

Original Articles

Atmospheric dispersion of trace metals between two smelters: An approach coupling lead, strontium and osmium isotopes from bioindicators



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ABSTRACT

Bioindicators, by naturally cumulating the impacts of chemical contaminants over time, have demonstrated their added value in evaluating environmental quality. We studied Pb, Sr and Os isotope systematics from *Cladonia rangiferina* lichens collected along a transect between two smelting complexes located in Rouyn-Noranda and Sudbury (Canada) to identify sources of these metals in the Abitibi region and to delineate the extent of their respective emission plumes. Results show that metals present in the study area are explained by the contamination of the regional background by deposition from the atmospheric emissions of the different smelters over distances up to 250 km. A rough estimate of the respective metal contributions of each smelter to the lichen samples was calculated. At low metal concentrations, lichen samples indicate that dispersion plumes may differ for the Pb and Os contamination, perhaps to be linked to differential volatility.

1. Introduction

Mining activities have been recorded as early as 500 BCE when Egyptians sank mineshafts in search for gold (Notton, 1974). Later, during the Copper/Bronze Age and the Roman Empire, mining continued releasing metals into the environment (Rauch, 2010). Mining in Canada has evolved from a Native American exploitation activity in the 1800's into an economic development lever between 1900 and 1960 (Hipwell et al., 2002). While within the last 50 years environmental concerns began shaping the mining industry there is still a need for monitoring and precisely characterising industrial activities in mining regions to establish metal background levels in the environment and to uncover potential zones of metal contamination (Lapalme, 2003). Mining in the Abitibi Gold Belt (Canada) started with the 1909 gold rush (Dixon, 1979). The Archean Abitibi greenstone belt forms the local bedrock and is mainly composed of old compressed and metamorphosed volcano-sedimentary rocks (Dimroth et al., 1984; Daigneault et al., 1990). The Horne copper smelter, located in Rouyn-Noranda (Quebec province) near the Ontario border, is one of the main active smelters in the region. The smelter processes local and worldwide ores. It also is the largest recycling facility for used electronic and computer parts in North America (Gallon et al., 2006). Previous studies have shown that the particles rejected into the atmosphere by the Horne smelter greatly influence the overall lead (Pb) budget of local and regional aerosols, sediments and flora (Simonetti et al., 2000; Carignan et al., 2002; Simonetti et al., 2004). Two other active smelters, Vale

Inco Copper Cliff and Sudbury Integrated Nickel Operation (Glencore), are located within the same geographical area ca. 300 km, in Sudbury (Ontario). The Vale Inco plant smelts nickel-copper bulk concentrates from various sources and the Glencore nickel-copper concentrates from Sudbury, Raglan and XNA (Australia) ores. The Glencore smelter also processes custom-feed materials in the form of concentrates and secondary products.

Environmental monitoring has been widely based on the study of elemental concentrations around mining activities to identify contamination resulting from atmospheric transport and deposition (e.g. Telmer et al., 2006). Recent studies however demonstrated that a multi-isotope approach could unambiguously backtrack sources of air pollutants and help characterise secondary processes occurring post-emission (e.g. Widory et al., 2004; Geagea et al., 2007). The isotope tracking of atmospheric pollutants usually involves direct sampling of both gases and filtered aerosols (e.g. Monna et al., 1997; Veron et al., 1999; Harrison, 2012), or indirect sampling of meteoric water or snow (e.g. Nakano and Tanaka, 1997). However, the use of bioindicators to monitor/assess the quality of different environments offers numerous advantages, such as the possibility of bio-concentrating both organic and inorganic contaminants and of accessing to time-integrated information (Conti and Cecchetti, 2001). Mosses and epiphytic lichens are widely recognised as reliable bioindicators for evaluating air quality due to their ability to accumulate chemical elements in amounts usually exceeding their physiological needs (Nimis et al., 2002). This attribute is due to physiological properties such as a lack of cuticle, the absence

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of protective organs (which could limit the adsorption of toxic substances) and a large exchange surface. This is also why they are capable of absorbing both soluble and insoluble mineral nutrients; they survive by maximizing their uptake of atmospheric aerosols and precipitations while minimizing loss (Gerdol et al., 2002). Limitation of the biomonitoring approach is that it yields a time-averaged value over the lifetime of the bioindicator that can be difficult to assess (Sutton et al., 2004).

Due to the toxic nature of the complexes it forms Pb adversely impacts human health, especially children who present greater intake rates (Yoshinaga et al., 2012). Pb stable isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb) have thus been widely studied for several purposes, including monitoring Pb accumulation in sediments (e.g. Gobeil et al., 1995; Poirier, 2006) and to trace its origins (e.g. Simonetti et al., 2000; Carignan et al., 2002), including in bioindicators (e.g. LeGalley et al., 2013). Studies are based on the possibility of discriminating the main atmospheric sources of Pb by their specific Pb isotope ratios. For example, in eastern North America the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of most of the major Pb vectors are well defined: i) Natural Pb (taken from sediments younger than 1802) vary from 1.210 to 1.216 (Gallon et al., 2005), ii) the average Canadian aerosols vary between 1.167 and 1.177 (Simonetti et al., 2000, 2004), iii) the average US aerosols vary between 1.173 and 1.195 (Simonetti et al., 2000; Bollhöfer and Rosman, 2001), iv) leaded gasoline which dominated emissions from about 1930 to 1990 in North America shows values from 1.15 to 1.183 (Gallon et al., 2005), and v) local Abitibi ores between 0.92 and 1.04 (Delouie et al., 1989; Franklin, 1983).

