haliburton lakes was estimated to be a result of long-range atmospheric transport from the United States (Sturges and Barrie 1989). In the model calculations we assume that pre-industrial and current Pb deposition rates are 1 mg m^{-2} year^{-1}; which likely exceeds the present-day rate of Pb deposition at the JMOEC. The total pollution Pb deposition burden at the JMOEC over the past 100 years was estimated to be 750 mg m^{-2}, although we attribute 20% uncertainty to deposition values in the model calculations. The inclusion of uncertainty values results in a Pb deposition burden of 600–900 mg m^{-2}, which should bracket the actual Pb burden at the JMOEC (750–860 mg m^{-2}; Watmough and Hutchinson 2003). Higher Pb burdens have been reported at forests in the northeastern United States; however, these sites are often located at higher elevations (Johnson et al. 1982; Friedland and Johnson 1985; Friedland et al. 1992; Miller and Friedland 1994) or close to major industrial, or urban areas (Pouyat and McDonnell 1991).

Modeled changes in Pb concentration in the forest floor of sugar maple and white pine stands at the JMOEC

Changes in Pb concentration in sugar maple and white pine litter over the past 100 years were modeled using Equation (3), with k values obtained from the tracer experiment and Pb deposition data presented in Figure 6. Changes in Pb concentration in the forest floor at both sites were very similar, increasing gradually from a pre-industrial value of ~2.0 mg kg^{-1} to ~15 mg kg^{-1} by 1940 (Figure 7). After 1940, model predictions indicate that Pb concentrations in the forest floor increased more rapidly, reaching a peak concentration of ~45–60 mg kg^{-1} in the early 1970s. Lead concentrations in the forest floor decreased rapidly during the 1970s and 1980s, and then more gradually during the 1990s reaching ~2.0 mg kg^{-1} by 2000. In effect, because of the high k values, changes in Pb concentration in the forest floor at the JMOEC closely mirror temporal changes in Pb deposition. As a result, response times for Pb in the forest floor at the JMOEC are extremely short; 1.8 years for the sugar maple plots and 3.1 years for the white pine plots. These response times are shorter than previously published rates of Pb loss, although the majority of earlier studies were conducted at sites with mor-type forest floors that are characterized by a thick humus layer and have relatively slow rates of organic matter turnover (Friedland et al. 1992; Miller and Friedland 1994). For example, Miller and Friedland (1994) report response times of Pb in the forest floor of 12.7 years in a northern hardwood forest and 77.0 years in a spruce–fir forest in northern New England.

Our model predictions were based on estimated changes in bulk deposition and do not include Pb that is returned to the forest floor in litter fall following uptake from the mineral soil. However, Pb concentrations in sugar maple and white pine foliage are low (~0.3 mg kg^{-1}), and even assuming that foliar Pb was entirely pollution-derived and was accumulated in plants through soil uptake rather than adsorption to leaf surfaces, pollution Pb inputs to the forest floor through litter fall are low (~0.12 mg m^{-2} year^{-1} assuming litter fall to be 0.4 kg m^{-2} year^{-1}), and should have a minimal influence on our calculations. Results of the isotope tracer experiment indicated a similar conclusion; redistribution of pollution Pb from the mineral soil to the forest floor in litter fall was considered to be minimal.

Model predictions of current Pb concentrations in the forest floor (~2.2–3.3 mg kg^{-1}), are much lower than measured Pb concentrations (~9.4 mg kg^{-1}) (Table 2). However, both %LOI values (65–70%) and ^{206}Pb/^{207}Pb ratios (~1.21) in the forest floor indicate that some mineral soil was present in the forest floor



