

# 35<sup>th</sup> Gananoque Environmental Sciences and Engineering Conference

#### **Presentations, Session A:**

Analysis of metals in lichens using ICP-MS and neutron activation analysis (NAA): different tales told by different means.

Francois Caron

RMC

Large industrial projects such as development of new mines or siting a nuclear reactor for energy and heat production require a thorough multi-contaminant monitoring program prior to, during, and after the project completion. Monitoring for contaminants (mostly metals and toxic elements) normally uses multi-elemental analysis techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and/or neutron activation analysis (NAA): both of which have advantages and shortcomings. For example, sample preparation for ICP-MS is tedious and the signals are often influenced by matrices, especially for environmental matrices. On the other hand, analysis is multi-elemental and fairly fast, but also multiple calibration curves are needed. Sample preparation is simple with NAA, multiple elements can be detected with one calibration curve, but counting times could be long, up to several weeks in some cases. Both techniques could tell different stories as not all the same elements can be detected, and therefore could complement each other. As well, ICP-MS is mainstream technology, whereas NAA requires a neutron source (a reactor) – only 3 are available in Canada.

This presentation will give the working principles of NAA, particularly in the context of the SLOWPOKE-2 reactor at the Royal Military College in Kingston. An example of application using lichens as a bioindicator will be discussed from a recent case study in the Sudbury and Elliot Lake area [1].

[1] Anderson et al., (2022), https://doi.org/10.1016/j.heliyon.2022.e11863

Sampling and analysing atmospheric particles for single particle inductively coupled mass spectrometry Katia Latariene, \*Patrick Hayes, Kevin J. Wilkinson Université de Montréal

Atmospheric particles, also know as particulate matter or PM, have an important world-wide impact on air quality and are a source of contamination when deposited on the ground or on urban surfaces. They can be emitted into the atmosphere naturally (volcanoes, ocean spray) or accidentally (wear of tires, industries, and car exhausts). The objective of my work is to develop techniques to measure these particles and quantify their chemical composition on a single particle basis. Single particle techniques are interesting because rather than obtaining information on the bulk sample, we can analysis the particles individually. For example, with these techniques, it is possible to discriminate between a suspension where 100% of the particles contain 1% As from another where 1% of the particles are pure As. Our work will focus on the use of the Coriolis-micro – air sampler and the characterization of the inorganic elements of fine and ultrafine particles by ICP-MS in single particle mode (SP ICPMS).

Platinum inorganic speciation in simplified freshwater medium as well as complexation by natural organic matter (NOM) investigated by HPSEC-ICP-MS coupling

Océane Hourtané ,\*Claude Fortin Institut national de la recherche scientifique

It has been widely demonstrated that the speciation of a dissolved metal, i.e. its distribution among the different chemical species, can be used to explain and even predict its effects on aquatic organisms. In this context, the determination of metal speciation seems to be of paramount importance. While speciation can be predicted more easily for well-studied metals, the task is more difficult when very few thermodynamic constants are available, as it is the case for platinum. To determine speciation, it is then necessary to turn to experimental methods. This work focuses on the speciation of platinum in the presence of four different freshwater natural organic matter (NOM) to capture heterogeneity amongst NOM sources. For this purpose, a high-performance size exclusion liquid chromatography (HPSEC) method coupled with inductively coupled plasma mass spectrometry (ICP-MS) for online metal detection was used. We explored the speciation of platinum (II and IV) at pH 5 and 6 and at 3 and 10 mg C/L NOM. By this approach, several inorganic forms of Pt were identified, with good separation and repeatability. These results suggest that reaching thermodynamic equilibrium of Pt(IV) is relatively long (>1 week), although this redox form is k nown to be unstable under our working conditions. Furthermore, the presence of NOM seems to accelerate or modify these changes, especially the reduction of Pt(IV) to Pt(II). Consequently, the presence of NOM, in addition to inducing the complexation of Pt, seems to be at the origin of variations in its inorganic speciation.