Strontium (Sr) isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) have also been used in environmental studies for tracing sources of aerosols (e.g. Geagea et al., 2007; Widory et al., 2010). Sr isotopes can be useful biological markers as there is no fractionation among soil, plants and herbivores (Flockhart et al., 2015). Natural sources have a large range of Sr isotope ratios, from 0.715 to 0.725 (or more) for granites, 0.707–0.709 for carbonates, 0.703 for fresh basalts and 0.7092 in the ocean (e.g. McArthur et al., 2001). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in atmospheric emissions from the main industrial sources also greatly vary: steel plants and chemical waste incinerators (0.7091 and 0.7087, respectively; Geagea et al., 2007), coal combustion and cement plant (0.709–0.710 and 0.7095–0.7175, respectively; Widory et al., 2010). Aerosols from the US have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.70819 to 0.71266 (Simonetti et al., 2000).

Osmium (Os), due to the harmful and volatile nature of its tetroxide (OsO_4) coupled to its increased usage or presence in various industrial products, including automobile (car catalytic converters) and mining, has also recently been studied for environmental issues (e.g. Poirier and Gariépy, 2005; Rodushkin et al., 2007). Os is a trace metal from the platinum-group elements (PGE) commonly found as an impurity among the other PGEs because of its strong association with them (Poirier and Gariépy, 2005). Rodushkin et al. (2007), coupling Os concentrations and their corresponding isotope ratios in bioindicators collected in Sweden, characterised the dispersion of the contamination plume from a nickel smelter up to 100 km away from it. In the Abitibi region (Canada) Os isotopes were mostly studied around the Sudbury region to characterize the $^{187}\text{Os}/^{188}\text{Os}$ ratios of local ores and host rocks (Morgan et al., 2002). The Sudbury basin formed following a meteorite impact about 1,8 Gy ago (Davis, 2008). It displays a crustal Os isotope signature ($^{187}\text{Os}/^{188}\text{Os} = 0.90\text{--}1.17$), (Morgan et al., 2002), consistent with impact-induced melting (Dickin et al., 1996). The Abitibi mining region extends across the Quebec-Ontario border and is formed by two major mining districts, the Abitibi gold belt (Au-Cu) from Wawa (Ontario) to Val d'Or (Quebec) and the copper-nickel (Cu-Ni) belt in Sudbury, Ontario. To our knowledge Os isotope ratios have not been published yet for this mining region.

Here we present Pb, Sr and Os concentrations and stable isotope ratios from bioindicators (i.e. lichens) collected along a transect between Rouyn-Noranda and Sudbury with the aim of characterising the

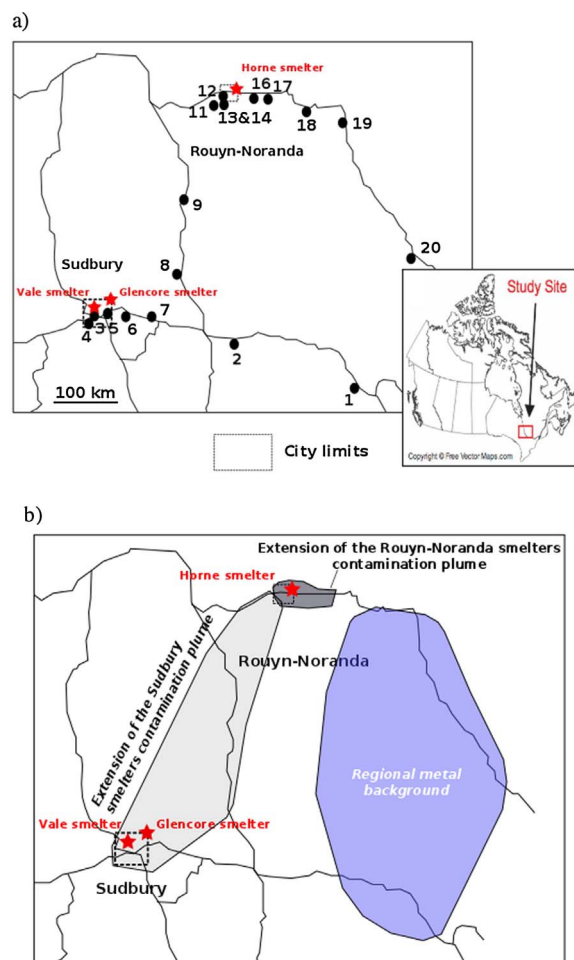


Fig. 1. A) Lichen samples locations in the Abitibi region. Numbers refer to sample numbers in Table 1. B) An assessment, based on the study of the Pb and Os isotope systematics, of the extension of the smelters contamination plume as well as of the regional background is shown. Samples 2 and 7 that are giving distinct conclusions are excluded from the assessment.

extent to which the two smelting complexes are impacting their surrounding environment.

2. Materials and methods

Eighteen *Cladonia rangiferina* lichen (also known as reindeer or caribou lichen) samples were collected (Fig. 1a) during the fall of 2014 along a transect between the two active smelters located 300 km apart in the cities of Sudbury (Ontario) and Rouyn-Noranda (Quebec). Five samples (1, 2 and 18–20) were collected far from the smelters (> 100 km) and not under dominant winds coming from them in order to try to characterise the regional background levels for Pb, Sr and Os. The *Cladonia rangiferina* is a terricolous (epigenous) lichen that was selected as i) it is widely spread in the study region and ii) soil contamination was minimised by taking the lobe tips as samples.

Lichens, not bigger than 5 cm in diameter or roughly younger than 10 years old (assuming a growth rate of $0.4\text{--}0.5\text{ mm year}^{-1}$; Scotter, 1963; Pegau, 1968), were sampled in cleaned plastic bags. For each sampling location at least 5 distinct lichen samples were collected. Samples were taken away from roads, in parks or hiking trails when possible. Lichen samples were first washed with ultrapure Milli-Q water, dried at $50\text{ }^\circ\text{C}$ for 24–48 h. Lobe tips were collected from the thallus and then crushed using an agate mortar. Because they potentially represent the main local sources of industrial contamination, three samples corresponding to the main ores processed in the Abitibi

Table 1
Lichen samples description, Pb and Os concentrations, Pb stable isotope ratios and $^{187}\text{Os}/^{188}\text{Os}$.

