Assessment of Airborne Lead Provenance in Northern Ontario, Canada, Using Isotopic Ratios in Snow and *Cladonia rangiferina* Lichens

T. Akerman · G. Spiers ⓘ · P. Beckett · J. Anderson · F. Caron

Abstract Fresh snow and lichens (*Cladonia rangiferina*) were collected along two ~300-km transects in a regional survey around two smelter areas in Northern Ontario, i.e., the Sudbury and Timmins areas, in 2009–2010, as a part of a monitoring program. The samples were analyzed for Pb isotope ratios in snow from 47 sites, and in lichens from 28 sites, for background airborne lead and to determine the influence of distance versus local sources of Pb on a regional scale. Moreover, the lichen samples were split into two portions, the top portion, corresponding to recent growth (2–4 years), and the lower portion (up to 10+ years old) to determine the regime of recent versus old deposition. The study also investigated whether the isotopic signature in fresh snow (~1–2 weeks old) could correlate to the lichens' recent growth. The Pb isotope signatures, reported as Pb isotope ratios $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, in both snow and lichen recent growth were uniform over the region, except for localized influences near Sudbury and Timmins, suggesting that the background Pb represented remote sources for most of the region. Three-isotope plots $^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$ of snow and lichens followed a linear model typical of mixing lines between two sources. As there are no statistical differences of Pb isotope ratios between fresh snow and recent lichen growth at neighboring stations, either type of sample may be used to describe the short-term record of airborne inputs. Finally, we found a strong relationship between the Pb isotope ratios of the recent growth (upper part) and old growth (lower part) of the lichens, with a slope of 0.9 between the lichen parts. This observation suggests either an isotopic segregation or the older parts of the lichens developed under different Pb source inputs in earlier times.

Keywords Pb isotopes · Snow samples · Lichens · Northern Ontario · Airborne lead · Atmospheric contamination

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1 Introduction

Airborne lead emissions to the environment originate from diverse anthropogenic sources such as coal combustion, mining and smelter emissions, urban industry, postcombustion, and re-suspension of leaded gasoline, waste incineration, light aviation fuel, and unleaded gasoline (Patterson and Settle 1987; Komárek et al. 2008; Cziczo et al. 2009; Bird 2011; Cloquet et al. 2015; Chrastný et al. 2018). Lead is present in atmospheric aerosols in the submicron-size particles that can be transported over long distances on local, regional, or intercontinental scales before being deposited (Bollhöfer and Rosman 2001; Graney et al. 2019) into the surface environment.

In northeastern North America, industrial Pb emissions from the USA and Canada have been documented as major pollution sources (Flegal et al. 1989; Cheyne et al. 2018). Specifically, the input from coal combustion, processing of Mississippi Valley-Type Pb ores and urban industry, was reported for Bondville, Illinois (Graney and Landis (2013), and for the Great Lakes and southern Ontario region (Cheyne et al. 2018). Sherman et al. (2015) suggested the importance of input from coal combustion and processing of Mississippi Valley-Type Pb ores for precipitation samples collected at various sites across the Great Lakes region. The input of several isotopically distinct anthropogenic lead sources including emissions from Canadian smelters, leaded gasoline from Canada, and the USA, and smelting activities in the Upper Mississippi Valley was documented for lake sediment cores in Québec, in the regions of Rouyn-Noranda, Québec City, Duchénier Faunal Reserve, Murdochville (Gobeil et al. 2013). Furthermore, the inputs of local Canadian smelting plants were recorded in lake sediments in central and northern Ontario (e.g., Cheyne et al. 2018). Transport from long-range and local sources was identified as significant contributors to atmospheric deposition in the Sudbury area, Northern Ontario (Chan and Lusis 1985; Adamo et al. 2002; Schindler and Kamber 2013). The zones of influence for the Sudbury and Noranda smelters (NE and upwind from Sudbury) were studied by Widory et al. (2018), who reported no significant input from Noranda smelter operations towards the Sudbury region. However, they concluded that the contamination plume from the Sudbury smelters may extend to the Rouyn-Noranda area, with distribution driven by the SW-NE regional wind pattern.

The four main stable lead isotopes are ^{208}Pb (52.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%), and ^{204}Pb (1.4%) (Bird 2011). Lead-204 (^{204}Pb) is primordial only, whereas the other isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) are both primordial and from the decay chains of ^{238}U, ^{235}U, and ^{232}Th, respectively (Faure 1986). The relative Pb isotope ratios vary with differences in the relative concentrations of the parent and daughter isotopes and the orebody age (Komárek et al. 2008; Sherman et al. 2015). Lead isotope ratios have been used as "fingerprints" to trace and attribute the potential sources of pollution using air samplers, water, precipitations, sediments, and lichens as point receptors (Sturges and Barrie 1987; Rosman et al. 1994; Graney et al. 1995, 2019; Bagur and Widory 2020). Lead released to the environment by mining, smelting, and other industrial processes retains the isotopic composition of the source ore deposit, thus allowing identification of the lead sources subsequently measured in environmental media (Bird 2011; Faure 1986).

Airborne lead environmental contamination in North America has been traced using different environmental matrices including snow and rainwater (Simonetti et al. 2000a, 2000b, 2000c), soils (Hou et al. 2006), and aerosols (Bagur and Widory 2020). Furthermore, lichens have been used to obtain records of recent (Carignan and Gariépy 1995; Carignan et al. 2002; Widory et al. 2018), and lake sediments of less recent contamination sources (Graney et al. 1995; Gobeil et al. 2013; Schindler and Kamber 2013; Cheyne et al. 2018). Wet precipitations, snow and rain, are efficient scavengers of fine suspended particles and aerosols (e.g., Francova et al., 2017; Liu et al. 2018). Snow, known to reflect recent local contamination (Francová et al. 2017; Chrastný et al. 2018), was reported to be a more efficient scavenger of particles than rain (Franz and Eisenreich 1998) due to larger surface area. Snow samples, analyzed to characterize metal deposition on a relatively short timescale, have been shown to be superior indicators for tracing metals and other contaminants in the atmosphere when compared to other environmental samples (Francová et al. 2017).

Lichens have been widely used for elemental analysis (Beckett et al. 1982; Zakshek et al. 1986; Garty 2001; Loppi et al. 2019). Metals may accumulate in the thalli of lichens as trapped particles or be present in water-soluble form (Beckett 1995). Lichens integrate deposition over long time scales and therefore may be used to trace long-term activity of local and remote pollution

sources (Francova et al., 2017; Graney et al. 2019). They are also used as short-term accumulators, in particular, in transplant experiments with known exposure times and pre-exposure values (Loppi et al. 2019), or as native samples with the outermost or recent growth of a lichen being commonly examined (Fortuna et al. 2020).

