

# Lead biogeochemistry in a central Ontario Forested watershed

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**Abstract** To determine the sources and sinks of atmospherically deposited Pb at a forested watershed (Plastic Lake) in central Ontario, Canada, Pb pools and fluxes through upland, wetland and lake compartments were measured during 2002/2003 and compared with previous measurements taken between 1989 and 1991. In 2002/2003, annual bulk deposition of Pb was  $0.49 \text{ mg m}^{-2}$  compared with  $1.90\text{--}1.30 \text{ mg m}^{-2}$  in 1989–1991. Annual Pb concentrations in stream water draining the upland part of the catchment were very low ( $0.04 \text{ } \mu\text{g l}^{-1}$ ) and were approximately half those measured in 1989–1991 ( $0.11\text{--}0.08 \text{ } \mu\text{g l}^{-1}$ ). Leaching losses in stream water were small and mass balance estimates indicate almost complete retention (>95%) of atmospherically deposited Pb in upland soils. In contrast, annual Pb concentrations in stream water draining a wetland were between  $0.38$  and  $0.77 \text{ } \mu\text{g l}^{-1}$ , with the highest concentration occurring in 2002/2003 and mass balance calculations indicate that the wetland is a net source of Pb in all measured years. Lead concentrations in the lake outflow were low and the average Pb concentration measured in 2002/2003 ( $0.09 \text{ } \mu\text{g l}^{-1}$ ) was approximately half the value recorded in 1989–

1991 ( $0.19 \text{ } \mu\text{g l}^{-1}$  both years). Annual mass balance estimates indicate that the lake retained between  $2.47 \text{ mg m}^{-2}$  (1989/1990) and  $1.42 \text{ mg m}^{-2}$  (2002/2003) and that in 2002/2003 68% of the Pb input to the lake is derived from the terrestrial catchment. These estimates are higher than sediment core records, which indicate around  $18 \text{ mg m}^{-2}$  Pb was retained in sediment during the 1990s. Nevertheless, Pb concentrations decrease with sediment depth and  $^{206}\text{Pb}/^{207}\text{Pb}$  concentrations increase with depth, a pattern also observed in mineral soils that reflects the substantial contribution of anthropogenic Pb to the watershed. Lead isotope data from soil and sediment indicate a recent anthropogenic Pb signal ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.185$ ) in upper soils and sediments and an older anthropogenic signal ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.20$ ) in deeper soil and sediment. Lead isotope data in sediment and vegetation indicate that practically all the Pb cycled in the forest at Plastic Lake is anthropogenic in origin.

**Keywords** Lead · Forest · Wetland · Lakes · Isotopes

## Introduction

The release of Pb into the environment caused the atmospheric concentration, long-range transport and atmospheric Pb deposition to increase by several

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orders of magnitude during the 20th century (Nriagu 1990). Lead, released from human activities, has been deposited to practically all parts of the globe and there are numerous reports of high Pb concentrations in remote locations in North America and Europe. Despite the well-documented decrease in Pb deposition in North America in recent decades, concern remains that the industrial burden of Pb may pose a risk to biota, particularly if transfer to surface waters occurs (Miller and Friedland 1994), and consequently enhancing our understanding of Pb biogeochemistry in forested watersheds is of considerable importance.

Many studies have reported on various aspects of Pb biogeochemistry in forested watersheds, and while some aspects of Pb biogeochemistry are becoming well established, other areas remain controversial. For example, Pb was originally expected to remain tightly bound to surface organic horizons, but recent reports indicate that the release of Pb from the forest floor and the mobility of Pb in soils may be faster than originally thought (Herrick and Friedland 1990; Miller and Friedland 1994; Watmough et al. 2004). Most studies agree that Pb is tightly retained in mineral soils, although the extent of downward movement of anthropogenic Pb is more debatable (Bindler et al. 1999; Erel 1998; Ettler et al. 2004; Wang and Benoit 1997; Watmough and Hutchinson 2004; Watmough et al. 2004). Dissolved organic carbon (DOC) is also known to play a major role in the transport of Pb through watersheds (LaZerte et al. 1989) although inorganic phases may also be important (Kaste et al. 2005). Quantifying natural Pb inputs to the Pb biogeochemical cycle through mineral weathering has proved problematic. Weathering inputs of Pb are considered low relative to inputs from deposition, although as Pb deposition declines the relative importance of Pb weathering may increase (Johnson et al. 2004; Starr et al. 2003). Organic soils are traditionally thought of as sinks for Pb (Vile et al. 1999) although Tipping et al. (2003) demonstrated that net release from organic soils may occur under certain climatic conditions. Lake sediments have been used to reconstruct historical Pb deposition under the assumption that Pb is relatively immobile in lake sediments (Brannvall et al. 2001a, b; Renberg et al. 1994; Siver and Wozniak 2001) although this assumption also remains controversial (White and Driscoll 1985).

Our understanding of Pb biogeochemistry has been greatly enhanced in recent decades by the use of stable Pb isotopes. Lead exhibits large natural variations in the proportions of its stable isotopes (atomic masses 204, 206, 207 and 208), which are related to the radiogenic ontogenies of the latter three isotopes. Different rock formations and Pb ore deposits thus contain Pb with characteristic isotopic ratios (Sangster et al. 2000). Numerous studies have used stable Pb isotopes to estimate the relative contribution of anthropogenic sources to Pb accumulated in lake sediment cores, aerosols, snow, vegetation, soils and lichen (Blais 1996; Carignan and Gariépy 1995; Ettler et al. 2004; Flegal et al. 1989; Gallon et al. 2005; Simonetti et al. 2000; Sturges and Barrie 1989; Watmough and Hutchinson 2004). In general, isotopic data indicate that the biogeochemical Pb cycle is dominated by anthropogenic Pb inputs.

In this study the biogeochemistry of Pb is examined in detail at the Plastic Lake watershed in central Ontario. Lead cycling in the upland forest, a conifer-*Sphagnum* swamp and the lake are considered separately and in combination and Pb isotopes are used to determine the relative importance of anthropogenic Pb compared with natural Pb to total Pb burdens. Lead concentrations and cycling measured during 2002/2003 are also compared with data collected between 1989 and 1991 to determine whether notable differences in Pb cycling have occurred between the two time periods. The goals of this study are to test the hypotheses that (a) upland, organic soils and lake sediment are sinks for atmospherically-deposited Pb; (b) weathering inputs of Pb are negligible and (c) the majority of Pb cycled within the watershed is anthropogenic in origin and is strongly associated with DOC.

## Materials and methods

### Study site

Plastic Lake is located in Haliburton County on a southern extension of the Precambrian Shield in south-central Ontario, Canada (45°11'N, 78°50'W), and is typical of acid-sensitive lakes in this region. The 32 ha headwater lake is fed by one major stream

Plastic Lake-1 (PC1) and 6 ephemeral streams, which together drain an area of approximately 90 ha. PC1 is the largest sub-catchment (23.3 ha) in the watershed, and is characterized by thin (average depth 0.37 m to bedrock) orthic humo-ferric and ferro-humic podzols, formed from thin, sandy basal tills. The forest at Plastic Lake is dominated by white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*), red oak (*Quercus rubra*), and red maple (*Acer rubrum*) in the upland areas, and by white cedar (*Thuja occidentalis*) and black spruce (*Picea mariana*) in the swamp. A 2.2 ha conifer-*Sphagnum* swamp is located approximately 50 m above the catchment outflow in PC1 and more than 85% of the runoff from the Plastic Lake catchment drains through the swamp before discharging to the lake (Fig. 1). A short (<250 m) ephemeral stream (PC1-08) drains the northeastern upland part of PC1 before discharging into the swamp.

