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Original article

Influence of climatic conditions and industrial emissions on spruce tree-ring Pb isotopes analyzed at ppb concentrations in the Athabasca oil sands region

L. Dinis[a,*], M.M. Savard[b], P. Gammon[c], C. Bégin[b], J. Vaive[c]

[a] Institut national de la recherche scientifique-ETE, 490 rue de la Couronne, Québec G1K9A9, Canada
[b] Geological Survey of Canada, Natural Resources Canada, 490 rue de la Couronne, Québec G1K 9A9, Canada
[c] Geological Survey of Canada, Natural Resources Canada, 601 Booth street, Ottawa K1A 0E8, Canada

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ABSTRACT

This study investigates Pb isotope ratios at low concentrations (parts per billion; ppb) in tree rings and soils in the Northern Athabasca Oil Sands Region (NAOSR), western Canada, to evaluate if: (1) climatic conditions influence on tree-ring Pb assimilation; and (2) such low Pb content allows inferring the regional Pb depositional history.

Our results reflect the influence of winter snow cover and the importance of minimum temperature and precipitation in spring and summer on the bioavailability of Pb and its passive assimilation by trees in sub-arctic semi-humid climatic conditions. Winter conditions can influence the state of root systems that subsequently impacts the following growth period, while spring and summer conditions likely control microbial processes and water source, and may thus impact Pb assimilation by trees. Thus, the results of tree-ring Pb concentrations show interesting correlation with cumulated snow from November of the previous year to February ($\rho = 0.53$; $P < 0.01$; $n = 36$). Likewise, the $^{206}Pb/^{207}Pb$ ratios inversely correlate with minimum temperature from April to September ($\rho = -0.67$; $P < 0.01$; $n = 40$) and precipitation from May to August ($\rho = -0.42$; $P < 0.01$; $n = 36$). The isotopic results also suggest that the effects of climatic variations are superimposed by regional industrial Pb deposition: Western North American Aerosols (WNAA) and fugitive dust from the oil sands mining operations appear to be the most likely sources.

Importantly, this study suggests that even at low Pb concentrations, tree-ring Pb isotopes are modulated by climatic conditions and potential input of regional and long-range transport of airborne Pb. These interpretations open the possibility of using Pb isotopes as an environmental tool for inferring the pollution history in remote regions, and improving our understanding of its natural cycle through the forest environment.

1. Introduction

The natural variations of ^{206}Pb, ^{207}Pb and ^{208}Pb in environmental materials are recognized to be minimally affected by physico-chemical and biological fractionation as a result of smelting and manufacturing processes (Sangster et al., 2000; Komárek et al., 2008). Those characteristics have led to an extensive use of Pb isotopes as an indicator of environmental changes in Pb cycling. The results of those studies provided a general history of Pb cycling between atmosphere, hydrosphere, pedosphere and biosphere, which is now relatively well understood in the context of global pollution (Komárek et al., 2008).

Environmental archives, such as tree rings, are a history of the Pb inventory of both the local area and more far travelled atmospheric sources that are commonly anthropogenic. Anthropogenic use of Pb such as alkyl-Pb production, industrial processing (e.g., coal combustion, waste incineration) and international trading results in anthropogenic Pb emissions whose isotopic composition is more reflective of an overall homogenisation of the natural variability of Pb-isotopic signatures found across the globe (Bollhöfer and Rosman, 2002). Such isotopically-homogenised Pb has been emitted to the atmosphere since the beginning of the industrial era

* Corresponding author. Present address: Institute of Geography and Geoecology, Karlsruhe Institute of Technology (KIT), Reinhard-Baumeister-Platz 1, 76131 Karlsruhe, Germany.
E-mail address: lauriane.dinis@kit.edu (L. Dinis).

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(Pacyna and Pacyna, 2001), with subsequent transport and deposition in forests.

Over the last two decades Pb concentrations and isotope ratios have been documented in multiple conifer tree-ring chronologies, which has helped reconstructing anthropogenic perturbations of the natural Pb cycle (e.g., Savard et al., 2006; Mihaljevič et al., 2008; Novak et al., 2010; Vanek et al., 2011; Doucet et al., 2012). Conifer tree-ring Pb isotopic studies have been used to investigate the environmental record for systems such as: point source emissions (e.g., mine smelters); urban areas (e.g., highway traffic); and diffuse pollution in peri-urban areas. These studies demonstrate the utility of conifer tree-ring Pb for investigating changes in the atmospheric and soil Pb chemistry.

Metal concentrations or isotopic ratios in a tree ring sequence can only be considered as an accurate chronological record if there has not been radial movement of the metal after tree ring formation. For some elements, particularly essential elements (e.g., P, K and S), it is clear that radial translocation does occur (Arp and Manasc, 1988; Meerts, 2002). A few studies have therefore questioned the use of tree-ring Pb characteristics as archival systems due to Pb accumulation in the heartwood of mature trees, or to mobility within the xylem in seedlings and young trees (e.g., Donnelly et al., 1990; Hagemeyer and Weinand, 1996; Watmough and Hutchinson, 2002; Bindler et al., 2004; Patrick and Farmer, 2006; Stille et al., 2012). However, as a non-essential element for trees, Pb is considered to be practically unaffected by translocation in many species; i.e. there is weak inter-ring Pb mobility, particularly in conifers (Cutter and Guyette, 1993). Compared to hardwood, conifer wood has a uniform anatomical structure that is principally composed of tracheids with less and shorter ray cells, which has also been inferred to limit the potential for radial translocation effect (Watmough, 1999; Bégin et al., 2010). Therefore, tree-ring Pb is generally considered to reflect changes in atmosphere and soil chemistry of the year of their formation (Amato, 1988).