Sample	Pb		$^{87}\text{Sr}/^{86}\text{Sr}$		$^{206}\text{Pb}/^{204}\text{Pb}$		$^{207}\text{Pb}/^{204}\text{Pb}$		$^{208}\text{Pb}/^{204}\text{Pb}$		$^{207}\text{Pb}/^{206}\text{Pb}$		$^{208}\text{Pb}/^{206}\text{Pb}$		$^{187}\text{Os}/^{188}\text{Os}$		
	ppb	ppt		2σ		2σ		2σ		2σ		2σ		2σ		2σ	
Lichens																	
1	795	11	0.71951	0.00004	18.390	0.02	15.609	0.02	38.481	0.04	0.849	0.0001	2.092	0.0001	0.930	0.010	
2	484	149	0.71213	0.00003	18.357	0.02	15.598	0.02	38.415	0.04	0.850	0.0001	2.093	0.0001	0.457	0.002	
3	31058	9000	0.71562	0.00016	17.931	0.02	15.595	0.02	38.559	0.04	0.870	0.0001	2.150	0.0001	0.437	0.001	
4	2230	562	0.71605	0.00004	17.597	0.02	15.537	0.02	38.126	0.04	0.883	0.0001	2.167	0.0001	0.396	0.002	
5	3063	442	0.71479	0.00032	17.495	0.02	15.520	0.02	38.029	0.04	0.887	0.0001	2.174	0.0001	0.361	0.001	
6	1855	72	0.71867	0.00003	18.125	0.02	15.586	0.02	38.174	0.04	0.860	0.0001	2.106	0.0001	0.453	0.007	
7	462	22	0.71628	0.00003	18.442	0.02	15.612	0.02	38.429	0.04	0.847	0.0001	2.084	0.0001	0.419	0.004	
8	2305	73	0.71448	0.00002	17.739	0.02	15.455	0.02	36.650	0.04	0.871	0.0001	2.123	0.0001	0.392	0.003	
9	1794	806	0.71457	0.00004	17.041	0.02	15.319	0.02	36.920	0.04	0.899	0.0001	2.167	0.0001	0.441	0.002	
11	3894	51	0.71643	0.00010	16.474	0.02	15.190	0.02	36.304	0.04	0.922	0.0001	2.204	0.0001	0.792	0.008	
12	6982	86	0.71274	0.00005	15.916	0.02	15.065	0.02	35.785	0.04	0.947	0.0001	2.248	0.0001	2.390	0.013	
13	2199	34	0.71226	0.00013	16.269	0.02	15.145	0.02	36.119	0.04	0.931	0.0001	2.220	0.0001	0.593	0.003	
14	2161	39	n.d.	n.d.	16.135	0.02	15.110	0.02	35.974	0.04	0.936	0.0001	2.230	0.0001	0.792	0.009	
16	15344	33	0.71260	0.00004	14.395	0.01	14.696	0.01	34.194	0.03	1.021	0.0001	2.375	0.0001	2.297	0.026	
17	6478	25	0.71132	0.00003	14.456	0.01	14.706	0.01	34.256	0.03	1.017	0.0001	2.370	0.0001	2.006	0.033	
18	2550	20	0.71462	0.00002	17.227	0.02	15.367	0.02	37.006	0.04	0.892	0.0001	2.148	0.0001	0.866	0.009	
19	624	8	0.71881	0.00003	17.655	0.02	15.445	0.02	37.594	0.04	0.875	0.0001	2.129	0.0001	0.519	0.010	
20	526	10	0.71572	0.00007	18.169	0.02	15.558	0.02	37.973	0.04	0.856	0.0001	2.090	0.0001	0.663	0.014	
Ores																	
CDN-ME-1208	n.d.	71596	0.70954	0.00002	17.096	0.02	15.456	0.02	36.925	0.04	0.904	0.0001	2.160	0.0001	0.227	0.001	
CM717	n.d.	n.d.	0.78841	0.00004	17.845	0.02	15.545	0.02	38.312	0.04	0.871	0.0001	2.147	0.0001	n.d.	n.d.	
CM955	n.d.	n.d.	0.75098	0.00003	13.297	0.01	14.469	0.01	33.156	0.03	1.088	0.0001	2.494	0.0001	n.d.	n.d.	
<i>Other potential sources taken from the literature (numbers between brackets indicate the overall range reported)</i>																	
SU-1a ^a																	1.200
Sudbury ores ^b																	0.020
Rouyn-Noranda ores ^c					14.351 (13.390–16.360)		17.219 (15.516–20.401)		34.291 (33.250–37.270)		1.027 (0.921–1.081)		2.057 (2.033–2.080)				
Pre-industrial soil ^d					18.51 (18.49–18.53)		15.273		37.400		0.840 (0.838–0.841)		2.081				
Average Canadian aerosols ^e					18.23 (17.93–18.44)		15.57 (15.46–15.62)		37.93 (37.56–38.18)		0.847 (0.835–0.855)		2.081				
Average US aerosols ^e					18.41 (18.23–18.65)		15.58 (15.51–15.73)		38.04 (37.70–38.45)		0.847 (0.835–0.855)		2.067				

^a Rodushkin et al. (2007).
^b Dickin et al. (1996).
^c Delouie et al. (1989).
^d Gallon et al. (2006).
^e Simonetti et al. (2000).

region were analysed: i) two ore deposits from the Sudbury and Du-magami Mines (samples CM717 and CM955 in Table 1, respectively) were obtained from a private collection, and ii) a pre-crushed mineral standard from the Raglan Mine (sample CDN-ME-1208 in Table 1) was acquired from the CDN Resource Laboratories Ltd.