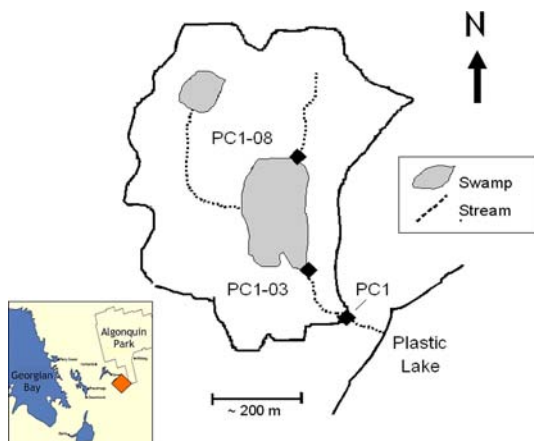
#### Sampling – 2002/2003

Deposition data were obtained from collections of bulk deposition ( $0.25 \text{ m}^2$ ) and samples were removed from collectors when there was sufficient volume for chemical analysis, typically weekly. Between September 1 2002 and August 31 2003, litterfall was collected 5 times at 20 ( $0.5 \text{ m} \times 0.5 \text{ m}$ ) litterfall collectors placed randomly throughout PC1-

08 and throughfall was collected (usually biweekly) from 20 throughfall collectors (8 cm diameter funnel with  $80 \mu\text{m}$  Nitex mesh) co-located with the litterfall collectors. Each litterfall collection was separated into foliar tissue, woody tissue and reproductive (seed, flowers) tissue for chemical analysis. Water level or stage at PC1, PC1-08 (upland outflow) and PC0 (lake outflow) was recorded continuously at weirs installed at each outflow, and daily stream discharge ( $\text{m}^3/\text{day}$ ) was computed using established stage-discharge relationships for all outflows. Flow at PC1-03 (immediately draining the wetland) was estimated from flow recorded at PC1 prorated to the discharge area. Water samples for chemical analyses were collected at the weir at regular intervals (at least biweekly) when there was flow, although sampling was more frequent during the spring melt period. Periodic comparisons were made between filtered ( $0.45 \mu\text{m}$ ) and 'coarse filtered' ( $80 \mu\text{m}$  only) stream samples collected during 2002/2003. Lead concentrations were generally comparable although coarse filtered samples tended to be slightly higher. Water samples were also collected at monthly intervals from the epilimnion, metalimnion and hypolimnion of Plastic Lake between June and October 2003. Samples were collected from the mid-point of each 2 m stratum and combined in proportion to the volume of that stratum, yielding volume-weighted samples for each of the 3 thermal zones. The measured concentrations in these 3 layers were then combined in proportion to the volume of each layer to yield a volume-weighted lake concentration for the summer of 2003. Lead concentrations were also analyzed in soil leachate from beneath the LFH and A-Horizon (Canadian Soil System of Classification 1998) using 6 zero tension lysimeters that had been installed in the upland part of the catchment in 1987. Samples were usually collected at the same time that stream water samples were obtained.

#### Sampling – 1989–1991

Lead concentrations were determined in bulk precipitation, PC1, PC1-08, PC1-03, PC0, LFH and A-horizon samples between 1989 and 1991 (LaZerte et al. 1989) using the same sampling procedures, approximate sample frequency and stream-discharge relationships used in 2002/03.



**Fig. 1** Map of the PC1 subcatchment showing stream sample collection sites at the outlet of the subcatchment (PC1), the outlet of the PC1 wetland (PC1-03), and the outlet of a representative upland area (PC1-08)

## Lake sediment

Sediment core samples were collected in 2002 from the deepest basin of the lake (16 m) using a Glew gravity corer. The core was sectioned into 0.3 cm intervals. The top 38 cm of the core was analyzed for Pb. After collection, samples were dried in an oven at 40°C. The top 18 cm of the core was dated using  $^{210}\text{Pb}$  based on the constant rate of supply (CRS) model which corresponds to the years 1840–1995. Although  $^{137}\text{Cs}$  was also measured in an attempt to validate  $^{210}\text{Pb}$  dates using  $^{137}\text{Cs}$  peaks in the 1960s (atmospheric thermonuclear tests) and 1986 (Chernobyl accident), the data fail to show clear peaks at the corresponding depths. Previous studies have shown that Cs may be mobile during sediment diagenesis and thus may not be a reliable tracer (Pinglot and Porchet 1995). Sediment accumulation rates were determined by combining measurements of Pb concentration with mass of sediment (per unit area) and correcting for sediment focusing using a previously established relationship for Plastic Lake (Dillon and Evans 1982). Details of chronology for the Plastic lake sediments can be found in Eimers et al. (2006).

## Pb pools and Pb weathering estimates

Lead pools in mineral soil were determined by horizon by combining estimates of soil mass (bulk density  $\times$  depth) and Pb concentration at 16 soil pits dug around the upland part of the catchment in 1999 (Watmough and Dillon 2004). Lead pools in the wetland were similarly obtained at 10 pits with samples collected from the OF, OM and OH horizons in each pit (Canadian System of Soil Classification 1998). Lead pools in forest biomass at Plastic Lake were estimated by combining estimates of forest biomass and Pb concentrations in tree parts (bark, wood, roots, stems, leaves) using methods described by Watmough and Dillon (2004). Litterfall inputs were determined by combining litterfall mass (foliage, wood, reproductive tissue) and lead concentration for each sample. Weathering rates for Pb were estimated using methodology adopted from European critical load protocols for heavy metals (Posch et al. 2001). In addition, for comparison, estimates of Pb weathering were obtained from Hendershot (*pers com.*) who determined mineral weathering rates based on laboratory analyses of C-horizon soil mineralogy.

## Chemical analyses

### 1989–1991

Between 1989 and 1991 Pb concentrations in water samples were determined using a Metrohm hanging mercury drop anodic stripping voltammeter (DPASV) using an E.G. and G. Rotel rotating glass carbon electrode (LaZerte et al. 1989). All DPASV calibrations were by standard addition. Detection limits for Pb were  $0.03 \mu\text{g l}^{-1}$ , although no samples measured between 1989 and 1991 were below the detection limit.

### 2002–2003

Soil, sediment, vegetation 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 deionized water, oven dried (65°C) for at least 72 h and ground prior to analysis. Sediment samples ( $\sim 50$  mg) were digested under reflux in 50%  $\text{HNO}_3$  at 100°C for 8 h. Vegetation and forest floor samples (0.2 g) were cold-digested in 2.5 ml trace grade  $\text{HNO}_3$  overnight and then digested under reflux at 100°C for 8 h. Soil samples were similarly cold-digested overnight in 2.5 ml  $\text{HNO}_3\text{:H}_2\text{SO}_4$  (2:1 molar ratio) and then digested under reflux at 100°C for 8 h. In addition soil samples were also digested using hydrofluoric acid (HF) although isotopic analysis was not conducted on these samples. All samples were diluted to 25 ml and filtered through Whatman No. 42 filter paper prior to analysis by ICP-MS. This analytical method used for water samples is different to that employed in 1989/1990 and we have no way to compare samples. However, during both periods reference standards were routinely run and Pb concentrations in all water samples were well above analytical detection limits so we are confident that differences in Pb concentration in precipitation, stream and lake samples are not due to different analytical procedures. Other chemical parameters (pH,  $\text{SO}_4$ , DOC etc.) were analysed in all water samples using methods described by the Ontario Ministry of Environment (1983).

## Pb isotopes

Lead concentrations and isotope ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$ ) in samples (2%  $\text{HNO}_3$ ) were measured using a Finnigan Element 2 high resolution single collector ICP-MS. For isotope ratio measurement, instrumental mass bias was corrected using Tl external isotopic standard. Based on repeated analyses of NIST-981, the precision of  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  measurements was estimated to be 0.05% and 0.1%, respectively. This precision, although not as high as those achievable by MC-ICP-MS or TIMS, is sufficient to detect Pb isotope variations in the environment, as the natural variation of Pb isotopes is quite large.

