Devenir des éléments métalliques en régions arctique et sub-arctique: exposition des écosystèmes et des populations nordiques

The fate of metal elements in arctic and sub-arctic areas: ecosystems and northern populations exposure

Our knowledge of the behavior of metals in the environment is critical for a number of social issues, namely economic, regulations, health of living organisms and humans, traditional way of life. The Arctic Metals project aims at developing tools (speciation, isotopes) to assess metals sources, mobility and reactivity in "remote" areas of the Arctic and sub-arctic AND to determine their bio-availability for northern biota and populations. The anthropogenic pressure, through mining exploration and exploitation in the Arctic and sub-arctic is high and will increase over the next decades. Thus, Arctic and sub-arctic living biota and population are exposed to several metallic pollutants. The estimation of "toxicity" pass through our knowledge of levels, chemical forms, reactivity and bio-availability of metals in the environment. The Arctic Metals project is focused on metal accumulation due to diffuse pollution, which covers millions of km^2 and is more difficult to appreciate than pollution from a punctual source (e.g. smelters). In a changing environment, re-mobilization of metals of both anthropogenic **and** natural origin may yield toxic exposure for biota and human populations.

The goal of our project is to understand the relationship between metals and the reactive organic matter in aquatic environments of the arctic and sub-arctic areas. This is because: 1) the arctic is submitted to a high anthropogenic pressure regarding mining exploration and exploitation; 2) the arctic is highly affected by climate change and global warming and the thawing of permafrost is/will change the stability fields of metals and enhance their mobility and interaction with the organic matter and biota; 3) we have evidence for higher metal contents (particularly Hg) in the Arctic biota and Aboriginal populations than any other population worldwide, so studying the behavior of metals in arctic and sub-arctic ecosystems is a priority for the global environment. The project do not intend to study the effects of the global warming for the environment and the ecosystems. Rather, we propose to study the consequences of the global warming climate in the arctic and sub-arctic environments regarding **the fate of natural and anthropogenic metals** stocked (and to be stocked) in water, soils, sediments and vegetation. Documenting the mobility of metals, the reactivity (primarily with organic matter) including bio-availability and bio-accumulation, the exposure of ecosystems and northern community to trace metal elements is our major goal.
The proposed project is a collaborative study between French, Canadian and Russian scientists (chemists, biologists, limnologists, ecologists, geochemists, soil scientists, doctor).

In general terms, our project aims at:

- Evaluating the source of metals present in aquatic ecosystems of northern areas (isotopes). Chemical and isotopic variations will be used to discriminated anthropogenic input from "natural" metal enrichment processes such as biotic and/abiotic scavenging. Up to now, isotope tracing is the only way to ascertain additional metal sources into the ecosystems. Measuring isotopic variations in various compartments of ecosystems, such as soils, water, sediments, vegetation, we hope to discriminate between physico-chemical processes during transfer between reservoirs and "tapping" different sources. For example, additional (anthropogenic) sources of metals to soils may mobilized easier than geogenic metals. In a favorable case, the bio-available pool of a given metal in soil will have a different isotopic composition from bulk soils and readily be identified by isotope tracing.

- Understanding the impact of metals on eco-geo-systems by developing tools that will highlight reactions between metals and organic matter (adsorption, transformation, bio-accumulation, ...). The ultimate goal here is to establish metal (Zn, Hg, Se, ...) global cycle from their source, through their pathways, to their storage, including biota and humans. Such data are critical for

evaluating potential toxicity. Indeed, using the results obtained in laboratory, we hope to quantify, from a given influx, the amount of a given metal (e.g. Hg, Se, Zn ,Ni, ...) that will be sequestered and the amount that will stay available for bio-accumulation and to the food web.