The present study is aimed at characterizing airborne Pb pollution on a local and regional scale in Sudbury and Timmins areas of Northern Ontario, areas well known for up to a century of smelting activities (Nriagu et al. 1982; Gunn 1995). The Sudbury region is also recognized for the environmental damage recovery successes consequent to industrial emissions reduction and improvement in air quality over the past decades (Gunn 1995; Wren 2012). The present work examines recovery and Pb pollution reduction in the region surrounding Sudbury by tracing changes in relative abundance on individual Pb isotopes. Lead isotopic ratios are one tool of choice in samples collected near presumed sources, up to a scale of influence of several hundreds of kilometers, as changes in measured Pb ratios reflect variation in source materials within an impact footprint, thus allowing a documentation of decreases in pollution loading from local or distant sources.

The analysis of recent snow samples and growth of lichen tissue as accumulators of airborne Pb (recent and old portions) enables a focus on shorter-term deposition history. The study documents isotopic data from analyses of snow and lichen samples along two transects in Northern Ontario, one to the west of Sudbury towards Sault Ste. Marie and the other to the north towards the Timmins area. For each transect, snow samples were analyzed to document Pb accumulation on a time scale of only days or weeks, whereas lichen samples may document the Pb isotope signature for a longer term from months to years. The study also investigates whether these diverse aerosol accumulators can cross-validate each other as media to monitor the recent dynamics of pollution using Pb isotope signatures.

2 Materials and Methods
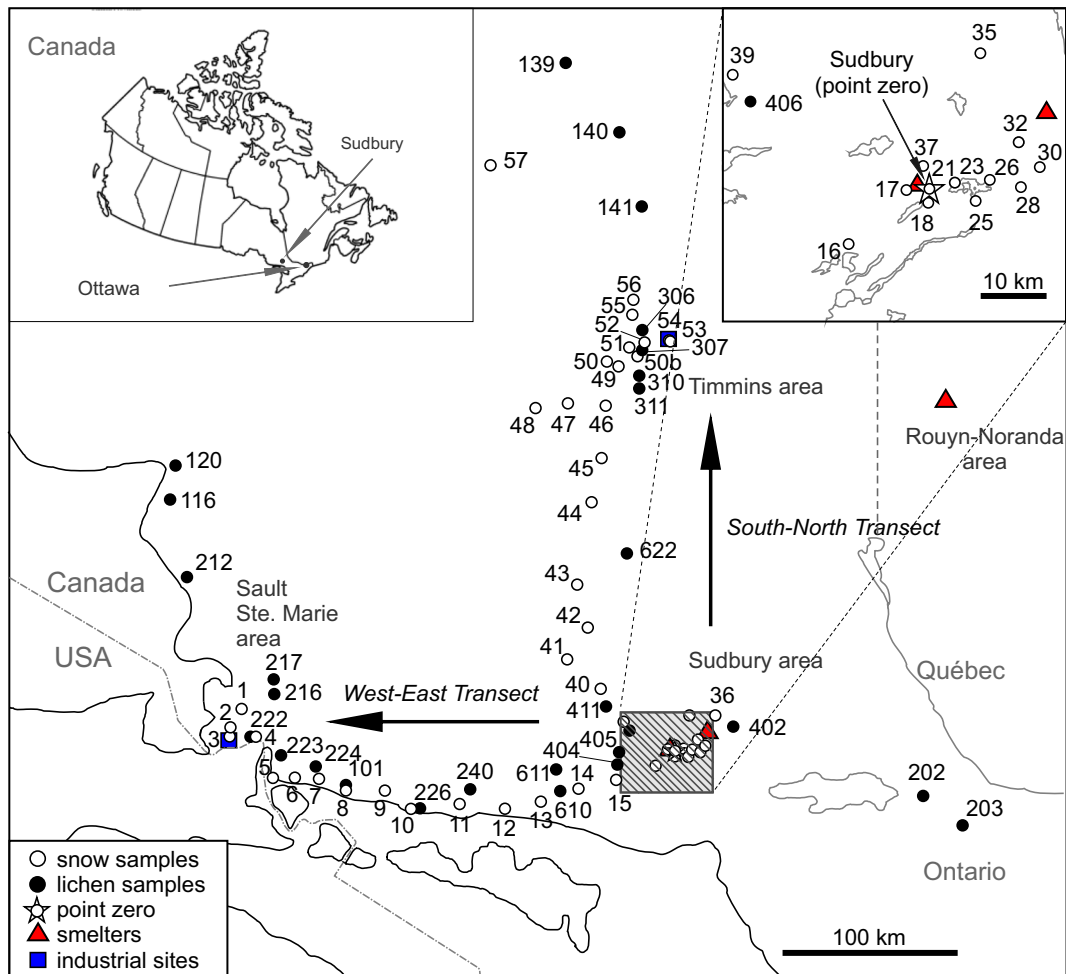
2.1 Study Area

Samples of snow and lichens were collected along two transects (Fig. 1) running west-east (WE) from Sudbury to the Sault Ste. Marie region on Lake Superior, and in a

south-north (SN) direction from Sudbury to the Timmins area, respectively. Transects were selected to span the potential impact region of the major regional smelters and industrial facilities of Northern Ontario (Tables 1, 2, 3, 4, 5, 6 and 7). Sample location 21, at ~2 km east of the Copper Cliff smelter, was chosen as the "zero" point of reference in this study (Table 3 and Fig. 1). Detailed information about sampling locations is in the supplementary materials (Table S1).

2.2 Sampling Procedures

Snow sampling at 47 sites was completed in January 2010 (Fig. 1), with multiple samples collected at a 20-km radius around the "zero" reference point when possible. The remote samples were collected from positions at least 250 m from industrial sites and arterial roads. Visually clean snow samples were collected from open zones within the local forest vegetation into double plastic bags, transported frozen to the laboratory, and melted overnight at 20 °C upon arrival in the laboratory facility. Each snow sample yielded approximately 3 L of melt water.

Samples of the abundant fruticose species *Cladonia rangiferina* (L.) F.H. Wigg, commonly known as reindeer or caribou lichen, were collected from 28 sites during the late summer of 2009 (Fig. 1). As suggested by Steinnnes et al. (1992), sampling sites were in openings between large trees at least 250 m from roads to optimize input from eolian sources. Replicate samples (5x) were retrieved at each site using a 15-cm diameter stainless steel ring as a cutting tool. Each sample was placed into labeled paper bags and air-dried at room temperature (~20 °C) upon returning to the laboratory, for at least 5 days. The samples were then carefully cleaned from debris such as pine needles, twigs, and leaves using isopropyl alcohol pre-cleaned nylon tweezers. Following the removal of senescent tissues (Trembley et al. 1997), the living tissues were excised for digestion and subsequent analysis. The separation of living portion of the podetium from the decaying portion was based on color differentiation (Scotter 1963). With an annual growth rate of ~4–6 mm per year for *Cladonia rangiferina* documented in studies from Northern Canada and Finland (Scotter 1963; Vasander 1981), we have estimated the uppermost part to represent the recent 2–4 year's growth and the lowermost part approximately 10 years. The top portion was dissected from the rest of the podetium, again using nylon scissors

Fig. 1 Study area and sampling locations. Numbers (along WE and SN transects) correspond to numbers of samples in Tables 1, 2, 3, 4, 5 and 6. The zero point of reference is the station 21

and tweezers. The two sections of the podetia, ground into a fine powder using a ceramic mortar and pestle, were stored for subsequent digestion and analysis.