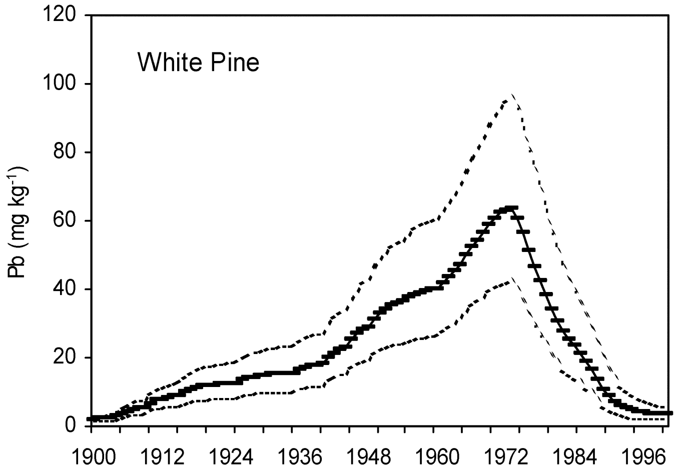


Figure 7. Predicted forest floor Pb concentration (mg kg^{-1}) in sugar maple (upper) and white pine (lower) plots at the JMOEC over the past 100 years. Dashed lines represent values obtained assuming 20% uncertainty in Pb deposition values and error associated with *k* values obtained from the tracer experiment. Upper dashed line is the predicted Pb concentration in the forest floor assuming maximum Pb deposition and lowest *k* value and lower dashed line is obtained from lowest deposition estimate combined with highest *k* value.

samples. Some mineral soil contamination in forest floor samples is unavoidable, particularly at the JMOEC where the forest floor is extremely shallow (~1.5–2 cm). However, the amount of contamination by mineral soil can be estimated using differences in ^{206}Pb/^{207}Pb ratios among the forest floor, surface soil (0–1 cm), vegetation and atmospheric deposition. The ^{206}Pb/^{207}Pb ratio in vegetation at the JMOEC averages ~1.19 (Watmough and Hutchinson 2003) whereas the

^{206}Pb/^{207}Pb ratio in surface (0–1 cm) soil is ~1.23. If Pb in the forest floor is derived solely from vegetation and surface soil, a simple mixing equation indicates that approximately 54% (maple) and 62% (pine) of Pb in the forest floor is from mineral soil (Table 2). This would mean that the actual Pb concentration in a 'pure' sample of the forest floor (which represents the modeled Pb concentration in the forest floor) would be 4.3 and 3.6 mg kg^{-1} in the maple and pine stands, respectively. Similarly, if Pb in the forest floor is derived entirely from deposition (assuming a ^{206}Pb/^{207}Pb ratio of 1.18 for deposition, estimated from lichen measurements and published deposition data; see Watmough and Hutchinson 2003) plus surface soil, Pb concentrations of 'pure' forest floor samples would be 3.1 and 2.6 mg kg^{-1} in the maple and pine stands, respectively. As Pb in the forest floor is derived from all three sources, data suggest that Pb concentrations in 'pure' forest floor samples should be between 3.1 and 4.3 mg kg^{-1} in the maple stand and between 2.6 and 3.6 mg kg^{-1} in the pine stand. These values are in close agreement with model predictions of 1.5–3.1 mg kg^{-1} for the maple stand and 2.1–5.8 mg kg^{-1} for the pine stand (Table 2). Similar values are obtained if the calculation is done using %LOI values and assuming that the ash content of a pure organic sample is 10%. This would mean that 20–25% of Pb in forest floor samples was due to mineral soil contamination, and since mineral soil (0–1 cm) has a Pb concentration of 22–24 mg kg^{-1}, approximately 4.4–6 mg kg^{-1} of forest floor Pb is of mineral soil origin.

Predicting Pb movement in the mineral soil

The close agreement between predicted and observed Pb concentrations in the forest floor at the JMOEC provides some confidence in the model prediction of rapid loss of pollution Pb from the forest floor. Importantly, this means that annual inputs of pollution Pb to the upper mineral soil (0–1 cm) can be equally well-predicted, using the simple formula$\mathrm{Pb}_{\mathrm{input}}\mathrm{year} = \mathrm{Pb}_{\mathrm{deposition}} - \mathrm{Pb}_{\mathrm{change}}\mathrm{FF}$,where $\mathrm{Pb}_{\mathrm{input}}$year is the annual input of pollution Pb to the surface mineral soil, $\mathrm{Pb}_{\mathrm{deposition}}$ is the Pb input in deposition and $\mathrm{Pb}_{\mathrm{change}}$FF is the change in forest floor Pb content from the preceding year. All units are mg m^{-2} year^{-1}. Inputs of Pb to the mineral soil closely resemble inputs to the forest floor at both the sugar maple and white pine sites because of the short residence time of Pb in the forest floor (Figure 8). Inputs of pollution Pb at both sites peaked at ~20 mg m^{-2} year^{-1} in the early 1970s and then decreased rapidly thereafter. The model indicates that virtually all of the pollution Pb (>99%) deposited at the JMOEC over the past 100 years has moved from the forest floor to the mineral soil. This prediction is consistent with measurements by Watmough and Hutchinson (2003) who reported that over 97% of the pollution Pb at the JMOEC was found in the mineral soil, with the majority, >85%, occurring in the upper (0–10 cm) horizon.

