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The isotopic evolution of atmospheric Pb in central Ontario since AD 1800, and its impacts on the soils, waters, and sediments of a forested watershed, Kawagama Lake

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Abstract

A peat core from an ombrotrophic bog documents the isotopic evolution of atmospheric Pb in central Ontario since AD 1804 ± 53 (^{210}Pb dating). Despite the introduction of unleaded gasoline in the mid-1970's, the ratio ^{206}Pb/^{207}Pb in atmospheric deposition has not increased as expected, but rather continues to decline. In fact, snowpack sampling (2005 and 2009) and rainwater samples (2008) show that the isotopic composition of atmospheric Pb today is often far less radiogenic than the gasoline lead that had been used in Canada in the past. The peat, snow, and rainwater data presented here are consistent with the Pb isotope data for aerosols collected in Dorset in 1984 and 1986 which were traced by Sturges and Barrie (1989) to emissions from the Noranda smelter in northern Quèbec, Canada's largest single source of atmospheric Pb. Understanding atmospheric Pb deposition in central Ontario, therefore, requires not only consideration of natural sources and past contributions from leaded gasoline, but also emissions from metal smelting and refining.

Lead in the streams which enter Kawagama Lake today (^{206}Pb/^{207}Pb $= 1.16 - 1.19$) represents a mixture between the natural values ($1.191 - 1.201$ estimated using pre-industrial lake sediments) and the values found in the humus layer of the surrounding forest soils (^{206}Pb/^{207}Pb $= 1.15 - 1.19$). In the lake itself, however, Pb is much less radiogenic (^{206}Pb/^{207}Pb as low as 1.09) than in the streams, with the dissolved fraction less radiogenic than particulate material. The evolution of Pb isotope ratios within the watershed apparently reflects preferential removal by sedimentation of comparatively dense, radiogenic, terrestrial particles (derived from the mineral fraction of soils) from the humus particles with lower ratios of ^{206}Pb/^{207}Pb (because of atmospheric Pb contamination). Despite the contemporary enrichments of Pb in rain and snow, concentrations of dissolved Pb in the lake are extremely low (sometimes below 10 ng/l), with Pb concentrations and Pb/Sc ratios approaching "natural" values because of efficient binding to particles, and their subsequent removal in the watershed.

1. INTRODUCTION

Ombrotrophic (i.e. rain-fed) peat bogs are excellent archives of atmospheric Pb and have provided the first complete, long-term record (15,000 years) of atmospheric Pb deposition in Europe (Shotyk et al., 1998, 2001). The isotopic composition of Pb in peat cores from such bogs has shown that human activities have dominated atmospheric Pb inputs in central Europe continuously for more than 3000 years (Shotyk et al., 1998, 2001). Moreover, they have also shown, using precisely dated peat cores from Denmark and the Faroe Islands, that the greatest contributions to atmospheric Pb contamination, at least in many parts of Europe, were mainly from industrialization (ore smelting and refining, and coal combustion), and not due to the use of leaded gasoline additives (Shotyk et al., 2001, 2003, 2005). With appropriate methods for sample collection,

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handling, preparation, and age dating (Givelet et al., 2004), peat cores have been used for detailed reconstructions of atmospheric Pb pollution histories (Le Roux et al., 2004). Studies of recent peat layers from a bog in southern Germany combined with Pb isotope measurements of the overlying snowpack, clearly show that even today, atmospheric Pb inputs continue to be dominated by anthropogenic signatures (Le Roux et al., 2005).

By far the majority of the published studies of the use of peat bogs as archives of atmospheric contamination have focused on Pb (e.g. Vile et al., 1995; Jensen, 1997; MacKenzie et al., 1997), with early work having been reviewed elsewhere (Shotyk et al., 1990, 1992; Jones and Hao, 1993; Shotyk, 1996a,b; Shotyk et al., 1998). A number of papers were published following the first international workshop on peat bog archives (Appleby et al., 1997; Brännvall et al., 1997; Espi et al., 1997; Farmer et al., 1997; Kempter et al., 1997; Küster and Rehfuess, 1997; Martinez-Cortizas et al., 1997; Norton et al., 1997; Shotyk et al., 1997; Steinnes, 1997; Weiss et al., 1997). Since then, the number of published studies using peat bogs as archives of atmospheric trace metals has continued to grow (Holynska et al., 1998; MacKenzie et al, 1998; Ettler and Mihaljevic, 1999; Kempter and Frenzel, 1999, 2000; Vile et al., 1999, 2000; Weiss et al., 1999a; Shotyk et al., 2000; Martinez-Cortizas et al., 2002; Mighall et al., 2002; Nieminen et al., 2002; Shotyk et al., 2002; Weiss et al., 2002; Klaminder et al., 2003; Novak et al., 2003; Bindler et al., 2004; Ukonmaanaho et al., 2004; Cloy et al., 2005; Coggins et al., 2006; Mihaljevic et al., 2006; De Vleeschouwer et al., 2007; Rothwell et al., 2007; Syrovetnik et al., 2007; Zaccone et al., 2007a,b; Ettler et al., 2008; Mihaljevic et al., 2008; Novak et al., 2008; Renson et al., 2008; De Vleeschouwer et al., 2009; Hutchinson and Armitage, 2009; Klavins et al., 2009; Kylander et al., 2009a,b). In addition to these studies employing peat cores from ombrotrophic bogs and two studies employing *Sphagnum* moss, the dominant peat-forming bog plant, from herbarium collections (Weiss et al., 1999b; Farmer et al., 2002), there has also been a number of retrospective studies of atmospheric Pb deposition using cores from minerotrophic wetlands such as marshes, swamps, and fens (Alfonso et al., 2001; Shotyk, 2002; Hettwer et al., 2003; Baron et al., 2005; Jackson et al., 2004; Monna et al., 2004; Kylander et al., 2007; Kamenov et al., 2009). Many of these publications include not only information about temporal changes in Pb concentrations, but also the isotopic composition of Pb which can be helpful in distinguishing between natural and anthropogenic sources of atmospheric Pb (Flegal et al., 1989; Sturges and Barrie, 1989; see Sangster et al., 2000 and Komarek et al., 2008, for reviews).

In contrast to the detailed reconstructions of atmospheric metal contamination in Europe (Brännvall et al., 2001a; Shotyk and Le Roux, 2005; Bindler et al., 2008a), much less work has been undertaken in North America. Except for recent studies of atmospheric Hg deposition reconstructed using peat cores from Ontario (Givelet et al., 2003) and Maine (Roos-Barraclough et al., 2006), there have been few studies of atmospheric Pb using peat cores from ombrotrophic bogs in North America (Norton et al., 1997; Benoit et al., 1998; Weiss et al., 2002; Kylander et al., 2009a).

Measurements of Pb in Greenland ice documented the global extent of atmospheric Pb pollution (Murozumi et al., 1969), with the first isotopic evidence of atmospheric Pb contamination in the Canadian Arctic dating back more than 3,000 years (Zheng et al., 2007). Given the intensity and extent of atmospheric Pb pollution, there is ongoing interest in the fate of anthropogenic Pb in forest soils throughout the temperate zone of the northern hemisphere (Siccama et al., 1980; Dörr and Münnich, 1989; Dörr et al., 1990; Friedland et al., 1992; Miller and Friedland, 1994; Johnson et al., 1995; Wang et al., 1995; Wang and Benoit, 1996; Wang and Benoit, 1997; Brännvall et al., 2001b; Semlali et al., 2001; Kaste et al., 2003; Semlali et al., 2004; Klaminder et al., 2008a,b; Kylander et al., 2008). One approach to understanding the transformations and fate of Pb in soils is to study the streams which drain their respective watersheds (LaZerte et al., 1989; Erel et al., 1990, 1991; Erel and Patterson, 1992, 1994; Tarvainen et al., 1997; Outridge, 2000; Emmanuel and Erel, 2002; Vinogradoff et al., 2005; Graham et al., 2006; Klaminder et al., 2006; Bindler et al., 2008b; Bur et al., 2009; Landre et al., 2009). Concentrations of total dissolved Pb in natural waters may be very low (Hirao and Patterson, 1974; Erel et al., 1991), with values reported for surface waters (Field and Sherrell, 2003) and recent groundwaters (Shotyk et al., 2010) below 1 ng/L. Any studies of Pb in forest soil solutions and stream waters remote from industrial activity, therefore, need to be able to reliably measure Pb in the part per trillion (ng/L) concentration range. The great difficulties associated with reliable measurements of Pb in this concentration range are well known (Settle and Patterson, 1980; Boutron, 1990; Nriagu et al., 1993; Benoit, 1994; Benoit et al., 1997) and can be performed by very few laboratories, and only when extreme care is taken to avoid sample contamination.

Recently, major strides have been made with respect to clean lab techniques and high sensitivity inductively coupled plasma-sector field mass spectrometry (ICP SMS) such that trace elements can now be measured reliably and routinely in arctic snow and ice (Krachler et al., 2004a, 2005). With detection limits approaching parts per quadrillion (pg/L), it is therefore possible to also measure Pb reliably in other dilute natural waters such as remote streams and lakes. Moreover, stable Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) can be measured directly, even in arctic snow and ice, using the same methods (Krachler et al. 2004b), allowing anthropogenic Pb to be clearly distinguished from natural Pb inputs (Shotyk et al., 2005). Here, we use the analytical strategy which was successfully applied to arctic snow and ice (Shotyk et al., 2005; Zheng et al., 2007), as well as pristine groundwater (Shotyk et al., 2010), to study the flows of Pb through a forested watershed.