- Tracing the source of metals in human populations by testing the potential of isotope tracing for Hg and Se in blood samples. Typical country food such as various parts of beluga will be analyzed for Hg and Se contents and isotopic compositions. Blood samples will be selected according to metal contents but also to geographical, social and gender criteria in order to link isotopic results to potential exposures and way of life of populations. Lead isotope signature was used to show that high blood Pb levels are likely due to the use of Pb shot in the hunting of traditional/country food (Dewailly et al. 2000). High concentrations of Hg and Se in northern Canadian population blood are explained by country food. Isotope tracing of these two elements may help to understand their relationship, not only in terms of source, but also regarding the role of Se as an antagonist to MeHg (Van Oostdam et al. 2005). We hope that chemical and isotopic (co-) variations of Hg and Se in blood will be used to discriminate sources and processes but our approach is exploratory.

- Developing a chemical and isotopic data base (including rate constants and isotope fractionation factors) for various metals in arctic and sub-arctic aquatic environments. We will use the Polar Data Catalogue as an international medium to the community.

- Training several postdoctoral, master and PhD students to state of the art methods applied to environmental studied focused on tracing metal behavior and fate in the environment.

- Making the project data and results available to the northern population, to the general public and to the stakeholders using a project web site with key results translated into French, English and Inuktituk.

DESCRIPTION DES PARTENAIRES

Partner 1. Takuvik (UMI 3376 CNRS-ULaval)
Takuvik - Centre International d'Etude et de Modélisation des Ecosystèmes et Géosystèmes Arctiques et Subarctiques - is the new international joint research laboratory between CNRS and University Laval, in Québec city, Canada. The staff comprises 6 CNRS and 8 Prof. from ULaval. Partner 1 researchers and engineers are also members of the inter-university "Centre d'études nordiques" based at ULaval. Researchers at the CEN (36 regular members) are world recognized specialists of high latitude environments. A unique network of automated climate and weather stations (SILA) equipped with permanent instruments in the field (77 stations acquiring climatic and environmental data), and eight field research stations (Qaujisarvik) and base camps created and operated by the CEN will be available to the UMI. Also available at Takuvik: corers for lake sediments, geophysics instruments, boats, 4X4 trucks, cold rooms for sample storage, radiochronology, (paleo)ecology, limnology & sedimentology laboratories as well as rooms for the preparation of samples for chemical and isotopic analyses. J. Carignan (project coordinator) is expert in elemental and isotopic geochemistry of metals, R. Pienitz and W. Vincent are ecologists specialists in limnology of arctic and sub-arctic lakes. Takuvik has other collaborators that will take part of the project: E. Dewailly, P. Ayotte, M. Lemire, are researchers at the Québec Hospital specialized in environment and population health and study Inuit exposure to metal contaminants.

Partner 2. CRPG (UPR 2300 CNRS)
CRPG - Centre de Recherches Pétrographiques et Géochimiques - is located in Nancy. For decades, CRPG researchers specialized in the development of new isotope systems to trace sources and processes in various geological environment, including ecosystems. CRPG has a strong international

reputation for his expertise in analytical developments and related science applications. Sample preparation labs (clean rooms) and all instrumentations necessary for elemental analyses and high precision isotopic measurements are available. Christophe Cloquet, a IR (CNRS) with an establish knowledge in isotope analysis and geochemistry, is the team leader. Partner 2 also includes Christian France-Lanord (DR CNRS), an isotope geochemist ($\delta^{34}S$, $\delta^{13}C$, $\delta^{18}O$, δD) specialized in the erosion of the continental crust and the CO_2 global cycle with an established international reputation, Barbara Marie and Delphine Yeghicheyan, both engineers specialized in analytical chemistry. Aymeric Schumacher is an assistant engineer specialized in isotopic measurement with MC-ICP-MS. CRPG has another collaborator that will take part of the project: T. Sterckeman is a research engineer (LSE - UMR 1120 INRA/INPL in Nancy) specialized in bio-availability and bio-accumulation of metal in plants.