All lichen and ore samples were prepared in a clean laboratory (class-100). Pb digestion and chemical purification followed the adapted procedure described in Font et al. (2012) using a biospin column and the Sr Spec resin. Pb concentrations were measured by HR-ICP-MS (Attom; Nu Instruments) with an error better than 5%. Detection limit for Pb determination was 3 ppt. The Pb isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$) were measured by MC-ICP-MS on a NuPlasma II with an Aridus II desolving membrane as the introduction system. All samples were doped with thallium (Tl) to correct for the mass bias (e.g. Belshaw et al., 1998). Measurement of the NBS-981 standard every five samples throughout the analytical sequence allowed getting a Tl-Pb mass bias relationship (Woodhead, 2002). Measurements of the in-house CGPb-1 standard yielded the following long-term averages (2σ , $n = 22$, over several years) $^{208}\text{Pb}/^{206}\text{Pb} = 2.0425 \pm 0.0003$; $^{206}\text{Pb}/^{204}\text{Pb} = 18.596 \pm 0.008$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.702 \pm 0.005$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.98 \pm 0.02$, and $^{207}\text{Pb}/^{206}\text{Pb} = 0.8444 \pm 0.0002$.

Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured by Thermal Ionisation Mass Spectrometry (TIMS) on a Thermo Triton plus. Sr was collected at the same time than Pb during the purification procedure described above. The Sr fraction was loaded on a Re filament using nitric acid and a tantalum activator (Birck, 1986). Mass bias was corrected by normalizing all ratios to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Analyses of the NIST SRM-987 standard yielded a long-term average $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.71026 ± 0.0003 (2σ , $n = 26$). Total procedural blanks were lower than 140 ppt for Sr.

Os concentrations were determined by Isotope Dilution Mass Spectrometry (IDMS), following the procedure described in Heumann (1992), during the Os isotope analysis (typical detection limit of a few ppt), typical blanks being < 0.5 pg. For the Os isotope analysis, samples spiked with ^{185}Re - ^{190}Os were digested with high-purity aqua regia at 300°C for 12 h in a High Pressure Asher (HPA) following the method described in Meisel et al. (2003). Bromine (Br_2) was added to the sample solution to separate Os under the form of OsO_4 , followed by micro-distillation before the mass spectrometry analysis (Birck et al., 1997). Os isotopes were measured by Negative Thermal Ionisation Mass Spectrometry (N-TIMS, Creaser et al., 1991) on a Thermo Triton Plus, by peak hopping on a secondary ion multiplier. Repeated measurement of standard material DROs yielded an average $^{187}\text{Os}/^{188}\text{Os}$ value of 0.1628 ± 0.0078 (2σ , $n = 8$, on 10–15 pg loads), which is consistent with Luguet et al. (2008).

Two reference materials were also analysed: BCR-482 and IAEA-336. Results we obtained are in agreement with data published by Aebischer et al. (2015), Sucharová et al. (2014) and Rodushkin et al. (2007): BCR-482: 4.24 ppm_{Pb}, 99 ppt_{Os}, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70842 \pm 0.00002$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.44 \pm 0.04$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.55 \pm 0.02$, $^{206}\text{Pb}/^{204}\text{Pb} = 17.59 \pm 0.02$, $^{187}\text{Os}/^{188}\text{Os} = 0.833 \pm 0.003$; and IAEA-336: 27.4 ppm_{Pb}, 43 ppt_{Os}, $^{87}\text{Sr}/^{86}\text{Sr} = 0.71181 \pm 0.00003$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.71 \pm 0.04$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.58 \pm 0.02$, $^{206}\text{Pb}/^{204}\text{Pb} = 17.82 \pm 0.02$, $^{187}\text{Os}/^{188}\text{Os} = 0.613 \pm 0.004$.

3. Results and discussion

3.1. Lead and strontium

Pb concentrations in lichen samples (Table 1) vary from 462 to 31,058 ppb with two locations showing higher Pb concentrations along our transect (Fig. 2). The first peak (Pb = 31,058 ppb) corresponds to the sample taken within 2 km from the Sudbury smelter (sample 3). The second peak located near the Horne smelter (25 km) gave a Pb content of 15,344 ppb (sample 16), consistent with the concentrations obtained

by Carignan and Gariépy (1995) on other lichens measured in the Abitibi region (1990–33,210 ppb). The authors observed the highest Pb concentrations in the vicinity of the city of Rouyn-Noranda and decreasing values away from the city. While most of the lichen samples studied here were taken more than 20 km away from the smelters, Telmer et al. (2006) showed, using the example of the Rouyn-Noranda smelter, that more than 90% of the atmospheric emissions are deposited within that distance from this smelter. Our lowest Pb concentrations, 462–795 ppb (average of 578 ± 136 ppb; $n = 5$; samples 1, 2, 7, 19 and 20), are similar to those reported for remote sites in Northern Canada (470 ppb; Chiarenzelli et al., 2001). Considering an atmospheric residence time of a few days (5–10 days) for Pb (Sturges and Barrie, 1987), a yearly average wind speed of 13 km h^{-1} in the region (data obtained from Environment Canada) and a daily average of 12 h of wind (data obtained from Environment Canada); Pb in aerosols could be transported by winds over a distance of up to 780 km. Our results indicate that the Pb plume signal may be observed up to 150–250 km from the smelters (calculated as the distance for Pb concentrations to decrease back to its background level measured in the lichens; Fig. 2).