2.3 Sample Analysis

The ground lichen samples were weighed (0.5 ± 0.02 g) into 50 mL Teflon™ tubes for pre-digestion with ultrapure distilled 6 mL HNO_3, 2 mL HCl, and 1 mL HF. The tubes, with reflux caps, were placed into holding trays for 16–24 hours in a fume hood for pre-digestion of the organic material. After this step, the samples were transferred to a digestion block (Environmental Express HotBlock Pro™ Model No. SC-180-1) that was programmed to slowly ramp the temperature to 105 °C, following by a holding time of 4.0 hours. The tubes were cooled to room

temperature overnight and brought to 50 mL with ultra-pure water. Sub-samples were diluted 10-fold with ultra-pure water prior to elemental analysis using a Varian 819 ICP-MS. Quality control and assurance samples consisted of a procedural blank, duplicate sample, and certified standard reference materials every 10 samples (NIST No. 1573a Tomato Leaves and 1570a Spinach Leaves).

The melted snow samples were filtered through a pre-cleaned 0.45 micrometer cellulose acetate filter and acidified with ultrapure HNO_3 to a pH of 2 ± 0.2. The samples were stored in pre-cleaned polyethylene bottles at approximately 4 °C until analysis, again using the Varian 819 ICP-MS. Quality control and assurance samples during the elemental analysis of the water consisted of a procedural blank, duplicate sample, and certified standard reference materials every 10 samples.

Table 1 Pb isotopic ratios and Pb concentrations for snow samples collected along WE transect

Sample number	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	Pb, µg/L
1	2.106	0.868	0.357
2	2.054	0.841	0.511
3	2.075	0.846	0.406
4	2.054	0.840	0.219
5	2.050	0.838	0.163
6	2.055	0.839	0.254
7	2.114	0.872	0.469
8	2.082	0.853	0.042
9	2.059	0.840	0.362
10	2.049	0.833	0.202
11	2.031	0.835	0.174
12	2.066	0.844	0.332
13	2.070	0.845	0.178
14	2.063	0.845	0.107
15	2.086	0.855	0.187
16	2.119	0.866	0.189

Table 3 Pb isotopic ratios and Pb concentrations for snow samples collected along common transect (Sudbury area)

Sample number	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	Pb, µg/L
17	2.134	0.875	0.165
18	2.122	0.873	0.109
21	2.208	0.903	0.114
23	2.150	0.879	0.228
25	2.214	0.912	0.203
26	2.194	0.914	1.664
28	2.209	0.922	0.297
30	2.310	0.959	0.252
32	2.262	0.945	12.086
35	2.132	0.877	0.184
36	2.245	0.927	0.217
37	2.147	0.879	0.135

SRM 982 (Equal-Atom Lead Isotopic Standard) were digested with ultrapure HNO_3 and diluted to 10 ppb for use to both correct for mass bias and to check for accuracy, respectively (Ulrich et al. 2010). The ICP-MS performance was optimized with ^{209}Bi, a mono-isotopic element close in mass to the Pb isotopes being analyzed. The measurement of isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb was completed using both Varian ICP 819 and Thermo X-Series quadrupole ICP-MS

National Institute of Standards and Technology lead wire isotopic standards (SRM 981 (Common Lead) and

Table 2 Pb isotopic ratios and Pb concentrations for lichens samples collected along WE transect ("lower" and "upper" columns stand for lower and upper parts of podetium in case of lichens)

Sample number	$^{208}Pb/^{206}Pb$		$^{207}Pb/^{206}Pb$		Pb, µg/g	
	Lower	Upper	Lower	Upper	Lower	Upper
120	2.281	2.056	0.842	0.841	1.440	1.373
116	2.065	2.062	0.842	0.843	2.353	1.129
212	2.054	2.064	0.839	0.842	1.162	0.581
217	2.035	2.050	0.832	0.837	1.673	1.405
216	1.958	2.040	0.804	0.834	1.634	1.048
222	2.051	2.062	0.839	0.844	1.545	0.884
223	1.950	1.967	0.772	0.787	1.826	1.254
224	2.066	2.063	0.844	0.842	1.706	1.771
101	2.059	2.064	0.841	0.845	1.609	1.145
226	2.058	2.058	0.843	0.843	2.027	1.654
240	2.051	2.059	0.836	0.841	1.094	0.677
611	1.943	1.980	0.750	0.775	1.978	1.083
610	2.075	2.079	0.848	0.851	2.037	1.459
203	2.091	2.092	0.853	0.857	0.835	0.618
202	2.079	2.068	0.846	0.845	4.032	2.742

Table 4 Pb isotopic ratios and Pb concentrations for lichens samples collected along common transect (Sudbury area) (lower" and "upper" columns stand for lower and upper parts of podetium in case of lichens)

Sample number	$^{208}Pb/^{206}Pb$		$^{207}Pb/^{206}Pb$		Pb, µg/g	
	Lower	Upper	Lower	Upper	Lower	Upper
404	2.116	2.116	0.858	0.862	1.281	1.072
405	2.095	2.102	0.852	0.854	3.743	2.633
406	2.115	2.124	0.856	0.862	1.802	1.215
402	2.116	2.117	0.857	0.859	2.115	1.535
411	2.063	2.104	0.838	0.856	1.434	0.973

instruments, with analysis of 2% HNO_3 digestion blank and the SRM 981 solution after every five samples as described in Ulrich et al. 2010. Repeated measurements of the 10-ppb solution of NIST 982 Equal-Atom Lead Isotopic standard yielded an external reproducibility of ±0.01 σ, and accuracy of the Pb isotope ratios were <0.16% for $^{207}Pb/^{206}Pb$ RSD, <0.29% for $^{208}Pb/^{206}Pb$ RSD, and <0.17% for $^{206}Pb/^{204}Pb$. The NIST NBS 982 was analyzed following every 15 samples along with the digestion blank. During the sample analysis, a 2% nitric

acid blank was run every five samples, before and after each NBS 981 analysis. The NIST 982 was used to minimize carry-over. A ^{209}Bi reference solution was used as an external drift monitor.

3 Results

The $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios measured for the snow and lichen samples collected along WE and SN transects, and the corresponding Pb concentrations, are presented in Tables 1, 2, 3, 4, 5 and 6. Figure 2 illustrates the Pb data as a function of the geographical transects (WE, SN) for (a) isotopic Pb ratios in snow and lichens (upper and lower parts), (b) Pb concentrations in the snow samples, and (c) Pb concentrations in lichens (also in upper and lower parts).