#### **Presentations, Session B:**

### Assessing the Accuracy of Available Geochemical Models: The Role of Precipitation and Organic Complexation in REE Speciation and Toxicity

Sam Zulian, \*Jim McGeer & D Scott Smith Wilfrid Laurier University

As technological and industrial applications of rare earth elements (REE) continue to be on the rise, the importance of understanding their chemical behaviour is becoming imperative. With the current climate crisis, and the trend toward green innovations, it is central for the technology sector to better understand the behaviour of REE aquatic speciation, persistence, and potential to cause toxicity within aquatic environments. For this reason, surface waters should be researched to determine the environmental implications of REE use. Key to REE risk assessment in aquatic systems will be the development of geochemical modelling methods to predict speciation, as different chemical forms of REEs will have different mobilities as well as toxicity in the environment. Speciation by fractionation was conducted. Size fractions included total, dissolved (<0.45  $\mu$ m), and free (<3kDa). Due to the variables that were manipulated including pH, DOC and CO32- the fractions can be defined as precipitated, organic bound, or inorganic bound & free. This information was compiled to assess the accuracy of the available geochemical model, CHEAQS (Chemical Equilibrium in Aquatic Systems). Based on specific conditions, modelled, and measured results do not align. The model should be adapted to reflect that. The complexity of heterogenous chemical systems continues to be a barrier to the development of environmentally accurate models for metal toxicity. As risk assessment tools, including toxicity prediction models such as the biotic ligand model, are developed for REE there is a strong need for validated chemical equilibrium modelling approaches for REE in water.

# Investigating the Effect of Rare Earth Elements Nd, Pr, & Y to *Daphnia magna* Celine Do, \*D Scott Smith & Jim McGeer Wilfrid Laurier University

Neodymium (Nd), Praseodymium (Pr), and Yttrium (Y) are rare earth elements (REEs) that occur naturally together in the mineral ore bastnaesite, the primary ore of Canada's first REE mine at Nechalacho, NT. These elements are increasingly being used in modern technologies therefore, there is an increasing concern for the potential environmental risk associated with anthropogenic contamination. There is very little data available for individual REEs, and there is also a lack of knowledge concerning REE mixtures. The objective of my study was to investigate the acute effects of Nd, Pr and Y as single metals and then in ternary mixtures to Daphnia magna. Standard 48-h acute tests following Environment and Climate Change Canada (ECCC) methods were conducted with D. magna neonates in an artificial soft water medium (hardness 50 mg CaCO3/L, pH 6.8 and 21°C) without added bicarbonate to determine the EC50 for each individual metal. The 48-h EC50 values were: 0.32 mg Nd/L (95% CI 0.03 – 0.56 mg/L), 0.69 mg Pr/L (95% CI 0.32 – 1.85 mg/L), and 0.70 mg Y/L (95% CI 0.58-0.83 mg/L). Mixture exposures were designed using a toxic unit (TU) approach, based on converting the EC50 concentrations to Tus and applying a matrix isobologram approach. For example, Tus of 0.2, 0.4 and 0.6 were prepared to observe whether the mixture responses would follow an additive interaction. This research is supported via a NSERC Alliance Grant with additional funding from ECCC and contributions from Cheetah Resources and Stantec Inc.

Competition Among Three Rare Earth Elements (Lanthanum, Cerium and Yttrium) for Uptake in *Chlamydomonas reinhardtii* Laurianne Pagé , \* Kevin J. Wilkinson Université de Montréal

Rare earth elements (REE) are increasingly used because of their unique optical, magnetic, and catalytic properties. The REEs mining sector is therefore growing and, it's important to know their environmental impacts. In environmental mixtures, the role of the competition must be studied as one means to verify that the biotic ligand model (BLM) can predict the bioaccumulation of REEs in natural samples. The objective of this study will be to measure the bioaccumulation of three REEs (La, Ce, Y), with a major focus on the competition among the ions for uptake sites. The conditions will range from well-controlled (synthetic waters in the laboratory) to real samples, taken from the first REE mine in Canada (Nechalacho in the Northwest Territories, Cheetah Resources). Chlamydomonas reinhardtii (C. reinhardtii), a unicellular alga, will be the model organism.

**3MT: Tox News: the BLM investigation**Océane Hourtané ,\*Claude Fortin
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#### **Poster Presenters Panel:**

Investigating the controls on microplastic accumulation in stormwater pond sediments.