The average $^{206}\text{Pb}/^{204}\text{Pb}$ ratio for these background samples (samples 1, 2, 7, 19 and 20) is 18.2 ± 0.3 ($n = 5$; from 17.6 to 18.4), similar to the isotope ratios obtained for lichen samples of Western Quebec (17.7–18.7; Carignan et al., 2002). The total sample set displays a large range of $^{206}\text{Pb}/^{204}\text{Pb}$ values, from 14.4 to 18.4, that seems to correspond to the two Pb concentration peaks (Fig. 2), in agreement with the hypothesis that atmospheric deposition from the smelters should translate into their corresponding Pb isotope ratios. The atmospheric emissions' signatures from the smelters are intimately related to the ores they are processing as Pb isotopes are not undergoing significant mass-dependent fractionation during high-temperature smelting operations due to the isotopes heavy mass and subsequently their small relative mass difference (Shiel et al., 2010). While Sudbury ores have a mean $^{206}\text{Pb}/^{204}\text{Pb}$ of 16.2 ± 1.5 (Dickin et al., 1996), the old rocks and ores of the Abitibi region processed by the Horne smelter have lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratios centered around 14.3 (Deloule et al., 1989).

Fig. 3a reports variations of the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in the lichens against the reciprocal of their Pb concentrations. In such diagram binary mixing relationships are represented by straight lines (Langmuir et al., 1978). The figure shows that lichen samples all plot within a ternary mixing between 3 end-members: 1) atmospheric emissions from the Sudbury smelter characterised by high Pb concentrations and a $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of 17.9 (represented by sample 3). This value is more radiogenic than the ones we measured in some typical ores supposedly processed in the smelter, CDN-ME-1208 ($^{206}\text{Pb}/^{204}\text{Pb} = 17.1$) and CM717 ($^{206}\text{Pb}/^{204}\text{Pb} = 17.8$), but the full natural isotope range of the ore is unknown. 2) atmospheric emissions from the Rouyn-Noranda smelter with high Pb concentrations and a $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of 14.4, (represented by sample 16), and 3) a third source characterised by relatively low Pb concentrations and a more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratio around 18.4 that we believe represents the regional Pb background level (i.e. dust from all sources, natural and anthropogenic, non-mine related). This $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of ca. 18.4 is similar to the value of 18.49 and 18.53 reported for pre-industrial sediments from the oligotrophic lakes Carpe and Despériers in the same region (the latest one being located close to Rouyn-Noranda; Gallon et al., 2006). The corresponding $^{206}\text{Pb}/^{207}\text{Pb}$ ratios reported by the authors are 1.190 and 1.193, which are also consistent with the same ratios measured in our five least Pb-contaminated lichens (1.17 ± 0.02).

The phasing out of leaded petrol in Canada started in the 1980s and leaded petrol was finally phased out in 1992 (Pacyna et al., 1995), this background $^{206}\text{Pb}/^{204}\text{Pb}$ ratio may thus also be interpreted as a binary mixture between typical Canadian ($^{206}\text{Pb}/^{204}\text{Pb} = 17.7$; Carignan et al., 2002) and US ($^{206}\text{Pb}/^{204}\text{Pb} = 18.85$; Carignan et al., 2002) aerosols measured circa 2000. Assuming that average Canadian and US aerosols contain similar concentrations of Pb (e.g. Han et al., 2012; Celo

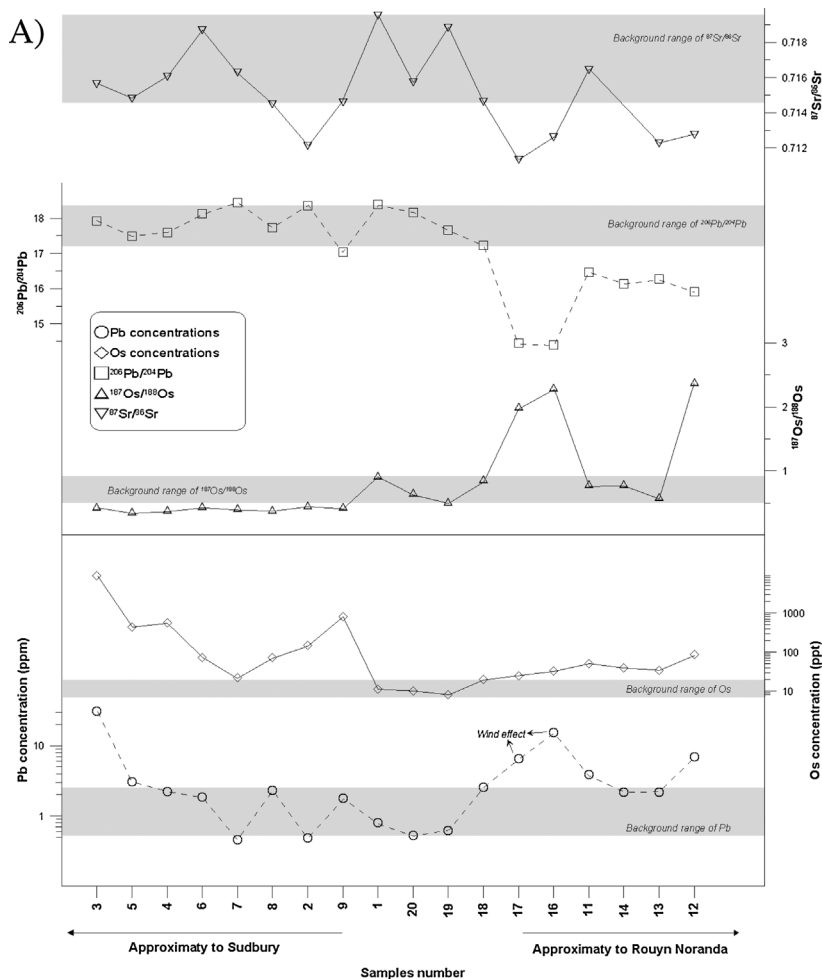
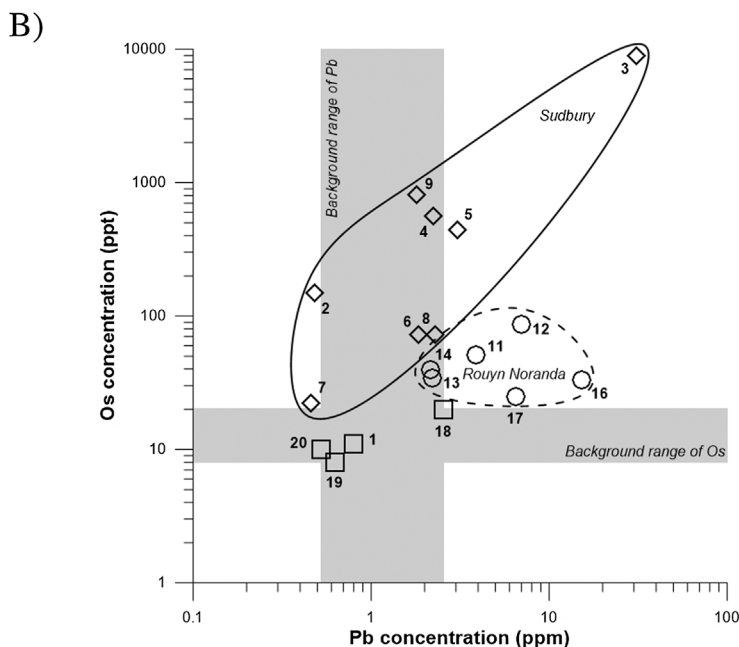