Our first objective is to document the changing isotopic composition of atmospheric Pb since industrialization, including its evolution since the elimination of leaded gasoline in the mid-1970's. In particular, we wish to evaluate the hypothesis that, during the three decades since the elimination of leaded gasoline, the isotopic composition of atmospheric Pb has begun to evolve back toward more radiogenic, pre-industrial values. Second, we wish to better understand the changes in atmospheric Pb deposition on a forested watershed. Given the reservoir of accumulated industrial Pb in the soils, does the isotopic composition of Pb in surface waters now reflect contemporary atmospheric inputs, or is anthropogenic Pb leaching from the soils into the lakes? To satisfy these objectives, we have undertaken an integrated study which includes both a reconstruction of the isotopic evolution of atmospheric Pb in central Ontario, as well as a multimedia study of the relevant components of a representative watershed (soils, waters, and sediments) within the Great Lakes-St. Lawrence forest region of central Ontario, Canada. Specifically, we used (i) a peat core from an ombrotrophic bog to provide the isotopic evolution of atmospheric Pb for the past two centuries, (ii) pre-industrial lake sediments to estimate the isotopic composition of natural Pb to the watershed, and (iii) samples of soil humus to help characterize the recent inputs of particulate material to the lake. Water samples from streams and lakes were measured for total and dissolved Pb and Sc concentrations, and Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb), to identify the predominant Pb sources and the processes affecting their fluxes.

2. MATERIALS AND METHODS

2.1. Brief description of the geology, soils, and ecology

Kawagama Lake ("lake of many sounds") is 180 km NE of Toronto and 220 km SE of Sudbury in the Haliburton Highlands of central Ontario (Fig. 1a). The bedrock geology of the area consists of Precambrian (1.45 Ga) granitic gneiss with distinct banding; pegmatite dikes with large crystals of potassium feldspar are common (Easton, 2000). The shallow (ca. 20–50 cm), poorly developed Brunisolic soils are developed from a locally derived glacial till and the predominant minerals are plagioclase feldspar (ca. 30%), quartz (30%), potassium feldspar (15%), hornblende (ca. 10%), biotite (ca. 5–10%), and goethite (ca. 2–3%). Plagioclase feldspar, hornblende, biotite, and potassium feldspar are responsible for most of the weathering which takes place, and the dissolution of these phases controls the chemical composition of the waters of this region (Kirkwood and Nesbitt, 1991).

This part of Ontario was inhabited by Native Peoples for at least 5,000 years, first by the Algonquin, then Iroquois and finally the Ojibway. The area was a wilderness dominated by old growth white pine until logging began toward the end of the 19th century. Settlement lands bordering Kawagama Lake were first applied for in 1885. Two logging dams built during 1890 which permitted logging companies to direct Kawagama Lake water into the Severn River, or Muskoka River waterways. By the late 1890's, the entire region was clearcut, reaching a climax in 1896 with the collapse of the David Gilmour Lumber Company. Since then, the area has become dominated by a mixed forest consisting of a remarkable diversity of coniferous (white and red pine, white spruce, balsam fir, hemlock, tamarack) and deciduous tree species (northern red oak, sugar, red, black, and striped maple, white ash, elm, beech, basswood, hop hornbeam, balsam and yellow poplar, and trembling aspen). Shrubs and small trees include pin and choke cherry, nannyberry, elderberry, and sumac, with black spruce, white cedar, willow and alder found in the wet sites. Soils are shallow, exposed bedrock is extensive, drainage is poor, and wetlands, mainly hardwood swamps and marshes, are common. The major land use since approximately the 1920's has been recreation, and today there are numerous summer cottages on most of the larger lakes. Not all lakes are accessible by road, and most of the smaller lakes in the watershed are effectively inaccessible.

At an elevation of 355 m asl, Kawagama Lake itself is up to 16 km long and 4 km wide, with numerous islands, peninsulas, and bays (Fig. 1b). It is a clear, cold lake, with a maximum water depth of approximately 69 m, surrounded by hills up to 475 m asl. The most important physical properties of the lake are given in Table 1. The main sources of surface water to the lake, as well as a brief description of the upper reaches of the watershed, are listed in Table 2. The volumes of water supplied by the streams, as estimated visually in the field, increases approximately in the order White Trout Bay << Loon Bay = Crumby Lake = East Jeannie Lakes = Harvey Lake < Wolfbane Lake < Sucker Lake = Fletcher Lake << East Hollow River. Although the topographic maps indicate that the inlet to White Trout Bay is a stream, in summer this site represents seepage from the soils, as there was no visible flow during any of the sampling periods. Water from the East Hollow River which enters the lake from the east, is the largest single tributary, followed by the inflows from Bear Lake; however, there is no quantitative hydrological data. The only outflow is the Hollow River which leaves Kawagama Lake and enters Lake of Bays at Dorset, 5 km west of Kawagama and the only town in the area. The total area of the Kawagama Lake watershed area is approximately 380 km^2. This watershed is just one part of the much larger Muskoka River Watershed (4660 km^2), which drains into Georgian Bay of Lake Huron, part of the Great Lakes system. Kawagama Lake lies ca. 175 m above the elevation of Lake Huron, and ca. 150 km to the east.

The pH values of the streams flowing into Kawagama Lake are depressed (as low as pH 5.2) compared to values for the lake itself (pH 6.9–7.0), reflecting inputs of dissolved organic acids from the surrounding forest soils, as well as the wetlands. The concentrations of total organic carbon range from approximately 4 to 12 mg/l, with the lowest values found in Kawagama Lake proper, and the highest values found in streams draining areas containing wetlands. The average annual temperature at Dorset is 4.8 °C, with 1070 mm of precipitation (280 mm as snow).

2.2. Sample collection

To describe and to understand the changes in predominant sources of atmospheric Pb to the watershed as well as the subsequent flows of Pb from the soils to the streams and lakes, and ultimately to the sediments, a multimedia sampling approach was used: atmospheric inputs to the watershed were studied using a peat core and snow samples from a nearby ombrotrophic bog, as well as a sample of *Sphagnum* moss and rainwater collected adjacent to Kawa-

