

Acronyme / Acronym	arctic metals		
Titre du projet	Devenir des éléments métalliques en régions arctique et sub-arctique: exposition des écosystèmes et des populations nordiques		
Proposal title	The fate of metal elements in arctic and sub-arctic areas: ecosystems and northern populations exposure		
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1. RÉSUMÉ DE LA PROPOSITION DE PROJET

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" passes through our knowledge of levels, chemical forms, reactivity and bio-availability of metals in the environment. The Arctic Metals project will focus on metal accumulation due to diffuse pollution, which covers millions of km² 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. To achieve our objectives, we defined 4 major tasks: 1- the project coordination will comprise a Steering Committee and will be dedicated to the organization of project and international meetings, project logistics (including field missions), progress reports, setting up training, data base and diffusion of information; 2- laboratory experiments will document conditions that govern reactions between metals and various organic matters, including chemical form transformations and isotopic fractionations; 3- metals biogeochemical cycle within various compartments of selected lake ecosystems in northern Canada and Siberia (Russia) will be assessed through chemical, speciation, isotopic data; 4- the metal exposure of northern populations will be addressed through the analyses of the isotopic composition (Hg, Se) of country food and human blood from a "sample bank" covering populations living in arctic and sub-arctic areas in Canada. Ambitious results are expected: i- evaluating the source of metals present in aquatic ecosystems of northern areas; ii- understanding the impact of metals on eco-geo-systems in relation to biodiversity by developing tools that will highlight reactions between metals and organic matter; iii- tracing the source of metals in human populations by testing the potential of isotope tracing for Hg and Se in blood samples; iv- developing a chemical and isotopic data base and chemodynamic models for various metals in arctic and sub-arctic aquatic environments. The project also aims at training several postdoctoral, master and PhD students to

state of the art methods applied to environmental studies. The project data and results will be available to the northern population, to the general public and to the stakeholders through a project web site with key results translated into French, English and Inuktituk.

2. CONTEXTE, POSITIONNEMENT ET OBJECTIFS DE LA PROPOSITION

The thawing of permafrost in response to global warming will lead to important changes of the polar and subpolar ecogeosystems. Anthropogenic activities, at large, impact and will be impacted by such changes. Positive or negative feedbacks on both sides, society and the environment, may therefore be identified. One of the negative feedback is the fate of soil metals in the context of thawing permafrost. Metals are naturally present but also accumulated in soils through the deposition of direct (proximal) and/or diffuse (long range) atmospheric pollution in these remote areas. The proposed project aims to study different aspects of metals behavior in arctic and sub-arctic regions, including sources and distribution in the various compartments of eco- and geosystems, as well as the exposition of northern population to metallic contaminants. We propose a collaborative study between French, Canadian and Russian scientists based on important scientific problems related to the behavior of metals in the environment: i- identifying level, distribution and speciation of metals and documenting fluxes in various environments that evidence the thawing of permafrost (e.g. thermokarst lakes); ii- using and developing natural isotopic abundances for tracing sources, including natural vs anthropogenic, and to highlight metal reactivity such as chemical and phase changes; iii- characterizing the isotopic composition of consumption products (country food and local traditional medicines such as red berries and plants for teas) and northern population blood to identify possible sources of metals presenting risks for Inuit health.

The mining activities and the subsequent exposition to metal pollution may directly impact Northern communities (including ~150 000 Inuits in total, ~45 000 in Canada; ~140,000 of small ethnic communities in Russia) and their economic/social development. Inuit populations are concerned about potential exposition to metallic pollution because it may have direct consequences on their traditional way of life. Mining companies have now to develop environmental policy/programs to minimize ecotoxicology problems. Such programs are elaborated through our knowledge of metal behavior in the ecogeosystems. Furthermore, territorial managers need information on the metallic pollution level and fate, particularly for the preservation and exploitation of ice-rich soils and wetlands in the changing arctic and sub-arctic environments.

2.1. CONTEXTE ET ENJEUX ÉCONOMIQUES ET SOCIÉTAUX

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. A changing environment will certainly change the fate of metals, causing remobilization, chemical and phase transformations. The Arctic has attracted growing attention from scientists, the public, and policy makers, because it is an environment where the effects of global climate change are accumulating and increasing. A group of specialists (Arctic Climate Impact Assessment; <http://www.acia.uaf.edu/>) published a 1042-page document including an inventory of climate changes and their major impacts on oceanic and terrestrial environments (ACIA 2005):

Temperature rise. The air temperature has risen almost twice as fast in the Arctic as compared to the rest of the world during the last few decades, probably in response to the increase in greenhouse gases in the atmosphere. In a scenario for moderate emissions, an increase in the average annual temperature of up to 7°C is predicted above the Arctic Ocean during the next century, which may lead to the ice-free summer ocean within the next 30 years.

Thawing of permafrost. The permafrost, which represents 25% of the continental surface of the northern hemisphere, has been observed to have undergone a temperature increase since the 1960s and, in many places, a gradual thaw. This thaw drives the mobilization of the sequestered organic carbon, a part of which is oxidized by bacterial action in the water and soil column. This anaerobic activity is a major source of methane, a gas with a greenhouse effect 23 to 63 times more important than that of CO₂ (per molecule). Changing soils redox conditions will displace stability fields of metal chemical species and increase their reactivity with the surrounding environment.

Changes in the anthropogenic activities. Mining activities in the Arctic are important contributors of geological materials, coal and metals to the global economy with major exploited deposits in Russia, Greenland, Alaska and Canada. The warming temperature and the resulting decrease of summer sea-ice is likely to facilitate some offshore operations, lengthen the shipping season and shorten routes. On land, permafrost thawing will increase the costs of maintaining infrastructure such as roads, airports, mills, tailing deposits and towns and of minimizing environmental impacts. Overall, metal mining and oil/gas industrial activities in the Arctic are likely to expand and impact the surrounding environment.

Anthropogenic activities related to metal mining in the North.

Today, mining activities in the arctic and sub-arctic areas are important contributors of geological materials, coal and metals to the global economy. Very large mining operations are active today in the Arctic, comprising one of the largest metal producers in the world. For example, the Red Dog Zn-Pb Mine in Alaska (USA) has an annual Zn production of 725 Ktons, probably one of the largest in the world (<http://www.reddogalaska.com/>); The Polaris and Nanisivik Zn-Pb mines in the Nunavut territory of the Canadian arctic archipelago produced together more than $3.5 \cdot 10^3$ Ktons Zn and 800 Ktons Pb between 1981 and 2002 (http://nunavutgeoscience.ca/eo/YrCmmdtyGrp/5/7_e.html); the Raglan Ni-Cu Mine in Nunavik (Canada), has an annual production of 10³ Ktons of ore, 22 Ktons Ni and 6 Ktons Cu (<http://www.mining-technology.com/projects/raglan/>); the Norilsk Nickel Company in Russia operates multiple mining sites in polar regions: Kola Peninsula, with an annual production of 110 Ktons Ni and 62 Ktons Cu, and Siberia, with an annual production of 122 Ktons Ni and 339 Ktons Cu (http://www.nornik.ru/en/our_products/).