Despite the relatively rapid transfer of Pb from the forest floor, the highest Pb concentrations are found in the uppermost layer of the mineral soil layer (0–1 cm). In addition, Pb concentrations decrease with depth, and are strongly correlated

Table 2. Measured and predicted Pb concentrations in the forest floor at the JMOEC.

			^{206}Pb/^{207}Pb					
	Pb$_{\mathrm{meas}}$ (mg kg^{-1})	Pb$_{\mathrm{pred}}$ (mg kg^{-1})	FF[1]	Veg[2]	Soil[3]	%soil Pb$_{\mathrm{v}}$[4]	%soil Pb$_{\mathrm{d}}$[5]	FF Pb −soil Pb[6] (mg kg^{-1})
Maple	9.4 (5.4)	2.2 (1.5–3.1)	1.212	1.193	1.228	54	67	3.1–4.3
Pine	9.4 (2.3)	3.3 (2.1–5.8)	1.216	1.193	1.230	62	72	2.6–3.6

[1] ^{206}Pb/^{207}Pb ratio in the forest floor (FF).

[2] ^{206}Pb/^{207}Pb ratio in vegetation (Veg) (Watmough and Hutchinson 2003).

[3] ^{206}Pb/^{207}Pb ratio in surface (0–1 cm soil) (Soil).

[4] % contribution of soil Pb to total forest floor Pb assuming the two mixing members are soil and vegetation.

[5] % contribution of soil Pb to total forest floor Pb assuming the two mixing members are soil and atmospheric deposition (^{206}Pb/^{207}Pb = 1.18).

[6] Pb concentration in forest floor if Pb contamination from surface soil is removed.

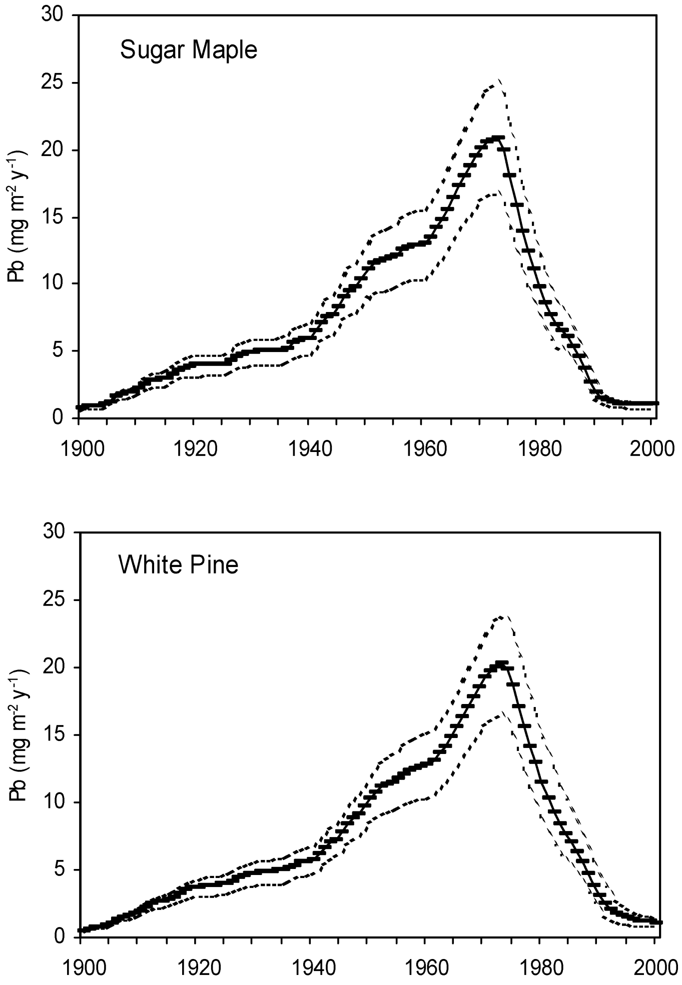


Figure 8. Predicted annual Pb input (mg m^{-2} yr^{-1}) to the mineral soil in the sugar maple (upper) and white pine (lower) plots at the JMOEC over the past 100 years. Dashed lines represent values obtained assuming 20% uncertainty in Pb deposition values and error associated with *k* values obtained from the tracer experiment (see Figure 7).