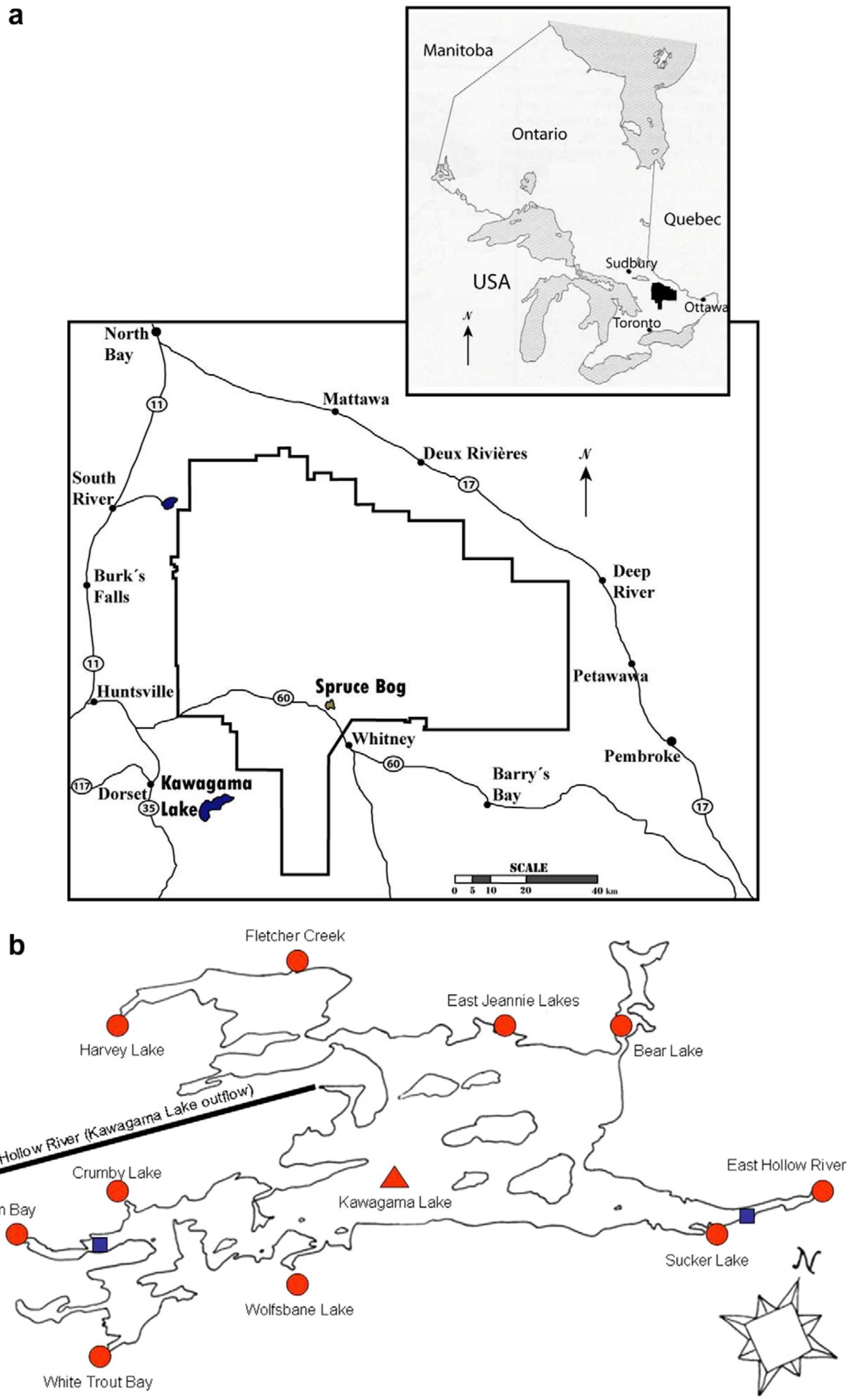

Fig. 1. (a) Location map. The closest town to Kawagama Lake is Dorset which is approximately half-way between Toronto and Sudbury, Ontario. The site where peat and snow samples were collected at Spruce Bog, Algonquin Park, is located approximately 500 m from Hwy 60. (b) Sampling locations, Kawagama Lake: stream water samples indicated by solid circles, lake water samples by solid triangle. The solid squares show the location of lake sediment cores. The solid arrow shows the approximate location of the Hollow River which is the only outflow from Kawagama Lake; the sampling location of the Hollow River is off the map. Humus samples were collected from soils nearby the entrance of the streams (solid circles) to the lake.

Table 1
Physical properties of Kawagama Lake.

Approximate location	45° 18′N, 78° 45′W
Elevation	355 m asl
Surface area	3184 ha (31.8 km^2)
Maximum depth	69 m
Mean depth	21.8 m
Perimeter	82.9 km
Volume	528 × 10^6 cubic metres
Total area of the Kawagama Lake watershed	380 km^2

gama Lake; aquatic and terrestrial inputs of Pb to the lake prior to industrialization were reconstructed using a sediment core; and contemporary inputs of Pb to the streams was obtained using humus samples collected around the lake. These data are then used to help interpret measurements of Pb, Sc, and Pb isotope ratios in the stream and lake waters.

2.3. Atmospheric inputs recorded by peat, *Sphagnum* moss, snow, and rain

A peat core from Spruce Bog, ca 45 km NE of Kawagama Lake, in Algonquin Provincial Park (Fig. 1a) had already been collected (10. July, 2000), sectioned, subsampled, dried, and milled according to the protocol described elsewhere (Givelet et al., 2004). The core is known to consist entirely of ombrotrophic i.e. rain-fed peat and had already been measured for ash content, degree of humification, Ti, and total Pb concentrations (Givelet et al., 2003). Using archived specimens of dried, milled peat samples from this same core, subsamples were digested in duplicate in a high pressure microwave autoclave (Krachler et al., 2002) and measured for total Pb as well as for ^{206}Pb, ^{207}Pb, and ^{208}Pb using ICP-SMS (Krachler et al., 2004c). The peat core was age dated using ^{210}Pb (Constant Rate of Supply model) after measuring the activity of ^{210}Pb using a low background gamma-spectrometer with Canberra model GCW4028 High-Purity Germanium (HPGe) well-type gamma detector. The acquisition time ranged from 20 to 45 h, depending on the ^{210}Pb activity. The relative error of the measurements ranged from ca. 5% in samples containing more than 300 Bq/kg ^{210}Pb, to 25% for samples containing less than 30 Bq/kg. The Pb concentrations presented here represent an average of the replicate measurements using ICP-MS ($n = 4$) and XRF ($n = 4$).

To supplement the peat core data and to provide an estimate of contemporary atmospheric Pb inputs, a snow pit was dug (24.3.05) at this same bog, and samples collected from three depths (ca. 0–10, 10–20, and 20–30 cm). In addition, a snow pit was also dug four years later (11.3.09), and samples collected in triplicate from two depths (14 and 21 cm below the top of the pit). The snow samples collected in 2005 were subjected to four different treatments including filtration (0.45 μm) which had no consistent effects on Pb concentrations and no effect on the Pb isotope ratios; the snow samples from 2009 were simply acidified upon melting in the lab, and not filtered. For comparison with the peat core and recent snow from Algonquin Park, a sample of *Sphagnum* moss was collected (24.8.04) adjacent to the stream which enters Kawagama Lake from Wolfsbane Lake. The moss sample was processed and measured for Pb isotopes as the peat samples described above. Finally, rainwater samples were collected in triplicate on 8. August and 9. August, 2008, on the shore of Loon Bay of Kawagama Lake, in acid-cleaned bottles, and processed in the same way as the other water samples.

2.4. Soils

Samples of soil humus were collected in August of 2004, in the vicinity of the stream sampling locations, after first removing the litter layer. In the lab, the soil samples were dried overnight at 105 °C, then sieved to obtained the <2 mm and <200 μm fractions. The samples were then milled in an agate centrifugal ball mill. Subsamples of the <200 μm fraction were digested in a high pressure micro-

Table 2
Description of the watersheds upstream of the sampling locations.

Sampling site (No.)	Watershed elements upstream
Loon Bay (1)	Small wetland
White Trout Bay (2)	Small pond
Wolfsbane Lake (3)	Three wetlands, three small ponds, one large pond, Wolfsbane Lake
Hollow River (4)	Exclusive outlet of the Kawagama Lake watershed
Sucker Lake (5)	Sucker Lake, Slipper Lake, Stocking Lake, three small wetlands, four ponds
Kawagama Lake (6)	
Crumby Lake (7)	Three wetlands, one small lake
Bear Lake (8)	Bear Lake, Kimball Lake, Livingstone Lake, Dividing Lake
East Jeannie Lakes (9)	Three small lakes, two wetlands
Fletcher Creek (10)	Wetland, three ponds, Lower Fletcher Lake, Fletcher Lake
Harvey Lake (11)	Four ponds, Harvey Lake
East Hollow River (12)	Numerous small lakes and wetlands as well as larger, headwater lakes (Wildcat Lake, South Wildcat Lake) as well as lakes and wetlands of the Southeast corner of Algonquin Provincial Park

Notes: Sites 1–3, 5, and 7–11 represent the inflows to Kawagama Lake; Site 4 is the only outflow; Site 6 is Kawagama Lake proper where samples were collected near the middle of the lake.

wave autoclave (Krachler et al., 2002) and measured for ^{206}Pb, ^{207}Pb, and ^{208}Pb using ICP-SMS (Krachler et al., 2004c).

2.5. Sediments

A sediment core was collected in August of 2005 from the eastern end of Kawagama Lake (45° 18′ 558″ N, 78° 40.020′ W) toward the East Hollow River. The core was collected from a water depth of ca. 3 m. A plexiglas tube (50 × 5 cm) was driven by hand into the sediments, yielding a sediment core ca. 29 cm long. After carefully removing the overlying water column, the cores were extruded manually, and sliced into increments of approximately 2 cm. Individual sediment samples were packed into ziplock plastic bags and kept refrigerated until they were returned to the laboratory. In the lab, the sediment samples were dried overnight at 105 °C, but not treated further. For chemical and isotopic analyses, sufficient quantities of the clay-sized fraction (<2 μm) was obtained by sedimentation from samples EHR 1 to 10; in samples EHR 11 to 16, however, insufficient material from this fraction was obtained, so the fraction (2–10 μm) had to be used instead.

2.6. Kawagama stream and lake waters

Water samples were collected during August of 2004, 2005, and 2006 from the locations indicated (Fig. 1b). Single samples were collected from each site during 2004 (as part of a pilot study), but in triplicate from each site in 2005 and 2006. The water samples representing Kawagama Lake itself (site 6) were sampled from the surface of the lake, at a position of 45° 18′ 0″ N, 78° 46′ 0″ W, on 26.8.04, 19.9.04, 17.8.05 and 24.8.06. For comparison with these data, bulk and filtered water samples were collected from the same location (site 6) on 10.8.08. The outflow from the lake was collected at the waterfalls on the Hollow River (45° 15′ 408″, 78° 51′ 534″ W) which is ca. 7 km downstream from the dam at River Bay; the dam is operated by the local electricity company (Ontario Power Generation) and is used to regulate the level of the lake.

2.6.1. 2004

In 2004, wearing appropriate clothing, hair net and polyethylene gloves, water samples were collected directly into pre-cleaned Falcon tubes containing 2 drops of high purity concentrated nitric acid. This acid is produced in-house, purified twice by sub-boiling distillation, and has an average Pb concentration of 800 pg/l. Addition of 100 μl of this acid to 100 ml of water is sufficient to acidify the water to pH <2 and stabilise the trace metals until the samples could be measured. The contribution of Pb to the sample from this acid is approximately 0.8 pg/l. To minimise the risks of contamination, none of the water samples were filtered. Each water sample was packed into three ziplock plastic bags and kept refrigerated until they could be transported to the laboratory in Germany for analyses. For transport, they were placed into an insulated plastic box containing freezer packs and shipped airfreight; the samples were still cool when they arrived at the lab.