Today, approximately 300 sites are slightly to heavily polluted by heavy metals in the Arctic region of USA, Canada and Greenland (http://www.robindesbois.org/arctic/polar_star_2_FR.html and references therein). Much less is known in Russia except for the regions adjacent to major Cu-Ni mining operations in Siberia (Norilsk smelter) and in the Kola Peninsula (de Carita et al. 1996; Kashulina and Reimann 2001). Boyd et al. (2009) reported high atmospheric emissions of metals from the Cu-Ni industry in these two arctic areas of Russia, reaching 1 to 2 ktons per year for Cu and Ni and 296 and 1860 ktons for SO₂ at Kola and Norilsk respectively. In comparison, Mount Etna, the larger SO₂ volcano producer in Europe, emits up to 1300 to 2200 ktons SO₂ per year (Salerno et al. 2009), which is in the range of the Norilsk smelter emissions. Anthropogenic SO₂ deposition may be transported through ecosystems and direct exposure is believed to be a major cause for significant vegetation damage (Kashulina and Reimann 2001; Kashulina et al. 2003).

In the next 20 to 25 years, the world demand of metals, particularly Cu and Ni, will increase so that the consumption of Cu for the next 25 years will be equal to the total consumption since the beginning of humanity (CRU data; <http://crugroup.com/Pages/default.aspx>). With the warming temperature, marine navigation (shipping) and mining activities in the North are likely to expand and impact the surrounding environment. For example, in 2009, 60 exploration projects for metals (base metals, gold, Iron, Ni-Cu-PGEs) were active within the Nunavut territory in the Canadian arctic archipelago (Fig. 1)

Diffuse metal pollution in the arctic and sub-arctic areas.

Cu emissions from Kola and Norilsk mining operations (Russia) **alone** (ca. 3400 tons per year; Boyd et al. 2009) would explain the total increase in Cu atmospheric deposition flux estimated at Baffin Island in the Nunavut territory over the last century (ca. 400 mg/m²/yr - Micheluti et al. 2009) for a territory almost twice as large as the whole Nunavut (8.5*10⁶ km² vs ~ 5*10⁶ km²). Enough Cu is emitted from these two mining plants to increase by a factor of 20 the atmospheric Cu deposition over the entire Baffin island (~ 0.4*10⁶ km²). Of course, metal emissions from mining exploitation and refineries are not uniformly dispersed and huge gradients are observed (e.g. Carignan and Gariépy 1995; Reimann and de Carita 2005).

Just to say that metal emissions related to mining industry worldwide have the potential to increase significantly metal contents in remote environments. For example, Telmer et al. (2004) estimated that **only** 49% Cu, 15% Pb, 23% Zn and 9% Cd of total emissions from a smelter in the mining area of Québec (Abitibi) reach the ground within a 50 km radius around the chimney stack. According to numerical models, Pb emissions may be dispersed within an area of up to 1.3*10⁶ km² around the smelter (Telmer et al. 2004). This was confirmed by Pb isotope tracing, more than 500 km north of the refinery (Carignan and Gariépy 1995).

Pb and other metals (Cd, Cu, Zn) concentrations in snow from Greenland also indicated enrichments because of the anthropogenic activities further south in North America and Europe for the last century (e.g. Rosman et al. 1994, 1993). Metal signal in Greenland snow seems to decrease since 1970-1980, thanks to environmental policies developed in industrial countries. However, the atmospheric Pb deposition in the high Canadian arctic is still buffered by anthropogenic sources (e.g. Shoty et al. 2005). Atmospheric fluxes remain small so that Pb, Zn, Cu, Cd, ... excess relative to geogenic input is small to non significant (0 to 19%) in some high arctic lake sediments (Outridge et al. 2002). However, in some other sites, excess Pb may reach up to 26% (also Cu, As, Ni excess), as reported in some lakes in Baffin Island (Micheluti et al. 2009). Measured metal excess in sub-arctic lake sediments in Nunavut and Nunavik Inuit territories of northern Canada as well as in Europe (Scandinavia, Greenland) is much more significant than the one measured in high arctic lakes (e.g. Outridge et al. 2002; Lucotte et al. 1995; Weiss et al. 2007; Camarero et al. 2009). In general terms, the increase in trace elements in modern with respect to pre-industrial lake sediments reflects the history of a long range contamination affecting the most remote locations (e.g. Camarero et al. 2009). In comparison to diffuse pollution, atmospheric deposition proximal to mining operations may yield metal enrichments in lake sediments reaching several orders of magnitude compared to pre-industrial natural input in Canada (e.g. Couillard et al. 2004; Outridge et al. 2011) and northern Europe (e.g. Veli-Pekka et al. 2006). These pollution "hot spots" metals may be remobilized through the hydrological system and thus access more remote areas and become available for biota and the food web (e.g. Loftis et al. 2007).

The case of Hg (also S & Se) is different compared to other metals, probably because of its stable volatile forms at low temperature and its high reactivity in the environment. Recent Hg increases in arctic and sub-arctic lakes have been attributed to global anthropogenic Hg emissions (e.g. Lucotte et al. 1995; Lockhart et al. 2005; Landers et al. 1995). However, it was proposed that the recent Hg increases in high arctic lake

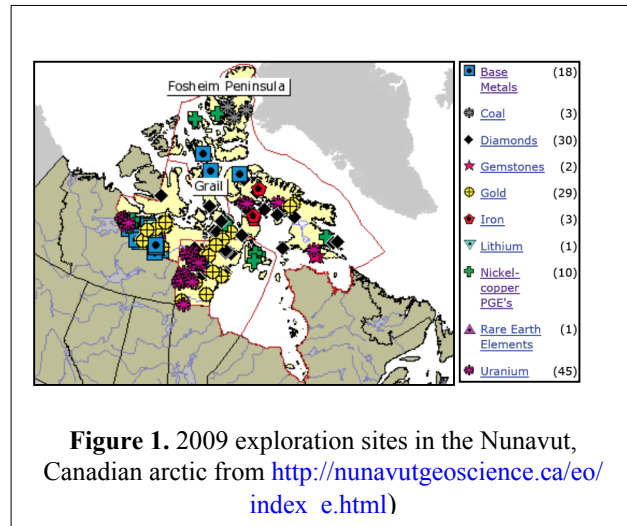


Figure 1. 2009 exploration sites in the Nunavut, Canadian arctic from http://nunavutgeoscience.ca/eo/index_e.html

sediments may be partly (up to 78%; Outridge et al. 2007) the result of elevated rates of Hg scavenging from the water column caused by markedly greater algal productivity, which in turn was driven by accelerating climate warming during the 20th Century (Outridge et al. 2005). This suggestion does not imply that anthropogenic Hg is insignificant in the current Arctic environment. In any case, it is clear that a changing environment may significantly change environmental metal cycles by altering soil-water balances, vegetation types, aquatic productivity and land-uses (e.g. Lofts et al. 2007).