($r^2 = 0.94$–0.96) with the distribution of organic matter at both the maple and pine plots (Figure 9). The distribution of Pb with depth which was observed at the JMOEC is inconsistent with the assumption that Pb moves as a pulse down the soil profile, because inputs of pollution Pb to the mineral soil peaked around 25 years ago (Figure 7). Previous studies have suggested that Pb movement in mineral soil could occur at rates varying from 0.39 to 19.7 mm year^{-1}, depending on soil type and depth (Dorr and Munnich 1991; Miller and Friedland 1994; Erel et al. 1997). If the minimum rate of 0.39 mm yr^{-1} is applied at the JMOEC, Pb concentrations in

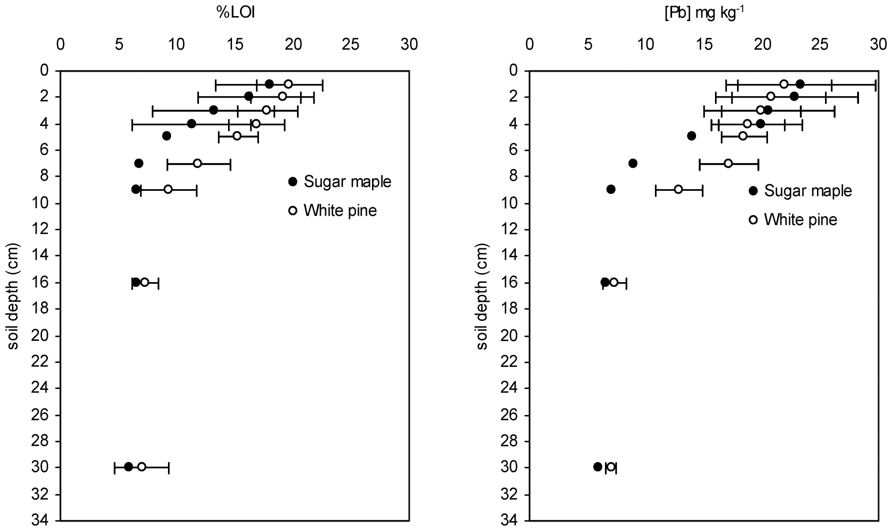


Figure 9. Loss on ignition (left) and Pb concentrations (right) in mineral soil in sugar maple and white pine plots at the JMOEC.

mineral soil should be very low in the upper (0–1 cm) soil horizon, peak at 1 cm depth (1–2 cm in this study), and virtually all of the pollution Pb burden should be present in the upper 3 cm. Clearly, this rate is inconsistent with the observed distribution of Pb at the JMOEC. Conversely, if a higher transport rate is applied, the maximum Pb concentration in mineral soil should occur at a much greater depth, which is also unrealistic.

Although the distribution of Pb in soil at the JMOEC cannot be explained by assuming that Pb moves as a pulse down the soil profile, the distribution of Pb in mineral soil could be explained if Pb moves down the profile, from layer to layer, using a series of first order rate constants. At a heavily contaminated site in England, for example, Martin and Coughtrey (1987), predicted the movement of Pb down the soil profile using a series of first order rate constants assuming that Pb moved from soil layer to soil layer in 1 cm increments. In their study, the rate of Pb migration down the soil profile was between 0.15 and 0.62 mm year^{-1} for 1 cm layers in the upper 10 cm of the mineral soil (Martin and Coughtrey 1987). At the JMOEC, the measured Pb content in the 0–1 cm layer could be explained assuming *k* values for this soil layer of 0.05 and 0.056 at the sugar maple and white pine sites, respectively. Different *k* values would be obtained for each subsequent soil horizon. However, this would mean that the response time for Pb in the 0–1 cm mineral soil layer is 20 years at the sugar maple site and 17.9 years at the white pine site. In contrast, just 1 year following tracer application, 9% of applied ^{207}Pb was detected in the 2–3 cm soil horizon at the maple stand in the JMOEC, indicating that Pb movement down the soil profile is more rapid than indicated by the aforementioned *k* value.

