Pooling tree-ring samples for determining Zn isotopic signatures in the Athabasca oil sands region

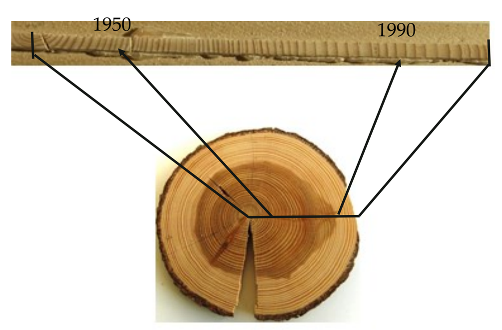
Dinis, L.[a], Savard, M. M.[b], Bégin, C.[b], Gammon, P.[c], Vaive, J.[c] and Girard I.[c]

[a] INRS-ETE, 490 rue de la Couronne, Québec (QC), G1K 2N9, Canada; [b] Geological Survey of Canada, 490 rue de la Couronne, Québec (QC), G1K 2N9, Canada;
[c] Geological Survey of Canada, 601 Booth St., Ottawa (ON), K1A 0E8, Canada

1. Introduction

Trees

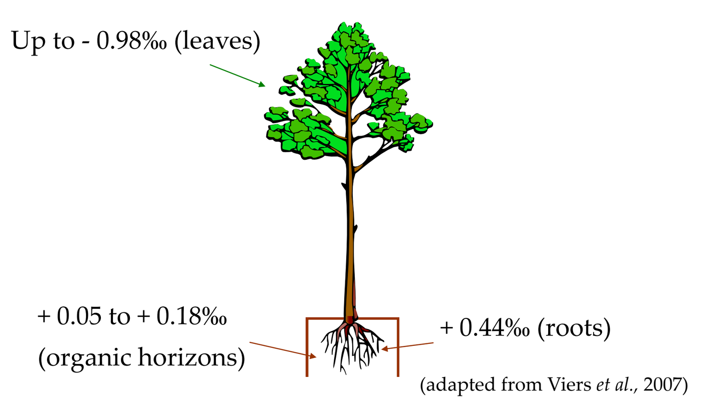
- Living systems sensitive to environmental conditions due to their position between atmosphere, pedosphere and biosphere
- Temporal records due to rhythmic growth producing annual rings



Natural records of environmental changes and climatic conditions

Zinc

- Micronutrient mostly assimilated through the root system
- Yearly assimilation depends on: tree characteristics (*e.g.* age, status in stand, etc.) and soil properties (*e.g.* pH, ectomycorrhizal fungi, Zn speciation, etc.)
- Roots are generally enriched in heavy Zn isotopes relative to soil organic horizons/nutrient solutions, while leaves are characterized by low δ^{66}Zn



(adapted from Viers *et al.*, 2007)

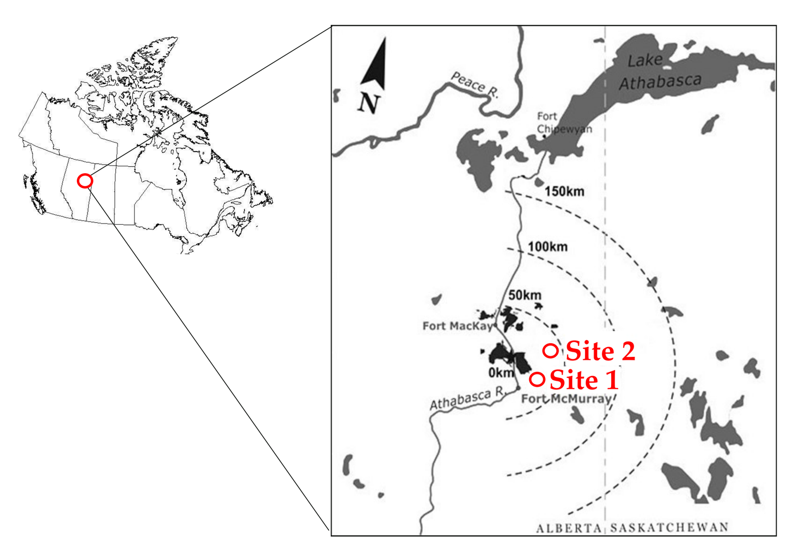
- Zn isotopes may be useful for distinguishing natural and anthropogenic sources
- Example: refining by smelting produces stack dust with δ^{66}Zn values (up to - 0.70 ‰) lighter than smelting residues (+ 0.13 to + 1.43‰; Sonke *et al.*, 2008)

Problematic

- Plant δ^{66}Zn has been considered as a possible indicator of environmental contamination (Weiss et al., 2005)
- Are white spruce Zn concentrations affected by radial translocation?
  - → If so, does translocation affects δ^{66}Zn similarly?