The changing arctic and sub-arctic environments.

The permafrost thawing will certainly affect the dynamics and fate of anthropogenic metals by changing the soil-water balances and making toxic elements available to bio-accumulation. The rise in global Arctic temperature has a strong impact on permafrost and may lead to the formation of thermokarst lakes and ponds - ground surface subsidence caused by thaw of ice-rich permafrost. These environments are real reactors for organic matter and are particularly suitable to study interactions between metals and dissolved organic matter and bacterio-plankton (e.g. Pokrovsky et al. 2010).

Northern biota and population metal exposure.

Arctic and sub-arctic living biota and population are exposed to several metallic pollutants, particularly Hg. Mercury and other metals are transported through the atmosphere and the hydrographic systems to lakes and oceans. Century scale studies of Hg trends in Arctic marine predators and humans, using teeth, hair, or feathers (Braune et al. 2005; Outridge et al. 2005b; Dietz et al. 2006) show that current concentrations are at least several-fold above pre-industrial levels, indicating that most of the Hg in present day Arctic biota is ultimately anthropogenic in origin.

Northern populations are particularly concerned by environmental changes, including exposure to environmental contaminants such as metals. The primary exposure pathway for contaminants for various toxic metals is through the traditional northern diet, in turn related to ecosystems surrounding populations. For the last decades, northern populations (e.g. Inuits) have higher Hg and Pb concentrations in blood and various organs than other, more south, populations (e.g. Van Oostdam et al. 2005; Dewailly et al. 2007; Johansen et al. 2007).

2.2. POSITIONNEMENT DU PROJET

According to the context cited above, 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 does 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). The present demand will cover expenses for the French teams exclusively. In addition to their scientific expertise, Canadian and Russian teams will provide field infrastructures and access to remote sites in the arctic and sub-arctic areas. Canadian and Russian collaborators are world recognized specialists of high latitude environments and have numerous on-going studies in fields related to the proposed project. One of the strengths, novelty and originality of our research is that it will span a broad range of Arctic environments, exposed to a variety metal atmospheric fallout, medium to long range transport from the source, in both Russia and Canada. Indeed, the project will comprise pre-selected and partially monitored sites by our Russian partners from the west of Ural mountain to the Taimur peninsula (ca. 2000 km in longitude) and a latitudinal coverage of more than 3000 km in Western and Central Siberia. In Canada, such a coverage will be made possible via the use and the development of 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 and base camps created and operated by the Centre d'etudes nordiques (**CEN** - partner #5) and available to our team. This CEN Network is part of the SCANNET circumpolar consortium of observation and research stations. The French team proposing this project will thus contribute and benefit from the Sustained Arctic Observing Networks (SAON) which is being developed and implemented by the nations of the Arctic Council (www.arcticobserving.org).

The proposed project will contribute to the **French initiatives in polar environments**, specifically some dealing with ecogeosystems in permafrost. For example, the **Groupement De Recherche International** project **CARWETSIB** aims to study the influence of climate warming on ecosystems and thermokarstic structures of Siberian wetlands, including the behavior of trace metals. Scientists involved (LMTG-GET Toulouse, Tomsk State University, Russian Academy of Science) are partners 3, 8 and 9 respectively of the proposed project. Our project also has links with many national and international projects developed in Canada. For example, the Canadian **Northern Contaminants Program- NCP** (<http://www.aicn-inac.gc.ca/nth/ct/ncp/index-eng.asp>) concerns human exposure to elevated levels of contaminants in wildlife species that are important to the traditional diets of northern Aboriginal peoples. One of our collaborator in partner 1 is deeply involved in the NCP. Also the Canadian Network of Centres of Excellence **ArcticNet** (<http://www.arcticnet.ulaval.ca/>), for which the central objective is to contribute to the development and dissemination of the knowledge needed to formulate adaptation strategies and national policies to help Canadians face the impacts and opportunities of climate change and globalization in the Arctic. All CNRS researchers from the Takuvik UMI 3376 CNRS-ULaval (coordinator CNRS lab) will be members of ArcticNet.

Position of the project in the CESA call for proposals

Firstly, our project perfectly fits many of the general and specific objectives of the CESA program. It is an academic research project devoted to our understanding of the fate of metals in the northern environments by characterizing the level, but also the speciation of metallic contaminants in aquatic ecosystems. We want to develop isotopic measurements and document isotopic fractionation factors related to specific reactions and chemical form and phase transformations in relation to metal-organic matter reactivity (e.g. adsorption, bio-accumulation). Isotopic tracing will also allow to estimate the nature and sources of metals, natural vs. anthropogenic. In addition to the impact of metal contaminants to ecosystems, one of our Tasks will concern human health and the exposure of Arctic and sub-arctic populations to metal contaminants. Our project will integrate research tasks in Theme #1 (metrology - chemical contaminants) of the CESA call, by developing isotopic and speciation measurements of metals (including organometallic molecules) and their level, bio-availability and bio-accumulation; Theme #2 (health and

contaminants: impact on communities and ecosystems), by studying the reactivity of ecosystems to metal contaminants through time (using sediment cores), by documenting metal transformation through biogeochemical cycles and by initiating Hg and Se isotope source tracing in human blood; Theme #5 (models, predictions,...) by developing a data base, including metadata and constraints for models from our isotope and speciation results.

Position of the project at the international level

Lots of **International projects in the Arctic** were initiated during the last few years, especially for the International Polar Year in 2007-2008 (<http://www.ipy.org/>). Many organizations and/or international Networks, such as **AMAP** (<http://www.amap.no/>), **UNEP** (<http://www.grida.no/polar/>), **ICOS** (<http://www.icos-infrastructure.eu/>) and the **IPA** - International Permafrost Association ([http://ipa.arcticportal.org/index.php/ Activities/](http://ipa.arcticportal.org/index.php/Activities/)) coordinate programs throughout the circum polar Arctic with environmental assessments, concerning, among other topics, anthropogenic contaminants.

Our collaboration with the CEN and Nasivvik Centers in Canada will ensure privileged links with the Inuit and with other stakeholders, which probably sets our program apart from others. Indeed, our project benefits from the support of Inuit institutions of Nunavik (see support letter from Makivik Corporation). Finally, we will have access to an international data base devoted to arctic data, the **Polar Data Catalogue** (<http://polardata.ca/>), host at the CEN in ULaVal. The catalogue is a database of metadata and data that describes, indexes and provides access to diverse data sets generated by Arctic and Antarctic researchers. The records follow Federal Geographic Data Committee (FGDC) standard format to provide metadata exchange with other data centers. This will ensure the highest visibility for our project.

2.3. ÉTAT DE L'ART

Note: references in bold comprise members of the team as author or co-author.