An alternate explanation for the movement and distribution of pollution Pb in surface mineral soil at the JMOEC is that Pb is tightly bound to organic matter and is therefore subject to mixing by biological activity in surface soil. This mechanism could explain both the current distribution of pollution Pb at the JMOEC and the movement of ^{207}Pb down the soil profile. Of course Pb dynamics will not be identical in all soil types. Wang and Benoit (1996) for example indicated that Pb movement in acidic podzols was characterized by a relatively slow release of pollution Pb from the forest floor (compared with this study), followed by rapid transport in colloidal and dissolved forms to the B-horizon where Pb is effectively retained.

Comparison of the JMOEC with other forested sites in eastern North America and central Ontario

The rate of Pb loss from the forest floor indicated in this study is far greater than any previously reported study in forest ecosystems (Martin and Coughtrey 1987; Miller and Friedland 1994; Johnson et al. 1995). As a consequence, Pb concentrations in the forest floor at other sites in eastern North America are generally much higher than values found at the JMOEC (Friedland and Johnson 1985; Friedland et al. 1992; Johnson et al. 1995). For example, Friedland et al. (1992) reported that the mean Pb concentration and Pb burden in the forest floor in 1980 at a number of sites in the eastern United States was $148\,\mathrm{mg\,kg^{-1}}$ and $1009\,\mathrm{mg\,m^{-2}}$, respectively, although the Pb content of the forest floor decreased by $\sim 11\%$ between 1980 and 1990. We believe that the relatively rapid loss of Pb from the forest floor at the JMOEC is due to the rapid breakdown of litter, which is typical of a mull-type forest floor.

In order to place the results for the JMOEC in context with other sites in south-central Ontario (and eastern North America), we measured Pb concentrations in the forest floor and foliage at 23 sites (11 sugar maple; 12 white pine) which represented a broad range of soil pH. Lead concentrations in the forest floor were between ~ 5 and $\sim 82\,\mathrm{mg\,kg^{-1}}$ (Figure 10). There was no difference in Pb concentrations between white pine and sugar maple stands, although Pb concentrations in the forest floor increased exponentially ($r^2 = 0.68$; $p < 0.001$) with decreasing soil pH (Figure 10). A similar relationship was reported for forest plantation stands in Scotland, and is probably due to the slower turnover of litter in more acidic soils (Billet et al. 1991). In the present survey, the pH gradient corresponds to a transition from mull to mor-type forest floors and at the most acidic sites, Pb concentrations in the forest floor were more comparable to previous values reported in eastern North America (Friedland et al. 1992; Johnson et al. 1995).

At one of the survey sites (PC1), the forest floor was re-sampled at 15 adjacent pits in 1983 and 1999 (Figure 11; Watmough and Dillon 2003). Over this 17-year period, the average Pb concentration in the forest floor decreased from 104 to $79\,\mathrm{mg\,kg^{-1}}$. Using deposition data presented earlier, a k value of 0.05 reasonably predicts the change in Pb concentration in the forest floor over the 17-year period (Figure 11). A k value of 0.05 corresponds to a Pb residence time of around 20