2.6.2. 2005

In 2005, triplicate samples were collected directly into acid-cleaned, 100 ml low density polyethylene (LDPE) bottles to which high purity HNO_3 (100 μl) had already been added. Again, to minimise the risks of contamination, none of the water samples were filtered.

2.6.3. 2006

In 2006, triplicate water samples were collected as in 2005, but in addition, triplicate samples of filtered water was also taken. To this end, 25 mm syringe-type membrane filters consisting of 0.45 μm PTFE (Millex LH, Millipore) were used. The filters as well as the plastic syringes were pre-cleaned under strict clean lab conditions, vacuum-packed in polyethylene, and then packed in ziploc plastic bags. One syringe and three filters were used per sampling location. Each filter was first rinsed with 10 ml of sample prior to collection. Depending on the site, between 10 and 20 ml of sample could be collected before the filters became clogged, with the stream water samples much more susceptible to clogging. Based on blank determinations employing MilliQ water, the Pb contribution from the clean 0.45 μm PTFE filters is negligible (<<1 ng/l).

2.6.4. 2008

As noted above, rainwater samples were collected on 8.8.08 and 9.8.08, and lake water samples (bulk and filtered, in triplicate) at site 6 of Kawagama Lake, using the same procedures as described above for 2006.

2.7. Stocking Lake and Dividing Lake

For comparison with Kawagama Lake, water samples were also collected from Stocking Lake, a nearby but much less accessible lake, in Haliburton Forest, a 27,000 hectare privately-owned nature reserve. Stocking Lake (389 m) is upstream of Kawagama Lake, and empties into Kawagama via Slipper and Sucker Lakes; site 5 of Kawagama Lake (Fig. 1b) represents the inflow from Sucker Lake. Triplicate water samples were collected from the two streams which enter Stocking Lake, as well as Stocking Lake proper, on 7.10.05.

The East Hollow River and Bear Lake, the main sources of water to Kawagama Lake, have their origins in the Dividing Lake Nature Reserve, in Algonquin Provincial Park. The DLNR is one of the more remote parts of Algonquin Park, and is the only part of the park which was never logged. Bulk and filtered water samples were collected in triplicate from the centre of Dividing Lake, and a stream entering Dividing Lake from the north, on 22.9.08, using the same field methods as described above.

2.8. ICP-SMS of trace metal concentrations and Pb isotope ratios

For ICP-SMS, a high efficiency sample introduction system (Apex) was used, along with a PFA low flow nebulizer operated in the self-aspirating mode (Krachler et al., 2005). With respect to Pb and Sc, the LODs were 0.06 and 0.005 ng/l, respectively. The ICP-SMS approach used here has two advantages compared to ICP-MS instruments equipped with quadrupole mass filter (ICP-QMS). First, the LOD for Pb is more than three orders of magnitude lower than the LODs recently reported (Klaminder et al. 2006; Vinogradoff et al. 2005). Second, Sc can be determined even at low ng/l levels: using a resolution setting of $m/\Delta m = 4000$, the severe spectral interferences which hampers the reliable quantification of Sc at m/z 45 using ICP-QMS, can be easily separated from the Sc signal (Prohaska et al., 1999). The LODs for Pb and Sc are approximately two to three orders of magnitude below the lowest Pb and Sc concentrations found during the course of this study. The certified water reference material SLRS-4 (National Research Council Canada) was analyzed at regular intervals during the analyses to guarantee the accuracy of the results. Good agreement between the certified and experimental values was obtained for all elements of interest.

Lead isotope ratios (^{206}Pb, ^{207}Pb, and ^{208}Pb) in the water samples were determined using ICP-SMS as described previously (Krachler et al., 2004b). The isotopic standard reference material NIST 981 analyzed before and after each sample was used to correct for mass discrimination effects during analysis. The precision of Pb isotope ratios varied between 0.05 and 0.1%. Because of the extreme sensitivity combined with low electronic noise and high ion extraction efficiency, the performance of ICP-SMS in terms of precision for Pb isotope measurements is roughly one order of magnitude superior to ICP-QMS. Taken together, ICP-SMS allows the straightforward assessment of concentration and Pb isotope data, even at the extremely low concentrations occurring in natural waters.

3. RESULTS

3.1. Isotopic evolution of atmospheric Pb

The peat core from Spruce Bog, Algonquin Park, represents approximately 200 years of atmospheric Pb deposition (Fig. 2). The most radiogenic value for the ratio ^{206}Pb/^{207}Pb is 1.227 ± 0.001 in the deepest peat sample dating from AD 1804 ± 53; this value is comparable to the estimated "background" (^{206}Pb/^{207}Pb) of the rocks and soils of this area (see below) and is taken to represent the isotopic composition of natural Pb in this sample supplied exclusively by atmospheric dusts. During the past two centuries, however, the ^{206}Pb/^{207}Pb ratios have shifted to lower values, reflecting the growing importance of atmospheric Pb contamination. There are two important dates regarding the history of atmospheric Pb pollution in North America: the introduction of leaded gasoline in the U.S. in 1923, and the elimination of leaded gasoline in the mid-1970's. Although the isotopic composition of atmospheric Pb was fairly stable around 1880–1920 (Fig. 2), with most Pb derived from industrial sources (smelting and coal burning), the signature became less radiogenic after the introduction of leaded gasoline in the early 1920's. For example, the most radiogenic sample of the 20th century dates from 1925 ± 10 (ALG 40) and yielded ^{206}Pb/^{207}Pb = 1.204. The phase out of leaded gasoline for automobiles which began in Canada by 1976. The most radiogenic sample of the recent decades, however, dates from 1983 (ALG 16) with ^{206}Pb/^{207}Pb = 1.185. Since then, the values have once again gone into decline, reaching ^{206}Pb/^{207}Pb = 1.160 in the most recent sample (corresponding to AD 2000 when the core was collected). The recent shift in Pb isotope signatures to less radiogenic values subsequent to the elimination of leaded gasoline more than 30 years ago, was unexpected.

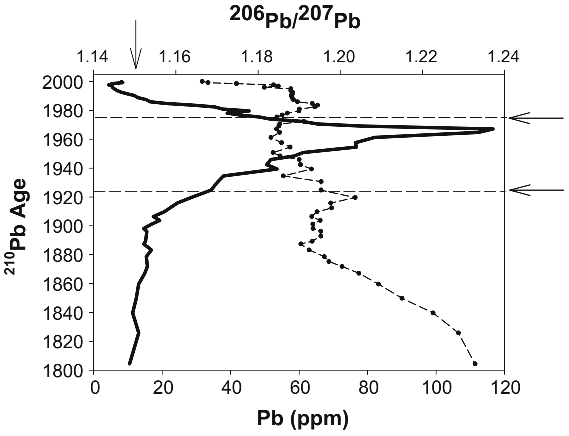

Fig. 2. Lead concentrations (solid line, ppm) and isotopic composition (^{206}Pb/^{207}Pb, dashed line) in acid digests of peat samples from a core collected in the Spruce Bog, Algonquin Park. The age dates were obtained using ^{210}Pb (Constant Rate of Supply model). The horizontal arrows indicate the depth corresponding to the introduction (1923) and elimination (1976) of leaded gasoline; the vertical arrow indicates the ^{206}Pb/^{207}Pb ratio of leaded gasoline used in central Canada (Sturges and Barrie, 1989). The top sample corresponds to AD 2000 when the peat core was collected. Notice that the ^{206}Pb/^{207}Pb ratio has continued to decline, despite the elimination of leaded gasoline in Canada, starting in 1976.

Confirmation of the low ratios of ^{206}Pb/^{207}Pb found in the top peat layers are provided by the snow samples collected from the Spruce Bog in 2005 and 2009 (Table 3). In addition to these samples, the *Sphagnum* moss sample collected near the stream which enters Kawagama Lake from Wolfsbane Lake yielded ^{206}Pb/^{207}Pb = 1.156 ± 0.001, a value which is consistent with the top sample from the peat core and further helps to constrain the isotopic composition of atmospheric Pb reaching the watershed today. For comparison with this data, the rainwater samples collected in 2008 at Kawagama Lake had ^{206}Pb/^{207}Pb = 1.112 ± 0.001 on 8.8.08 and ^{206}Pb/^{207}Pb = 1.148 ± 0.001 on 9.8.08 (Table 3). Despite the elimination of leaded gasoline, therefore, the isotopic composition of atmospheric Pb has not shifted back in the direction of natural values.

3.2. Isotopic composition of natural inputs of terrestrial and aquatic Pb

The isotopic composition of the natural terrestrial and aquatic inputs of Pb to Kawagama Lake from the watershed was estimated using the clay-sized fraction (<2 μm) of sediments pre-dating the onset of industrialization. Specifically, samples EHR 1–EHR 4 contain no measurable unsupported ^{210}Pb and are therefore older than AD

Table 3
Summary of snow pit and rainwater data.

