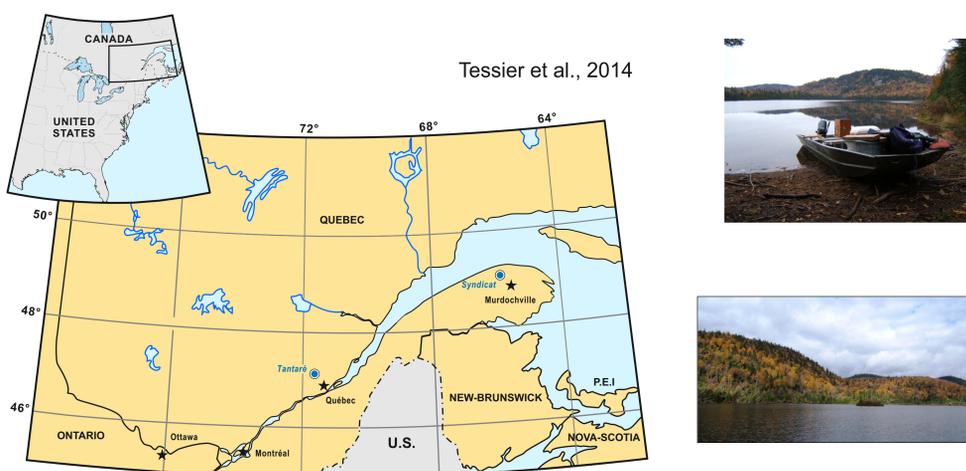


## 1. Rationale

Gallium is a trace element whose use has grown in several high-tech sectors over recent decades. As a consequence, waste incineration and recycling of technological equipment may represent potential sources of environmental contamination by this element. Base metals smelters could also be significant emitters of anthropogenic Ga. So far, however, the environmental geochemistry of this trace metal is too poorly documented to properly assess these concerns.

In this M.Sc. research project, we propose (i) to determine Ga net reactions rates in lake sediments near potential contamination sources, (ii) to quantify its post-depositional redistribution in the sediment column and (iii) to reconstruct the chronology of its deposition at the sediment-water interface. To reach these goals, the profiles of Ga will be determined in dated sediment cores and in sediment porewater collected by *in situ* dialysis. The profiles of dissolved Ga in the interstitial water of the sediments will serve as sensitive indicators of reactions involving Ga subsequent to deposition and will be modeled through both thermodynamics and reactive-transport approaches.

## 2. Study sites



**Figure 1:** Sediment cores and porewater samples were collected in two oligotrophic lakes receiving contaminant inputs only via atmospheric deposition, since their watersheds have always been uninhabited and undeveloped. One of this lake (L. Tantaré) is located on the Canadian Shield at about 40 km from Québec City (~500 000 inhabitants), while the other (L. du Syndicat) is situated in the Appalachian region, at about 25 km from a small industrial city (Murdochville; ~3000 inhabitants) where a smelter was operational between 1952 and 2002.

## 3. Methods

### Sediment sampling and analysis

- Sediment cores were obtained at the deepest site of the lake basins by divers with 9.5 or 12-cm internal diameter butyrate tubes and they were sectioned on the shore at 0.5-cm intervals from the sediment surface to 10 cm or 15 cm depth and then at 1-cm intervals from this horizon to the bottom of the cores.
- Aliquots of sediments were completely digested with a mixture of ultra-clean concentrated  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{HF}$ , evaporated to dryness and redissolved in diluted  $\text{HNO}_3$ . Gallium concentrations were determined by ICP-MS. Precision was better than 3% ( $n=10$ ).
- Details on the determination and corroboration of sediment ages as well as on the appraisal of sediment accumulation rates ( $\text{g cm}^{-2} \text{a}^{-1}$ ) by  $^{210}\text{Pb}$  geochronology are available in Tessier et al. (2014).