Thu Hang Nguyen, \*Fereidoun Rezanezhad University of Waterloo

In urban watersheds, stormwater runoff is a major carrier of microplastics to downstream water bodies, which are collected in stormwater ponds (SWPs). As expected, recent studies have reported high microplastics retention efficiencies in SWPs. However, the variability in the retained microplastic types and sizes among, and within, SWPs remain understudied. The aims of this study are to (1) assess the variability in microplastics types, sizes, and abundances within SWP sediment samples, (2) determine the influence of sediment properties on microplastics accumulation in sediments within and between SWPs, and (3) relate microplastics loads in stormwater runoff to upstream land use. Thus far, we have collected sediment samples from five SWPs with variable catchment land use types (commercial, industrial, and residential) in the City of Kitchener in Ontario. The preliminary results at one of the industrial ponds show that microplastic fragment accumulation rates decreased from 9x107 particles m-2 yr-1 in the inlet forebay to 2x107 particles m-2 yr-1 in the main basin. Moreover, ponds in the industrial catchments exhibited the highest sediment burial and organic carbon accumulation rates, followed by ponds receiving stormwater from residential and commercial areas. Our ongoing research will shed light on the contribution of urban catchments to microplastic pollution and the factors controlling microplastics retention by SWPs.

How will decreasing winter snow cover affect agricultural soil nitrogen cycling and loss: Results from a lysimeter study Danielle Green \*Fereidoun Rezanezhad & Philippe Van Cappellen University of Waterloo

In cold regions, climate change is expected to result in warmer winter temperatures and increased temperature variability. Coupled with changing precipitation regimes, these changes can decrease soil insulation by reducing snow cover, exposing soils to colder temperatures and more frequent and extensive soil freezing and thawing. Freeze-thaw events can exert an important control over winter soil processes and the cycling of nitrogen (N), with consequences for soil health, nitrous oxide (N2O) emissions, and nearby water quality. We conducted a lysimeter experiment to assess the effects of winter pulsed warming and soil texture on N cycling in agricultural soils. We monitored the subsurface soil temperature, moisture, porewater geochemistry, and N2O flux es from four agricultural lysimeter systems, alongside air temperature and precipitation, at the University of Guelph's Elora Research Station over one winter. The lysimeters featured two soil types (loamy sand and silt loam) which were managed under a cornsoybean-wheat rotation with cover crops. Additionally, ceramic infrared heaters located above two of the lysimeters were used to melt fallen snow and mimic snow-free winter conditions. The results from the snow removed lysimeters were compared to those of lysimeters with snow. The removal of the insulating snow cover resulted in more intense soil freeze-thaw events, causing increased dissolved N loss from the lysimeter systems. N loss was in the form of N2O in silt loam lysimeters due to de novo processes and via NO3– leaching from loamy sand lysimeters due to the larger pore size and lower water retention capacity of this soil type.

Methane oxidation in landfill cover soils under variable moisture and temperature conditions Christina Lam, \*Fereidoun Rezanezhad University of Waterloo

Landfills are one of the largest anthropogenic sources of methane (CH4), comprising over 20% of Canada's CH4 emissions. Hot-spots of CH4 emissions in landfill cover soils have shown an enrichment of microbes that consume CH4 and produce carbon dioxi de (CO2) through CH4 oxidation, which can act as a natural solution to reduce CH4 emissions. CH4 oxidation is affected by soil moisture and temperature, although their simultaneous effects on CH4 oxidation rates have not been well-studied. Here, we conducted a closed-headspace batch experiment with cover soil from a former landfill in Waterloo, Ontario, to measure CH4 oxidation and CO2 efflux rates associated with variations in soil moisture and temperature simultaneously. The soil samples were prepared under 5 soil moisture contents (% WFPS; water-filled pore space), ranging from 11 to 47% WFPS, and incubated following a regime whereby temperatures increased from 1 to 35°C (Phase I) then decreased from 35 to 1°C (Phase II). Every 2 days, the temperature was adjusted to the next value for a 24-hour acclimation period while open to the atmosphere, then the headspace was closed and spiked with CH4 (150 ppm). Headspace CH4 and CO2 concentrations were measured over 2 hours to calculate apparent CH4 oxidation and CO2 efflux rates. The maximum CO2 efflux rate was observed at the maximal WFPS and temperature conditions of this experiment (91.5 nmol h-1 g dry wt.-1 at 47% WFPS and 35°C). In contrast, the maximum CH4 oxidation rates were observed at intermediate WFPS and temperature conditions (1.86 nmol h-1 g dry wt.-1 at 25% WFPS and 25°C). These experimental results provide insight into favourable WFPS and temperature conditions for CH4 oxidation, and therefore into how seasonal changes in WFPS and temperature could impact CH4 oxidation.