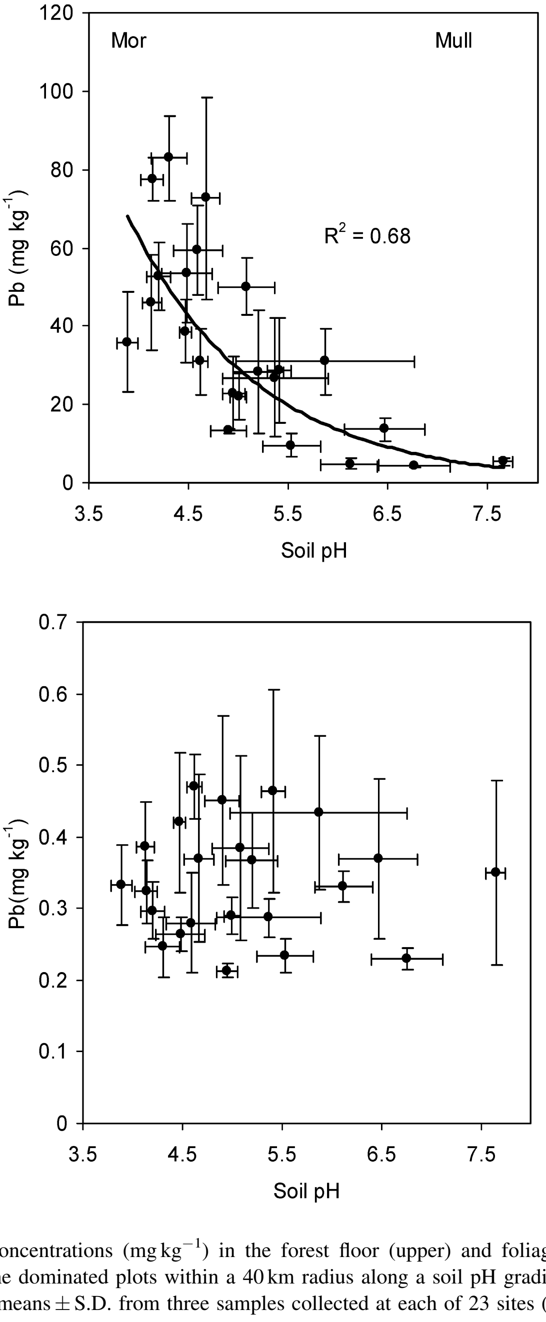


Figure 10. Lead concentrations (mg kg^{-1}) in the forest floor (upper) and foliage (lower) of sugar maple and white pine dominated plots within a 40 km radius along a soil pH gradient in south-central Ontario. Values are means ± S.D. from three samples collected at each of 23 sites (11 sugar maple; 12 white pine).

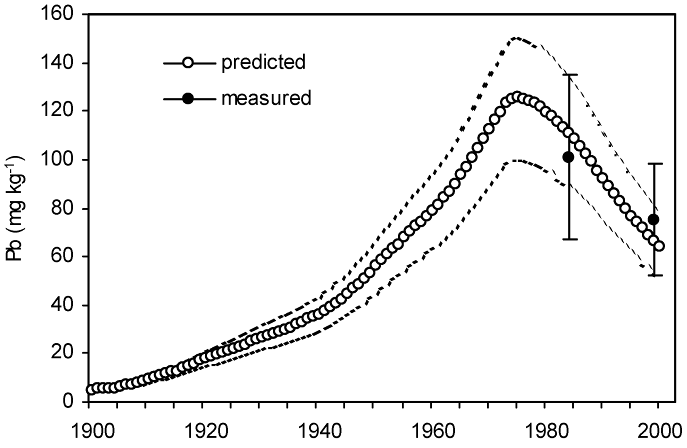


Figure 11. Predicted Pb concentration (mg kg^{-1}) in the forest floor at PC1 in south-central Ontario. Solid circles represent measured Pb concentrations in 1983 and 1999. Values are means ± S.D ($n = 15$). Dashed lines represent values obtained assuming 20% uncertainty in Pb deposition values.

years and compares favorably with values reported by Miller and Friedland (1994) for forests in Vermont. There is some uncertainty associated with this k value at PC1, although it is clear that it must be considerably lower than k values at the JMOEC. The model predicts that a maximum Pb concentration of 120 mg kg^{-1} would have occurred in the forest floor at PC1 in the early 1970s. A further point to note is that the mass of the forest floor at acidic sites (with mor-type forest floors) is much greater than at the JMOEC. Even without correcting for mineral soil contamination, pollution Pb burdens in the forest floor at PC1 are ~25 times greater (~250 mg m^{-2}) than Pb burdens at the JMOEC (~10 mg m^{-2}). If corrections for mineral soil are applied, the difference between the two sites is even greater (~100 times) because the correction would decrease the Pb concentration in the forest floor at the JMOEC and increase the concentration at PC1 (mineral soil Pb concentration at PC1 is only ~20 mg kg^{-1}). There was no relationship between Pb concentrations in the forest floor and foliar Pb levels, and there was no difference in Pb concentrations between pine needles and maple leaves. This demonstrates that higher Pb concentrations in the forest floor are not reflected in foliar Pb concentrations supporting the argument that recycling of Pb by trees will have only a minor influence on Pb concentrations in the forest floor.