Three-isotope plots ($^{208}Pb/^{206}Pb$ versus $^{207}Pb/^{206}Pb$) for the snow and upper parts of lichens are presented in Figs. 3a and b. The $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios are compared for snow and the upper parts of lichens from neighboring stations in Fig. 4. In Fig. 5, the Pb isotope ratios are compared for the uppermost and lower part of the lichens. The detailed isotopic data for all samples is documented in the supplementary material (Tables S2, S3).

3.1 Pb Isotope Ratios Along Transects

WE Transect The Pb isotopic ratios of snow samples varied along the WE transect, with ranges of 0.833 to 0.872 for $^{207}Pb/^{206}Pb$ ratio and 2.031 to 2.119 for $^{208}Pb/^{206}Pb$ ratio, respectively. Samples collected in the immediate vicinity of Sault Ste. Marie were not isotopically different from those further to the east. The isotopic ratios measured for the lichen samples were close to those of the snow samples (Fig. 2). The two data

Table 5 Pb isotopic ratios and Pb concentrations for snow samples collected along SN transect

Sample number	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	Pb, µg/L
39	2.098	0.860	0.066
40	2.090	0.856	0.196
41	2.115	0.869	0.390
42	2.119	0.876	0.024
43	2.109	0.869	0.662
44	2.082	0.854	0.172
45	2.097	0.862	0.280
46	2.089	0.858	–
47	2.245	0.944	0.165
48	2.102	0.868	3.064
49	2.159	0.899	0.394
50	2.140	0.886	0.037
50b	2.194	0.917	–
51	2.143	0.885	0.040
52	2.299	0.977	3.017
53	2.378	1.020	1.809
54	2.163	0.898	0.459
55	2.348	1.005	1.605
56	2.159	0.898	0.254
57	2.097	0.871	2.046

Table 6 Pb isotopic ratios and Pb concentrations for lichens samples collected SN transect ("lower" and "upper" columns stand for lower and upper parts of podetium in case of lichens)

Sample number	$^{208}Pb/^{206}Pb$		$^{207}Pb/^{206}Pb$		Pb, µg/g	
	Lower	Upper	Lower	Upper	Lower	Upper
622	2.119	2.126	0.872	0.877	1.958	1.907
311	2.216	2.228	0.913	0.938	1.208	0.893
310	2.198	2.187	0.922	0.917	4.140	2.303
307	2.266	2.294	0.953	0.941	5.494	2.263
306	2.260	2.263	0.953	0.956	3.831	2.082
141	2.178	2.189	0.908	0.916	1.065	0.693
140	2.118	2.125	0.873	0.880	0.850	0.699
139	2.122	2.113	0.876	0.873	1.816	0.867

sets, one near Espanola (station 611) and one near Sault Ste. Marie (station 223), appear as outliers; these two sampling stations are in proximity to smaller local emission sources, namely a pulp and paper mill and an iron ore smelter, but the concentration data do not appear to corroborate abnormal Pb levels. Also, the other outlier at station 120, exhibiting higher values only of $^{208}Pb/^{206}Pb$ ratio and only for lower parts of lichen, remains unexplained.

Sudbury Area The snow samples from the Sudbury area, in contrast to samples collected along WE transect, showed a higher $^{207}Pb/^{206}Pb$ ratio compared to other locations of the transect, from 0.873 to 0.959 (Fig. 2). Those high values were near the "zero" reference point, the Copper Cliff smelter. The isotope ratios of the lichen samples follow a pattern similar to that documented for the snow samples. These ratios are generally slightly higher than those for other samples of the WE transect, although the difference of the Sudbury signature is much less pronounced than for the snow samples.

SN Transect The $^{207}Pb/^{206}Pb$ isotopic ratios for snow samples collected along the SN transect between Sudbury to the north of Timmins ranged from 0.854 to 1.020, with pronounced high values near Timmins (Fig. 2). Interestingly, the Pb concentration in snow was the highest for the same area. Otherwise, the isotopic signatures of snow samples collected along the SN transect do not appear to bear a local signature. The lichen samples collected along the SN transect also exhibit distinct isotopic signatures in the Timmins area, compared to those in Sudbury area and the SN transect.

3.2 Pb Concentrations in Snow and Lichens

The lead concentrations in snow were generally below 1 µg/L (Fig. 2). Only six of the samples had a higher Pb concentration (~1–3 µg/L), near Sudbury and Timmins, and one high value near Sudbury at ~12 µg/L. The Pb concentrations in lichens were variable in the transects, with most values between ~1–3 µg/g. Two sets of lichen samples (one in Sudbury and one in the Westwards

Table 7 Release of lead and its compounds for 2009 from some of presumed point sources. The data taken from NPRI, National Pollutant Release Inventory, Government of Canada

Industry	Location	Release into air, kg
Algoma Steel Inc.	Sault Ste. Marie, ON	194
Domtar Inc./Espanola Mill	Espanola, ON	19
Vale Canada Limited/Copper Cliff Smelter Complex	Sudbury, ON	8083
Glencore Sudbury Integrated Nickel Operations, formerly Xstrata Nickel at Falconbridge	Sudbury, ON	5074
Kidd Metallurgical Site	Timmins, ON	23058
Kidd Mine Site	Timmins, ON	65

transect) exhibited a higher concentration than for the rest of the samples in the transect, but there was no apparent correspondence with the isotope ratios or Pb concentration in the snow. The three samples of lichens near Timmins exhibited higher Pb concentrations, compared to the other locations in the area. The results also indicated that Pb concentrations were higher in the lower parts of lichens, compared to the levels in the upper part. Plots of Pb concentrations in the upper part versus the lower part gave a linear relationship ($Pb_{(upper\ part)} = 0.463Pb_{(lower\ part)} + 0.403$; $R^2 = 0.743$; see supplementary material, Fig. S3).

3.3 Comparison of Isotope Ratios in Snow and Lichens

Figure 4 represents the comparison of $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ isotopic ratios for snow and lichens from neighboring locations, with only 16 locations being sufficiently close to one another to make meaningful

comparisons. Those points were located within 10 km from each other, because winter road conditions partially controlled access to the snow sampling sites. As a general trend, the isotope ratios for snow and lichens were similar to one another for these stations. The difference between $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios for the snow and lichen samples in the "paired" locations was not statistically significant ($^{208}Pb/^{206}Pb$ ratio: t-score=−0.273, t-critical = 2.131, two-tailed, $\alpha = 0.05$; $^{207}Pb/^{206}Pb$ ratios: t-score=0.610, t-critical=2.131, two-tailed, $\alpha = 0.05$; Student's t-test performed using MS Excel analysis ToolPak). This similarity is illustrated in Pearson's correlation plots (see the supplementary information, Fig. S1).