	Pb (ng/l)	Sc (ng/l)	Pb/Sc	206/207	Std dev	208/206	Std dev
Snow Pit, 2005, Spruce Bog, Algonquin Park							
AG 0–10 cm acidified + filtered	318	1.7	186	1.164	0.001	2.101	0.002
AG 0–10 cm not acidified + filtered	241	4.0	61	1.163	0.001	2.099	0.002
AG 0–10 cm acidified + not filtered	322	1.1	281	1.163	0.001	2.102	0.002
AG 0–10 cm not acidified + not filtered	224	2.3	96	1.163	0.001	2.093	0.002
Average	*276*	*2.3*	*156*	*1.163*	*0.001*	*2.099*	*0.002*
Standard deviation	*51*	*1.2*	*99*				
AG 10–20 cm acidified + filtered	237	1.2	192	1.174	0.001	2.081	0.002
AG 10–20 cm not acidified + filtered	103	3.1	34	1.171	0.001	2.082	0.002
AG 10–20 cm acidified + not filtered	245	1.0	247	1.172	0.001	2.083	0.002
AG 10–20 cm not Acidified + not filtered	81	2.3	36	1.167	0.002	2.086	0.004
Average	*167*	*1.9*	*127*	*1.171*	*0.001*	*2.083*	*0.003*
Standard deviation	*86*	*1.0*	*109*				
AG 20–30 cm acidified + filtered	166	1.5	111	1.231	0.001	2.008	0.002
AG 20–30 cm not acifidied + filtered	93	1.6	58	1.231	0.001	2.005	0.002
AG 20–30 cm acidified + not filtered	160	0.7	222	1.231	0.001	2.006	0.001
AG 20–30 cm not acidified + not filtered	119	1.3	95	1.231	0.003	2.006	0.004
Average	*134*	*1.3*	*121*	*1.231*	*0.002*	*2.006*	*0.002*
Standard deviation	*35*	*0.4*	*71*				
Rainwater, 2008, Kawagama Lake							
(unfiltered rainwater, 8.8.08; pH 4.12)							
UFRW 8808 1	339	3.0	113	1.099	0.000	2.174	0.001
UFRW 8808 2	638	3.6	179	1.137	0.000	2.126	0.001
UFRW 8808 3	383	3.8	101	1.099	0.001	2.178	0.001
Average	*453*	*3.5*	*131*	*1.112*	*0.001*	*2.159*	*0.001*
Standard deviation	*161*	*0.4*	*42*				
(unfiltered rainwater, 9.8.08; pH 4.10)							
UFRW 9808 1	168	3.1	54	1.150	0.001	2.101	0.002
UFRW 9808 2	225	3.3	67	1.154	0.001	2.095	0.001
UFRW 9808 3	265	6.4	42	1.141	0.001	No data	
Average	*219*	*4.3*	*54*	*1.148*	*0.001*	*2.098*	*0.002*
Standard deviation	*49*	*1.8*	*13*				
Snow Pit, 2009, Spruce Bog, Algonquin Park							
Algonquin LHS 110309 1	548	0.59	932	1.151	0.001	2.107	0.002
Algonquin LHS 110309 2	104	0.32	326	1.168	0.001	2.087	0.001
Algonquin LHS 110309 3	128	0.41	310	1.170	0.001	2.081	0.003
Average	*260*	*0.44*	*522*	*1.163*	*0.001*	*2.092*	*0.002*
Standard deviation	*250*	*0.14*	*355*				
Algonquin RHS 110309 1	140	1.33	106	1.179	0.001	2.073	0.002
Algonquin RHS 110309 2	155	0.41	380	1.182	0.001	2.063	0.003
Algonquin RHS 110309 3	151	0.65	233	1.179	0.000	2.074	0.001
Average	*149*	*0.79*	*239*	*1.180*	*0.001*	*2.070*	*0.002*
Standard deviation	*8*	*0.48*	*137*				

1839 ± 40; the isotopic composition of Pb in these samples ranges from 1.191 ± 0.000 to 1.201 ± 0.001 (Table 4). These data are consistent with Pb isotope data (^{206}Pb/^{207}Pb = 1.22 and ^{208}Pb/^{206}Pb = 2.10) for sediment samples pre-dating the Industrial Revolution (as indicated by ^{210}Pb-age dating) from Plastic Lake which is 8 km south of Kawagama Lake (Watmough and Dillon, 2007). For comparison with these values, the natural "background" isotopic composition of lithogenic Pb in the watershed can be estimated considering the age of the rocks (1.45 Ga) and the evolution of ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb of the Upper Continental Crust (Zartman and Doe, 1981) yielding values of ^{206}Pb/^{207}Pb = 1.238 and ^{208}Pb/^{206}Pb = 2.016. The differences between bulk rock, bulk sediment (Watmough and Dillon, 2007) and the fine fraction of sediments from Kawagama Lake (this study) are most likely be

Table 4
Summary of lake sediment data, Kawagama Lake.

Sample No.	Weight gram	^{137}Cs counts per g	Unsupported ^{210}Pb Bq per kg	^{210}Pb integral	Age years	Error ± years	Calendar year	^{206}Pb/^{207}Pb	Std dev	^{208}Pb/^{206}Pb	Std dev	Pb (mg/kg)
East Hollow River sediment core												
EHR-16	4.130	155.21	41.71	159.53	0.0		2005	1.144	0.000	2.120	0.001	42.1
EHR-15	4.094	85.74	23.72	117.82	9.7	2.0	1995	1.192	0.001	2.075	0.001	40.4
EHR-14	2.924	98.15	25.25	94.10	17.0	3.0	1988	1.199	0.001	2.071	0.001	33.8
EHR-13	2.678	53.02	23.36	68.85	27.0	5.0	1978	1.199	0.002	2.072	0.001	32.3
EHR-12	2.626	36.94	26.85	45.48	40.3	5.0	1965	1.199	0.001	2.077	0.002	22.9
EHR-11	4.157	22.61	0.88	18.63	69.0	10.0	1936	1.199	0.001	2.077	0.002	18.7
EHR-10	6.019	0.00	9.75	17.74	70.5	10.0	1934	1.212	0.001	2.114	0.001	15.6
EHR-09	6.721	0.00	3.75	7.99	96.1	15.0	1909	1.212	0.001	2.124	0.001	14.9
EHR-08	5.970	0.00	0.00	4.24	116.5	20.0	1888	1.194	0.001	2.131	0.001	21.6
EHR-07	6.455	0.00	2.59	4.24	116.5	20.0	1888	1.189	0.001	2.150	0.001	18.3
EHR-06	7.498	0.00	0.75	1.64	146.9	30.0	1858	1.183	0.001	2.142	0.001	14.0
EHR-05	7.998	0.00	0.90	0.90	166.3	40.0	1839	1.197	0.000	2.139	0.001	8.5
EHR-04	8.277	0.00	0.00	0.00				1.200	0.000	2.152	0.001	9.4
EHR-03	8.324	0.00	0.00	0.00				1.191	0.001	2.170	0.000	11.6
EHR-02	8.210	0.00	0.00	0.00				1.201	0.000	2.164	0.001	10.6
EHR-01	8.875	0.00	0.00	0.00				1.199	0.000	2.193	0.000	8.5

Notes: EHR-01–EHR-10, <2 micron fraction; EHR-11–EHR-16, 2–10 micron fraction.

due to the kinds of mineralogical- and grain-size effects which have been documented in sediments and soils by other investigators (Shirahata et al., 1980; Erel et al., 1990) e.g. preferential weathering of radiogenic minerals such as apatite.

The amount of clay-sized (i.e. <2 μm) material which could be extracted from samples EHR 11 to EHR 16 was insufficient for chemical and isotopic analyses, possibly because of the re-establishment of vegetation cover following deforestation. However, the fraction 2–10 μm was sufficient; measurements of this fraction show that the isotopic composition of Pb in this size fraction did not change significantly between 1936 and 1995 (Table 4). This finding contrasts with the results obtained using the peat core which receives Pb exclusively from the atmosphere. In contrast to the peat core where Pb concentrations increased by a factor of 10 during the past two centuries, Pb concentrations in the lake sediments changed only by a factor of five. Compared to the peat core from the bog, therefore, the lake sediments are a much less sensitive indicator of atmospheric change; they are, however, a valuable indicator of the isotopic composition of natural Pb derived from terrestrial and aquatic inputs in the past.

3.3. Isotopic composition of soil humus

The < 200 μm fraction of the humus layer of the soils around the Kawagama Lake watershed (Table 5) are much less radiogenic than the pre-industrial lake sediment samples (Table 4): all values show ^{206}Pb/^{207}Pb < 1.19 and four yielded values <1.16. The average isotopic composition of Pb in atmospheric aerosols collected in Dorset during the 1970's and 80's was ^{206}Pb/^{207}Pb = 1.148 ± 0.007 which reflected the impact of leaded gasoline used at that time in central Canada (Sturges and Barrie, 1989), and the isotopic composition of Pb in the humus layers of the soils today represents a mixture between natural Pb derived from the underlying soils, with significant contributions of atmospheric derived from industrial sources.