Tracing metal enrichments in the environment

Heavy metals in the environment may have natural or anthropogenic origins, related to the exploitation of ore deposits or other industrial activities such as refineries and power plants or simply to the global urban or agriculture activities. Emissions and dispersion will be punctual or diffuse, directly into the hydrographic system or through atmospheric depositions, involving short- or long-range transport. Today, mining activities in the arctic and subarctic areas are important contributors of geological materials, coal and metals to the global economy. Although heavy metal emissions to the atmosphere from these industries are (partly) estimated, we have scarce information on atmospheric deposition fluxes and the impact on eco-geosystems for remote areas like the Arctic and sub-arctic. For example, pre-industrial atmospheric fallout fluxes in a high arctic lake basin were close to zero (0.012 mg/m²/yr; Outridge et al. 2007) whereas post-industrial fluxes range between 3.3 and 51.6 mg/m²/yr in many Arctic lakes (Landers et al. 1998; Muir et al. 2009). A regional Hg inventory around Hudson Bay in Canada indicates that the atmospheric deposition flux increased from 0.1 to 1.5 ton/year between pre-industrial and industrial times and that rivers input passed from 0.6 to 1.9 tons/year over the same period, probably related to higher atmospheric deposition and higher mobilization in soils due to climate warming (Hare et al. 2008).

Determining if a given metal concentration contained in soils or sediments results from an additional input of anthropogenic origin is not a trivial task, especially in remote areas. Comparing to regional geochemical background, or normalizing to a crustal element (Al, Sc, Th) and calculating enrichment factors (EF), may be used to estimate additional sources to the natural ones (e.g. Laperrière et al. 2008). However, backgrounds and EF may be difficult to interpret properly because of the natural heterogeneity

and the reactivity of some metals with organic matters (Reimann and de Caritat 2000, 2005; Reimann and Garrett 2005). Regional studies in polar and subpolar environments in the Kola Peninsula mining area (Russia) suggested that, except in the surroundings of refineries, the regional distribution of pH and many metals in soils has not an evident direct link to smelter activities (Reimann et al. 2000). Concentrations and EF only thus have strong limitations. Combining isotopic compositions to EF is much more powerful in terms of source discrimination (e.g. **Baron et al. 2006** for Pb in peat sediments, **Sterckeman et al. 2006** for Pb in soils and **Cloquet et al. 2006** for Cd in soils). For example, although there was no strong correlation with Pb EF, **Carignan et al. (2002)** used the Pb isotopic composition of lichens to document the sources of atmospheric Pb and the distribution of atmospheric fallout in the Laurentian area in Québec. Pb isotopes in lichens, in aerosols and in snow demonstrated the long-range atmospheric transport of Pb emitted from smelters (e.g. Sturges et al. 1989, **Carignan and Gariépy 1995**, **Simonetti et al. 2000a**) and from industrial areas of the northern hemisphere (e.g. Rosman et al. 1994). Studying Pb isotopes in snow packs from the boreal forest areas of Québec, **Simonetti et al. (2000b)** suggested that some metals (Pb, Zn) originated from Eurasia and were transported to Canada over the pole via the Arctic vortex (haze). In high arctic lakes of Baffin Island (Canada), increases of deposition metal fluxes are small (Pb, Zn, Cu, ...) but are marked by a change in the Pb isotopic composition, suggesting anthropogenic sources (Micheluti et al. 2009). At a larger scale, anthropogenic Pb and Hg were identified in marine Arctic sediments (Gobeil et al. 2001; **Carignan et al. 2008**). Sediments from west-central Fram Strait record the material outflux from the arctic Ocean to the North Atlantic Ocean (**Carignan et al. 2008**). Pb and Hg concentrations along a sediment core in this area strongly suggest an enrichment in surface sediments related to anthropogenic input. Contrary to what was proposed by Gobeil et al. (1999) for Hg enrichment in surface Arctic sediments, Hg in Fram sediments is not related to Fe or Mn variations and Hg excess cannot be the result of some redox reaction within the sediment pile (**Carignan**, unpublished data). Furthermore, **Carignan et al. (2008)** reported a change in the Pb isotopic composition of surface sediments from this core, strongly suggesting anthropogenic input. These metal excess certainly originate from watersheds and rivers surrounding the Arctic Ocean (**Maccali et al. in prep.**), suggesting the transfer of metals deposited on land to the aquatic and oceanic systems.

Source, transport and transformation processes are key factors in controlling the fate of heavy metals, including their exposure to receptors. Field investigations, including leaching fluxes and solid-solution partitioning, are research priorities (Lofts et al. 2007). In particular, metal stable isotopes (e.g. Fe, Cu, Zn, Se, Hg, Pb) can be used for our understanding of origin and transformation fluxes of local and global pollutants in soil and vegetation (**Viers et al., 2007 - Cu-Zn; Carignan and Cloquet 2009 - Zn;**) but this research area is still in its infancy. In particular, our knowledge of Hg isotope geochemistry greatly expanded for the last 5 years (e.g. Foucher and Hintelman 2006; Blum and Bergquist 2006; Kritee et al. 2007; Zheng et al. 2007; Gosh et al. 2008; Smith et al. 2008; Zombardi et al. 2008; **Estrade et al. 2009**) with the discovery of both mass dependent and independent isotopic fractionation (Bergquist and Blum 2007). Environmental studies using Hg isotopes succeeded in tracing back sources in the atmosphere (**Carignan et al. 2009; Estrade et al. 2010**), soils (**Estrade et al. 2011**) and aquatic systems (Foucher et al. 2009; Gehrke et al. 2010). Gantner et al; (2009) and Gehrke et al. (2011) used isotopes to show that sediment is a primary source of Hg to lake and nearshore aquatic food web.

Metals in thawing permafrost lakes and wetlands

Permafrost is part of the ground (soils, sediments, rocks) permanently frozen for several years. Present in polar and subpolar areas, it covers between 10 and 20% the Earth's land surface. In the Northern Hemisphere, permafrost covers large areas of Canada, Russia and Alaska, USA totalizing approximately 23 x 106 km² (~20 to 50% of basin surface; Zimov et al., 1997; Hinkel et al., 2003; Riordan et al., 2006).

Due to accelerated air warming, permafrost thaws and the potential consequences on natural ecosystems as well as human lives and activities, although widely acknowledged, are still not fully apprehended because of a lack of knowledge on the functioning and the dynamics of these soils in such changing climatic conditions. In some regions of the Arctic, ponds are draining or drying up through permafrost erosion (Smith et al. 2005) and shifts in the Precipitation/Evaporation balance (Williamson et al. 2009), and the net change in total freshwater surface area of the Arctic is presently unknown. According to the warming scenario, the lakes will be drained to the hydrological network as climate gets warmer and wetter; as a result, all metals enclosed in remote isolated basins in the water column and in the sediments may be delivered closer to the human infrastructure, for example.

