(GC21C-0883)

Multiple Tree-Ring Isotopes as Environmental Indicators of Diffuse Atmospheric Pollution in a Peri-Urban Area

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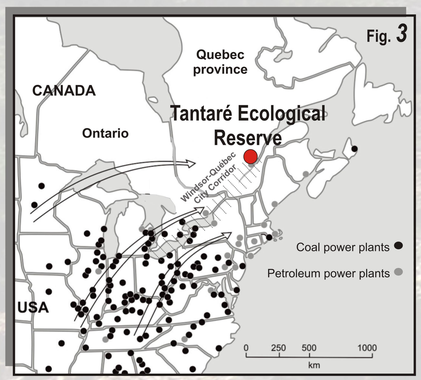
I. Introduction

The chemical composition of tree-ring series represents, at least partially, the chemical composition of its environment and perhaps perturbations of this environment. This has been shown in several studies for trees growing near point-source air pollutants. Here, we verify if trees growing in peri-urban areas are sensitive enough to diffuse atmospheric pollution to reflect pollution sources. To address this question, we combine the analyses of tree-ring **$\delta^{13}C$, $\delta^{18}O$, $\delta^{15}N$, $^{206}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$ and $^{206}Pb/^{208}Pb$ isotope ratios, and Cd, Zn and As concentrations** of three red spruce specimens from the Tantaré ecological reserve located in the peri-urban area of Québec City (Canada), with the **aim of reconstructing environmental conditions and unraveling past air-quality changes of the 1840-2007 period**.

II. Study Site and Selection of Specimens

- Three red spruce trees of 191, 207 and 216 years (Figs. 1-2).
- Protected area of the Tantaré ecological reserve.
- 40 km NW of Quebec City, in the NE part of the WindsorQuébec City Corridor (hatched surface; Fig. 3).
- Corridor highly populated and industrialized, one of the three most polluted zones in Canada.
- Significant concentration of eastern American industries, including an important number of coal power plants, in the southern part of the corridor.
- Related atmospheric emissions transported over the corridor by the southwest to northeast dominant winds (arrows, Fig. 3).



III. Methodology

Laboratory manipulations

- Tree rings of cores separated with clean stainless blades (1840-2007; n = 121), ground with a Wiley mill.
- Cellulose extracted from wood samples to analyse their $\delta^{18}O$ and $\delta^{13}C$ values.
- Wood pre-treated (removal of resins) to analyze the $\delta^{15}N$ values.
- Total digestion of tree rings before analyzing the tree-ring metal concentration and lead isotope ratios.

Objective of Statistical approach

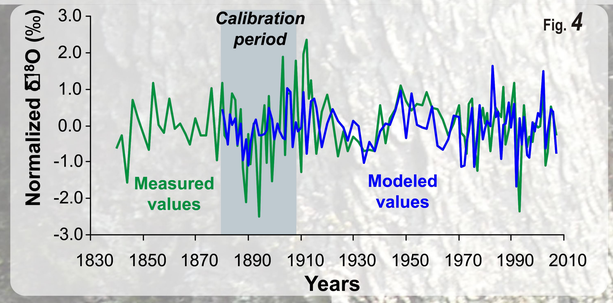
To separate the geochemical patterns induced by natural conditions from those generated by anthropogenic perturbations.

***Statistical approach*:**

- Apply a linear regression between the most explicative meteorological parameters and the $\delta^{18}O$ and $\delta^{13}C$ series for the period of no (low) pollution (1880 to 1909).
- If there is a good fit between measured and modeled data, the regression-derived equations are applied to generate a modeled geochemical climatic series for the recent period (1910 to 2007).
- For that period, if the modeled geochemical trends match the measured ones, the trees are considered to be solely influenced by natural (climatic) conditions.
- A strong departure between the modeled and measured data indicates an environmental perturbation.
- To verify if the departure can be caused by anthropogenic emissions, we applied a linear regression between the residual of the predicted values from regression with climatic parameters and anthropogenic emissions. Then, the modeled values from meteorological parameters and pollution data are combined to verify if they match the measured isotopic values.