Precision and accuracy for Pb measurements were confirmed by repeated analysis of reference sugar maple leaf material (NIST 1515) and San Joaquin soils (NIST 2709). Recovery was >96% for leaf material, but only 75–85% for reference soil samples (>90% for HF digests). Digestion in  $\text{HNO}_3/\text{H}_2\text{SO}_4$  does not obtain 100% Pb recovery from soil samples, although this method is suitable for extracting anthropogenic Pb from soils (Erel et al. 1997). In this study it is assumed that the small amount of residual (i.e. silicate) Pb is from natural sources and is consistent throughout the soil profile.

## Statistical analysis

All streamwater and throughfall concentrations are presented as volume-weighted monthly concentrations and fluxes. Values were combined to give average annual volume-weighted concentrations and annual flux (annual volume weighted concentration  $\times$  annual water flux). Mass balances for upland soils (PC1-08), the *Sphagnum*-conifer swamp and lake for 1989/1990, 1990/1991 and 2002/2003 were estimated by subtracting annual inputs; i.e. bulk deposition only (PC1-08) or bulk deposition plus area-weighted inflows (wetland and lake).

## Results and discussion

### Bulk deposition

Annual bulk deposition of Pb declined by approximately 75% between 1989/1990 and 2002/2003 (Table 1). The decline in Pb deposition in eastern

North America due to the restrictions of alkyl-Pb additives in gasoline is well documented (Johnson et al. 1995; Loranger and Zayed 1994), but notably the majority of the decline in Pb deposition occurred during the 1980s, prior to the onset of this study. For example, Loranger and Zayed (1994) reported that based on gasoline sales (mobile sources), emissions of Pb in Canada declined from around 9 megatonnes in 1980 to around 1 megatonne in 1990 before Pb was completely phased out of gasoline by 1991. Over a similar period, the input of Pb in bulk precipitation at Hubbard Brook in New Hampshire declined by 97%, from  $39.6 \text{ mg m}^{-2}$  in 1976 to  $1.27 \text{ mg m}^{-2}$  in 1989 (Johnson et al. 1995). This latter value is comparable to bulk Pb deposition inputs at Plastic Lake during the same time period. Jeffries and Snyder (1981) reported that annual Pb deposition in the Muskoka-Haliburton region in the late 1970s was approximately  $10 \text{ mg m}^{-2}$ ; therefore, it is highly likely that Pb deposition at Plastic Lake was up to an order of magnitude higher in the mid 1970s and early 1980s. This is supported by the sediment data (see below).

### Upland forest cycling

The Pb pool in upland forest biomass is approximately  $99 \text{ mg m}^{-2}$  (data not shown). This value is similar to other studies in eastern North America. For example, Smith and Siccama (1981) reported that the Pb content in the forest at Hubbard Brook was approximately  $125 \text{ mg m}^{-2}$ , while Friedland and Johnson (1985) reported that the Pb content of above-ground biomass at Camels Hump, a high elevation site in Vermont was approximately  $89 \text{ mg m}^{-2}$ . Throughfall and litterfall data were only available for 2002/2003, but the combined annual inputs of throughfall ( $0.33 \text{ mg m}^{-2}$ ) and litterfall ( $0.69 \text{ mg m}^{-2}$ ) were approximately double the inputs recorded in bulk deposition (Tables 1 and 2). The majority of the Pb input in litterfall occurred in woody tissue (including bark) despite the much larger input of foliage to the forest floor (Table 2). Lead concentrations are higher in wood than in foliage or reproductive tissue, which generally have low and comparable Pb concentrations (Table 2). Similarly, Pb concentrations were considerably higher in bark and root tissue compared with wood and foliar tissue (data not shown) in the dominant tree species at Plastic Lake. Higher Pb concentrations in woody

**Table 1** Annual volume-weighted Pb concentrations ( $\mu\text{g l}^{-1}$ ) and annual fluxes ( $\text{mg m}^{-2}$ ) at various locations in the Plastic Lake Watershed (refer to Fig. 1 for location of weirs)

Concentration/Fluxes	1989/1990		1990/1991		2002/2003	
	$\mu\text{g l}^{-1}$	$\text{mg m}^{-2}$	$\mu\text{g l}^{-1}$	$\text{mg m}^{-2}$	$\mu\text{g l}^{-1}$	$\text{mg m}^{-2}$
Bulk deposition	2.12	1.90	1.17	1.30	0.58	0.49
Throughfall	n.d.	n.d.	n.d.	n.d.	0.50	0.33
Litterfall	n.d.	n.d.	n.d.	n.d.	n.a.	0.69
PC1-08	0.11	0.05	0.08	0.05	0.04	0.02
PC1-03	0.72	0.36	0.58	0.34	0.61	0.23
PC1	0.63	0.32	0.38	0.22	0.77	0.37
PC0	0.19	0.09	0.19	0.10	0.09	0.03
Weathering	n.d.	n.d.	n.d.	n.d.	n.a.	0.02–0.36
<hr/>						
Pools/Mass balances	1989/1990		1990/1991		2002/2003	
	$\text{mg m}^{-2}$	$\text{mg m}^{-2}$	$\text{mg m}^{-2}$	$\text{mg m}^{-2}$	$\text{mg m}^{-2}$	$\text{mg m}^{-2}$
Upland	n.d.	+1.85	n.d.	+1.25	1942	+0.47
Wetland	n.d.	−1.12	n.d.	−1.53	4753	−1.57
Lake	n.d.	+2.47	n.d.	+1.55	1481 <sup>a</sup>	+1.42
Watershed	n.d.	+1.81	n.d.	+1.20	n.a.	+0.46

Lead pools ( $\text{mg m}^{-2}$ ) in various compartments and annual mass balances ( $\text{mg m}^{-2}$ ) for the upland, wetland, lake and entire watershed are also shown

n.d. Not determined

n.a. Not applicable

<sup>a</sup> Lake sediment pool (1870–present)

**Table 2** Pb concentrations (*standard deviation*) and input in litterfall at Plastic Lake in 2002/2003

		Date				
		Oct-02	Oct-29	April-23	June-12	Sept-09
[Pb] $\mu\text{g g}^{-1}$	Leaves	0.79 (0.24)	0.71 (0.65)	1.25 (0.26)	0.80 (0.41)	2.07 (1.93)
	Bark	20.2 (24.3)	NC	8.15 (6.34)	7.45 (6.38)	12.49 (19.62)
	Repro.	0.52 (0.49)	NC	1.08 (0.48)	1.90 (1.10)	4.66 (1.70)
Litterfall ( $\text{g m}^{-2}$ )	Leaves	102.9	40.4	52.4	6.5	25.6
	Bark	4.93	NC	18.5	3.5	9.8
	Repro.	4.03	NC	2.7	3.4	8.7
	Total	112	40.4	73.6	13.5	4.4
Pb input ( $\mu\text{g m}^{-2}$ )	Leaves	81.0	28.7	65.5	5.3	53.1
	Bark	102	NC	150	26.3	122.5
	Repro.	2.1	NC	2.9	6.4	40.6
	Total	185	28.7	219	38	216

NC None present/collected

tissue probably reflect the fact that bark tissue can accumulate atmospherically deposited Pb over a number of years and therefore Pb burdens in bark reflect years when Pb deposition was higher.

The greater combined input of Pb in throughfall and litterfall compared with bulk deposition may be explained by a combination of internal forest cycling and dry deposition. Although we are unable to



distinguish between the two sources, the low bio-availability of Pb (Adriano 2001) and the fact that the highest concentrations are found in woody tissue suggest that the majority of the difference is due to dry deposition and that bulk deposition collectors likely underestimate total Pb inputs to the forest floor by about 50%. In a detailed review of the literature, Galloway et al. (1982) reported that the dry fraction of total Pb deposition ranged from 0.3 in rural areas to 0.2 in urban areas. Lindberg and Turner (1988) reported that the relative contribution of Pb inputs in dry deposition compared with wet deposition at four deciduous watersheds in the southeastern United States was approximately 40–50%. Huang and Matzner (2004) similarly report that throughfall input of Pb to a Norway spruce (*Picea abies* [L.] Karst.) forest in Germany was more than double the input in bulk deposition and litterfall accounted for about 60% of the total Pb input to the forest floor.