The nature of the lakes also evolve through time, from its formation (eutrophic) to its more "mature" stage (oligothrophic), which may change the relationship between the available metals, dissolved organic carbon and groups of bacterio-plankton (Shirokova et al. 2009; Pokrovsky et al., 2010) and the redox conditions of both water column and sediments. Indeed, Shirokova et al. (2010) showed that some biologically important trace metals (e.g. Mo, Mn, Co, Cd) in a northern Russian lake were subject to sinusoidal diurnal variations reflecting their speciation in solution and their affinity to aquatic micro-organisms. Most trace elements in lake water are present essentially in colloidal large-size fraction (0.45 μm - 10 kDa) whereas some divalent metals show high affinity to small-size (< 1 kDa) colloidal fraction (Pokrovsky et al. 2010). Indeed, there is an increase of small size organic ligands binding divalent metals (e.g. Cu, Cd) produced by the phytoplankton at the mature stage of ecosystem development. This late stage marks the expense of bacterio-plankton mineralization of large colloidal size allochthonous humic and fulvic complexes (Fig. 2).

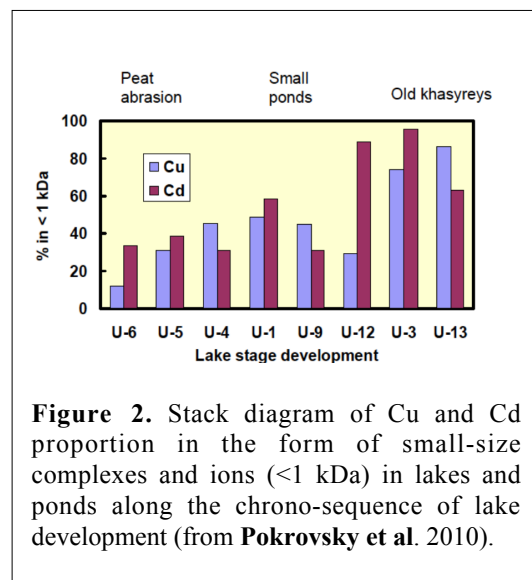


Figure 2. Stack diagram of Cu and Cd proportion in the form of small-size complexes and ions (<1 kDa) in lakes and ponds along the chrono-sequence of lake development (from Pokrovsky et al. 2010).

This late stage marks the expense of bacterio-plankton mineralization of large colloidal size allochthonous humic and fulvic complexes (Fig. 2). Speciation calculations for divalent metals for Siberian and European boreal forest lakes suggest that $\pm 30\%$ bound with organic ligands and $\pm 30\%$ with the kDa–0.45 μm fraction colloids (Vasyukova et al., 2010; Pokrovsky et al. 2010). The speciation of some trace elements in colloids may be controlled by interaction with Fe oxy(hydr)oxides rather than DOC as suggested by positive relationships between Fe and other metals. However, it was suggested that the presence of organic matter may considerably slow down adsorption rates onto Fe oxy(hydr)oxides within the sediment pore water, at least for As (e.g. Redman et al. 2002; Couture et al. 2010).

Metals deposited in lake sediments may also have various relationships with other elements indicative of speciation. Feyte (2008) studied the distribution of some trace elements along sediment cores retrieved from permafrost thaw lakes in the Hudson Bay area, Canada. The total Cd concentrations are highly related to total S contents suggesting a speciation relationship (Fig. 3). Both Cd/Al and S/Al increase sharply in the first top 4 cm of the sediments core (~60 to 150 a), probably the onset of thermokarst sedimentation. It is interesting to note that the composition of suspended matter do not fall on the sediment trend suggesting another Cd-S relationship within the water column. This might be because of the dissolved O₂ stratification of waters for these lakes, ranging from near 0 mg/L at the sediment-water interface to more than 10 mg/L closer to the surface (Laurion et al. 2010).

Sulfur speciation in lake sediments comprises acid-volatile sulfides (AVS), mostly FeS (S may also bond

to Zn, Cd, Pb, ...), generally formed by sulfate reducing bacteria (Rickard et Morse, 2005), generally in transition between sulfate (oxic environments) and insoluble sulfides (reduced environments). Sulfur may also be incorporated in the structure of organic matter (e.g. Urban 1999). Isotope tracing ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of SO_4^{2-}) suggest that drought induced pulses of SO_4^{2-} from a Canadian wetland mostly originate from the oxidation of organic S, previously reduced and store in the wetland (Schiff et al. 2005). Selenium has a similar behavior as S but have slightly different stability field in the Eh-pH diagram so that combined S-Se data may yield more information on the redox environment and reactions (e.g. Johnson 2004). Dissolved S-Se species in aquatic environments are +4 and/or +6 ions that can be reduced by bacteria or plankton to S^{2-} - Se^{2-} and eventually volatile organic molecules DMS, DMSe and even DMSSe (e.g. Tessier et al. 2002; Amouroux et al. 2001). Evidently, the chemical speciation of S and Se is a critical prerequisite in assessing environmental reactivity as the bioavailability and toxicity of S and Se are greatly affected by their chemical forms. As for S, Se isotopes trace redox reactions in aquatic and geological environments (Johnson 2004; Wen and Carignan 2011) with identified isotopic fractionation related to specific biotic and abiotic reactions (e.g. Johnson et al. 1999, 2003; Ellis et al. 2003).

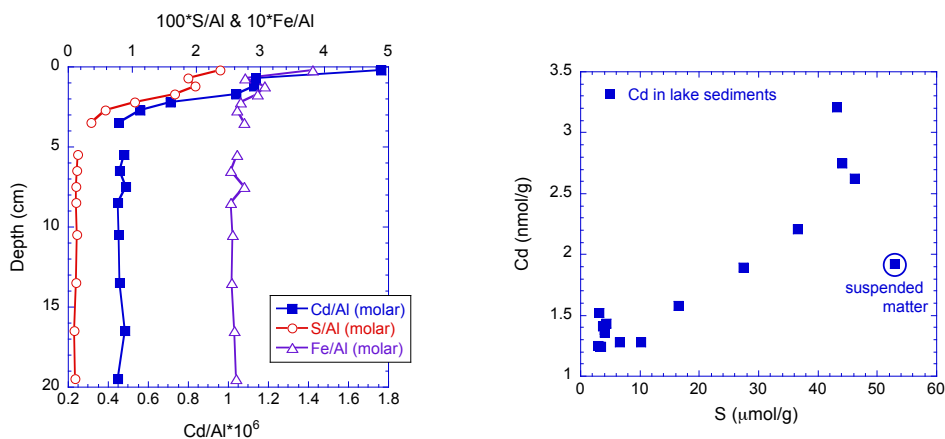


Figure 3. (left) Cd, S and Fe normalized to Al profile in permafrost lake sediments from a sub-polar area around Hudson Bay, Canada; (right) Cd vs S molar concentration relationships in the lake sediments. Note that suspended matter do not fall on the sediment trend. Data from Feyte (2008).

Northern biota and population metal exposure.