3.4. Lead in the surface waters

3.4.1. Pb, Sc, and Pb/Sc

The inter-site variations in Pb concentrations during the three seasons (2004, 2005, 2006) show consistent differences. The data for 2006 are representative, and are summarised in the form of Pb and Sc concentrations, and the Pb/Sc ratios, for bulk and filtered samples, in Fig. 3. The greatest concentrations of Pb are found in the streams entering the lake, with the concentrations in the lake itself (site 6) much lower (Fig. 3a). The greatest concentrations of Pb (up to 1210 ng/l in 2005) were always found in the stream entering Kawagama Lake from Crumby Lake; this sampling location is downstream from a small wetland (beaver pond) which apparently has a disproportionate effect on the supply of Pb to the lake. In fact, the streams contributing the greatest Pb concentrations, all have wetland components in their watersheds (Table 2); similar findings have been reported by others working in the region, including LaZerte et al., 1989, Watmough and Dillon (2007, and Landre et al. (2009). Concentration data alone, however, must be viewed with care as they are undoubtedly affected by water flow rates. For this reason, it is desirable to compare the Pb concentrations to another lithogenic element.

Because Sc has no anthropogenic source and behaves conservatively during chemical weathering in soils (Shotyk et al., 2001), the variations in Sc throughout the watershed provide an indication of the variations in the concentrations of mineral particles and colloids (Fig. 3b). The greatest Sc concentrations are seen in the streams entering Kawagma Lake from Wolfsbane Lake and Crumby Lake, and the lowest concentrations in Kawagama Lake proper

Table 5
Pb concentrations and Pb isotope ratios, humus and moss.

Sample ID	Location	Sample type	Pb (ppm)	$^{206}Pb/^{207}Pb$	Std. dev	$^{208}Pb/^{206}Pb$	Std. dev
lbk-3	Loon Bay	Humus	39.3	1.147	0.001	2.129	0.003
wtbk-2	White Trout Bay	Humus	25.5	1.156	0.001	2.133	0.002
wik-2	Wolfsbane Lake	Humus	19.9	1.154	0.001	2.148	0.002
sk-3	Sucker Lake	Humus	27.9	1.175	0.002	2.091	0.004
clk-3	Crumby Lake	Humus	14.7	1.185	0.000	2.076	0.002
ejl-3	East Jeannie Lake	Humus	151.4	1.179	0.001	2.085	0.001
fc-3	Fletcher Creek	Humus	68.2	1.173	0.001	2.091	0.003
ehr-3	East Hollow River	Humus	81.9	1.182	0.001	2.084	0.003
wik-3	Wolf Island	*Sphagnum* moss	9.0	1.156	0.001	2.136	0.003

Notes: (1) Humus samples represent <200 micron fraction. (2) Concentrations obtained using XRF except for *Sphagnum* moss (ICP-SMS).

(site 6) and the outflow of the Hollow River; similar trends are seen in Al (not shown). The Pb/Sc ratios show that all of the water samples except those at White Trout Bay (seepage water) and Bear Lake are enriched, compared to crustal proportions (Fig. 3c).

3.4.2. Total vs. dissolved metal concentrations

Sampling during 2006 allowed both the total as well as dissolved (<0.45 μm) concentrations of trace metals to be determined (Fig. 3). Although the dissolved Pb concentrations are generally much lower than total Pb concentrations, even the dissolved Pb fraction in the streams entering Kawagama Lake are much greater than in the lake itself. For example, the stream from Crumby Lake yielded dissolved Pb concentrations of 188 ± 40 ng/l, compared to Kawagama Lake itself (site 6) which showed as little as 10 ng/l (Fig. 3a). Scandium shows much smaller differences between the bulk water samples and the dissolved fraction (Fig. 3b).

The ratios of Pb to Sc in these fractions show spatial variations consistent with those found during 2005 and 2004. Taking the stream from Crumby Lake again as an extreme example, the Pb/Sc ratio in the bulk water samples is as great as 25 (Fig. 3c), and in the dissolved fraction as much as 10 (Fig. 3d), compared to the seepage water at WTB with Pb to Sc ratios in both fractions of ca. 1:1 (in 2006). Compared to the seepage water at WTB, therefore, all of the inflows to Kawagama Lake, are significantly enriched in Pb, relative to Sc.

3.4.3. Isotopic composition of Pb in the streams versus lake

The Pb isotope data for the stream and lake water samples are summarised as the ratio $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ (Fig 4). In general, the spatial differences in Pb isotope ratios are very reproducible during all 3 years of water sampling. The very low $^{206}Pb/^{207}Pb$ values for the water samples from Kawagama Lake (site 6) are particularly noteworthy. The streams have $^{206}Pb/^{207}Pb$ values in the range 1.15 to 1.19. The $^{206}Pb/^{207}Pb$ values for the lake itself (site 6) were measured in samples collected in August as well as September of 2004, and the values were identical ($^{206}Pb/^{207}Pb = 1.124$). Although the water samples collected in 2005 at this site show some variation (Fig. 4), the average value ($^{206}Pb/^{207}Pb = 1.121 \pm 0.011$) is very similar to that of 2004. In 2006, one of the water samples showed the lowest ratio of $^{206}Pb/^{207}Pb$ measured in Kawagama Lake to date (1.097 ± 0.001). In the samples collected from the same site in 2008, the bulk waters averaged $^{206}Pb/^{207}Pb = 1.159 \pm 0.002$ and the filtered waters $^{206}Pb/^{207}Pb = 1.149 \pm 0.002$. The very low ratios of $^{206}Pb/^{207}Pb$ found in the lake water samples (ca. 1.10–1.15) compared to the streams (up to ca. 1.19) suggests that the fractionation processes which are removing Pb (Fig. 3) and other trace metals (not shown) from the streams relative to the lake, have a pronounced effect on the isotopic composition of Pb.

3.4.4. Isotopic composition of dissolved versus particulate Pb

The data from 2006 shows that the bulk water samples (i.e. not filtered) are typically much more radiogenic than the filtered water samples (Fig. 5). Again, the picture which emerges is that the streams deliver particulate Pb which contains both natural, radiogenic mineral particles as well as organic-rich particles from the soil surface which are contaminated by industrial Pb. Again, rocks in this area are assumed to have $^{206}Pb/^{207}Pb = 1.238$ compared to the leaded gasoline signature of central Canada in the 1970's when $^{206}Pb/^{207}Pb = 1.148 \pm 0.007$ (Sturges and Barrie, 1989). As soil-derived mineral and organic particles are removed from the water column by sedimentation or coagulation, apparently proportionately more of the radiogenic mineral particles are removed, giving rise to less radiogenic Pb isotope signatures in the water. As these particles are removed from the water column of the lake by physical and chemical processes at the interface between the stream and the lake, Pb in the lake waters becomes less radiogenic, and the sediments more radiogenic, relative to the streams. The physical and chemical fractionation of colloids and particles, therefore, has a profound effect on the isotopic composition of Pb in the streams and lakes of this forested region.

4. DISCUSSION

4.1. Kawagama Lake watershed

With several hundred summer cottages on Kawagama Lake, it is important to consider the possibility of Pb contamination from local sources. However, the stream entering Kawagama Lake from Crumby Lake consistently