Lead concentrations in upland forest soil decreased with soil depth and higher Pb concentrations were measured in HF digests (Table 3). Digestion using HF likely dissolves silicate bound Pb, which is likely natural in origin although some recalcitrant deposited Pb may be contained within this fraction. Accordingly, total Pb burdens in soil estimated using the HF digest were approximately 2.5 times greater than Pb burdens estimated using a  $\text{HNO}_3/\text{H}_2\text{SO}_4$  digest (Table 3). Clearly, estimates of Pb burdens in soil are strongly dependent upon the method used to digest soils and so comparisons between studies should be made with these differences in mind. Total Pb pools in mineral soil and the forest floor estimated using the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  digest were 1824 and 87.8  $\text{mg m}^{-2}$ , respectively, which likely overestimate to some extent the amount of pollution Pb

in soil. Numerous studies have shown that Pb accumulates in upper soil horizons during periods of high deposition, and Pb concentrations typically decrease dramatically with soil depth reflecting the relative immobility of Pb in soils (Brannvall et al. 2001c; Erel 1998; Huang and Matzner 2004; Navratil et al. 2004; Nowack et al. 2001; Watmough and Hutchinson 2004). The average Pb concentration in the forest floor at PC1 (HF digest) was  $75 \mu\text{g g}^{-1}$ , which is far below the lowest biological effect level for Pb of 225–250  $\mu\text{g g}^{-1}$  reported by Bringmark and Bringmark (2001).

A number of recent studies have suggested that Pb release rates from the forest floor and the downward movement of Pb through the soil profile may be greater than previously thought (Bergkvist 2001; Miller and Friedland 1994; Klaminder et al. 2005; Watmough et al. 2004). For example, Friedland et al. (1992) reported that the amount of Pb in the forest floor in the northeastern United States declined by approximately 12% between 1980 and 1990. Similarly, Bergkvist (2001) reported that Pb pools in the O-horizon of Swedish forests are declining by 0.1–0.2% annually. Lead that is being distributed from the forest floor to mineral soil may also be moving down the soil profile. Brannvall et al. (2001c) reported that pollution Pb had penetrated to depths of 20–60 cm in Swedish forest soils. Transport velocities between 0.39 and 0.83  $\text{mm year}^{-1}$  were reported for forest soils in Europe (Dorr and Munnich 1991), 5  $\text{mm year}^{-1}$  in Mediterranean soils (Erel et al. 1997) and rates between 8.2 and 19.7  $\text{mm year}^{-1}$  were reported for different depths in a hardwood forest in Vermont (Miller and Friedland 1994). Close to a metal smelter in the Czech Republic, Ettler et al. (2004) reported that Pb had moved down the soil profile at a rate of 3–3.6  $\text{mm year}^{-1}$ . These studies

**Table 3** Lead concentrations (*standard deviation*) and pools in soil sampled in 1999 at Plastic Lake

Horizon	Hydrofluoric acid		$\text{HNO}_3/\text{H}_2\text{SO}_4$	
	[Pb] $\mu\text{g g}^{-1}$	Pb burden ( $\text{mg m}^{-2}$ )	[Pb] $\mu\text{g g}^{-1}$	Pb burden ( $\text{mg m}^{-2}$ )
LFH	74.7 (23.8)	145	45.2 (21.6)	87.8
A (Ahe)	39.0 (6.3)	729	21.0 (13.9)	302
A (Ae)	25.1 (6.6)		10.8 (6.7)	
B (upper)	18.2 (3.2)	3549	8.7 (3.0)	1359
B (lower)	16.8 (3.2)		5.4 (1.6)	
BC	14.0 (9.4)	819	2.8 (0.7)	163
Total		5042		1912

have raised concern that the large amounts of Pb deposited to soils over the past century may eventually move through the soil profile and contaminate surface or ground waters (Kaste et al. 2003). It is also debateable whether the use of transport velocities is appropriate to describe the downward movement of Pb in mineral soil as this implies some constant rate of movement over time, when in fact Pb may initially move rapidly down the soil profile before becoming bound to soil and rendered relatively immobile.

Although a direct comparison cannot be made, the Pb content in the forest floor in 1999 (HF digest) was  $\sim 25 \text{ mg m}^{-2}$  higher than in 1983 (Lozano 1987; estimated using a nitric/perchloric digest). Lead concentrations in soil leachate draining the forest floor and A-horizon are strongly related to DOC concentration (Fig. 2) although this relationship changes both with soil depth and sampling period. In the forest floor leachate data, the relationship suggests that there was  $0.19 \text{ }\mu\text{g}$  of Pb associated with each  $\text{mg}$  of DOC in 2002/2003 compared with  $0.33 \text{ }\mu\text{g mg}^{-1}$  DOC in 1989–1991, representing a decrease of approximately 40%. A-horizon leachate data indicate  $0.05 \text{ }\mu\text{g}$  Pb was associated with every  $\text{mg}$  of DOC in 2002/2003 (median Pb concentration  $1.3 \text{ }\mu\text{g l}^{-1}$ ) compared with  $0.12 \text{ }\mu\text{g mg}^{-1}$  DOC in 1989–1991 (median Pb concentration  $2.0 \text{ }\mu\text{g l}^{-1}$ ). While Pb fluxes in soil leachate cannot be calculated due to the lack of a soil water model application at Plastic Lake, these data suggest that Pb is moving from the forest floor to the mineral soil, but that the amount of Pb transferred from the organic horizon to the mineral soil has decreased over the study period.

Lead concentrations in stream water draining PC1-08 were much lower than in bulk precipitation, throughfall or soil lysimeters (Table 1). Annual volume-weighted concentrations in PC1-08 were  $0.11 \text{ }\mu\text{g l}^{-1}$  in 1989/1990,  $0.08 \text{ }\mu\text{g l}^{-1}$  in 1990/1991 and  $0.04 \text{ }\mu\text{g l}^{-1}$  in 2002/2003; a reduction of approximately 50% between the two study periods. Relationships between Pb deposition and stream Pb concentrations are not generally observed due to the relative immobility of Pb in soil (Navratil et al. 2004; Johnson et al. 1995) but considerable inter- and intra-annual variation in Pb concentration in streams has been noted (Smith and Siccama 1981). Wang et al. (1995) suggest that over 80% of the Pb in streams draining the Hubbard Brook forest was derived directly from surface debris. As the percentage

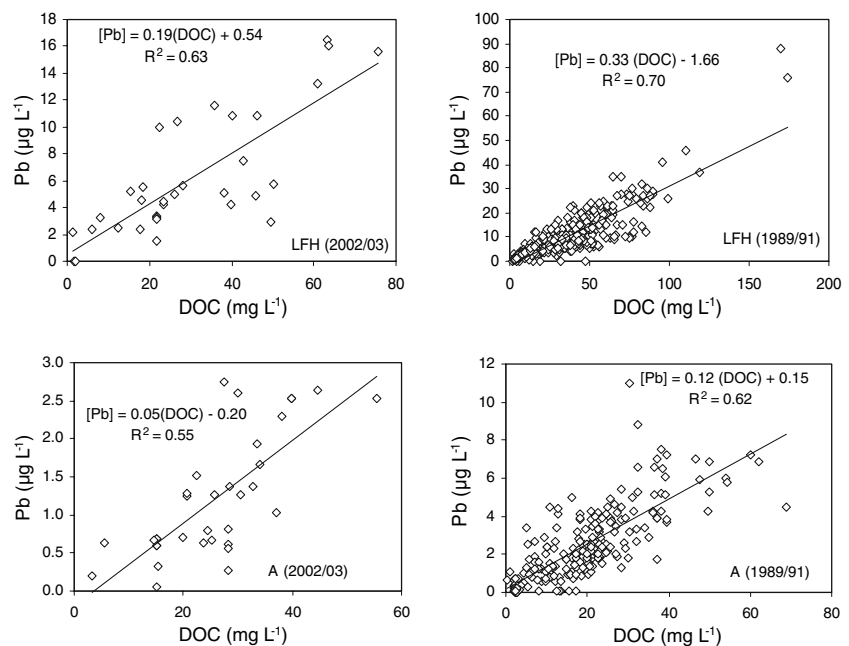
reduction in Pb concentration in PC1-08 ( $\sim 50\%$ ) is similar to that observed in forest floor and A-horizon leachate ( $\sim 40\%$ ), and Pb concentrations in the forest floor have also declined, it is possible that the decrease in Pb levels in PC1-08 was caused by lower Pb inputs in overland flow and/or surface debris, although the influence of changes in pH or DOC cannot be discounted. Aastrup et al. (1995) reported that only 55% of the current Pb deposition was retained within a forested catchment in southwestern Sweden but that some of this Pb may be derived directly from surface soil horizons.