Although the increase of Hg concentration in the arctic biota is evident between pre- and post-industrial times, the THg and MeHg trends found in arctic biota for the last 20-30 years is somewhat more inconsistent with significant increases for some animals (Beluga - Outridge et al. 2005b; polar bears in Canada - Rush et al. 2008) and a relative stability for other ecosystems for the last 20 years (arctic char - Muir et al. 2005). This contrasts with the decline of atmospheric inputs estimated for the last 2 or 3 decades (Evans et al; 2005). Because of the inconsistency in trends observed in some biota during the last 20-30 years, it was proposed that anthropogenic inputs might be not the exclusive source for higher Hg contents in living organisms but that environmental changes due to climate warming might play a role (e.g. Braune et al. 2005). For example, relatively high mercury levels appear to be due to a combination of relatively old fish populations (because of light fishing pressures) and tend to be more prevalent in smaller lakes where warmer summer water temperatures and watershed influences result in greater mercury and methyl mercury inputs (Evans et al. 2005). Hence, better estimates of metal inputs (atmospheric, river inflow, re-suspension), losses (sedimentation, volatilization), and biological pathways in the changing

environment are crucial for a better understanding of contaminant trends in the arctic biota and the actual exposure of ecosystems. This is particularly true for Hg because of its bio-magnification along the food web (e.g. Campbell et al. 2005). Country food comprises meat and fish, ducks, marine mammals, wild plants, etc... (e.g. Van Oostdam et al. 2005). For example, Hg concentrations in the liver and kidneys of Greenlanders are elevated compared to the mean levels reported for the population in several European countries (Johansen et al. 2007). The THg and MeHg contents in humans might vary considerably among different regions in the Arctic but also among ethnicity or social groups within communities because diet is related to ecosystem variety and cultural preferences (Van Oostdam et al. 2005; Dewailly et al. 2007). Because traditional food diet is often related to social, cultural and spiritual way of life for northern Aboriginal populations, the risks of exposure to environmental contaminants through diet is not a simple problem because the perception of exposure might be biased (Van Oostdam et al. 2005). However, the significant decrease in Inuit blood mercury content is primarily interpreted as the result of dietary changes for the population of the Nunavik territory in Northern Québec (Fontaine et al. 2008).

2.4. OBJECTIFS ET CARACTÈRE AMBITIEUX OU NOVATEUR DU PROJET

The global objective here is to develop 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 estimation of "toxicity" passes through our knowledge of levels, chemical forms, reactivity and bio-availability of metals in the environment. Contrarily to highly contaminated areas related to intense industrial activities, metal accumulation due to diffuse pollution, which covers millions of km², is more difficult to appreciate. In a changing environment, re-mobilization of metals of anthropogenic origin **and** naturally present may yield toxic exposure for biota and human populations (for example the natural source of As contamination in the Ganga basin waters; e.g. Acharyya et al. 2000; Pal et al. 2002). To achieve our objectives, we will use laboratory experiments to document conditions that govern reactions between metals and various organic matters, including chemical form transformations and isotopic fractionations. We will also document metal composition of various compartments in selected lake ecosystems in northern Canada and Siberia (Russia). Finally, we will analyze the isotopic composition (Hg, Se) in human blood from a "sample bank" covering populations living in the Nunavik territory in Canada.

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 discriminate 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. By 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 be 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 studies 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.

3. PROGRAMME SCIENTIFIQUE ET TECHNIQUE, ORGANISATION DU PROJET

3.1. PROGRAMME SCIENTIFIQUE ET STRUCTURATION DU PROJET

The project is structured in 4 tasks. Relationships between tasks are illustrated in Fig. 4.

Task 1 - Coordination of the project

Task 1 is the project coordination including project meetings and dissemination of the results (project website, data base). It is described in section 3.2. Task 1 will monitor work progress, collect data for the project database, and check the flow of information between the different tasks (see section 3.2).

Task 2 - Laboratory experiments

Laboratory/field experiments will be done to document kinetics of key reactions of phase transformation of some metals and possible related isotopic fractionation. The data obtained in task 2 will be delivered to task 1 (project data base). The results obtained will be used to build a conceptual framework for interpreting data obtained from task 3 and 4. All the systems studied are related to metal - organic matter reactions. Task 2 is divided in 3 sub-task:

Task 2a - Reduction & bio-accumulation kinetics and isotopic fractionation of Se (and S) during the formation of DMS_e (DMS) by the bacterio-plankton.

Task 2b - Evaluation of the mercury methylation by microbial biomass from biofilms and surface sediments of permafrost thaw lakes.

Task 2c - Isotopic fractionation during metal (Ni, Hg, Se) bio-accumulation by plants grown in controlled conditions in the laboratory.

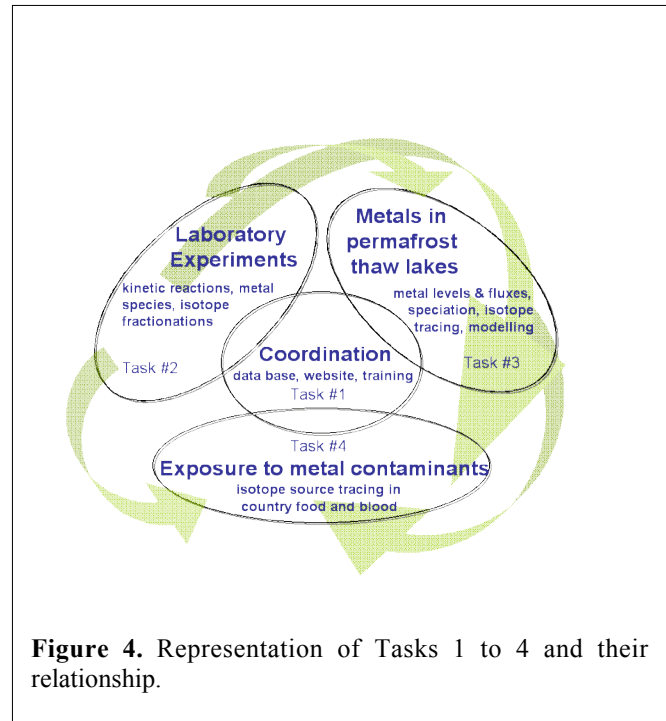


Figure 4. Representation of Tasks 1 to 4 and their relationship.

Task 3 - Biogeochemical cycle of metals in permafrost thaw lakes: inventory of phases, species & reactions

This task aims to document the level and the dispersion of various metals in the permafrost thaw lake environments from Canada and Russia. Samples will be collected during devoted field work and from existing sample banks, if the storage was compatible with the type of analyses performed. The data obtained in task 3 will be delivered to task 1 (project data base). Results from task 3 will be used to establish a reference scheme for the chemical and isotopic compositions of potential source reservoirs in relation to the exposition of metal contaminants for Northern populations, studied in task 4. Task 3 comprises 4 sub-tasks according to type of measurements:

Task 3a - The analyses of major and trace element concentrations in water, suspended matter, sediments (surface and core), soils, vegetation. Paleo-ecology data from core sediments.