#### Determination of Cupric Ion Electrode Detection Limit as a Function of pH and Dissolved Organic Carbon

Michelle Tai, \*Scott Smith Wilfrid Laurier University

The toxicity of metals in environmental conditions was controlled by various parameters including metal concentration, pH, and inorganic and organic ligands. The determination of free copper concentrations was significant for the evaluation of copper toxicity. As copper was known to exhibit strong affinity for natural ligands, an Ion-Selective Electrode (Cu-ISE) method was presented for analytical determination of the speciation. The detection limit of ISE depends on the sample characteristics though; this study aims to quantify cupric ISE detection limits as a function of total copper, pH and dissolved organic carbon concentration. The detection limit is expected to be lower as the cupric ion buffer capacity increases but the question remains, is the detection limit low enough for application of cupric ISE as a probe for bioavailable cupric ion monitoring.

### Fingerprinting the environmental distribution of microplastic: a procedure for extracting and analyzing microplastics from water, soil and sediment.

Asal Jaberansari, \*Shuhuan Li University of Waterloo

Quantifying the distribution of microplastics in environmental compartments is crucial for predicting the fate and transport of microplastics. However, a major challenge is that microplastics are integrated within their environmental matrices and separation is required using methods that (1) do not damage the surface chemistry of the particles and (2) that separate all the microplastics within the sample with a high recovery efficiency. Our optimized extraction method combines density separation (using zinc chloride brine solution) with wet peroxide oxidation to isolate microplastics from their soil, sediment and water matrices. Following separation, the particles are analyzed for size and polymer type using laser direct infrared (LDIR) spectroscopy. LDIR maps the population of microplastics within a sample to generate their size and polymer type distribution allowing for the interpretation of the potential source (s) and extending of degradation/weathering of the microplastics. Using sample spiking, we found that the recovery efficiency decreases with decreasing particle size. This effect can be corrected by continuing to spike microplastic standards of different sizes to extractions of environmental samples and correcting the microplastic concentrations of different sizes we are quantifying using LDIR. We also validated that the extraction method did not damage the surface chemistry using Raman and infrared spectra of representative polyethylene particles. Overall, the method effectively separates particles with a reproducible high recovery efficiency that can be corrected and without damaging the surface chemistry properties, enabling the accurate characterization and quantification of microplastics in environmental samples.

#### **Presentations, Session C:**

#### Quantification of metallic nanoparticles in wastewater

Houinne Kim, \*Kevin J. Wilkinson Université de Montréal

The aim of the project is to determine the concentrations of anthropogenic metal-based nanoparticles (NPs) in the influents and effluents of some Canadian wastewater treatment plants. Indeed, we intend to develop techniques and strategies to distinguish between naturally occurring and anthropogenic NPs in wastewaters at the influent and after passage through the water treatment plant (effluent). SP-ICP-MS is used to measure the elemental ratios and size distribution of NPs sampled from the waters collected in the influents and effluents. The results will provide insights about origins of novel forms of pollution, specific to locations in the country and pollution levels.