Regardless of whether Pb inputs to the stream pass through the soil column, mass balance estimates indicate that upland soils at PC1-08 retain between  $0.47$  and  $1.85 \text{ mg m}^{-2} \text{ year}^{-1}$  based on bulk deposition estimates and approximately double these values if throughfall and litterfall inputs are considered. This represents  $>95\%$  retention in mineral soils, a value consistent with most other reports in the literature (Navratil et al. 2004; Johnson et al. 1995; Wang et al. 1995). Based on the mass balances above, Pb appears to be accumulating in mineral soil as Pb concentrations in the forest floor decline.

Complete mass balance estimates for mineral soils require consideration of Pb input through mineral weathering. Weathering rates for trace metals such as Pb are rarely estimated, although Johnson et al. (1995) estimated Pb inputs from weathering to be  $0.7 \text{ mg m}^{-2} \text{ year}^{-1}$  at Hubbard Brook. In later work, Johnson et al. (2004) revised this estimate to  $0.1$  to  $0.12 \text{ mg m}^{-2} \text{ year}^{-1}$ . Starr et al. (2003) reported weathering rates around  $0.30 \text{ mg m}^{-2} \text{ year}^{-1}$  for Haplic Podzols in eastern Finland. In this study, Pb weathering rates of  $0.02$  and  $0.11 \text{ mg m}^{-2} \text{ yr}^{-1}$  were estimated from rates of base cation weathering and Pb concentrations in parent material (C-horizon), depending on the method of acid digestion (Table 4). These values are similar to those estimated by Johnson et al. (2004) using a similar approach, but Johnson et al. (2004) accounted for changes in natural Pb concentration with soil depth. Our values are lower than those reported by Starr et al. (2003) using identical methods with the exception that Starr et al. (2003) determined Pb concentration in parent material using a mixed acid (HF and  $\text{HClO}_4$ ), which would more fully dissolve silicate minerals. Lead weathering rates reported by Hendershot (*pers com.*) based on laboratory leaching experiments are much



**Fig. 2** Relationship between Pb concentration and DOC concentration in LFH (upper) and A-horizon (lower) leachate samples collected in 2002/2003 compared with samples collected in 1989/1991



greater, and range from 0.34 to 0.36 mg m<sup>-2</sup> year<sup>-1</sup>. Lead weathering estimates obtained in this study are generally higher than Pb fluxes in upland-draining stream water (PC1-08), and we suggest that some of the Pb recorded at PC1-08 may be directly derived from surface soil horizons, having bypassed the mineral soil. As it appears that weathering reactions are not notably contributing to Pb accumulation in the sediment or to plant uptake (see later section on isotopes), and given the uncertainty in these estimates, weathering rates are not considered in our mass balance calculation for upland soils.

### Wetland

The total Pb pool in the 2.2 ha *Sphagnum*-conifer swamp is estimated to be 4725 mg m<sup>-2</sup> of which forest biomass accounted for 27.5 mg m<sup>-2</sup>, or 0.6%

**Table 4** Estimated weathering rates for Pb in upland mineral soil at Plastic Lake

Method	Pb <sub>w</sub> mg m <sup>-2</sup> year <sup>-1</sup>
Reinds et al. (2001)	0.02 <sup>a</sup> ; 0.11 <sup>b</sup>
Hendershot (unpublished)	0.34–0.36

<sup>a</sup> HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> digest

<sup>b</sup> Hydrofluoric acid digest

of total Pb in the swamp. The Pb pool in the swamp is much higher than in the upland, likely because in addition to direct atmospheric deposition, 85% of the water draining PC1 passes through the wetland, so over time even small losses from the upland could accumulate in organic peat soils. The average Pb concentration in the OF horizon was 21.4 µg g<sup>-1</sup>, compared with 66.7 µg g<sup>-1</sup> in the OM horizon and 42.2 µg g<sup>-1</sup> in the OH horizon. Organic soils are usually thought to be a net sink for Pb due to the high affinity of Pb for organic matter (Vile et al. 1999). However, wetlands also release large amounts of DOC that may result in high concentrations of Pb (Tipping et al. 2003). In the present study, Pb concentrations in water draining the wetland (PC1-03) and PC1 were much greater than Pb concentrations measured in PC1-08 (Table 1). Similar to soil leachate, Pb concentrations in PC1-03 and PC1 were linearly related to DOC concentrations (Fig. 3) with  $r^2$  values ranging between 0.23 (PC1, 1989–1991) and 0.67 (PC1, 2002/2003). Regression analysis indicates that the relationship between Pb and DOC in the wetland outflow is much lower than that observed in upper mineral soil leachate (A-horizon), and that this ratio has decreased between the two study periods. For example the slopes of the regression were 0.05 and 0.07 for PC1 and PC1-03, respectively in 1989–1991 and 0.04 and 0.03 in

2002/2003. This also indicates that between 0.03 and 0.07  $\mu\text{g Pb}$  was associated with each mg of DOC compared with up to 0.33  $\mu\text{g Pb mg}^{-1}$  DOC in forest floor leachate.

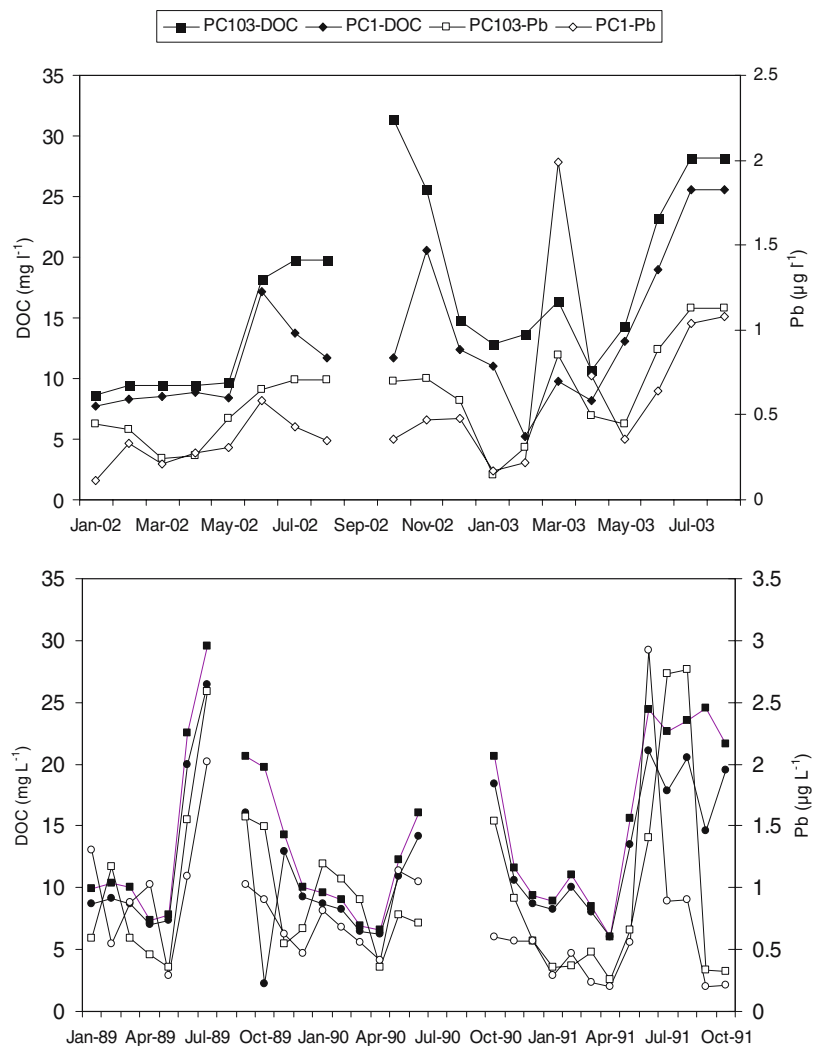
Changes in Pb/DOC ratio within the catchment indicate that approximately 10 times more Pb is associated with a given amount of DOC in LFH leachate compared with stream water draining the wetland. This change may reflect greater retention of Pb compared with DOC in the wetland and/or a change in the structure and hence complexation capacity of DOC for Pb caused by changes in parameters such as pH or competition with Al and Fe. These values translate to fluxes of Pb from the wetland (PC1-03) of  $0.36 \text{ mg m}^{-2} \text{ year}^{-1}$  in 1989/