Task 3b - The analysis of organometal molecules in water and sediments (DMS, DMS_e, MeHg), metals bond to reactive OM, inorganic speciation and bio-availability of metals in soils and sediments by selective leaching.

Task 3c - Isotopic measurements (C, S, Pb, Hg, Se, Cu, Zn, Ni, Fe) in water, suspended matter, sediments (surface and core), soils, vegetation.

Task 3d - Modeling the impact of metals on the ecosystem and biodiversity: data synthesis and box/chemodynamic models.

Task 4 - Exposure to metal contaminants for Northern population

This task will aim to make links between metal contaminants in the environment and the exposure of populations of the circum-arctic by using isotope tracing. The data will be interpreted in consideration of geographical repartitions, levels of contamination, social status, age and gender of the population studied. The data obtained in task 4 will be delivered to task 1 (project data base). Results obtained in task 4 will

be used to build biogeochemical box models done in task 3. Task 4 comprises 2 sub-tasks:

Task 4a - Analyses of metal concentrations and isotopic compositions (Hg, Se) in a selected local consumption product - beluga.

Task 4b - The characterization of Hg and Se isotopic compositions of Inuit blood for metal source affiliations.

3.2. MANAGEMENT DU PROJET

Coordination of the project: Jean Carignan (Takuvik Québec, partner 1)

Task 1 (project management) will be coordinated by Jean Carignan. The project steering committee (SC) will be formed by the principal investigators of the project (J. Carignan Takuvik-Québec, C. Cloquet CRPG-Nancy, O. Pokrovsky & J. Viers GET-Toulouse, D. Amouroux & M. Bueno IPREM-Pau, F. Jorand LCPME-Nancy, J. Schafer EPOC-Bordeaux); and by international collaborators: I. Laurion (INRS-ETE, Québec, Canada); E. Dewailly (Axe Santé des Populations et Environnement, Centre de Recherche du CHUQ et Université Laval, Québec, Canada); W. Vincent & R. Pienitz (Takuvik & Centre d'études nordiques, Université Laval, Québec, Canada). All decisions will be taken jointly within the SC.

Task 1 will be dedicated to:

- **Organization of international meetings**
 - Project kick-off international meeting: 2 days international workshop (in a partner laboratory) with all project partners, associated international collaborators as keynote speakers.
 - A workshop in Québec city during the annual meeting of the Centre d'études nordiques and the opportunity to meet Inuit people and authorities to present preliminary results of the project.
 - A final project international meeting in France: organization of a symposium on "metals biogeochemical cycles in arctic and sub-arctic environments" at the "Réunion Nationale des Sciences de la Terre".
- **Coordination of project logistics**

Canada and Russia field work is planned for Task 3 (Biogeochemical cycle of metals). Task 1 will coordinate project logistics and subcontracting for field work (expedition guide, translation, records) and translations if necessary. This task will have in charge to establish relationships with other related projects in order to share field expenses, resources, and objectives. For example, the CEN has many field work programs into which part of our project may be integrated. Task 1 will also organize the travel for keynote speakers for meetings.
- **Monitoring of project progress and reporting**
 - Tele conferences (email, phone and/or videoconferences) will be organized with a time step of 3 months between project partners.
 - Annual project meetings (SC members or representatives) will be organized each fall (October).
 - Scientific annual reports will be prepared and sent to ANR.
 - Abstracts for conferences and for papers to be submitted will be available to the project members before submission so that internal feedbacks can be provided.
 - Annual report adapted for the diffusion of information for Northern communities and authorities.
- **Set up training, data base and diffusion of information**

Task 1 will establish a project website, participate to the international interactive (meta)data base (Polar Data catalogue), keep relationships with northern authorities. It will be compulsory for all

project participants to provide the data and model analyses results to the project database.

The project website will comprise:

- A description of the "Arctic Metals" project and its general objectives.
- The different Tasks and the related contacts.
- For partners, all project results under the requirement of passwords.
- Public results and the project "news and views".
- Available MSc, PhD and post-doc positions directly related to the project and to other projects in similar fields.
- Tutorials on selected topics of the project for undergraduate and graduate students.

3.3. DESCRIPTION DES TRAVAUX PAR TÂCHE

3.3.1 TASK 1 - PROJECT COORDINATION

Task 1 is the coordination of the project: see section 3.1 above

3.3.2 TASK 2 - LABORATORY EXPERIMENTS:

Partners in charge 2a. D. Amouroux (IPREM-Pau, partner 4); 2b. F. Jorand (LCPME-Nancy, partner 5); 2c. C. Cloquet (CRPG-Nancy, partner 2)

Laboratory/field experiments will be done to document kinetics of key reactions of phase transformation of some metals and possible related isotopic fractionation. All the systems studied are related to metal - organic matter reactions. Task 2 is divided in 3 sub-tasks into which different aspects of metals-organic matter will be studied: 2a) the production of volatile organometallic molecules (DMSe) by bacteria/plankton and the related isotopic fractionation; 2b) the production of organometallic molecules (MeHg) by bacteria/plankton; 2c) Ni, Hg, Se, Zn bio-accumulation processes in plants and lichens.

Task 2a - Reduction & bio-accumulation kinetics and isotopic fractionation of Se during the formation of DMSe (DMS) by bacteria/plankton (D. Amouroux; E. Tessier; M. Bueno; J. Carignan, M. Levasseur; C. Cloquet).

This sub-task aims to better understand interactions between dissolved Se species and bacterio-plankton by studying the reduction of Se(IV-VI) into Se(-II) and the formation of organometallic volatile molecules (DMSe, DMDS₂, ...). Isotopic fractionation factors related to these reactions will be determined. Indeed, Se reduction reactions have shown important isotopic fractionation effects that might be expressed in the environment (e.g. Johnson 2004). Results from this sub-task will be used for the interpretation of data obtained from tasks 3 and 4.

Se bio-volatilization and isotopic fractionation experiments: Experiments will be conducted in the laboratory (at IPREM-Pau, partner 4) in presence of bacterio-plankton cultures resistant to Se inorganic concentrations from 10 to 100 µg/L. The bacterio-plankton will be selected from an available culture collection of more than 50 strains of filamentous cyanobacteria from the Arctic and Antarctica (from W. Vincent, Partner 1). Most of these are in the order Oscillatoriales and are the main biomass constituents of benthic microbial mats, complex microbial consortia that often dominate total ecosystem biomass and productivity in high latitude lakes, ponds and rivers.

Se Biovolatilization: Selenite (SeO_3^{2-}) and/or selenate (SeO_4^{2-}) (to be determined as a function of the results of measurement campaigns) will be added to the cultures (six strains will be selected from available collection) in a stationary growing phase in an oxygenated but gas-tight environment. After 24-48 hours of incubation, the dead volume of the culture will be sampled with a gas-tight syringe and directly injected and analyzed for Se gas components (DMSe, DMDS), S components (DMS) and mixed components (DMSSe) using a GC-QICP-MS. An additional preconcentration step by the mean of headspace solid phase microextraction (HS-SPME) combined to the GC-QICP-MS technique has also been developed (Bueno & Pannier 2009) to improve the determination of the low concentrated volatile species. In the same way, dissolved selenium speciation will be determined to identify potential precursors to the formation of volatile selenides. Figure 5 gives example chromatograms of determination of volatile Se, Te and S species in direct headspace analysis of marine microbes pure cultures, by GC-QICP-MS.