Fig. 2. Pb and Os concentrations and isotope ratios measured in the lichens. Corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios are also reported. Samples are ranked according to the distance to the nearest smelters. A) Shows that, 1) Pb and Os concentrations decrease with increasing distance to the smelters; 2) transport of Pb with prevailing wind can be observed in samples 16 and 17; 3) Pb concentrations fall in the range of background in most samples; and 4) Os concentrations higher than the background values in most samples. B) Samples were classified according to the distance to the nearest smelters. Samples 1, 18, 19 and 20 are background samples.



and Dabek-Zlotorzynska, 2010), we can calculate using a simple mixing equation ($\%_{\text{US}} \times ^{206}\text{Pb}/^{204}\text{Pb}_{\text{US}} + \%_{\text{CAN}} \times ^{206}\text{Pb}/^{204}\text{Pb}_{\text{CAN}} = 18.1$) that a $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of 18.1 corresponds to a rough 65% contribution of Canadian aerosols and of 35% for the US ones. This is in agreement

with Carignan et al. (2002) who reported that US aerosols contributed for up to 35% in Pb found in epiphytic lichens in the Rouyn-Noranda region.

From Fig. 3a we can thus assume that the three end-members

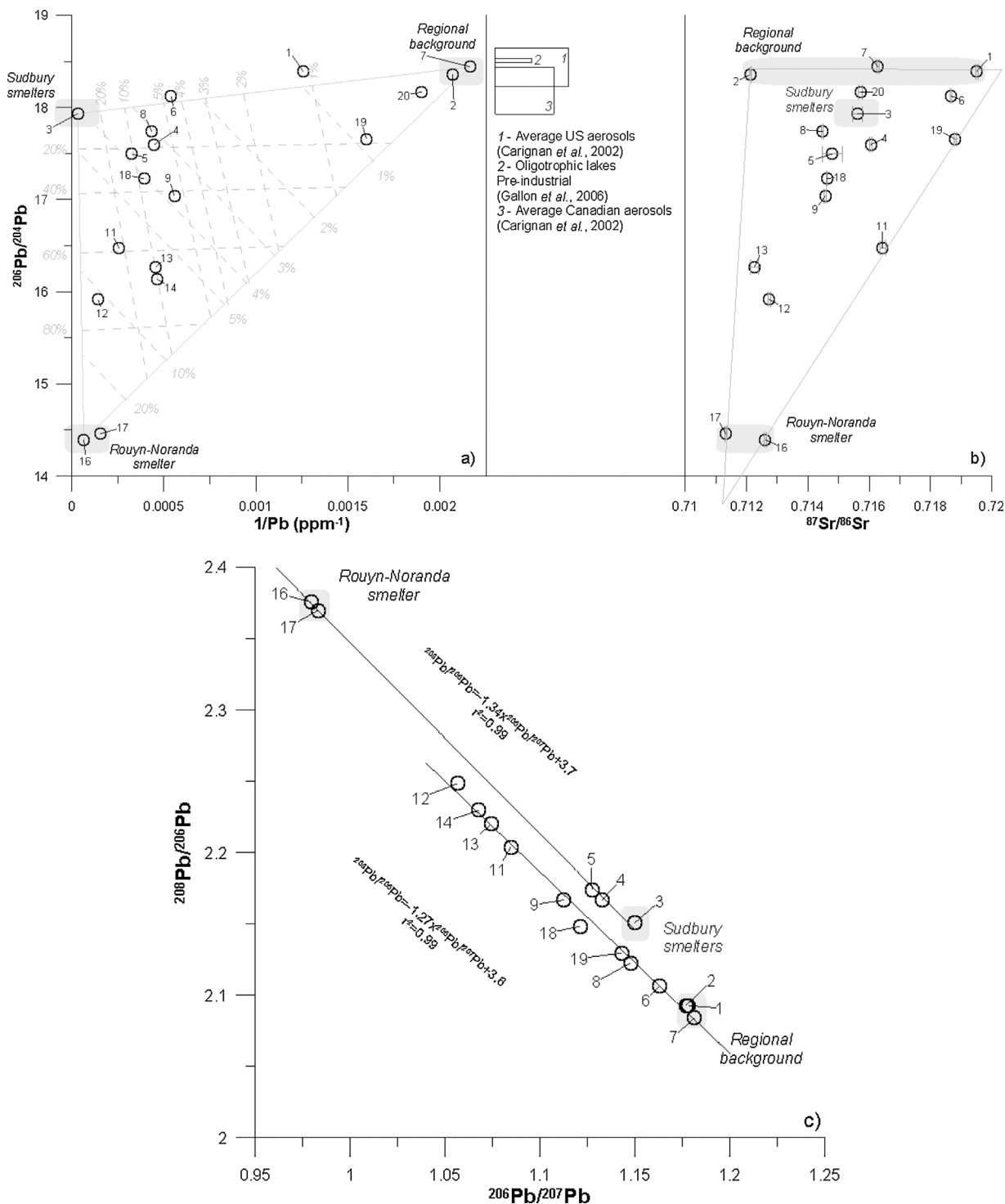


Fig. 3. Variations of the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in the lichens. A) vs variations of the corresponding Pb concentrations. B) vs variations of the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. $^{206}\text{Pb}/^{204}\text{Pb}$ characteristics of local oligotrophic lakes, of typical US and Canadian aerosols as well as modeled binary mixing relationships are also reported. C) Classical $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$ diagram. A mixing line between the two smelters is defined by a suite of samples, while another suite plots between the Abitibi ore (that comprises the Rouyn-Noranda smelter) and a regional background that seems to be affected by the “type-1 Pb” end-member of Gallon et al. (2006), as measured by this last study in the local Despériers lake.

previously discussed have the following characteristics: 1) Emissions from the Sudbury smelter, represented by sample 3: $[\text{Pb}] = 31,058$ ppb and $^{206}\text{Pb}/^{204}\text{Pb} = 17.9$, 2) Emissions from the Rouyn-Noranda Horne smelter, represented by sample 16: $[\text{Pb}] = 15,344$ ppb and $^{206}\text{Pb}/^{204}\text{Pb} = 14.4$, and 3) the regional Pb background, represented by the lichen sample with the lowest Pb concentration 7: $[\text{Pb}] = 462$ ppb and $^{206}\text{Pb}/^{204}\text{Pb} = 18.4$. We can then model mixing relationships for these three end-members using mass balance equations, and ultimately

estimate their corresponding contributions for each sample. The equation of mixing for a k component system for isotope ratios I can be expressed in the following way (Douglas and Schilling, 2000):

$$I = \frac{\sum_{i=1}^k z_i n_i I_i}{\sum_{i=1}^k z_i n_i} \tag{1}$$

with $\sum_{i=1}^k z_i = 1$ and $0 \leq z_i \leq 1$, and where I is the isotope ratio in the

mixture, I_i the isotope ratio in each end-member component, z_i the mass fraction of component 1, 2, 3... and n_i the relative enrichment of element I in component 1, 2, 3... relative to component k (i.e. $n_i = c_i/c_k$; where c is the concentration of element I).

As expected, results (Fig. 3a) indicate that lichens taken away from the smelters (samples 1, 2, 7 and 19, 20) present low Pb concentrations that are mostly corresponding to the regional background origin we previously defined. Other samples are impacted by atmospheric deposition of emissions from either the Horne smelter (samples 11, 13 and 14) or the Sudbury smelters (samples 4, 5, 6, 8). Corresponding Pb contributions from the smelters are generally ranging between 5 and 20%. Sample 11 is intriguing as while it was collected close to the Horne smelter its $\text{Pb-}^{206}\text{Pb}/^{204}\text{Pb}$ characteristics prove that it is still impacted by the atmospheric emissions from the Sudbury smelter (~40%). This could indicate the extent of the contamination plume from this latter smelter, which is consistent with the Southwestern wind patterns in the region (Carignan et al., 2002).