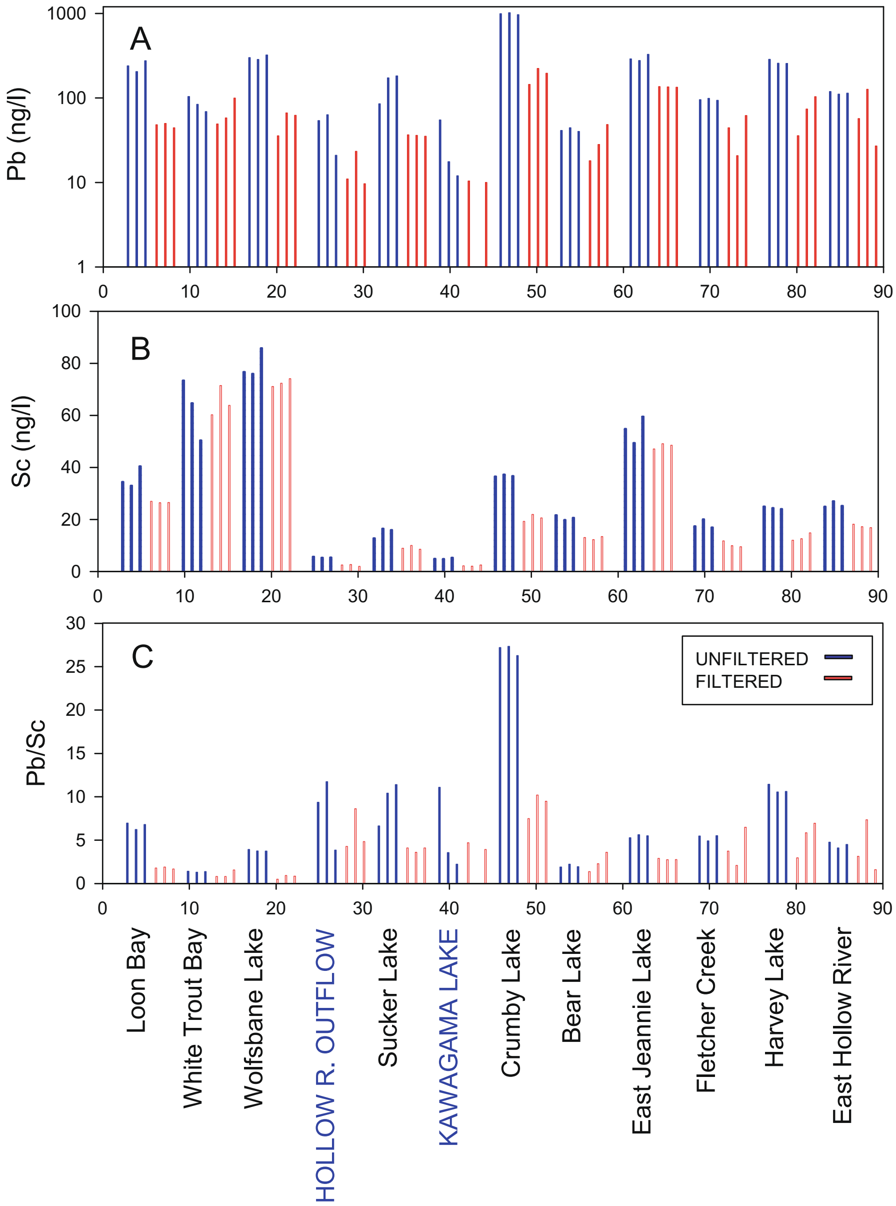

Fig. 3. Concentrations of total (unfiltered) and dissolved (0.45 μm) Pb and Sc (ng/l), and their corresponding Pb/Sc ratios, for the 2006 water samples.

yielded the greatest Pb concentrations, yet there is no road access and there are no cottages on Crumby Lake. The same is true of other inlets, for example the stream which enters Kawagama Lake from Loon Bay, and the stream which originates in Wolfsbane Lake. In fact, Wolfsbane Lake is within the Frost Centre, a 24,000 hectare, government-owned nature reserve used primarily for outdoor education. Although Kawagama Lake itself is populated, particularly in the summer months when the samples were collected, this is not true of some of the watersheds upstream.

Moreover, the water samples which were collected from Stocking Lake in the Haliburton Forest nature preserve, are also much less radiogenic than the estimated "background" values for this region. Specifically, the isotopic composition of Pb in this lake, expressed as the ratio $^{206}Pb/^{207}Pb$, as well as the two streams which enter it from the east and from the west, were found to be 1.175 ± 0.005 ($n = 3$), 1.176 ± 0.004 ($n = 3$), and 1.170 ± 0.009 ($n = 3$), respectively. The water samples collected from Dividing Lake which is the most remote and least accessible of the sites visited during this study, yielded $^{206}Pb/^{207}Pb = 1.176 \pm 0.002$ ($n = 3$) for the bulk water samples, and 1.159 ± 0.001 ($n = 3$) for the dissolved samples. Given the number of streams and lakes which were sampled upstream of Kawagama Lake and well beyond any significant local influences, the Pb isotope data presented here may be representative and therefore broadly valid for the streams and lakes of this mixed forest region of central Ontario.

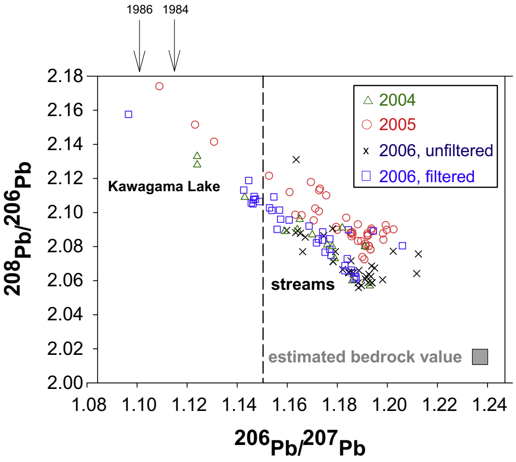

Fig. 4. Isotopic composition of Pb in water samples collected in 2004, 2005, and 2006 (filtered and not filtered). This plot of $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ shows that all water samples are well removed from the estimated isotopic composition of natural Pb in the watershed, as indicated by the solid square (estimated bedrock composition). The vertical dashed line corresponds to the isotopic composition of leaded gasoline used in the past, in central Canada (Sturges and Barrie, 1989). The samples lying to the left of the vertical dashed line are from Kawagama Lake proper (site 6), and are even less radiogenic than leaded gasoline additives, showing that other sources of industrial Pb have impacted the lake. The two vertical arrows represent the $^{206}Pb/^{207}Pb$ values for aerosols collected in Dorset in 1984 and 1986 (Sturges and Barrie, 1989) when the air mass trajectories were predominantly from the Noranda area of Quebec (see text for discussion).

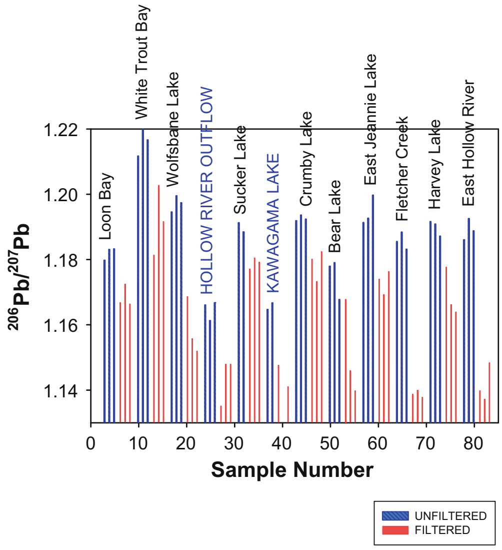

Fig. 5. Isotopic composition ($^{206}Pb/^{207}Pb$) of Pb in the bulk water samples versus the filtered samples (dissolved fraction). Each fraction was collected in triplicate, from each sampling location, in 2006. The particulate material which is present in the bulk samples is clearly more radiogenic than the corresponding dissolved fraction. The diagram illustrates how particle scavenging in the water column leads to Pb in the lake waters becoming less radiogenic, and Pb in the lake sediments more radiogenic, compared to Pb in the streams.

4.2. Comparison of the peat bog and lake sediment Pb records

The declining $^{206}Pb/^{207}Pb$ values observed during the past two decades in the peat core from Algonquin Park are not seen in the recent layers of sediments from nearby Plastic Lake: in fact, the top sediment layer, which is least radiogenic, shows a $^{206}Pb/^{207}Pb$ of 1.19 (Watmough and Dillon, 2007, Fig. 4). The peat core, taken from an ombrotrophic (i.e. rain-fed) *Sphagnum* bog, receives Pb exclusively from atmospheric deposition (Givelet et al., 2003). Moreover, the peat has been accumulating rapidly, with the top 60 cm representing only ca. two centuries of peat growth (Fig. 2). As a consequence, the peat core provides a sensitive and high resolution reconstruction of the isotopic evolution of atmospheric Pb. In contrast to the peat bog, lake sediments receive inputs of Pb from both atmospheric as well as aquatic sources (Bindler et al., 2001; Eades et al., 2002). The isotopic composition of streams entering Kawagama Lake are much more radiogenic than the lake water samples (Fig. 4), and contain much higher Pb concentrations (Fig. 3). The Pb removal process at the stream/lake interface, therefore, not only has a profound impact on the isotopic composition of Pb in the lake waters, but also in the sediments. In fact, the sediments must be receiving and accumulating Pb-bearing particles which are more radiogenic than the Pb in the streams.

The comparison of the streams and lake water data presented here, helps to explain why the top layers of the sediment record from Plastic Lake, do not show any $^{206}Pb/^{207}Pb$ values below ca. 1.19. As noted by Watmough and Dillon (2007), there is a “disconnect” between atmospheric deposition, and recent changes in Pb concentrations, and Pb isotope ratios, in the lake sediments, a finding that has been reported in several other studies (Shirahata et al., 1980; Johnson et al., 1995; Outridge et al., 2002; Yang et al., 2002).

4.3. Lead in streams

There are several recently published studies of the abundance of Pb in streams (Erel et al., 1990, 1991; Vinogradoff et al., 2005; Graham et al., 2006; Klaminder et al., 2006; Pokrovsky et al., 2006). The detection limits reported by Vinogradoff et al. (2005) of 90 ng/l and Klaminder et al. (2006, 2008) of 200 ng/l are inadequate for studying the natural abundance of Pb in streams. However both reports include Pb isotope ratios: in the watershed from Sweden (Klaminder et al., 2006) as well as that from Scotland (Vinogradoff et al., 2005), the isotopic composition of Pb is much less radiogenic than host rock values, providing a clear indication that Pb in the streams is predominantly anthropogenic in origin. In streams from a remote part of Siberia, Pokrovsky et al. (2006) reported Pb concentrations as low as 40 ng/l, with the majority of this Pb associated with the particulate fraction. The association between Pb in streams with particles and colloids is well documented (Erel et al., 1991; Graham et al., 2006), and the results presented here (Fig. 3) are consistent with these earlier studies. We assume that most of the industrial Pb in the waters, whether it is particulate or colloidal, is bound to organic matter (Tyler, 1981; Lazerte et al., 1989; Taillefert et al., 2000).