1990,  $0.34 \text{ mg m}^{-2} \text{ year}^{-1}$  in 1990/1991 and  $0.23 \text{ mg m}^{-2} \text{ year}^{-1}$  in 2002/2003 (Table 1). Higher Pb concentrations and Pb fluxes were observed in PC1 in 2002/2003 compared with 1989–1991, but this is due to high Pb concentrations measured during spring runoff (March) and likely reflects Pb contribution from upper soil horizons due to overland flow in this year (Fig. 3).

### Lake

Lead concentrations in the lake outflow were much lower than concentrations in the inflow (PC1) and bulk deposition (Table 1). Mean annual Pb concentration in the Plastic Lake outflow was  $0.19 \mu\text{g l}^{-1}$  in

**Fig. 3** Monthly volume weighted Pb and DOC concentrations in PC1 and PC1-03 in 2002/2003 (upper) compared with 1989/1991 (lower)



both 1989/1990 and 1990/1991, compared with  $0.09 \mu\text{g l}^{-1}$  in 2002/2003. The decline in Pb concentration between the 2 time periods ( $\sim 50\%$ ) was similar to that observed in the upland part of the catchment. Mass balance estimates indicate that Pb was retained in the lake in all years of study, and retention ranged from 1.42 to  $2.90 \text{ mg m}^{-2} \text{ year}^{-1}$ . Between 80 (1990/1991) and 91% (2002/2003) of Pb input to the lake was retained and approximately 33% of Pb input to the lake in 1989/1991 was derived from the terrestrial catchment compared with 68% in 2002/2003. Using Pb concentration and isotope data, Kober et al. (1999) similarly reported substantial fluvial transfer of Pb into Lake Constance in central Europe, and that the catchment shifted from a net sink of atmospheric Pb deposition to a net source. Clearly, Pb inputs to lakes will not necessarily match deposition patterns in areas that have received moderate amounts of atmospheric pollutant Pb in the past, and the use of sediment cores to monitor changes in Pb deposition must be interpreted with this in mind.

During the summer of 2003, Pb concentrations were also measured in the epilimnion, metalimnion and hypolimnion of Plastic Lake, which had average volumes of  $16.4$ ,  $8.2$  and  $1.4 \text{ m}^3 \times 10^5$ , respectively (Table 5). Lead concentrations increased with lake depth and were  $0.04$  and  $0.09 \mu\text{g l}^{-1}$  in the epilimnion and metalimnion, respectively, which are comparable to values measured in the lake outflow (Table 1). In contrast, Pb concentrations in the hypolimnion were much higher, averaging  $0.36 \mu\text{g l}^{-1}$  during 2002/2003, and although this layer contained by far the smallest volume of water, the Pb content of the hypolimnion was comparable to the amount of Pb held in each of the epilimnion and metalimnion

(Table 5). The volume-weighted lake concentration for 2002/03 was  $0.07 \mu\text{g L}^{-1}$ , a value very similar to that measured in the lake outflow. Expressed on a lake area basis the total amount of Pb present in lake water is only  $0.56 \text{ mg m}^{-2}$ .

Relatively high Pb concentrations observed in the hypolimnion may be a result of one or a combination of two processes. Firstly, high Pb concentrations in the hypolimnion may simply be a result of settling out of Pb from the upper water column and a concentration effect as a larger mass of Pb transported from upper water layers settles into a smaller volume of water. As noted earlier, the amount of Pb in the hypolimnion is comparable to the amount in the upper layers. Secondly, the higher Pb concentration in the hypolimnion may be a result of remobilization of Pb from bottom sediment. A number of studies have recently suggested that Pb may be remobilized from lake sediments, and several mechanisms have been proposed (Benoit and Hemond 1991; Gallon et al. 2004; Widerlund et al. 2002). White and Driscoll (1995) similarly showed that Pb concentrations increased with lake depth during summer stratification in a dilute, acidic lake in the Adirondack Mountains in New York. The authors suggested that the apparent upward flux of Pb may be a significant process that increases water column concentrations and has implications for the interpretation of patterns and rates of Pb deposition in acidic lakes. While it appears that some remobilization of Pb from sediment at Plastic Lake is likely, the extent to which this may impact the sediment record is unclear. For example, Gallon et al. (2004) reported that diagenetic processes such as remobilization, molecular diffusion, bioturbation and bioirrigation occurred in a Canadian Shield lake with similar properties to Plastic Lake (pH 5.3–5.6; oligotrophic and hypolimnion remains oxic throughout the year) but had a negligible impact on the solid phase Pb profile in sediment.