When $^{206}\text{Pb}/^{204}\text{Pb}$ are coupled to their corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 3b), samples are still plotting within a ternary plot but with slightly different end-members. Samples 16 and 17, collected close the Horne smelter, present isotope characteristics similar to those previously reported for this smelter ($^{87}\text{Sr}/^{86}\text{Sr} = 0.712$, Simonetti et al., 2000, and $^{206}\text{Pb}/^{204}\text{Pb} = 14.5$, Gallon et al., 2006), but significantly different from the ore (CM955) we analysed, that presented a very radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7509) and a lower $^{206}\text{Pb}/^{204}\text{Pb}$ (13.3) values. Samples 1, 2, 7 and 20, which were identified as defining the regional background in Fig. 3a, represent the other two end-members. They have similar $^{206}\text{Pb}/^{204}\text{Pb}$ at ca. 18.5 but variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, ranging from 0.7121 to 0.7195. This isotope range is consistent with an origin that would be free of anthropic influence as such anthropogenic emissions are expected to have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios < 0.710 in Eastern Canada (Simonetti et al., 2000). It also fairly compares to the isotope range reported by Millot et al. (2002 for rivers in Canada which can be seen as a good estimate of the average range of $^{87}\text{Sr}/^{86}\text{Sr}$ for the Canadian bedrocks from which our atmospheric Sr background is hypothesised to originate from. Sample 3, which represents emissions from the Sudbury smelter in Fig. 3a has characteristics in Fig. 3b that are not significantly distinguishable from the regional background. Its $^{87}\text{Sr}/^{86}\text{Sr}$ is also intermediate between the isotope ratios measured in the ores that are representative of the ones processed in the smelter: CM717 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7884$) and CDN-ME-1208 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7095$). Using a binary isotope balance equation, we can then estimate from our Sr data that the Sudbury smelter may incorporate about 8% of the CDN-ME-1208 ore in the ores it is processing.

The identification of three end-members, drawn from Fig. 3a and b, is comforted by the study of the Pb multi-isotope ratios ($^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{206}\text{Pb}/^{207}\text{Pb}$; Fig. 3c). Emissions from the Rouyn-Noranda smelter (represented by samples 16 and 17) are significantly discriminated, showing the highest $^{208}\text{Pb}/^{206}\text{Pb}$ and lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, from the samples corresponding to the regional background we previously defined (samples 1, 2 and 7) that yielded the lowest $^{208}\text{Pb}/^{206}\text{Pb}$ and highest $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. In Fig. 3c we apparently have two distinct mixing lines: one sharply between the two smelters, encompassing samples 3, 4 and 5, and 16 and 17, while the other samples fall between our regional background and seems affected by a source close to the Rouyn-Noranda smelter signature, but not the exact one seen by samples 16 and 17. This could be attributed to a change in the smelter's ore signature over time, or simply to the fact that Abitibi rocks contains many showings and mining potentials that have a broader range of isotopic values that make up the regional natural background (e.g. the "type II source, Abitibi ores" from Gallon et al., 2006). Sample 3, which represents emissions from the Sudbury smelters in Fig. 3a, has intermediate $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. Data obtained from the other bioindicator samples show isotope ratios that are consistent with mixings between these three end-members.