4.4. Pb in lake water

The concentrations of dissolved Pb in Kawagama Lake may be as low as 10 ng/l or less: two samples in 2006 yielded 10 ng/l and one sample in 2008 contained 6 ng/l. Although these concentrations approach "natural" values, the isotopic composition of these samples (^{206}Pb/^{207}Pb = 1.156 ± 0.003, 1.149 ± 0.003 and 1.156 ± 0.003, respectively) are far removed from the expected isotopic composition of natural Pb (see below). The discrepancy between the measured ratios and the values estimated to represent natural Pb, indicates that even in the samples containing very low Pb concentrations, most of the Pb is industrial in origin. Based on the Sc concentrations and the ratio of Pb/Sc in the Upper Continental Crust (Wedepohl, 1995), the natural abundance of dissolved Pb may have been as low as 2 ng/l, with the concentrations in the lake and especially in the streams today well beyond this value.

4.5. Isotopic evolution of Pb in waters of the Kawagama Lake watershed

Natural Pb in the soil solutions and streams of the watershed are derived from the chemical weathering of feldpars (plagioclase and potassium feldspar) as well as biotite. Measurements of Pb, Sr, and Ba in feldspar samples, and comparison with the corresponding values in the waters, however, shows that weathering inputs of Pb to the streams and lakes are negligible (data not shown). The Pb-bearing colloids and particles, whether they consist of phyllosilicate clay minerals, amorphous Al and Fe oxides and hydroxides, organic matter, or a mixture of all three components, should resemble the isotopic composition of the clay fraction (<2 μm) removed from the sediments pre-dating industrialization (Table 4), namely ^{206}Pb/^{207}Pb = 1.19–1.21.

The streams which enter Kawagama Lake today, however, are much less radiogenic than this, with most values for ^{206}Pb/^{207}Pb between 1.16 and 1.19 (Fig. 4). As a result, some other source of Pb, in addition to the natural Pb derived from chemical weathering, must be invoked to explain the Pb isotope data from the stream samples. Leaded gasoline used in the past in Canada had a ^{206}Pb/^{207}Pb of approximately 1.15 (Sturges and Barrie, 1989), and comparable values are seen in the humus samples from several sites in the Kawagama Lake watershed. The Pb/Sc ratios of the humus samples, combined with the Pb isotope data, show that the humus layers are contaminated by anthropogenic Pb, a conclusion reached earlier in other studies of the soils of this region (Watmough and Hutchinson, 2004). The stream waters, with ^{206}Pb/^{207}Pb varying between 1.16 and 1.19 (Fig. 4), represent a mixture of natural Pb supplied by mineral particles (^{206}Pb/^{207}Pb = 1.19–1.21) and humus particles derived from the soil surface which have been impacted by leaded gasoline (ca. ^{206}Pb/^{207}Pb = 1.15). The stream water values are generally closer to the leaded gasoline values which indicates that a large part of the Pb entering the lake is from contamination, and not from natural sources.

The isotopic composition of Pb in the waters from Kawagama Lake itself (^{206}Pb/^{207}Pb = 1.09–1.15) are not only much lower than the streams (1.16–1.19) and the humus layers of the soils (1.15–1.19), but are even lower than the values attributed to leaded gasoline (vertical dashed line in Fig. 4). To explain the isotopic composition of Pb in Kawagama Lake today (Fig. 4), however, there must be an additional source of industrial Pb which is less radiogenic than leaded gasoline.

4.6. Contemporary inputs of anthropogenic, atmospheric Pb

With the elimination of leaded gasoline in Canada beginning in the mid-1970's, it could reasonably be expected that the isotopic composition of atmospheric Pb supplied to the Kawagama Lake watershed would evolve back in the direction of the natural values characteristic of the deepest, oldest section of the peat core from Spruce Bog (Fig. 2) which, in turn, approach the values representative of the metamorphic rocks of this region of Ontario (^{206}Pb/^{207}Pb = 1.238). In the studies published by Carignan and Gariépy (1995) and Simonetti et al., 2000, for example, leaded gasoline was thought to be by far the dominant source of anthropogenic, atmospheric Pb in this part of northeastern North America. In fact, the peat core shows that the Pb isotope values, since the phase out of leaded gasoline, expressed as the ratio ^{206}Pb/^{207}Pb, are moving in the opposite direction (Fig. 2) toward less radiogenic values. The low ratios of ^{206}Pb/^{207}Pb seen in the top layers of the bog have since been validated by the snow samples collected at the same site during 2005 and 2009 (Table 3), as well as the sample of *Sphagnum* moss collected at Kawagama Lake in 2004 (Table 5), and the rainwater samples collected at Kawagama Lake in 2008 (Table 3). If the Pb isotope ratios are not evolving in the direction of natural Pb supplied by soil dust particles derived from rock weathering, what is the dominant source of atmospheric Pb today ? In her study of lake sediments of this region, Blais (1996) realized that even in the early 1980's, an important source of atmospheric Pb contamination, especially in Quebec, was the smelting and refining of Ni and especially Cu ores.

The paper by Sturges and Barrie (1989) includes Pb isotope ratios for aerosol samples collected in Dorset in 1984 and 1986. The lowest ^{206}Pb/^{207}Pb reported in their study (ca. 1.12 in 1984 and 1.10 in 1986) corresponded to the periods when air masses were arriving from the smelter at Noranda, more than 400 km to the north, and the largest single source of atmospheric Pb in Canada. We note that many massive sulphide ore deposits in northern Ontario and Quebec are non-radiogenic, with half a dozen significant ore bodies having ^{206}Pb/^{207}Pb below 1.0, and some as as low as 0.91 (Russell and Farquahr, 1960). With atmospheric Pb contributions from leaded gasoline having been effectively eliminated, it stands to reason that other industrial sources of Pb have become relatively more important. The Sudbury basin lies approximately 220 km to the NE of Kawagama Lake, and although the smelting and refining of metal sulphide ores in this region may be a significant source of atmospheric Pb (and other trace metals) to the Kawagama Lake watershed. Sturges and Barrie (1989), however, indicated that the Pb isotope ratios of aerosols from Sudbury are not significantly different from the leaded gasoline values ie. $^{206}Pb/^{207}Pb = 1.15$. Given the very low $^{206}Pb/^{207}Pb$ in the lake waters from Kawagama (Fig. 4), as well as the snow and rainwater samples (Table 3), Pb inputs from the Sudbury area alone, cannot explain the Pb isotope data. Sturges and Barrie (1989) provided convincing data 20 years ago that Pb-bearing aerosols from Noranda were arriving at Dorset. There have been many recent studies of atmospheric pollution in the vicinity of the smelter at Rouyn-Noranda (Telmer et al., 2004; Kliza et al., 2005; Zdanowicz et al., 2005; Telmer et al., 2006), and even though there have been reductions in Pb emissions from the smelter in the past decades, the data presented here shows that smelting and refining activities in northern Ontario and Quèbec are still having a significant impact on the lakes in central Ontario because of long-range atmospheric transport.

Unlike the top of the peat bog (Fig. 2), a lake sediment core collected 700 km east of Noranda shows no $^{206}Pb/^{207}Pb$ values below 1.185, but this core was collected in 1994, so any changes in Pb isotope ratios during the past decade would anyway be impossible to see (Gallon et al., 2005). A sediment core taken from a lake 300 km east of Noranda also shows no evidence of smelter impacts, even in the topmost layers (Gallon et al., 2006), but this may once again simply be another indication, as noted above, that lake sediments are far less sensitive archives of atmospheric Pb inputs than peat from ombrotrophic bogs.

4.7. Fate of industrial Pb in forested watersheds

In the decades following the gradual elimination and eventual ban on leaded gasoline use for automobiles, several studies reported declining Pb concentrations in the surface layers of forest soils in northeastern North America (Yanai et al., 2004; Evans et al., 2005). Partly based on similar results, it had been suggested that there may soon be a soil-derived pulse of anthropogenic Pb arriving in streams and eventually groundwaters (Miller and Friedland, 1994; Kaste et al., 2003). While the results presented here show unambiguously that the streams draining the forests of central Ontario are contaminated with anthropogenic Pb, it is important to note that much of this Pb is associated with particles which are removed from the water column, with much of this likely taking place at the stream/lake interface. The concentrations of Pb dissolved in the lake, therefore, tend generally to be much lower than those of the streams. Moreover, the Pb concentrations and Pb/Sc ratios which are typical of the water from the surface of Kawagama Lake are dwarfed by the corresponding values in contemporary rain and snow. Thus, despite the elevated inputs of atmospheric Pb even today, the Pb/Sc and Pb isotope data from the surface waters show that Pb removal processes in the watershed are very efficient. Although the Pb isotope data and Pb/Sc ratios indicate that Pb dissolved in the surface waters of the lake is predominantly anthropogenic in origin, the Pb concentrations may be so low (sometimes below 10 ng/l) that even today, most labs are not capable of measuring them. To put these Pb concentrations into perspective, they are within a factor of two of the average "natural background" Pb concentration in Arctic ice dating from the mid-Holocene (Zheng et al., 2007). Moreover, even at these very low Pb concentrations, much, if not most, of the Pb may be colloidal (Lead and Wilkinson, 2006). An evaluation of the environmental significance of industrial Pb leaching from forest soils, therefore, needs to take these factors and processes into consideration.

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