Partner 3. GET (UMR 5563 CNRS-UPS)
GET - Géosciences Environnement Toulouse (former LMTG) is a large CNRS laboratory from (UMR 5563, A+), University of Toulouse and IRD that comprises more than 200 people. A large group of scientists are actively involved in field studies of soil, waters and plants, together with others specialist of experimental methods aiming at reproducing field observations and numerical modelers. This laboratory is also at the forefront in the exploration of new geochemical tracers, like Fe isotopes, thanks to state of the art analytical equipments (high resolution MC-ICP-MS, collision cell ICP-MS, ultra-fast laser ablation systems). This laboratory is probably the only one in France that systematically perform geochemical (ground) research in arctic and sub-arctic zone of Russia, in tight collaboration with numerous Russian colleagues (more than 10 Research Institutes). This collaboration is fostered by existing of two long-term structures – European Associated Laboratory LIA LEAGE (2006-2014) and Group of International Research GDRI CAR-WET-SIB, those objectives completely coincides with the topic of the present project. Oleg Pokrovsky (CR CNRS) and Jérôme Viers (Prof.) are internationally known scientists in biogeochemistry and isotope geochemistry and will lead the partner team. Partner 3 includes Russian collaborators: S. Kirpotin (UTomsk), A. Prokushkin & L. Shirokova (Russian Academy of Science).

Partner 4. IPREM (UMR 5254 CNRS-UPPA)
LCABIE has a strong expertise in analytical and environmental sciences. This research unit has been pioneering the development of innovative methods of speciation analysis since now more than 2 decades with the objective of understanding biogeochemical cycles and environmental impacts of trace elements and metals in the environment. Part of its work is based in laboratory experiments to better characterize the molecular forms of trace elements and metals, the mechanisms of their transformations and the relative contribution of biotic and abiotic processes. To improve the knowledge on the origin, anthropogenic contribution of chemical forms of trace metals in the environment and, study the environmental mechanisms of isotopic fractionation, analytical methods are also developed to determine the isotopic composition of trace elements and metals "at the molecular level". LCABIE team lean on various analytical means including electrochemistry and several equipments of mass spectrometry: elemental (QICP-MS), molecular (ESI QTOF, ESI MS/MS, MALDI TOF MS) and isotopic (MC ICPMS). Participants have a strong expertise both in the development of analytical methods as well as a very large experience in field monitoring or reactivity studies on metallic compounds in the environment.

Partner 5. LCPME (UMR 7564 CNRS-UHP)
LCPME (Laboratory of physic chemistry and Microbiology for the Environment) is a multidisciplinary laboratory internationally recognized in the biofilm research topic and located in Nancy. The LCPME currently conducts multidisciplinary approach for biofilm characterization and properties studies in environmental or industrial fields. It aims to study physico-chemical and microbial reactions at the interfaces water-solids in the environment. The researchs are transversal and conducted by the physico-chemists and microbiologists of the lab. F. Jorand is an associate professor specialized in the biofilm studies and in the bacterial interactions with the iron species especially in the anaerobic environments. Material for anaerobic cultures of bacteria is available in the lab (Coy chambers for controlled atmosphere, anaerobic and/or microaerobic). H. Guilloteau is an engineer

specialized in microbiology and water analysis. A PhD grant thesis will be provided from ministery (allocations MSER, école doctorale BioSE for 2012) and dedicated to the project at 66%. The student will be supervised by F. Jorand and working in collaboration with J. Schäfer for mercury analysis.
Recently, LCPME had conducted with the laboratory EPOC (G. Abril & J. Schäfer, Bordeaux, F) a research program on the biomethylation of mercury by the biofilms from tropical lake and river (Huguet, PhD thesis, F. Jorand, supervisor), and collaborated with the CRPG and IPREM (Nicolas Estrade, PhD thesis) on the isotopic fractionation of mercury during its reduction by a FeII-FeIII mineral.