3.4 Comparison of Isotope Ratios of Upper and Lower Parts of Lichens

The $^{208}Pb/^{206}Pb$ and Pb^{207}/Pb^{206} isotopic ratios of the uppermost parts of podetium from all lichen samples are

Fig. 2 $^{207}Pb/^{206}Pb$ isotope ratios for snow and lichen samples (a) and Pb concentrations in snow (**b**) and lichens (**c**) for the WE and SN transects
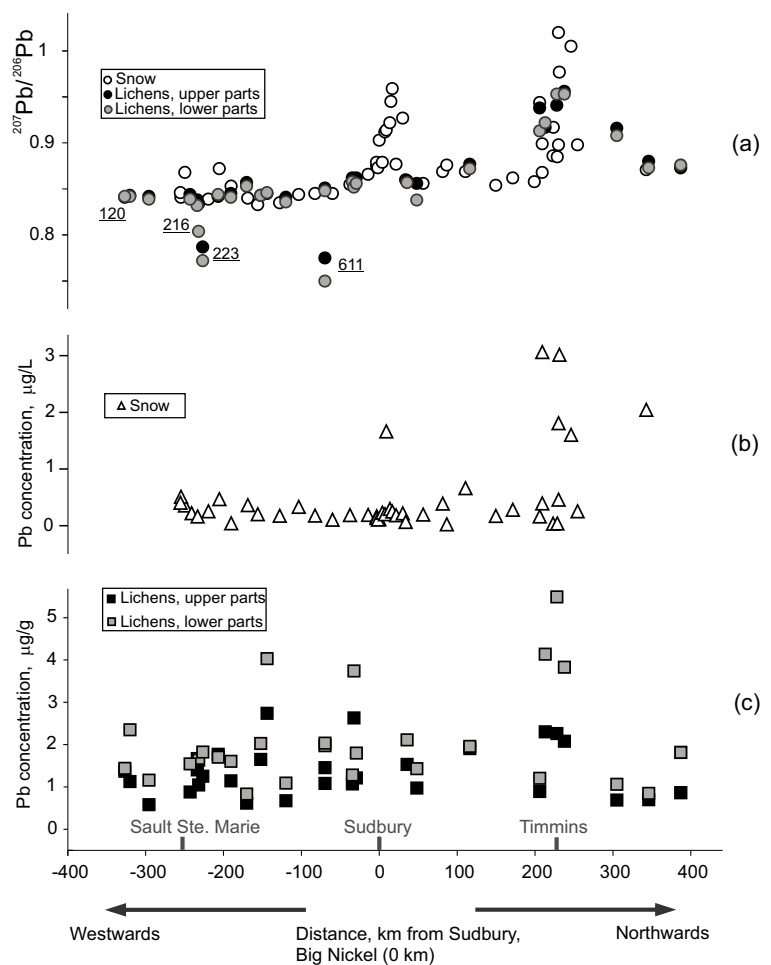
Fig. 3 ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb isotope ratios in snow and lichen samples (upper parts) collected along the WE transect (**a**) and along the SN transect (**b**), compared to selected data for the North America: **a** ores from Timmins area (Franklin et al. 1983); **b** ores from several mines from Noranda area (Franklin et al. 1983); **c** Sudbury ores (Dickin et al. 1996); **d** US and Canadian coals (Díaz-Somoano et al. 2009); **e** ores from the Upper Mississippi Valley District (Millen et al. 1995); **f** lead data for upper continental crust (Zartman and Haines 1988; Asmerom and Jacobsen 1993; Hemming and McLennan 2001; Millot et al. 2004); **g** Noranda smelter emissions (Simonetti et al. 2004)
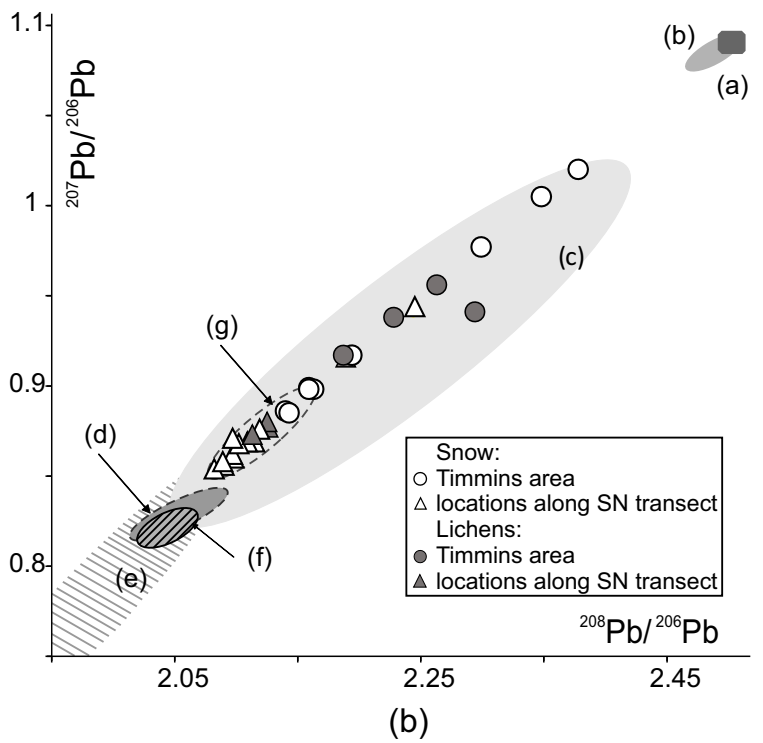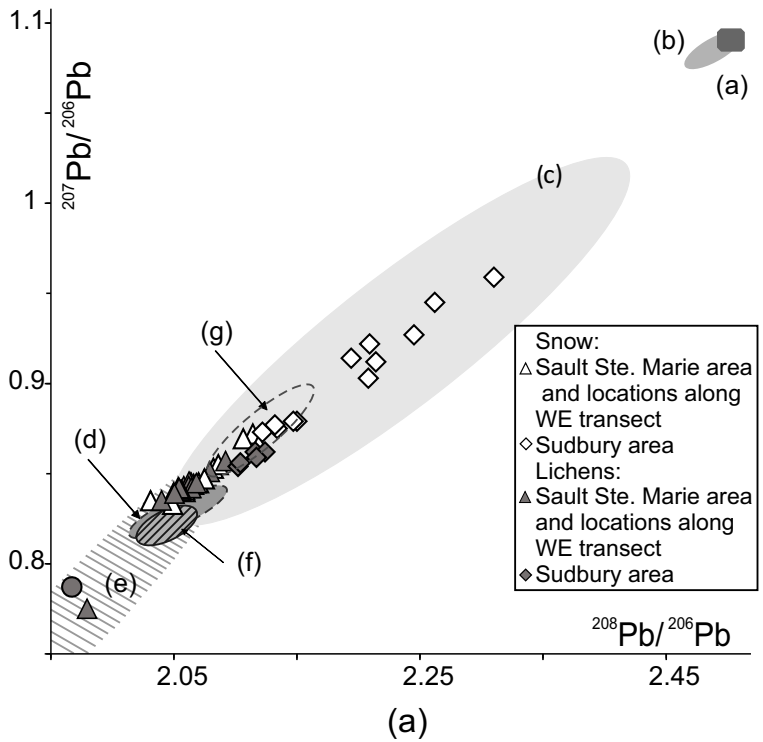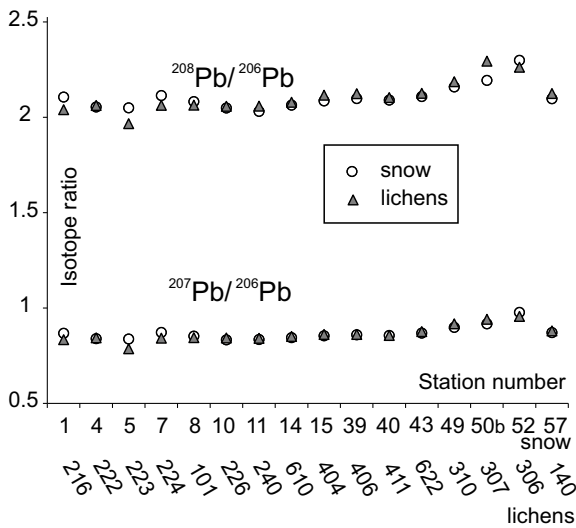
Fig. 4 Pb isotope data for snow and upper parts of podetia of lichen samples collected from relatively proximate locations along WE and SN transects (see Fig. 1 and Tables 1, 2, 3, 4, 5 and 6 for details). Station numbers are given for snow and lichens samples