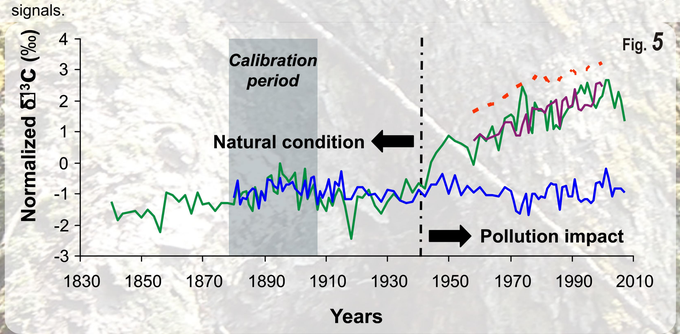
IV. Tree-ring $\delta^{18}O$ Results

- Modeling based on a linear regression with total precipitation (r = -0.39; P < 0.05) and maximal temperature (r = 0.34; P < 0.05) of July and August (Fig. 4).
- The good fit with the measured tree-ring $\delta^{18}O$ values suggests that the assimilation of oxygen by red spruce trees is mostly controlled by natural conditions and that the influence of pollution on the red spruce $\delta^{18}O$ values is minor.



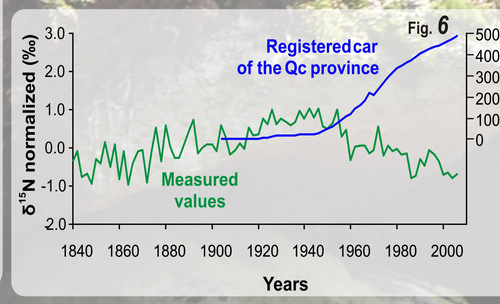
V. Tree-ring $\delta^{13}C$ Results

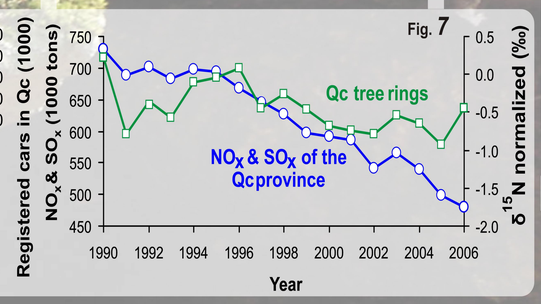
- Modeling based on a linear regression with annual total precipitation (r = -0.62; n = 30) and maximum temperature (r = 0.45; n = 30; Fig. 5).
- Considerable departure between measured and predicted $\delta^{13}C$ values suggests that the $\delta^{13}C$ values of tree rings of the post-1942 period harbour an anomalous behaviour for which climatic conditions are not the primary driver.
- Combination of the predicted $\delta^{13}C$ values from pollution data (Canadian fossil fuel consumption from 1958 to 2000) and those from climatic parameters do not match exactly, but the results strongly support the hypothesis that there is a natural and an anthropogenic portion in the tree-ring $\delta^{13}C$ signals.



VI. Tree-ring $\delta^{15}N$ Results

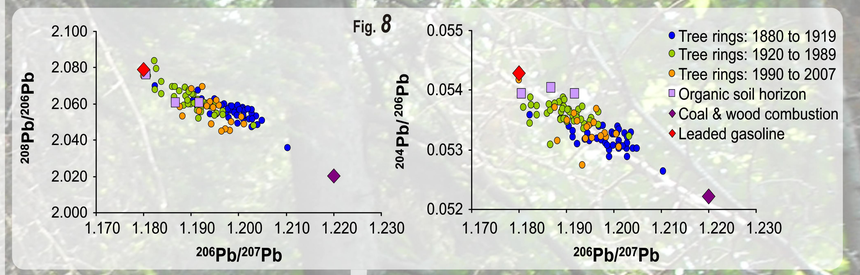
- The $\delta^{15}N$ trend (Fig. 6) of the 1840-41 to 1954-55 period reflects a mixture of natural conditions with coal combustion emissions (+4.8 to 13‰).
- The decrease of the $\delta^{15}N$ series corresponds to the increase of the number of cars in the Quebec province. This argument is supported by the fact that NO_x from car exhausts have more negative $\delta^{15}N$ values (-13 to +4‰) than natural ones (+1 to +9‰), and by the high negative Pearson coefficient correlation (PC = -0.74; P < 0.001; n = 52) between nitrogen values and the number of the Quebec registered vehicles (Fig. 6).
- The short-term (GLK of 75%; P < 0.05; n = 16; Fig. 7) and long-term (*r* of 0.69; P < 0.01; n = 17) variations of the red spruce $\delta^{15}N$ series correlated with the measured amounts of provincial N and S emissions for the 1990 to 2006 period, the longest direct measurements available.