3.2. OSMIUM

Osmium concentrations in the lichen samples varied between 8 and 9000 ppt (Table 1). While the highest concentrations were measured around the Sudbury smelter (9000 ppt; sample 3), samples collected around the Rouyn-Noranda smelter (samples 1–20) yielded significantly lower and relatively constant Os concentrations (8–86 ppt; average value of 34 ± 24 ppt), with the highest Os concentration measured in sample 12 collected 8 km from the smelter. The relatively low Os concentrations measured in lichens around Rouyn-Noranda suggest that atmospheric emissions from the smelter contain low Os concentrations. Rodushkin et al. (2007) reported a rapid decrease in Os concentrations in lichens away from a smelter in Sweden, from > 10,000 ppt close to the smelter to contents < 100 ppt when further than 100 km from it. A similar decrease is observed in the Sudbury region from 9000 ppt (sample 3) down to 149 ppt (sample 2) in less than 200 km.

Corresponding $^{187}\text{Os}/^{188}\text{Os}$ ratios show opposite trends with relatively constant values around the Sudbury smelter (from 0.392 to 0.457; average of 0.416 ± 0.03) and larger variations around the Rouyn-Noranda smelter (0.519–2.390; average of 1.478 ± 0.84). Samples collected the closest to the Horne smelter yielded the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratio (2.390, sample 12) but we observe a rapid decrease down to ratios of 0.5–0.8 within a radius of 100 km from the smelter. The highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ value for the emissions of the Horne smelter may be explained by the presence of rhenium-rich minerals, such as molybdenite (MoS_2) in the smelted ore material. Occurrences of MoS_2 have been documented within the Abitibi Gold Belt (Dubé and Gosselin, 2007; Ispolatov et al., 2008). Molybdenite contains up to several percents of rhenium (Mitchell et al., 1989), from which the radioactive ^{187}Re isotope decays into ^{187}Os over geological time (half-life $T_{1/2} = 41.6$ Gy; Smoliar et al., 1996), ultimately producing highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios (e.g. $^{187}\text{Os}/^{188}\text{Os} = 1054$; Zhang et al., 2005). Previous studies showed that ores from the Sudbury region have crustal $^{187}\text{Os}/^{188}\text{Os}$ ratios from 0.909 to 5.947 (Morgan et al., 2002), a range that is significantly more radiogenic than the Os isotope ratios we measured in the surrounding lichens. This isotope difference may result from the fact that the Sudbury smelter mixes ores from the Sudbury region to ores from the Raglan mine located in northern Québec in its smelting process. The Raglan ore deposit (sample CDN-ME-1208) showed a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.227 for an Os concentration of 71,596 ppt (Table 1). The Sudbury ores that were analysed by Rodushkin et al. (2007) yielded an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 1.20 ± 0.02 for an Os concentration of 10,000 ppt. If we assume that the $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.437 we measured in sample 3 represents actual emissions from the Sudbury smelter (Fig. 3a), then a simple isotope balance equation (Eq. (1)) shows that the Horne smelter may incorporate about 10% of the Raglan ores into the Sudbury ones in its smelting process. This is in agreement with the proportion we previously calculated using the Sr isotope systematic (e.g. ~8%).

Fig. 4 reports Os concentrations and $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios in the lichen samples. Results show that data are mostly plotting onto two distinct binary mixings. Samples from the Sudbury region (sample 3–7) plot on a linear trend characterised by a relatively constant $^{187}\text{Os}/^{188}\text{Os}$ (average of 0.416 ± 0.03) coupled to large variations of Os concentrations (from 22 to 9000 ppt). This may be interpreted as the result of contamination of the regional background (represented by sample 19) by atmospheric emissions from the Sudbury smelter (represented by samples with the highest Os concentrations; samples 3–5). The corresponding $^{187}\text{Os}/^{188}\text{Os}$ ratio for the regional background ([Os] = 8 ppt and $^{187}\text{Os}/^{188}\text{Os} = 0.519$; sample 19) is similar to the one defined by Rodushkin et al. (2007) for the Swedish airborne osmium background, at [Os] < 100 ppt and $^{187}\text{Os}/^{188}\text{Os} = 0.44 \pm 0.08$, that the authors attributed to the product of mixing emissions from low-intensity local sources, natural background (e.g. accretion of extra-terrestrial particles) and long-range atmospheric transport from remote sources. Samples 1

the extent of the contamination plume for each smelter. Results also indicated that for some of the low metal concentrations, Pb and Os isotopes identified distinct origins. This is probably related to the different atmospheric dispersion pathways between the insoluble particulate species containing Pb and the Os species that are soluble and quite probably volatile.

- Unexpectedly a dual isotope approach based on the study of the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios proved to have more limitations, as emissions from the Sudbury smelters and the regional background were not isotopically distinguishable.

Our study confirms that bioindicators, lichens here, are excellent passive samplers that can be studied to tackle environmental issues, in particular air contamination. Strategies of air quality control would benefit from adding them to their monitoring schemes, especially if they are complementing them with the added value brought by the isotope methodologies. Limitations of this approach mainly consist on the relatively superficial knowledge on the age of the lichens that are studied (mainly based on an estimated growth rate) and on the fact that they are giving information that is averaged over the lifetime of the bioindicators.

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