### Porewater sampling and analysis

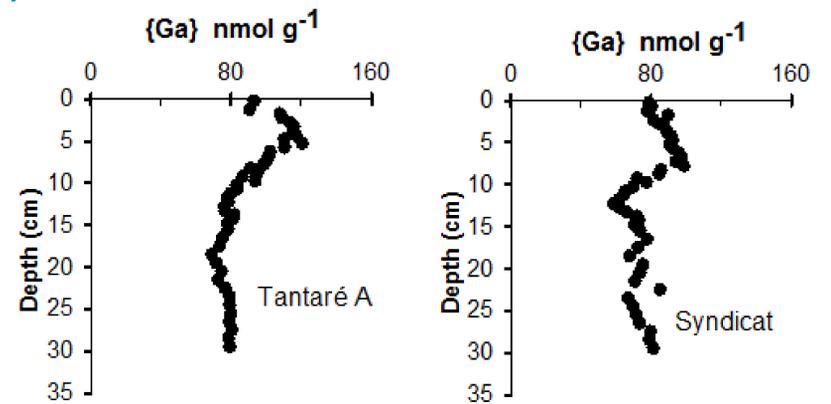
- Porewater samples were collected by *in situ* dialysis at a 1-cm vertical sampling resolution using acrylic peepers. The peepers were deployed for 21 days to collect samples down to 10 cm below the sediment-water interface and up to 5 cm above this interface.
- Immediately upon retrieval, the peepers were sampled in order to obtain two or three replicate profiles of sulfide (S(-II)), pH,  $\text{SO}_4$ , major cations, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC).
- Dissolved Ga concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Instrument X7).

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## 4. Preliminary Results

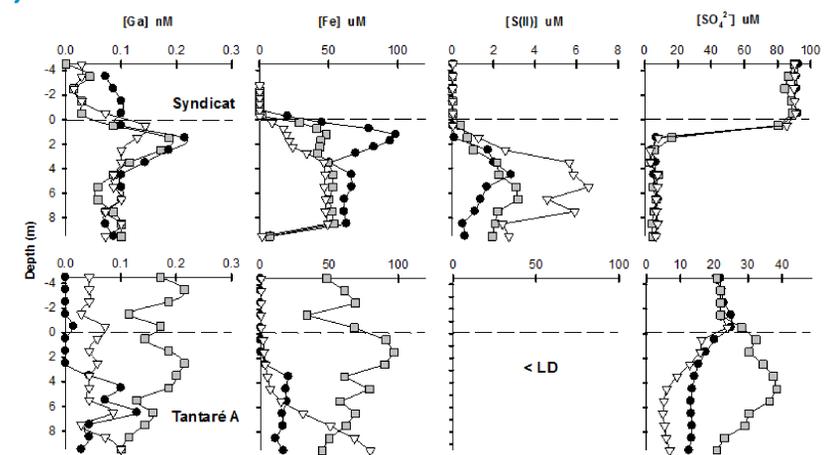
### a) Sediments



**Figure 2:** Vertical profiles of Ga in the sediments of Lakes Tantaré and du Syndicat.

- Solid-phase Ga concentrations range between  $60 \text{ nmol g}^{-1}$  and  $120 \text{ nmol g}^{-1}$  (Fig. 2). At the two study sites, sediment concentrations of Ga increase upwards from a nearly constant background value at the bottom of the cores, reached a maximum between 3 and 8 cm depth, and then decrease progressively towards the sediment surface. The background Ga/Al ratio is in the order of that of the continental crust ( $\sim 2 \times 10^{-4} \text{ g/g}$ ; Rudnick & Gao, 2014).
- These observations suggest that Ga deposition of the water-sediment interface has varied over time, maybe as a result of anthropic inputs.

### b) Porewater



**Figure 3:** Triplicate depth-profiles of Ga, Fe, total S(II) and  $\text{SO}_4^{2-}$  in the sediment porewater of Lakes Tantaré and du Syndicat. The horizontal dashed lines represent the sediment-water interface.

- All of the dissolved Ga concentration profiles measured show low concentrations of Ga in the overlying water and much higher values at or below the sediment-water interface, where they reach up to  $0.2 \text{ nM}$  for Ga. (Fig. 3).
- Parallelism between Ga and Fe profiles suggest that Ga is involved in the diagenetic redox cycle of the Fe oxyhydroxide in the sediments.

## 6. Next Steps

- Thermodynamic calculations will be achieved with the computer code "Windermere Humic Aqueous Model" (WHAM 6; Tipping, 2002) in order to estimate the speciation of Ga in the porewater and its diffusion coefficient.
- To determine the depth intervals in the sediment column where dissolved Ga is produced and consumed and net reaction rates, the reactive transport of dissolved Ga will be modeled using a one-dimensional mass balance equation assuming steady state.
- Results of this modeling will be used to quantify the post-depositional redistribution of Ga in the sediment column and then reconstruct the chronology of the Ga deposition at the sediment-water interface.

## 7. Conclusion

- Gallium in the solid-phase suggests that Ga deposition at the sediment-water interface has varied over time, maybe as a result of anthropic inputs.
- Parallelism between [Ga] and [Fe] profiles indicate that Ga is involved in the diagenetic cycle of the Fe oxyhydroxide in the sediments.
- The results of this research will allow to quantify the post-depositional redistribution of Ga in the sediment column and to reconstruct the temporal evolution of its deposition in two Southern Québec lakes which receive contaminants only via atmospheric deposition.

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