Climatic conditions influence how trees assimilate nutrients and non-essential elements by controlling physiological functions such as stomatal closure (Hari and Mäkelä, 2009). When conditions are suitable for stomatal opening, the ascension of xylem sap occurs, which actively transports dissolved soil nutrients from the roots up to the leaves for metabolic assimilation (Kolari et al., 2009). At the same time, non-essential elements can be passively incorporated and fixed into tree rings (Lepp, 1975; Watmough, 1997). Therefore, given that: (1) Pb isotopic fractionation through biogeochemical processes is practically negligible; (2) Pb is a non-essential passive element; and (3) Pb uptake and fixation in trees is substantially controlled by xylem sap ascension, then the climatic conditions that influence stomatal opening and evapotranspiration will at least partially control tree-ring Pb concentration and isotopic variations. The Pb isotopic ratios of Pb assimilated in trees should reflect the external environmental conditions to the trees in terms of presence of Pb types and bioavailability (Savard et al., 2006). In this sense, only a few tree-ring Pb isotope studies have suggested a link between Pb isotopic ratios and climatic conditions (Bindler et al., 2004; Savard et al., 2006). Poszwa et al. (2003) have found that drought may indirectly and partly control Pb sources in soils by forcing roots to use deeper water sources, which results in Pb uptake from horizons with different Pb concentrations and isotopic ratios. The relationship between the processes driving Pb uptake, climatic parameters and tree growth are poorly described or understood.

Most previously cited studies of Pb isotopes in tree rings have been conducted in strongly contaminated sites with tree-ring concentrations at parts per million (ppm), which enables tree-ring separation at high resolution (between 2 and 5 years). However, there is substantial scope to use Pb isotopes as contamination indicators in localities with trees containing much lower Pb concentrations to give a temporal perspective. Consequently, there is a need to develop sampling and treatment protocols that enable producing tree-ring time series of Pb isotopes at such low concentrations (parts per billion; ppb), without sacrificing the precision and accuracy of results.

Airborne emissions from the oil sands industry to the Northern Athabasca Oil Sands Region (NAOSR) are reported to have low metal content (Kelly et al., 2010; Guéguen et al., 2011; Edgerton et al., 2012). The average Pb concentration in lichens was 2.45 ppm for distal and 2.92 ppm for proximal samples, with 1.12 ppm as the lowest value (Edgerton et al., 2012; Graney et al., 2012). This contrasts with lichens surrounding urban or mining centers where reported concentrations range from 150 to 1200 ppm (Spiro et al., 2004). However, the temporal perspective for isotopic Pb deposition is as yet unknown for this region.

In light of the above, the objectives of this paper are: (1) to generate a long baseline chronology of Pb (concentrations and isotopic ratios) in the NAOSR; (2) to determine how Pb concentrations and isotopes of spruce tree rings may be related to environmental conditions; and (3) to evaluate the possibility of using Pb concentrations and isotopic ratios in trees and soils as a retrospective monitoring tool of environmental conditions in the context of very low Pb concentrations and depositional fluxes, such as in the NAOSR. Our approach combines the tree-ring chronological perspective of white spruce trees with samples of soil profiles to document and interpret the long-term Pb concentrations and isotopic trends (1878–2009) obtained at the high precision ppb level.

2. Material and methods

2.1. Field context

The NAOSR in Alberta hosts the largest oil sands deposits in the world. The first open pit-mining operations started in 1967, with a production of 45 000 barrels per day (bbl/d) (Suncor, 2013). In 2012, open mining and *in-situ* oil recovery projects produced 330 and 263 million barrels respectively (total of 1.62 million bbl/d), while 71,500 ha of forest have been disturbed principally by mining activities and tailing ponds expansion (Government of Alberta, 2013). Since 2002, the three largest producers (Syncrude Canada Ltd., Suncor Energy Inc. and Canadian Natural Resources Limited) have monitored their Pb emissions, with their estimated figures reported on the National Pollutant Release Inventory (NPRI; Environment Canada, 2013a). The lowest estimated emissions were in 2004 (219 kg released to the air), and the highest in 2010 (852 kg) with an average of 504 kg over the 2002–2011 period. In comparison to total Albertan Pb atmospheric emissions, oil sands emissions represent 13 and 21% for 2004 and 2010, respectively. For comparative purposes, the Horne Zn–Pb smelter in Rouyn-Noranda, Québec respectively emitted 45,747 and 70,088 kg for the same years (Environment Canada, 2013a). Therefore, oil sands emissions generally contain low Pb level.

The region is characterized by a subarctic semi-humid climate with a mean annual temperature of 0.7 °C and a mean relative humidity of ∼67%. The annual average precipitation is 489 mm, of which snowfall represents 29% (Ok et al., 2007; Environment Canada, 2013b). The selected site is located in the Boreal Plains ecozone (Wiken et al., 1996), which is generally characterized by two main environments: peatlands and upland forests, the latter being dominated by jack pine (*Pinus banksiana*) and trembling aspen (*Populus tremuloides*). Summer wildfires are common in the region making old-growth stands uncommon (Larsen, 1997). On the other hand, low-lying wetland areas are hosting black (*Picea mariana*) and white spruce (*Picea glauca*) trees. These last two species are