In this study we have assumed that changes in Pb concentration in the forest floor can be described as a linear first-order rate process for a single reservoir system (Martin and Coughtrey 1987; Miller and Friedland 1994). This may not be applicable if conditions in the forest floor have changed significantly over time, affecting the rate of litter decomposition and/or Pb leaching from the forest floor. Factors that may affect Pb movement from the forest floor either directly or indirectly include high Pb concentration, pH, temperature and N deposition. High Pb concentrations may inhibit microbial activity in the forest floor, although significant effects have only been reported at extreme Pb concentrations. Bringmark and Bringmark (2001) for example, reported a 10% reduction in soil respiration in forest floor samples containing 225–245 mg kg^{-1} Pb. Based on model predictions, it is unlikely that Pb concentrations in the forest floor at the JMOEC were ever high enough to inhibit microbial activity; although Pb concentrations at the more acidic sites of the survey would have been higher ($\sim$120 mg kg^{-1}), particularly during the period of peak Pb deposition. Even so, maximum predicted Pb concentrations at the acidic survey sites are still lower than levels reported to be inhibitory to microbial activity at other sites in eastern North America (Friedland et al. 1986).

Johnson et al. (1995) reported that changes in Pb content in the forest floor at Hubbard Brook could not be explained by a single value of k, and suggested that the recent rapid loss of Pb from the forest floor greatly exceeded model predictions. They argued that other factors such as changes in acid deposition altered Pb dynamics in the forest floor, making the use of a linear model with a single k value invalid. It is unlikely that decreasing pH of precipitation would affect Pb losses from the forest floor at the JMOEC, because the site overlies limestone and is well-buffered to acid deposition. Changes in forest floor pH may have occurred at the more acidic survey sites that overlay the Precambrian Shield; although it is unclear whether any such changes would be sufficient to significantly alter Pb mobility in the forest floor. Nevertheless, the potential impact of acid deposition and other factors such as N deposition and temperature should be considered when interpreting the model results from this study. For example, both increased N deposition and higher temperatures (or precipitation) could alter rates of litter decomposition (Berg et al. 1993; Berg and Matzner 1997) and consequently affect Pb dynamics in the forest floor. However, it remains to be established whether changes in N deposition, Pb concentration, pH and temperature over the past 100 years have significantly altered Pb dynamics in forest soil.

Conclusions

Excess ^{207}Pb applied as a tracer to the forest floor in a white pine and sugar maple stand in south-central Ontario was rapidly lost from the mull-type forest floor. Applying first-order rate coefficients (k) of 0.57 (maple) and 0.32 (pine) obtained from the tracer study, and using estimates of Pb deposition in the region, current predicted Pb concentrations in the forest floor were 1.5–3.1 and 2.1–5.8 mg kg^{-1} in the maple and pine plots, respectively. These values compare favorably with measured concentrations (corrected for mineral soil contamination) of 3.1–4.3 and 2.6–3.6 mg kg^{-1} in the maple and pine stands respectively. The rapid loss of Pb from the forest floor at the JMOEC is much greater than previously reported studies and is probably due to the rapid rate of litter turnover that is characteristic of mull forests. In a survey of 23 sites in south-central Ontario, Pb concentrations in the forest floor increased exponentially as soil pH decreased and as sites graded from mull-type to mor-type forest floors despite receiving similar levels of Pb deposition. Lead concentrations in the forest floor at the most acidic sites we surveyed were approximately 10 times greater ($\sim 80\,\mathrm{mg\,kg^{-1}}$) than at the JMOEC and pollution Pb burdens are up to 25 times greater than at the JMOEC. The difference is even larger (~ 100 times) if Pb burdens in the forest floor are corrected for mineral soil contamination. Despite the rapid loss of Pb from the forest floor at the JMOEC, maximum pollution Pb concentrations were detected in the upper (0–1 cm) mineral soil horizon. Lead concentrations in the upper 30 cm of the mineral soil were strongly correlated with the distribution of soil organic matter. This demonstrates that pollution Pb does not move as a single pulse down the soil profile and contamination of groundwater at the JMOEC by the large input of pollution Pb between 1950 and the mid-1970s is unlikely.

Acknowledgements

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