## Dissociation kinetics of inorganic Pt and Pd complexes and its influence on toxicity and accumulation Julien Michaud-Valcourt , \*Claude Fortin INRS-ETE

The unique properties of platinum-group elements (PGE) have led to an increasing worldwide demand and subsequent release in the environment. Typically, in metal toxicity studies, it is assumed that thermodynamic equilibrium in the medium is reached rapidly. This may not be true for Pt and Pd due to their slow kinetics. If the time needed to reach equilibrium is significant compared to total exposure duration, aquatic organisms could be mostly exposed to the complexes present at the initiation of the test rather than to those present at equilibrium. Hence, in this project, using the unicellular green alga *Pseudokirchneriella subcapitata*, we determined the accumulation and toxicity of Pd and Pt added from stock solutions in which amino- or chloro-complexes are the dominant species (Pt(IV)Cl<sub>6</sub><sup>2-</sup>, Pt(II)Cl<sub>4</sub><sup>2</sup>, Pt(II)(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, Pd(II)Cl<sub>4</sub><sup>2-</sup> and Pd(II)(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>). Changes in metal speciation were thereafter investigated by UV-visible absorbance.

Our results point at the rapid dissociation of Pd complexes leading to a similar toxicity and accumulation regardless of the forms tested. On the other hand, all three Pt sources tested resulted in similar accumulation but only  $Pt(IV)Cl_6^{2-}$  led to a significant growth inhibition

after 96 h. Interestingly,  $Pt(II)(NH_3)4^{2+}$  was shown to be stable in our medium for at least 96 h whereas  $Pt(II)Cl_4^{2-}$  was much less stable with indications of dissociation occurring within 24 h. This suggests that for Pt(II) complexes, initial speciation does not affect toxicity up to 150 µg/L (i.e. maximum exposure concentration). The  $Pt(IV)Cl_6^{2-}$  toxicity was potentially linked to free radical species formed during the reduction to Pt(II).

#### Toxicity of Radium 226 on the great pond snail embryos

Léna Guimard , \*Anne Crémazy & Claude Fortin Institut national de la recherche scientifique

The Anthropocene is associated with profound changes in ecosystems, including an increase in the presence of radioactive elements in natural waters. Among these elements, there is radium-226 (226Ra), which is released during activities such as mining and milling of uranium ores, or extraction of coal, oil and gas. However, no water quality guidelines for the protection of aquatic life exist to regulate the presence of this element in freshwater in Canada. To address this gap, we are using the great pond snail (Lymnaea stagnalis), a pulmonate snail that is widespread in Canadian fresh waters and extremely sensitive to metals. We will characterize the bioaccumulation and chronic toxicity of radium with this model organism in the laboratory. It is expected that this calciphilic organism will take up 226Ra in large amounts, since 226Ra is a calcium analog. The consequences of this bioaccumulation will be studied at different biological levels (e.g. oxidative stress, growth, fecundity, etc.) and on several life stages (embryos, juveniles, adults). I will present preliminary results on chronic toxicity testing with embryos of Lymnaea Stagnalis. This PhD project will contribute essential data on radium toxicity and improve water quality standards for the protection of aquatic life in Canada.

#### Application of RNA-Cleaving DNAzymes for Bioavailable Metal Sensing

Gagan Gill, \*Scott Smith Wilfrid Laurier University

The on-site and real-time detection of metal ions is important for environmental monitoring and risk assessment. For appropriate management decisions, it is necessary to specifically sense the bioavailable fraction of metal rather than total metal. DNA-based sensors (so called DNAzymes) are a promising new technology for possible bioavailable metal monitoring that have not yet been fully tested in real waters. In clean, buffered, laboratory waters specific DNAzymes interact with specific metal ions and produce a signal (e.g., fluorescence) that can be used to determine total metal concentration. In more complex, natural, solutions it is likely that the free ion concentration is reduced by complexation (e.g., to dissolved organic matter, DOM) and the signal would not be proportional to total metal, but possibly proportional to the bioavailable fraction of total metal; i.e., the fraction of met al available to interact with the DNAzyme. Our research utilizes an existing metal specific RNA-cleaving DNAzyme for Pb2+ (GR5) in test waters representative of natural solutions. In GR5 lead acts as a specific co-factor in DNA catalyzing the cleavage of RNAcontaining fluorogenic substrate. In these samples we systematically vary pH, ionic strength and DOM concentrations and assess changes in DNAzyme generated fluorescence signal compared to calculated lead speciation. There is some ambiguity about what species of lead GR5 actually responds to. To resolve this uncertainty, calibrations were performed assuming different species and combinations (e.g., Pb<sup>2+</sup>, PbOH<sup>+</sup>, Pb<sup>2+</sup> and PbOH<sup>+</sup>, ...) generated the analytical signal. Each calibration was applied to titration data for the same solution chemistry but with added DOM. This data was compared to Windermere Humic Aqueous Model (WHAM) modelled lead for the same water chemistry, including DOM. The best R<sup>2</sup> value between predicted and observed speciation was found when it was assumed that GR5 fluorescence signal was caused by both lead and lead hydroxide species. After this assessment of DNAzyme responses in natural waters, it will be possible to start comparison testing of DNA-signal to toxicity test results as a "true" measure of bioavailability and to eventually develop tools for real-time, on-site detection of bioavailable metals. Funded by Global Water Futures.