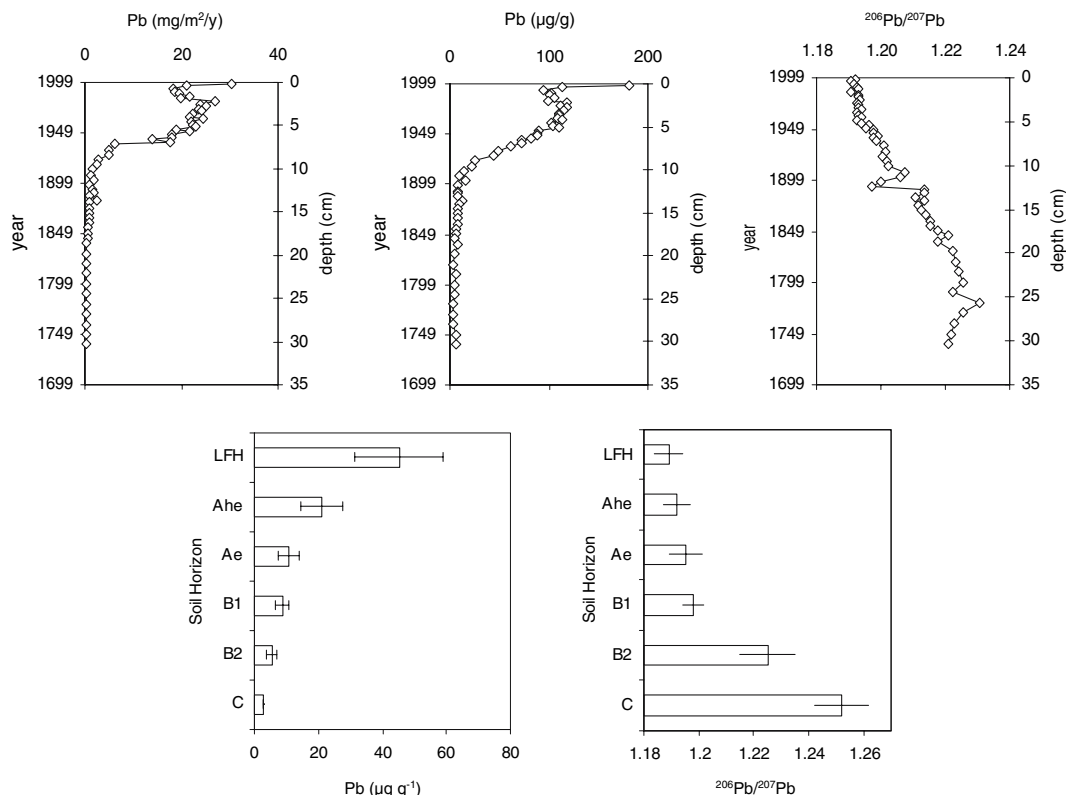
#### Lake sediment

Lead concentrations in lake sediment were stable below about 13 cm depth ( $\sim 1900$  based on  $^{210}\text{Pb}$  dating) and ranged between 3 and  $10 \mu\text{g g}^{-1}$  (Fig. 4). After this period, Pb concentrations increased upcore, particularly from about 8 cm depth ( $\sim 1930\text{s}$ ). This date approximately coincides with the large-scale

**Table 5** Volume weighted Pb concentrations and Pb content in Plastic Lake (average June–September 2003)

	Volume ( $\text{m}^3 \times 10^5$ )	Pb concentration ( $\mu\text{g l}^{-1}$ )	Pb content (g)	Pb content ( $\text{mg m}^{-2}$ )*
Epilimnion	16.4	0.04	65.6	0.20
Metalimnion	8.2	0.09	73.8	0.23
Hypolimnion	1.4	0.36	50.4	0.16
Whole lake	26	0.07	182	0.56

\* Expressed as Pb content of each layer divided by lake surface area (32.3 ha)



**Fig. 4** Lead concentrations ( $\mu\text{g g}^{-1}$ ), estimated accumulation rates ( $\text{mg m}^{-2}$ ) and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in Plastic Lake sediment (upper) and Pb concentrations and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in surrounding soil (lower)

introduction and usage of leaded gasoline in North America. Lead concentrations were relatively stable ( $100\text{--}110 \mu\text{g g}^{-1}$ ) between 2 and 5 cm depth (estimated to have been deposited in the 1940s and 1980s), and then decreased slightly toward the sediment surface. In total, approximately  $1480 \text{ mg m}^{-2}$  Pb is estimated to have been deposited since 1870 (Table 1). By comparison, if we assume that the Pb concentration in the BC horizon is uncontaminated and that the amount of natural Pb is consistent within the upland soil profile, between  $1270$  and  $1500 \text{ mg m}^{-2}$  of Pb in soil is of anthropogenic origin.

Similar patterns in sediment Pb concentration have been observed at a number of lakes in North America and Europe and appear to reflect changes in atmospheric Pb deposition (Renberg et al. 2002; Siver and Wozniak 2001). Sediment cores almost universally show an increase in Pb concentration coinciding with the onset of industrial activity and in some cases, particularly in Europe, increases in Pb concentration in deeper profiles are associated with human activ-

ities occurring several thousand years ago (Brannvall et al. 2001a; Renberg et al. 2002). Although some studies have reported decreases in Pb concentrations in response to declining Pb deposition (Brannvall et al. 2001a; Renberg et al. 2002), in many cases, these studies were undertaken when Pb deposition was still elevated, and lacked the resolution to evaluate the recent observed decline in Pb deposition that occurred over much of Europe and North America (Gallon et al. 2004; Siver and Wozniak 2001). We are unaware of any study that has reported a decline in Pb sediment concentration consistent in magnitude with the observed reduction in Pb deposition that has occurred over the past 2–3 decades. Continued input of Pb stored in the terrestrial catchment may partly be responsible for the apparent disconnect between atmospheric deposition and recent trends in Pb concentrations in upper sediment.

In the present study, increases in Pb deposition appear to have been preserved in the sediment record with Pb fluxes increasing from  $<1 \text{ mg m}^{-2} \text{ year}^{-1}$  prior to 1880 up to  $\sim 20 \text{ mg m}^{-2} \text{ year}^{-1}$  between the 1940s

and 1980s (Fig. 4). While sediment core estimates of peak deposition ( $\sim 20 \text{ mg m}^{-2} \text{ year}^{-1}$ ) are reasonably consistent with the estimated Pb deposition rate for the latter part of this period (1970s) and are similar to estimates from lake sediment profiles taken in other parts of Ontario and eastern Canada including the Muskoka-Haliburton region (Dillon and Evans 1982; Evans and Dillon 1982; Evans et al. 1986), the temporal record appears to be somewhat blurred. For example, Pb deposition fluxes peaked earlier (start  $\sim 1940$ ) and remained high for a longer period ( $\sim 40$ – $50$  years) than expected compared with estimates of Pb emissions and air concentrations (Miller and Friedland 1994) that generally indicate a 20-year peak deposition period between the mid 1950s and mid 1970s. Notably, Pb fluxes measured in upper sediments are  $18 \text{ mg m}^{-2} \text{ year}^{-1}$ , which is almost an order of magnitude greater than estimates based on the lake mass balance work presented earlier. While there is uncertainty in our lake mass balance estimates which is difficult to quantify due to the fact that Pb concentrations were measured in only 1 of 7 inflow streams (but have similar pH and DOC concentrations based on 1980s measurements) error in mass budget calculations is unlikely to fully explain the large difference in Pb deposition estimates. Overall, sediment core data indicate that Pb input to the lake is recorded in the sediment profile, but that the temporal pattern is smeared (perhaps over years or decades) due to possible remobilization of Pb in the sediment. Release of Pb from lake sediment could also account for relatively high Pb concentrations in the hypolimnion.

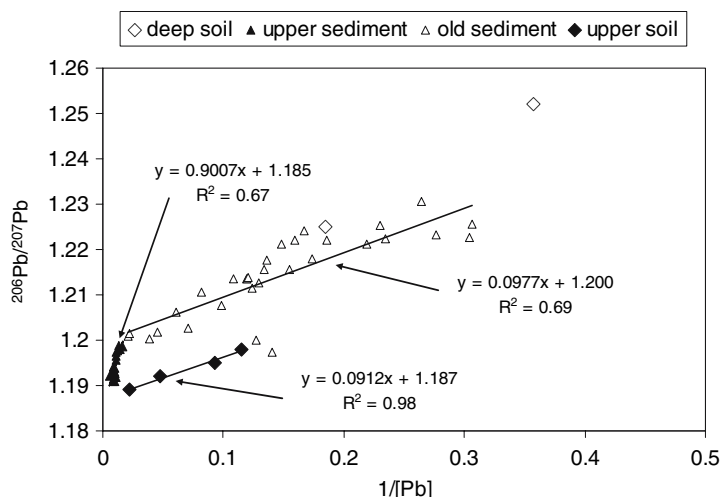
### Lead isotopes

Coincident with changes in Pb concentration in sediment,  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios decreased from 1.22 to 1.23 in sediment deposited prior to 1850 to  $\sim 1.19$  in the most recent sediment deposits (Fig. 4). A number of studies have shown that Pb isotopic ratios and Pb concentrations change with depth and these shifts have been attributed to the input of anthropogenic Pb deposition that has a different isotopic signature than geogenic Pb (Brannvall et al. 2001c; Erel 1998; Ettler et al. 2004; Hansmann and Koppel 2000; Watmough and Hutchinson 2004). Lower  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios and higher Pb concentrations have also been observed in sediment cores from lakes in the lower Canadian Arctic which is completely remote from pollution

sources (Outridge et al. 2002). The isotopic pattern observed in Plastic Lake sediment is similar to the pattern observed in upland mineral soil. Lead concentrations decreased with depth and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios increased, reflecting the input of pollution Pb from deposition (Fig. 4). It is noteworthy that the Pb isotopic composition of peat also changed with depth, from  $1.191 \pm 0.001$  in the upper OF horizon, to  $1.199 \pm 0.001$  in the OM horizon and  $1.202 \pm 0.013$  in the deepest OH horizon. Soil data are consistent with sediment data and indicate that Plastic Lake has been contaminated with pollution Pb and that the majority of pollution Pb has remained in the upper mineral soil horizons, although some pollution Pb can be detected in lower (lower-B horizon) soil horizons.