4 Discussion

4.1 Three-Isotope Plots

The isotope data shown in Fig. 2, with higher values in the vicinities of Sudbury and Timmins, probably reflects local influences. In contrast, the rest of the samples, especially those from the WE transect, have a fairly similar Pb isotopic signature. The data, when placed in three-isotope plots (Fig. 3), fall in a linear pattern. We have superimposed literature data representing various sources of lead to our data. Most of our isotope data are close to regions representing Sudbury ores (Dickin et al. 1996; region (c) in the figure), which are processed locally. Other relevant isotope ratios are represented by (a) ores from the Timmins area and (b) Rouyn-Noranda, approximately 200 km NE of Timmins (Franklin et al. 1983), US and Canadian coals (Díaz-Somoano et al. 2009; region (d)), US ores (Millen et al. 1995; region (e)), and upper continental crust (f), representing natural lead (Zartman and Haines 1988; Asmerom and Jacobsen 1993; Hemming and McLennan 2001; Millot et al. 2004). Smelter emissions from the Horne smelter (Rouyn-Noranda; Simonetti et al. 2004) are represented by region (g).

Using the isotope data fields (regions) of the plot, we have used an isotope model to determine the potential mixing of Pb sources. Using ranges of isotope ratio from literature sources, the plots suggest that a two-way mixing model (adapted from Monna et al. 1997; Komarek et al. 2008) may estimate relative contributions from sources at a given location.

compared with those for lower parts in Fig. 5. As the uppermost parts of podetium reflect the recent growth and the lower parts may represent several previous years of growth, the atmospheric contaminant deposition recorded by the lichens may exhibit inter-annual differences. Our results show that the isotope values are very close between the upper and lower parts at most locations. The regression analysis of the ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios for upper and lower parts yielded linear relationships of $y = 0.909x + 0.200$ ($R^2 = 0.946$) and $y = 0.898x + 0.093$ ($R^2 = 0.962$), respectively, for the isotope ratios (supp. information, Figure S2).

Fig. 5 Pb isotope data (^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb) for upper and lower parts of podetia for lichens samples collected along WE and SN transects versus station number

$$X_{(sample)} = \frac{\left(^{207}/_{206}\right)_{(sample)} - \left(^{207}/_{206}\right)_{(em2)}}{\left(^{207}/_{206}\right)_{(em1)} - \left(^{207}/_{206}\right)_{(em2)}}$$

where $X_{(sample)}$ is the contribution of end-member 1 in the analysed sample, (207/206) is the isotope ratio $^{207}Pb/^{206}Pb$, subscript (sample) is the isotope ratio of sample, (em1) is the isotope ratio for end-member source 1, and (em2) is the isotope ratio for end-member source 2.

The model can use the $^{208}Pb/^{206}Pb$ ratios independently. The mixing model represents an order of magnitude estimate of relative contributions of end-members. We have used the end-member isotope data and examples of calculations in Tables 8 and 9 to show how this model can be used. Our discussion below is based on these calculations; the attribution values should be taken as estimates.

WE Transect Almost all data points of this transect (Fig. 3a) fall within region (c), "Sudbury ores." Most of the data points, however, are concentrated in a region whose isotope ratios have been reported for the combustion of coals in thermal power plants (region (d)), lead data from upper continental crust (region (f)), and Noranda smelter emissions (region (g)).

For example, Snow sample No. 1 has an isotope ratio ($^{207}Pb/^{206}Pb$) of 0.868 (Tables 1, 2, 3, 4, 5 and 6). This ratio could be explained by the linear combination of two end-member sources, the centroid of the "Sudbury ores" (c) region and the centroid of the "US, Canadian coals" (d) region (see Tables 8 and 9). This combination would suggest a 42% contribution from the "Sudbury ores" (c), and a 58% contribution from "US, Canadian

Table 8 Calculations for the model. Examples of end-member isotope values

End-member (em) used in the calculation examples	Isotope ratios used in the calculation examples	
	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
(a) Timmins ores	1.09	2.50
(b) Noranda ores	1.085	2.488
(c) Sudbury ores	0.92	2.23
(d) US and Canadian coals	0.83	2.05
(e) US ores	0.756	1.934

coals" (d). Other combinations are possible and are not necessarily limited to only two end-members.

For the bulk of the analysed samples, using centroid values of the "Sudbury ores" in the model, with end-member (d) in Fig. 3, the Sudbury sources would be around 10%, and up to around 30–40% for some of snow samples in the transect. If the end-members are "USA ores" (region (e) in Fig. 3) (Millen et al. 1995) and the "Sudbury ores (c)," the contribution from Sudbury could be around 50–60% for most of the samples. Thus, from consideration of both two-way mixing models, the estimate of the contribution of local sources (Sudbury) into WE transect could range from 10 to 60%, with the rest (90–40%) being from remote sources.

Sudbury Area The Pb isotopic data for most snow samples from the Sudbury area fall within the range of the "Sudbury ores" (c) (from Dickin et al. 1996). Ores represented by the "Timmins ores" (a) and "Mines from Noranda" (b) (Franklin et al. 1983) may contribute to the Pb isotope signal in snow samples, but only if these ores are processed in the Sudbury area. Releases from the Noranda area ("g" in Figure 3) do not offer a satisfactory explanation as the prevailing winds generally do not come from the NE towards the Sudbury area. Calculations using the "Sudbury ores" (c) and other remote sources (d, e, or f in Fig. 3) suggest that most of the Pb in the snow samples in the Sudbury area (50–95%) is local. The rest would be explained by influences from remote sources.