#### **Presentations, Session D:**

Impacts of natural organic matter on the bioaccumulation of lanthanum by Chlamydomonas reinhardtii.

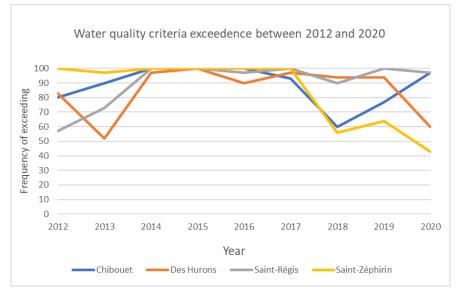
Marie-Hélène Brunet \*Kevin J. Wilkinson University of Montreal

Rare-earth elements (REE) are in high demand given their applications in the medical, green energy and high-tech industries. Canada has started to mine for REE, and it is important to ascertain the risk that such activities represent for our environment. Current bioavailability models such as the Biotic Ligand Model (BLM) were designed for divalent cations and therefore need to be validated for REE (mainly trivalent). The BLM considers that internalisation and biological effects are directly proportional to free ion concentration. We studied the bioaccumulation of lanthanum (La), a REE, through the measurement of internalisation fluxes for *Chlamydomonas reinhardtii*. Lanthanum bioaccumulation decreased in the presence of natural organic matter (NOM). However, this decrease is less significant than what is predicted by calculated La<sup>3+</sup> concentration. Furthermore, impacts of NOM varied with their origin. Therefore, dissolved organic carbon concentration is not sufficient to predict the impact of NOM on La bioaccumulation, it's nature must also be considered. We will further characterise the NOM samples in the hope of acquiring enough data to adjust speciation calculations. In addition, we will attempt to evaluate free ion concentrations using an ion exchange resin. Our goal is to determine if a modified BLM can be used to predict La bioavailability and if so, what parameters need to be measured in order to better protect our environment from potential REE contamination.

#### Impacts of pesticides mixtures on freshwater organisms

Antoine Faure, \*Anne Crémazy
Institut national de la recherche scientifique

Biodiversity loss in freshwater is a major environmental issue. Among different environmental disturbances, water contamination by pesticides is an important driver of biodiversity loss. In Québec in fresh waters, pesticides concentrations often exceed water quality criteria for aquatic life protection. Pesticides environmental risk is generally assessed through studies involving a single pesticide, with contamination occurring via water exposure. However, fresh waters are commonly contaminated with pesticides mixtures and organisms are exposed not only through water but also through contaminated food. Thus, there is a probability for the environmental risk of pesticides to be underestimated. To investigate this issue, we will carry out toxicity bioassays with pesticides mixtures representative of Québec's rivers, with freshwater mollusks: the great pond snail Lymnaea stagnalis and the mussel Elliptio complanata. Mixtures effects will be compared with individual pesticides effects. Moreover, an algal biofilm yielded in laboratory will be contaminated with pesticides mixtures, and used to feed the model organisms in order to assess the role of trophic network in pesticides contamination. These results aim to help decision making in terms of pesticides agricultural use regulation.



<u>Figure:</u> Frequencies of water quality criteria exceedance from 2012 to 2020 in four Québec rivers. Each river is sampled 30 times a year during summer, and a sample is labelled as exceeding water quality criteria when at least one pesticide exceeds its threshold for aquatic life protection

**Evaluating the Risk of Gadolinium in the Grand River Watershed**Johann Memmel, \*Jim McGeer
Wilfrid Laurier University