2. Objectives

1. Evaluate if tree-ring Zn isotopes can be used as a retrospective monitoring tool to reconstruct historical changes in the Lower Athabasca Oil Sands Region (LAOSR).
2. Evaluate if Zn concentrations and isotopes are affected by lateral transport in white spruce.
3. Estimate the possibility of pooling tree-ring sub-samples from several specimens to obtain site-averaged Zn-isotopic analyses.

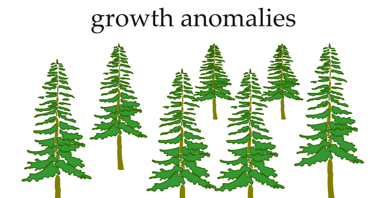


Location of the studied sites relative to the main open mining area in the LAOSR

3. Methodology

1. Sampling collection

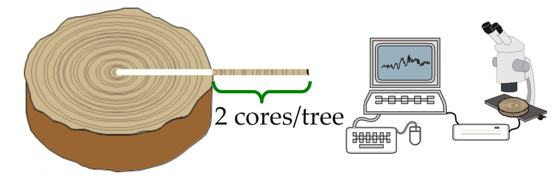
Mature and dominant trees with no growth anomalies



2. Measurement of ring width

Reference for the next steps

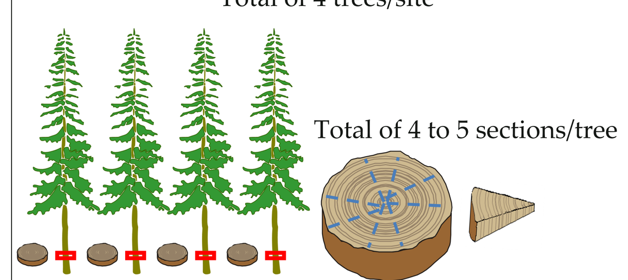
Total of 17 trees



Dendrochronology

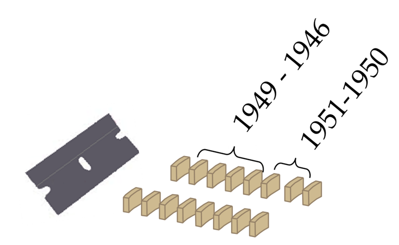
3. Cut of sections

Total of 4 trees/site



Dendrogeochemistry

4. Separation of tree rings

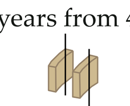


Resolution: 4 years & bisannual

5. Weighing of samples for individual trees

6. Pooling of tree

Sub-sampling and grouping tree rings of same years from 4 trees



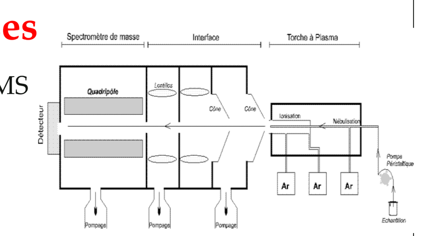
1920-1921

7. Processing

Total digestion (ashing + HNO_3, HCl & HF)