SN Transect The Pb isotopic data for most of the samples also fall within the range of the "Sudbury ores" (c) (from Dickin et al. 1996), but the other regions (d, e, f) representing remote sources from the WE cannot be discarded. Most of the points coincides with the region (g) (Noranda emissions; Simonetti et al. 2004). The mixing models using regions (a) and (d) as end-members, and possibly (e) and (c) as potential end-members, the mixing model equations would suggest the contribution of emissions from Timmins ore processing at around 10–30%.

Timmins Area The isotopic data anomalies highlighted in the SN transect for the Timmins area could reflect the influence of local smelter sources, but this could be limited. The influence from the Timmins area is intuitive, especially considering that atmospheric releases were highest in the region at the time of

Table 9 Calculations for the model. Examples of calculation with the isotope model (using the $^{207}Pb/^{206}Pb$ ratios)

Sample No.	Ratio	Em1	Em2	Contribution 1	Contribution 2
224 lichen	0.842	(c) Sudbury ore	(d) US, Can. coals	13%	87%
1 snow	0.868	(c) Sudbury ore	(d) US, Can. coals	42%	58%
45 snow	0.862	(a) Timmins ore	(d) US, Can. coals	12%	88%

sampling (NPRI n.d.) (Table 7). As an example of calculation, using the end-member values from Tables 8 and 9 for local ores and US and Canadian coals (regions (a) and (d)), and the extreme top-right snow sample of Figure 3 (#53, $^{207}Pb/^{206}Pb$ = 1.020, $^{208}Pb/^{206}Pb$ = 2.378), the model yields ~75% of local Timmins sources. Similarly, the local Timmins ores and Sudbury ores (end-members (a) and (c) in Tables 8 and 9) would indicate ~50% of local Timmins influence for the same snow sample. Only a few samples show these high values (top right of region (c) in Fig. 3). For most of the samples in this transect at the extreme "lower" points of the plot ($^{207}Pb/^{206}Pb$ = 0.85-0.9, $^{208}Pb/^{206}Pb$ = 2.09–2.18), a similar calculation with the (a) and (d) end-members suggest a ~10-25% of local Timmins influence. Therefore, most of the samples in the SN transect do not reflect local sources but rather reflect distant sources. Only in some extreme cases shown above, we have calculated up to 50–75% of local Timmins influence.

On a regional Eastern North America scale, lead emissions from various sources include contributions from coal-fired power plants, ore processing, and urban industries (Cheyne et al. 2018; Sherman et al. 2015; Graney and Landis 2013), with some inputs from terrigenous Pb (Bagur and Widory 2020). The Sault Ste. Marie area, discussed in the present study, is close to the US border and located downwind from a variety of emission sources that includes coal-fired power plants (Sherman et al. 2015). The isotope compositions of Pb in snow from our study are near the values reported by Sherman et al. (2015), for daily precipitation samples in Michigan and Ohio. They suggested that these Pb isotope values were from sources of either coal combustion or processing of Mississippi Valley-Type Pb ore deposits.

Our data for lichens collected at most locations of the two transects are in the same range of those presented by Widory et al. (2018). The authors reported $^{207}Pb/^{206}Pb$ ratios of 0.847 to 1.021 and $^{208}Pb/^{206}Pb$ ratios of 2.084–2.375 for *Cladonia rangiferina* lichens between the

Noranda (Québec) and Sudbury smelters. They suggested that samples collected near smelters were impacted by local emissions, whereas those taken at a distance from smelters contained Pb reflected mostly a regional background origin. The isotope values in our study in snow and lichens from the Sudbury area are close to the values in sediment cores from Vermillion Lake near Sudbury in 2008 (Schindler and Kamber 2013). They reported $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios of 0.862 ±0.001 and 2.107±0.002, respectively, which place these values at the lower left-hand of the "Sudbury area" (c) in Fig. 3. The authors suggested that this contamination was from a combination of several sources, including acid-mine drainage, smelter emissions, combustion of gasoline, and drainage of fertilizers.

Local Pb isotope fingerprint was only evident closer to the Timmins and Sudbury areas (Fig. 2), and it was mostly episodic, i.e., in snow. Local emissions are influenced by episodes of snowfall, potentially scavenging heavier particles close to a point source, and leaving behind smaller particles that would be carried regionally. For example, the 381-m "Superstack" at the Sudbury Copper Cliff smelter resulted in the reduction of emissions of SO_2 and particulate matter locally, and transporting of pollutants over longer distances (Schindler and Kamber 2013; Chan and Lusis 1985). These emissions would follow a regional SW-NE wind pattern (Chan and Lusis 1985; Pearson and Pitblado 1995). This pattern was estimated to extend to the vicinity of Rouyn-Noranda (Widory et al. 2018). Snow samples were reported to integrate the input of the local point sources, higher in the atmosphere (as smelter emissions; see Chrastný et al. 2018; Francová et al. 2017), supporting our observations that Pb contamination would have only a local influence.

We did not quantify the possible input of natural lead in our samples (area (f) in Figs. 3a and b; Zartman and Haines 1988; Asmerom and Jacobsen 1993; Hemming and McLennan 2001; and Millot et al. 2004). Although we cannot disregard the contribution of natural sources, anthropogenic atmospheric lead was reported to

dominate over natural sources (Patterson and Settle 1987; Bird 2011; Cloquet et al. 2015) by at least 1–2 orders of magnitude (Komárek et al. 2008 and references therein).

4.2 Pb Concentrations in Snow and Lichens

As mentioned before, most of the Pb concentrations in snow were below 1 µg/L across the study area (see Tables 1, 3, 5 and Fig. 2,), with a few isolated samples above ~1–2 µg/L near Timmins and Sudbury. These higher values could be attributed to local and/or episodic events, similarly to our earlier observation from the isotopic signatures. The high lead content value for Sudbury (site 32, 12.1 µg/L, see Table 3, not shown on the figures) was in the vicinity of a smelter; however, the other nearby stations (26, 28, and 30) did not show increases of similar magnitude. In addition, the isotope data did not show an anomaly for this station. In general, the lead concentrations in our snow samples were in the same range as those reported in the province of Québec, 0.05 to 2.5 µg/L (Simonetti et al. 2000a), from eastern Ontario, Québec, the Maritime provinces (Canada), and northeastern USA, 0.01 to 1 µg/L (Simonetti et al. 2000b).

The lead concentrations in lichens from our study ranged between 0.58 and 2.74 µg/g (upper parts) and 0.84 and 5.49 µg/g (lower parts). In general, these concentrations are in the same order of magnitude as the values reported by Tomczuk (2010) and Widory et al. (2018) for the Sudbury area. For instance, Widory et al. (2018) reported Pb concentrations of ~0.46 to 31.1 µg/g in *Cladonia rangiferina* lichens in a Sudbury to Rouyn-Noranda transect. The samples with the highest Pb levels were within 2 km of the Sudbury smelter. In our study, the lichens samples were collected at least 15 km from the urbanized and/ or industrial area. The Pb concentration in our study, however, is much lower than those for *Cladonia rangiferina* lichens from the Elliot Lake and Agnew Lake areas, about halfway in the WE transect (20–88 µg/g; see Boileau et al. 1982). These locations were associated with uranium mining operations that have been closed for at least two decades. The Pb concentrations that we are reporting are also lower than that for *C. rangiferina* lichens from various locations across the eastern Canada (3–21 µg/g) reported by Zakshek et al. (1986).