Parnet 6. EPOC (UMR 5805 CNRS-UBordeaux)
EPOC (Environnements et Paléoenvironnements Océaniques et Continentaux) is a multidisciplinary laboratory, represented in this project by the "Transferts Géochimiques des Métaux" (TGM; 2 PR, 1 MDC, 2 IE) team working on Geochemistry and Ecotoxicology of metals in aquatic systems. EPOC-TGM has performed internationally recognized research on trace metal cycles (e.g. sources and fate, reactivity, speciation, bioaccumulation, etc.) in complex natural aquatic systems. Coupling aquatic geochemistry and ecotoxicology implies the development of new experimental methods (in-situ and laboratory), based on high performance analytical techniques (e.g. operational and molecular metal speciation, incubations with stable isotopes, modelling) and the related equipment (e.g. clean rooms, GC-ICP/MS). Cécile Bossy and Lionel Dutruch are specialized in speciation analyses of metals in natural samples by ICP/MS. Gérard Blanc and Jörg Schäfer have already successfully (>5 publications, 2 in prep.) collaborated with LCPME and GET members (Partners 3 and 5), e.g. on stable Hg isotopes in sediments and Hg methylation kinetics/potential of biofilms and plankton microbia. Experienced in Hg biomethylation in tropical and temperate systems, the team is highly motivated by contributing their specific competences to this project.