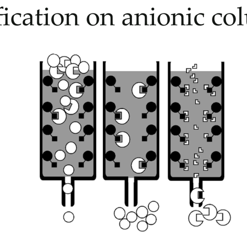
8. Analyses

[Zn] by ICP-MS



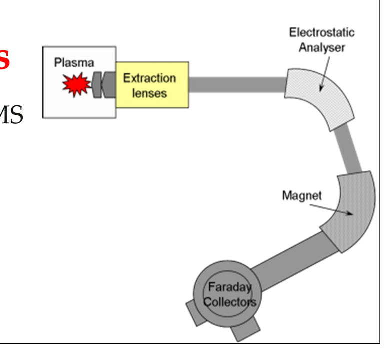
9. Processing

Purification on anionic columns



10. Analyses

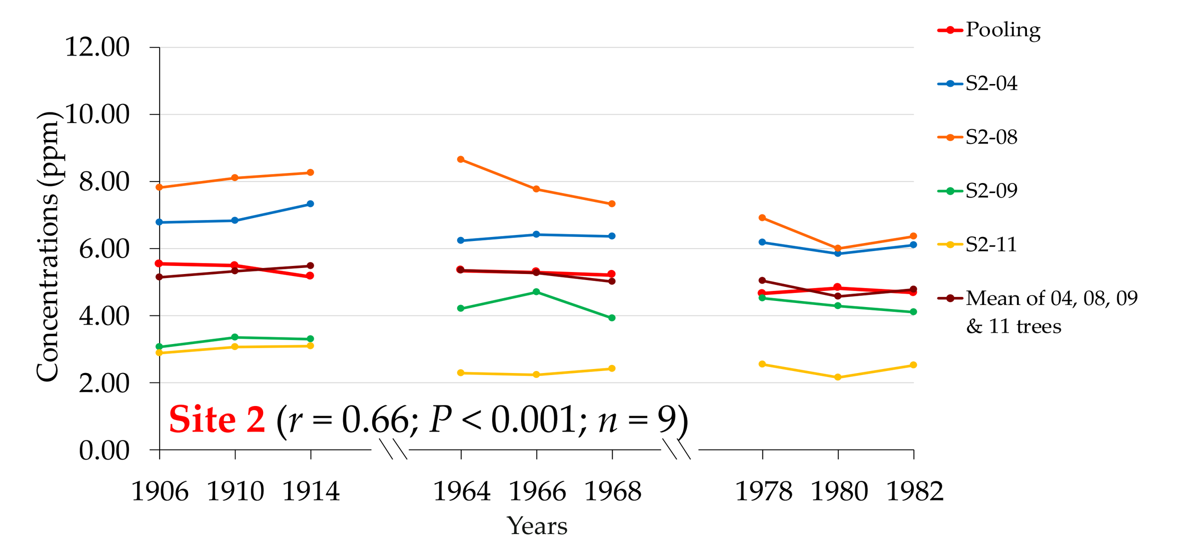
δ^{66}Zn by MC-ICP-MS

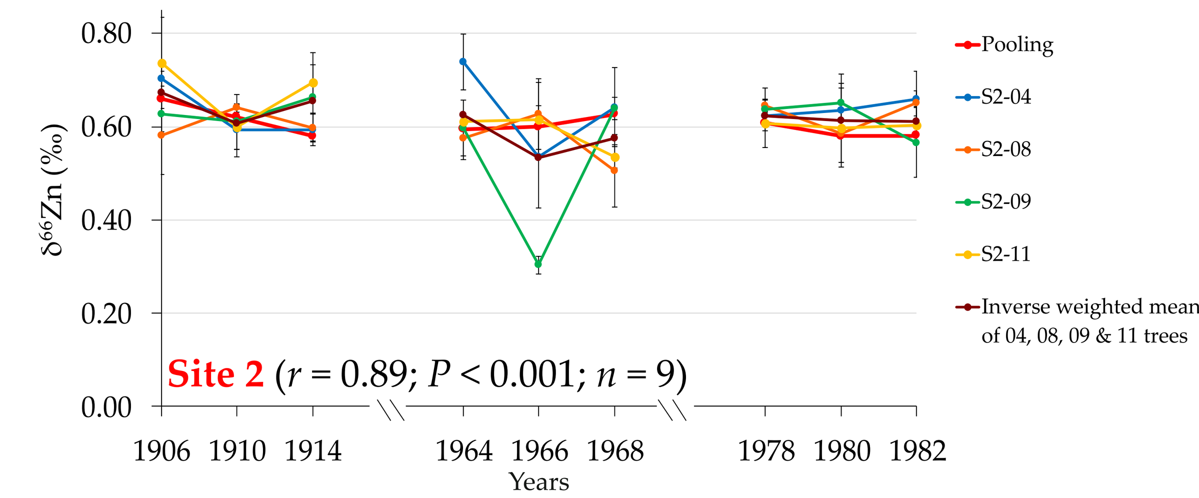


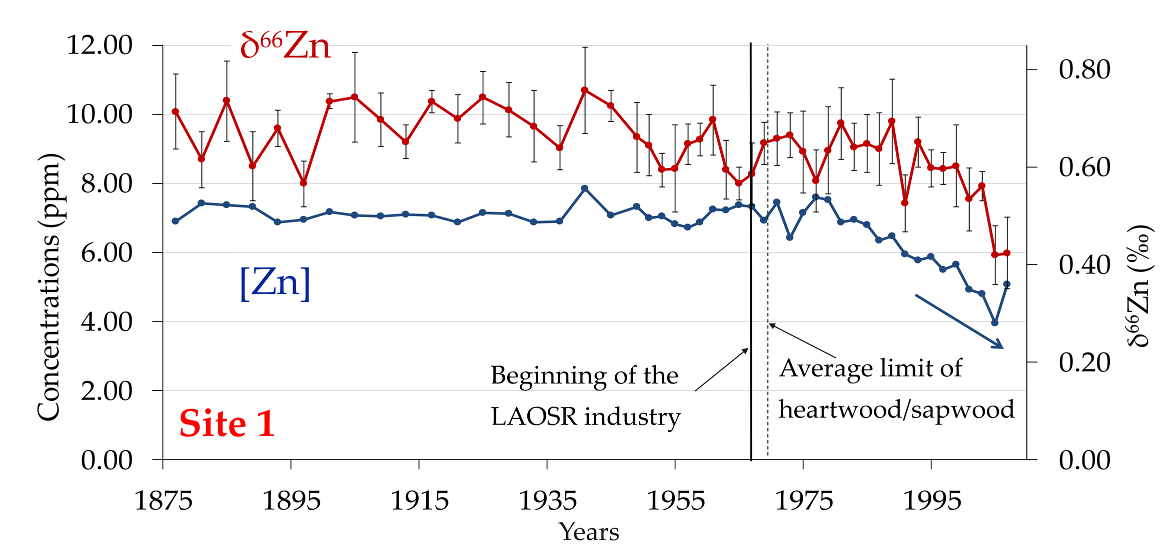
- Reproducibility of the protocol and quality of the analyses have been assessed using standard BCR-CRM 482 (lichen) throughout each steps (δ^{66}Zn = + 0.04 ± 0.07‰; n = 4) against the NIST SRM 683.
- The values obtained here are in agreement with reported measurements by Viers *et al.*, (2007) (δ^{66}Zn is + 0.07 ± 0.03‰) and Sonke *et al.*, (2008) (δ^{66}Zn is + 0.02 ± 0.04‰).
- Standard Lyon JMC has been introduced with every analytical batch of samples, and the δ^{66}Zn values were found to be - 0.12 ± 0.04‰ (n = 20), which compare well with measurements by Tanimizu *et al.*, (2002) (δ^{66}Zn of - 0.07 ± 0.01‰).