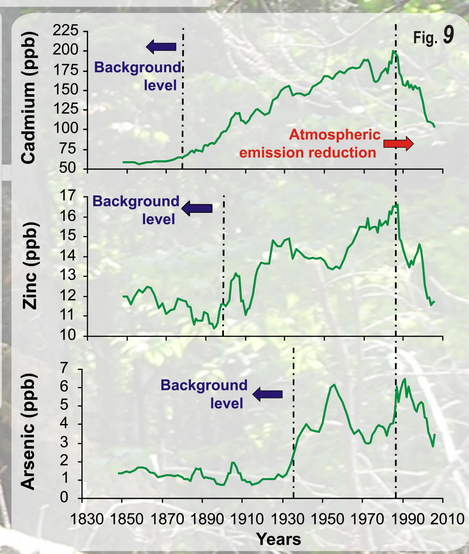
VII. Tree-ring Pb Isotope Ratios

- $^{208}Pb/^{206}Pb$ and $^{204}Pb/^{206}Pb$ as function of $^{206}Pb/^{207}Pb$ ratios of the 1880 to 1919 period reflect a mixture of natural lead from the mineral soil horizon and anthropogenic lead mostly from northeastern America coal combustion (Fig. 8).
- Lower Pb ratios of the 1940 to 1989 correlate well with the introduction of leaded additives to gasoline (allowed in North America from 1923 through 1990), and characterized by lower ratios relative to coal combustion.
- Increasing lead ratios of the 1990 to 2007 period reflect a return towards the higher ratio of coal combustion, the combustion of recycled lead material corresponding to a mixture of Pb ratios from different ore sources or the natural lead from mineral soil.



VIII. Tree-ring Cd, Zn and As Concentrations

- The tree-ring metal concentrations all reflect the urban and industrial combustion of fossil fuels of the last decades (Fig. 9).
- The Cd and Zn concentrations show higher values during the economic expansion of the 1900s and the increasing production linked to World Wars I and II.
- The tree-ring As concentrations mainly reflect the increasing use of As-containing pesticides in agriculture in the 1930s-1950s and its use in the industry of pressure-treated wood since 1980.
- All the tree-ring metal concentrations decline quickly after the implementation of restrictive governmental regulations on emissions of air pollutants in the 1980s.



IX. Conclusions

- **First integration of complementary environmental indicators showing that trees are sensitive records of environmental changes.**
- Tree-ring $\delta^{18}O$ values are mainly controlled by climate and are not significantly sensitive to atmospheric pollution; they reflect a natural behaviour.
- Assimilation of C and N is affected by diffuse atmospheric pollution, apparently in an important manner, by Canadian fossil fuel consumption (emissions of NO_x and SO_x).
- The early lead isotope trend of red spruce trees reflects a mixture of natural lead from the mineral soil horizon and anthropogenic lead from north-eastern American coal combustion (1880-1919).
- The lower Pb ratios reflect the introduction of leaded additives to gasoline (1920-1989).
- The late Lead isotope trend likely derives from three main sources (1990-207): coal combustion, burnt recycled material and natural lead present in soils.
- The tree-ring Cd, Zn and As concentrations are first linked to economic developments, and later sensitive to the diminution of atmospheric emissions occurring in the 1980s.

X. Acknowledgements

We would like to thank A. Smirnoff of the Delta-Lab at GSC-Québec for her support in this project. We want to acknowledge the financial support provided by the Environment & Health Program and the Environmental Geoscience Program of ESS/NRCan, and by Natural sciences and engineering research council of Canada NSERC.