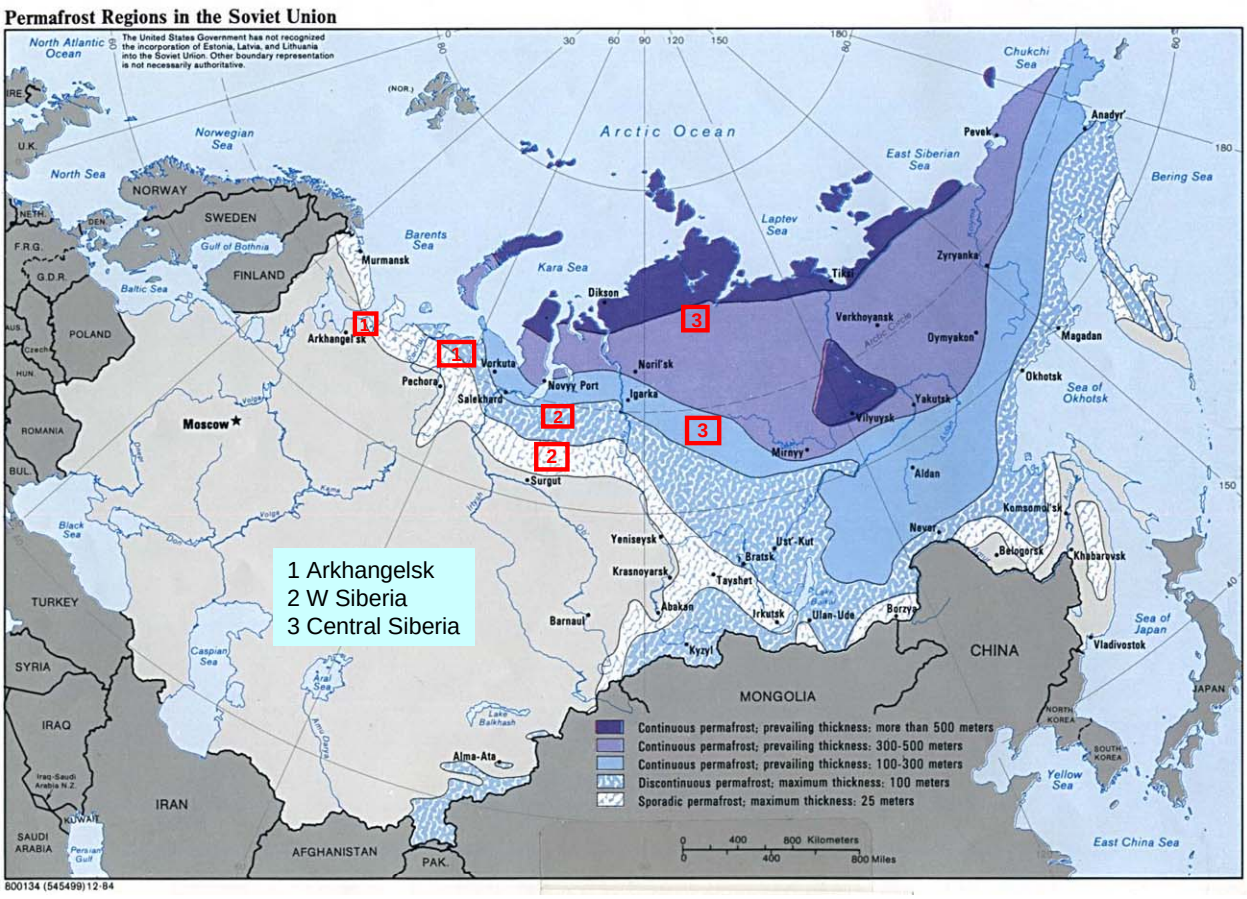
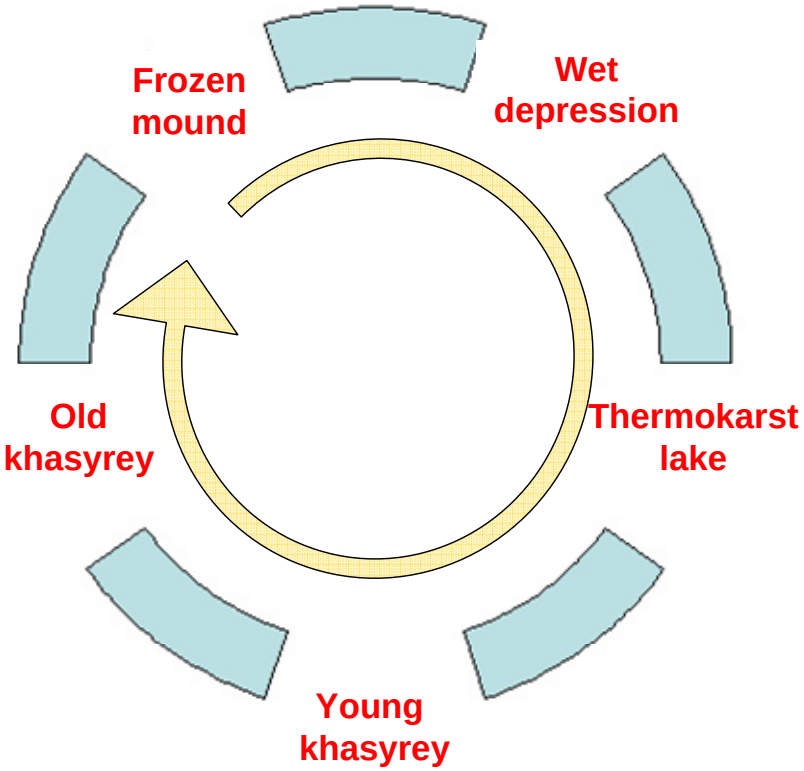
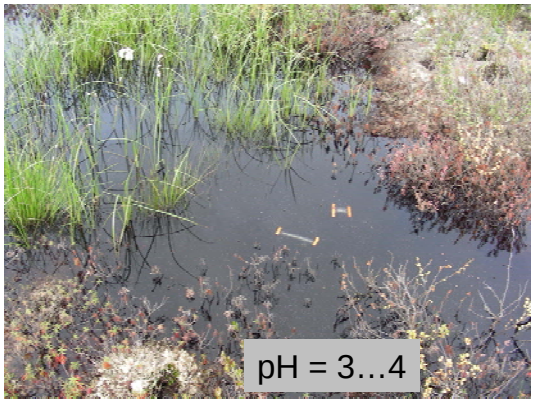