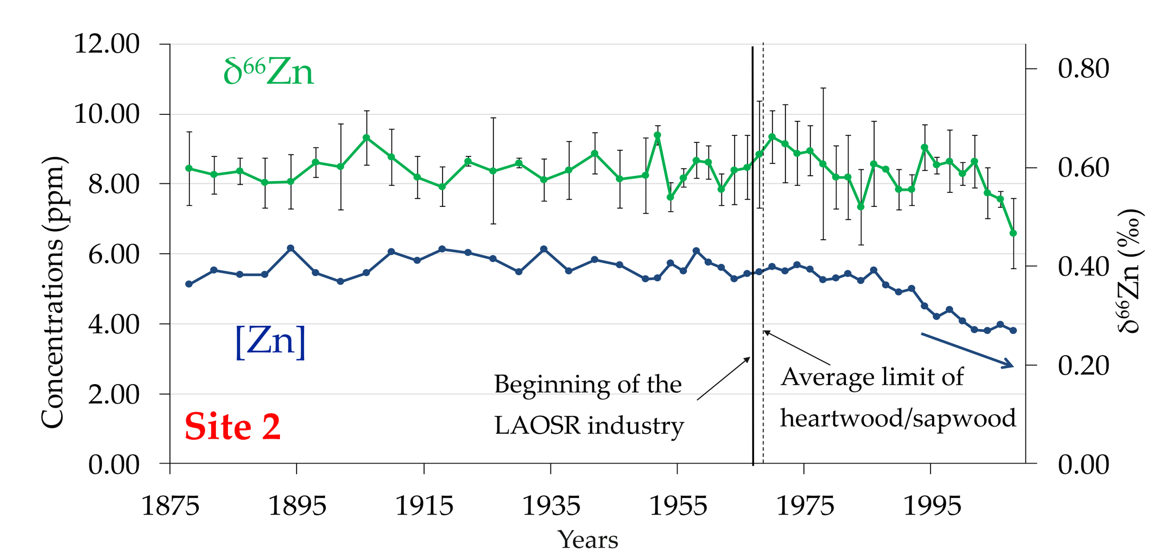
4. Results

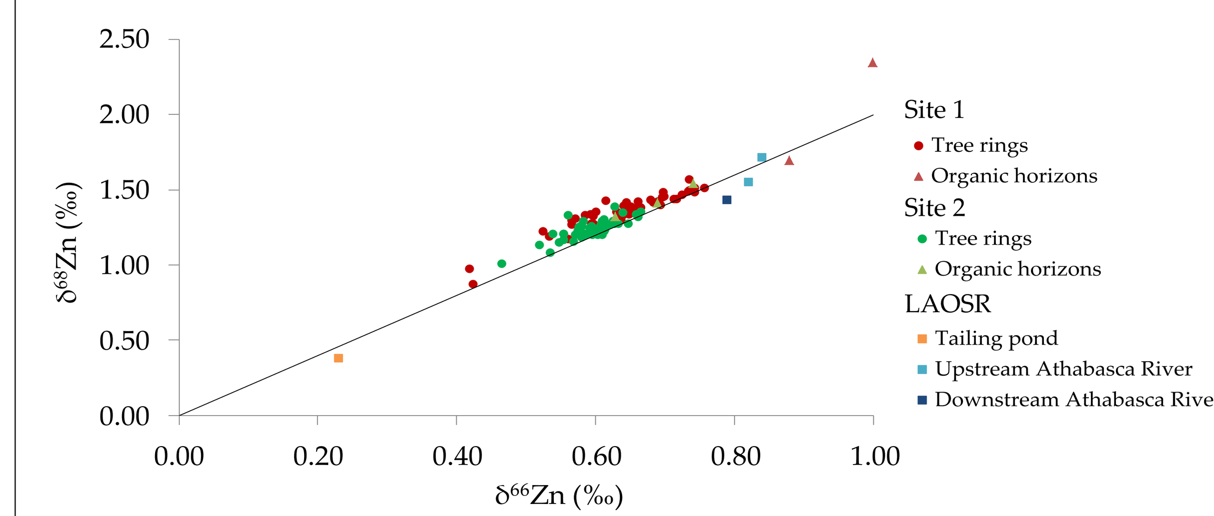
	Organic soils	Tree rings
Site 1		
[Zn] range (ppm)	0.2 to 10.2	3.95 to 7.86
δ^{66}Zn range (‰)	0.88 to 1.00	0.42 to 0.78
Site 2		
[Zn] range (ppm)	1.2 to 15.3	3.79 to 6.15
δ^{66}Zn range (‰)	0.63 to 0.74	0.47 to 0.66











Data of the LAOSR have been generated by the study of Savard *et al.*, 2012

5. Interpretations

LAOSR

- There is no evidence of airborne Zn-bearing Oil Sands contamination to the studied sites.

[Zn]

- The decreasing concentration after 1985 at both site likely represents a radial translocation of Zn within the stem.

δ^{66}Zn

- Spruce stemwood δ^{66}Zn values (at 1 m) of these boreal sites show a depletion in heavy isotopes relative to the exchangeable fraction of soil. Such an isotopic decrease is in accordance to what has been found in higher plants and tropical trees (*e.g.* Viers *et al.*, 2007). This is likely due to diffusion and ion exchange during xylem transport.
- Through time, δ^{66}Zn varies within the analytical errors.

Methodology

- Pooling tree-ring Zn isotopes is suitable for representing site-specific Zn concentration and δ^{66}Zn.

6. Conclusions

At this step of the project, Zn concentrations in our white spruce tree rings are likely affected by translocation while δ^{66}Zn values probably show an homogenization within the profile. This study put forward that Zn cannot be used as an indicator to reconstruct environmental changes in the studied sites. Further researches are necessary using different tree species and/or indicators.

7. References

Savard *et al.*, 2012. A local test study distinguishes natural from anthropogenic groundwater contaminants near an Athabasca Oil Sands mining operation. GSC Open file 7195.

Sonke *et al.*, 2008. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter. Chemical geology, 252: 145-157.

Tanimizu *et al.*, 2002. Absolute isotopic composition and atomic weight of commercial zinc using inductively coupled plasma mass spectrometry. Analytical Chemistry, 74: 5814-5819.

Viers *et al.*, 2007. Evidence of Zn isotopic fractionation in a soil-plant system of a pristine tropical watershed (Nsimi, Cameroon). Chemical Geology, 239(1-2): 124-137.

Weiss *et al.*, 2005. Isotopic discrimination of zinc in higher plants. New phytologist, 165: 703-710.

8. Contact information

Lauriane Dinis, PhD candidate in non-traditional isotopes in environmental research

Email: lauriane.dinis@ete.inrs.ca