4.3 Pb Isotope Ratios in Snow and Lichens

There were only small differences between the isotope signatures of snow and lichens collected in the same area—albeit we have recognized that the sampling locations were not exactly the same (Fig. 4). Specifically, both sets of isotope ratios ($^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$) were correlated between the lichens (recent growth) and snow samples at the corresponding stations. In fact, the $^{208}Pb/^{206}Pb$ in lichens versus snow plots had a slope of ~1.05, and the corresponding slope using the $^{207}Pb/^{206}Pb$ ratio was ~1.005 (supplementary information, Figure S1). We found no correlation between any of the isotope ratios and concentrations in snow and lichens (supplementary material, Figure S4). Moreover, we found no correlation between the Pb concentrations in either snow or the upper or lower parts of lichens (Figure S5).

As mentioned before, the Pb concentrations in snow samples were all low with the exception of a few sites, while there was more variability in lichen samples in the transects. The low variability of Pb concentrations in snow samples and the higher variability of Pb concentrations in lichens were also reported in a similar study in Norway (Chrastný et al. 2018). Francová et al. (2017) have reported a larger variability of isotope compositions in snow samples, compared to other environmental samples (particulate matter and lichens). The similarity of Pb isotopic compositions between snow and lichens was also reported by Simonetti et al. (2000a). They compared the Pb isotopic compositions of epiphytic foliose lichens and snow samples collected in Québec (in the St. Lawrence Valley). They did, however, report differences between snow and lichens for a transect extending from Noranda to the James Bay region. This dissimilarity was explained by different time scales for integration of the atmospheric deposition by snow and lichens, by acquiring the atmospheric input at different altitudes, or by the presence of a local pollution source.

Snow samples have been reported to represent short-term inputs of local point sources, while lichens have been considered longer-term accumulators of airborne pollution, integrating both local and remote sources (Chrastný et al. 2018; Francová et al. 2017). We recognize that the snow and lichen samples were not from the same exact location in our study. We also recognize that these types of environmental samples would capture and integrate airborne Pb over different time periods and in different ways. Snow integrates the scavenging of Pb-

containing particles for a period of a few days up to a few weeks, whereas the upper living portion of the podetium in lichens would reflect uptake of a few recent years of growth. Despite these different mechanisms and integration periods, the two sets of samples can be cross-validated (Fig. 4; Figure S1). The present study, therefore, indicates that reindeer lichens can be good short- to medium-term samplers for airborne Pb (up to a few years), whereas snow would represent a short-term sampler (up to a few weeks).

4.4 Upper Versus Lower Parts of Lichens

The upper part of lichen has isotopic ratios slightly lower than for the bottom part, with a slope of ~0.9 (Fig. 5). Although this difference is statistically significant, we do not know whether a different source of Pb was accumulated in prior years, whether planned shutdown of a local smelter might have affected the data, or if there is translocation, losses, and/or isotope discrimination of Pb between the different parts of the lichen. The Pb concentrations were generally higher in the lower part of lichens, compared to the upper part, with a weak but significant correlation. Other studies have made similar observations, albeit for different *Cladonia* species: Garty, (2001, and references therein for *Cladonia arbuscula*); Strakhovenko et al. (2008), especially in the dead podetia of *Cladonia* lichens; Osyczka et al. (2016) reported higher lead concentrations in lower parts compared to upper segments *C. cariosa*, *C. pyxidata*, and *C. rei*. We believe this observation of isotope segregation between the upper and lower parts of lichens is a novel finding. This finding, coupled with the concentration data, needs to be further investigated, especially if lichens were utilized as suitable passive airborne monitors to record recent (2–4 years) or older (up to 10+ years) exposure to industrial pollutants.

5 Conclusions

The lead isotopic fingerprint in fresh snow and lichens (recent and older growth) was investigated in two transects (west-east and north-south) in Northern Ontario, in 2009–2010. The Pb isotopic compositions in these samples followed a linear three-isotope model of ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb. We used an isotope mixing model to explain the origins of anthropogenic Pb emissions of remote regional sources transported by prevailing winds from the south-west, with smaller inputs from presumed local sources. The input of remote sources, presumably from North American industrial regions, could be traced across several hundreds of kilometers along both WE and SN transects. Local emissions, presumably from the Sudbury and Timmins areas, only had a local isotope ratio signature reflective of the ore feed to the smelters. Our model suggested that remote influences of airborne Pb could be dominant upwind from the local smelters. In the westernmost part of the transect, our model suggests that up to 90% of the airborne Pb comes from remote sources. This model is limited, however, without actual data on point sources of airborne Pb.

The two types of environmental samples, snow and lichens, provided two important points of information: (1) snow, which integrates recent airborne deposition (over days to weeks), and the recent growth of lichens, integrating somewhat recent deposition (2–4 years), showed a significant correlation in Pb signals, for neighboring stations. The second point (2) showed an isotopic discrimination between the recent growth (2–4 years) and older growth (>10 years) in lichens. We believe both these observations to be novel findings from this study. These findings suggest that, in the short-term at least, Pb isotopes in lichens can corroborate the data obtained from analysis of fresh snow samples or can be used to confirm any apparent anomalies in snow or rain samples.

The Pb concentrations in snow and in lichens showed background concentrations, similar or lower than literature sources from the same area, or from similar settings. Only a few samples showed a potential local influence from point sources. We found no statistically difference in Pb isotopic ratios and Pb concentrations between fresh snow and the recent or old growth of lichens.

Finally, this study provides background data using diverse sample matrices collected over a large area in a boreal setting in Canada. We believe we have shown that isotope data can be a useful discrimination tool that complements concentration data alone, in environmental monitoring sample matrices such as lichens and snow which are common in northern regions. There are concerns in some jurisdictions that a return from nuclear plants to coal-fired power plants would increase the loads of metals and radionuclides in airborne pollution. In addition, should small nuclear reactors (SMRs) be used in off-grid mining camps or remote communities in Northern regions, the U isotopic signal (up to 19.50% enrichment) would be quite different from background U. In fact, Tadmor (1986) and Papastefanou (2010) indicated that airborne U and Ra

could also increase from large-scale burning of coal, an observation similar to that documented for build up of U levels in soils as result of the use of phosphatic fertilizers in agriculture (McBride and Spiers 2001). The findings reported here could be an important tool, for example, to monitor the recovery from coal plant emissions, or for remote mining operations, especially if small nuclear reactors (SMRs) are implemented—with an enriched ^{235}U fuel. The natural U background is distinct from that of enriched fuel, and thus, isotope measurement must be obtained for monitoring samples in addition to more routine elemental concentration estimates.

Declarations

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