Figure 1. Map of Russian sites studied within the Arctic-Metals project

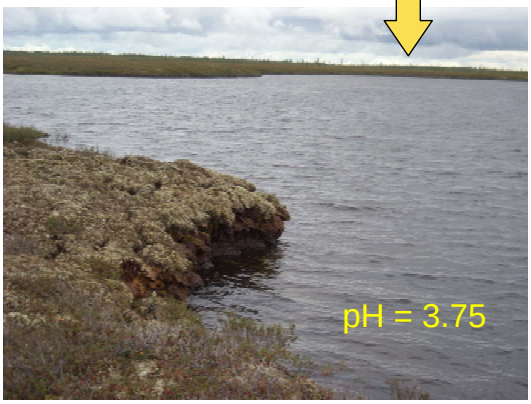
Scheme of cyclic succession of development of flat and mound bogs



Chronosequence of thermokarst lake evolution in NW Siberia

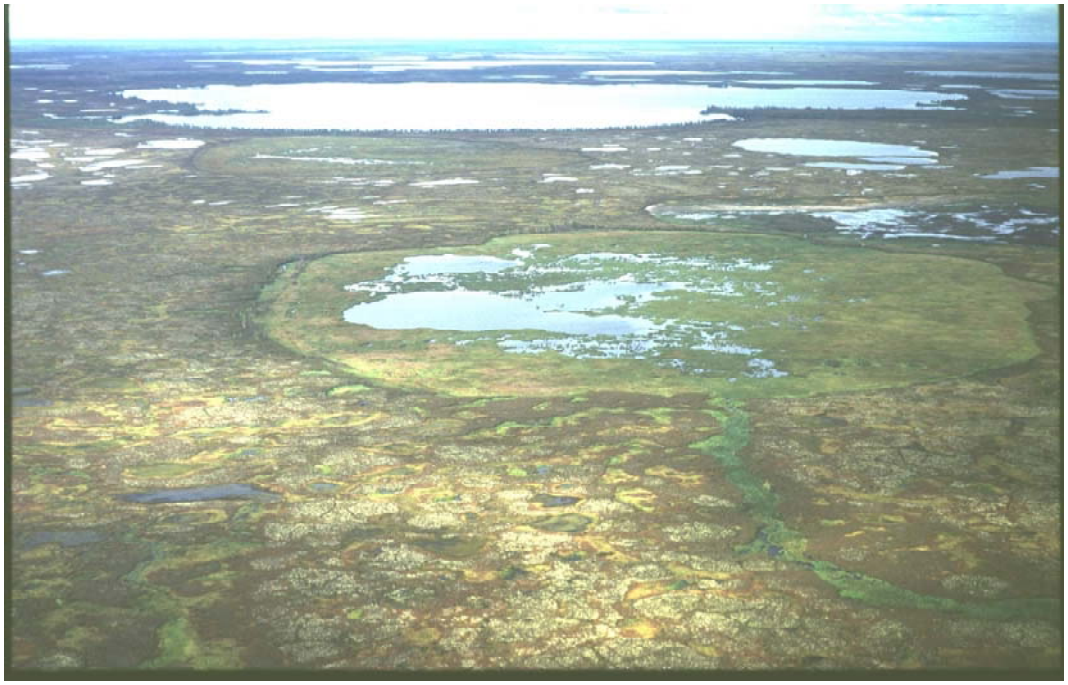


Acidic waters, peat leaching



Third stage of cyclic succession of permafrost degradation: round thermokarst lake (photo S.N. Kirpotin)

Khasyrey: drained lake
(4th stage of cyclic succession - photo S.N. Kirpotin)



Methodology

Sampling and in-situ filtration and dialysis

~ 10 samplesx

<u>Filtration frontale et ultrafiltration</u>:
5 µm, 2.5 µm, 0.22 µm, 100 kDa, 10 kDa, 1 kDa

<u>Dialyse in-situ</u>: *1 et 10 kDa*

<u>Composition chimique</u>:

Éléments traces (ICP-MS)
Cations majeurs (AAS)
Anions majeurs (HPLC)
Silicium (colorimétrie)
Carbone organique dissout
Alcalinité

<u>Isotopie</u> du Sr:

TIMS

Sediment sampling