If Pb isotopic ratios in soil and sediment can be explained by the mixing of two (constant) sources (pollution Pb and natural Pb) then a plot of the inverse of Pb concentration against  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio should be linear and separate plots for soils and sediment should produce the same intercept that indicates the signature of pollution Pb (Hansmann and Koppel 2000). While a linear plot could be fit through both sets of data, it is apparent that there is a marked difference in slope between ‘upper’ ( $>1930$ ); and ‘lower’ ( $<1930$ ) sediment and plots for soil and sediment do not produce similar estimates of a pollution Pb signature (Fig. 5). However, if data are separated such that only the upper sediment and upper mineral soils are compared, intercepts are 1.185 and 1.187, respectively, suggesting a more recent pollution Pb isotopic signature around 1.18–1.19 (Fig. 5) which reflects a mixture of pollution Pb derived from Canadian and US sources (Sturges and Barrie 1989). This value is also consistent with atmospheric measurements taken in the Dorset area (Sturges and Barrie 1989), recent lichen measurements for central Ontario (Watmough and Hutchinson 2004), snow samples from eastern Ontario (Simonetti et al. 2000) and isotopic ratios in surface sediment of lakes in the region (Blais 1996). Furthermore,  $^{206}\text{Pb}/^{207}\text{Pb}$  data suggest that most of the Pb measured in recently deposited sediment is of anthropogenic origin and since up to 68% of the Pb input to the lake is from the terrestrial catchment, leaching fluxes of Pb from soil are dominated by pollution Pb and the influence of Pb derived from natural weathering processes is minimal.

**Fig. 5** Relationship between  $1/[Pb]$  and  $^{206}Pb/^{207}Pb$  ratios in sediment and soil samples from the Plastic Lake Watershed (see text for further details)



By contrast, the intercepts of linear plots of  $1/[Pb]$  vs.  $^{206}Pb/^{207}Pb$  in deep sediment and deeper soil horizons (2 samples only) are higher ( $\sim 1.20$ ) suggesting a different, 'older' pollution source. The isotopic signature of atmospheric Pb in Europe and North America is known to have changed over time based on aerosol, sediment, ice core and peat core samples (Brannvall et al. 2001a; Dunlap et al. 1999; Monna et al. 1997; Novak et al. 2003; Rosman et al. 1993). Other studies using lake sediment cores from the Great Lakes and Quebec have similarly suggested that the isotopic signature of atmospheric Pb in southern Canada has changed over time with lower  $^{206}Pb/^{207}Pb$  values associated with more recently (late 20th century) deposited Pb (Gallon et al. 2005; Graney et al. 1995). For example, Gallon et al. (2005)

of 1.22 and was derived from coal combustion. The second which was not detectable before 1880 and reached a maximum in the mid 1970s is characterized by a  $^{206}Pb/^{207}Pb$  ratio of 1.179 and was derived from gasoline and industrial sources.

As the pollution Pb signature appears to have changed over time, the amount of pollution Pb in soils and vegetation relative to 'natural' Pb cannot be accurately determined using two constant end-members. However using the following simple mixing equation; and assuming a pollution Pb signature of 1.185 and a background ratio identical to that measured in the deepest (BC) soil horizon the  $^{206}Pb/^{207}Pb$  isotope values are consistent with most (at least  $1270 \text{ mg m}^{-2}$ ) of the Pb in soil being of anthropogenic origin; a conclusion consistent with

$Pb_{\text{pollution concentration}}$

$$= \left( \frac{^{206}Pb/^{207}Pb_{\text{sample}} - ^{206}Pb/^{207}Pb_{\text{background}}}{^{206}Pb/^{207}Pb_{\text{pollution}} - ^{206}Pb/^{207}Pb_{\text{background}}} \right) \times \text{total } Pb_{\text{sample}} \quad (1)$$

analyzed a sediment core from a Canadian Shield lake in Quebec and concluded that anthropogenic Pb deposited since pre-industrial time can be modelled as a mixture of two isotopically distinct types. The first, which was not detected before 1850 and reached a maximum in 1950 had a  $^{206}Pb/^{207}Pb$  isotopic ratio

sediment data and estimates based on changes in soil concentration presented earlier (Table 6). As there is evidence of an older, but less extensive pollution signature in the deepest sediment and soil that has a slightly higher  $^{206}Pb/^{207}Pb$  isotopic ratio, this calculation probably slightly underestimates the total



amount of pollution Pb in soil at Plastic Lake. Similarly,  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic signatures in vegetation samples at PC1 are consistently between 1.17 and 1.22 indicating that the majority of Pb in vegetation is from a pollution source, which has a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio between 1.18 and 1.20 (data not shown). Most other studies that have considered Pb isotopic ratios have similarly concluded that the majority of Pb measured in forest vegetation, even in remote sites, is of anthropogenic origin (Klaminder et al. 2005; Watmough and Hutchinson 2004). Brannvall et al. (2001a, b) for example, determined Pb concentrations and isotope ratios in sediment cores, peat samples and surface soils at boreal forests in Sweden and concluded that Pb enrichment in recent sediments, peat and in the mor (forest floor) layer are caused by pollution and not natural processes.

#### Summary watershed mass balance

Combination of mass budgets for the upland catchment, wetland and lake indicates that between 93% and 98% of the Pb deposited to the Plastic Lake Watershed in bulk deposition is retained. This is likely an underestimate as dry deposition is not accounted for in these estimates. In support of our

hypotheses, upland soil retained more than 95% of the Pb input in bulk deposition, however contrary to expected, the wetland was a net source of Pb in all measured years. As predicted, DOC played an important role in transporting Pb through the watershed, but the relationship between Pb and DOC changed both spatially within the watershed and between the two sampling periods. Lake sediment was a net sink for atmospherically deposited Pb and between 80% and 91% of the Pb input to Plastic Lake was retained. However, contrary to our predictions, up to 68% of the Pb entering the lake was derived from the terrestrial catchment. Lead isotope data show that Pb cycling at the Plastic Lake Watershed is dominated by Pb of anthropogenic origin, but two distinct anthropogenic signatures exist and inputs of Pb from mineral weathering are likely negligible. In summary, the Plastic Lake Watershed is effectively retaining atmospherically deposited Pb, but this Pb is being redistributed within the watershed, moving from the forest floor to the mineral soil and from the wetland to lake sediment.

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**Table 6** Estimated Pollution Pb burden using Pb concentrations and  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratios in  $\text{HNO}_3\text{:H}_2\text{SO}_4$  soil digest

Horizon	Pollution Pb concentration ( $\mu\text{g g}^{-1}$ )	Pollution Pb burden ( $\text{mg m}^{-2}$ )
LFH	42.5	82.5
A (Ahe)	18.8	270
A (Ae)	9.2	
B (upper)		5.9
921		
B (lower)		2.2
BC	0	0
Total		1274

Background  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio assumed to be that measured in the BC horizon

Pollution  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio assumed to be 1.185. (The true pollution  $^{206}\text{Pb}/^{207}\text{Pb}$  isotopic ratio likely varied in time with a higher ratio estimated for lower soil horizons so pollution Pb burdens are probably underestimated)

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