Se isotopic fractionation:

Experiments with higher yields of volatile Se species will be selected for isotopic work. For these, experiments will be re-conducted with selenite and/or selenate previously characterized for their Se isotopic composition. This will be used as the initial composition of the reaction for isotopic fractionation factor calculations. Incubations will be continuously degassed for 24h to 48h and gases will be trapped by an acid oxidizing solution ($\text{HNO}_3/\text{H}_2\text{O}_2$) in order to get in solution the Se volatile components. After Se purification, if needed (Marin et al. 2003), this solution will be analyzed for its Se isotopic composition using the on-line hydride generation MC-ICP-MS technique at CRPG-Nancy (partner 2) (Rouxel et al. 2002; Carignan and Wen 2007). Alternatively, purged gases will be stocked in adsorbent and/or cryogenic traps and directly analyzed by GC-MC-ICP-MS after thermodesorption at IPREM-Pau (partner 4) (e.g. Amouroux et al. 1998 and in progress for the use of MC-ICP-MS).

Risks: the production of Se organic volatile molecules might be too small for isotopic measurements. Pre-concentration might be needed or, depending on the measured reaction kinetics, a longer gas purge time might be necessary.

Task 2b - Evaluation of the mercury bio-methylation of permafrost thaw lakes (EPOC-Bordeaux: Jörg Schäfer, Gérard Blanc, Cécile Bossy, Lionel Dutruch ; LCPME-Nancy: Frédéric Jorand, Hélène Guilloteau, Rémi Guyonneaud)

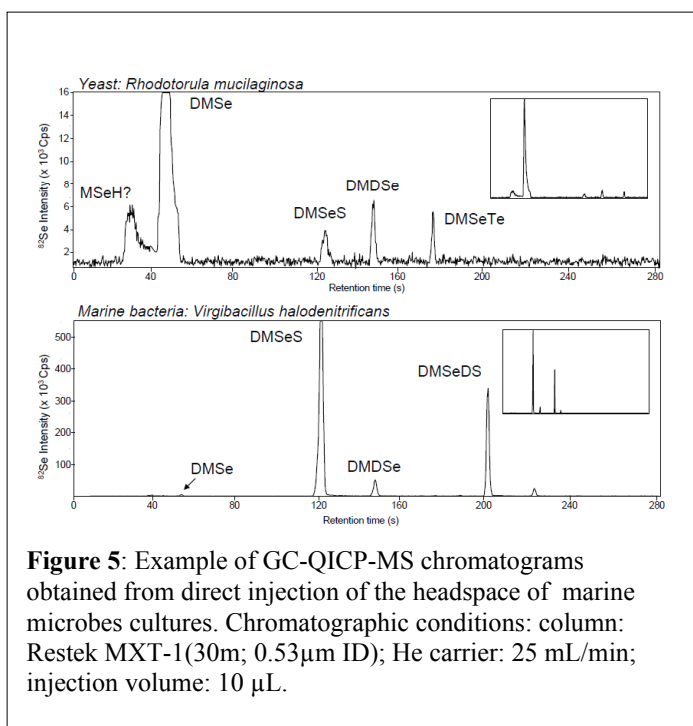


Figure 5: Example of GC-QICP-MS chromatograms obtained from direct injection of the headspace of marine microbes cultures. Chromatographic conditions: column: Restek MXT-1(30m; 0.53 μm ID); He carrier: 25 mL/min; injection volume: 10 μL .

This sub-task aims at (i) quantifying the Hg methylation/demethylation potential of the different microbial biomass compartments (suspended micro-organisms, sediments and biofilms) and (ii) identifying the main microbial activity involved (i.e. sulfate reducing activities (SRB); iron reducing activities (IRB); and methanogens) and (iii) evaluating the role of both exo-cellular polymers and inorganic compounds of biofilms in Hg net methylation.

Mercury bio-methylation in aquatic environments: It is well known that the microbial biomass of aquatic anoxic environments hosts most of the mercury methylators/demethylators such as sulphate- and Fe^{III}-reducing bacteria or methanogens (Compeau & Bartha, 1985). However, it remains unclear to what extent each group of anaerobic bacteria contributes to the net methylation (Avramescu *et al.*, 2011). Bacteria mostly form mixed communities, e.g. in biofilms and sediments, where several species implied in methylation/demethylation activities may be closely associated. Indeed, co-cultures of bacteria may show much higher methylation potential than pure strains (Pak and Bartha, 1998). Therefore, the capacity of natural microbe communities to methylate/demethylate Hg needs to be appreciated as a whole. Moreover, the organic and inorganic matrixes constituting biofilms, suspended particles or sediments (e.g.: exo-cellular polymers, minerals resulting from anaerobic respiration, e.g. Fe^{II}-Fe^{III} minerals, etc.) may influence the Hg biotransformation either by decreasing Hg bio-availability (Huguet *et al.*, 2010) or by a direct reaction (O'Loughlin *et al.*, 2003; Estrade *et al.*, 2009). Accordingly, microbially-driven methylation/demethylation processes probably depend on community properties and on the type of natural aquatic system hosting them. The increasing intensity and length of permafrost thawing periods, suggest that the related aquatic systems will soon play a key role in arctic methylmercury production. Therefore, it is crucial to quantify and understand the control of each microbial compartment (biofilm, sediment or plankton cells, Huguet *et al.*, 2010) on net Hg methylation, a key process of the Hg cycle in the changing Arctic environment.

Hg bio-methylation experiments: The material used for the incubation experiments will be suspended solids (SS), biofilms and sediments from anaerobic zones at the Whapmagoostui-Kuujuarapik Site, i.e. where the bio-methylation potential is expected to be the highest. Adapted sampling and experimental protocols will allow maintaining the anaerobic conditions until the end of the incubation periods (Huguet *et al.*, 2010). Biofilms will be collected from both natural surfaces on-site and artificial substrata (glass plates previously implanted during 12 or 18 months). Sediment incubations will be optimised, ideally at different water depth according to results obtained in Task 3 (e.g. different degree of sulfate depletion, AVS-zone, etc.; Schäfer *et al.* 2010) to focus on specific relations between methylation/demethylation rates and the dominant bacterial activity. Part of the incubation experiments will be performed on-site, whereas other experiments will be run at LCPME (partner 5), whenever useful (reduction of field trips, better infrastructure) or necessary (specific sample pre-treatments, e.g. preconcentration of microorganisms or sterilization). Dissolved and particulate Hg(II) and MMHg measurements will be done at EPOC by species-specific isotope-dilution GC-ICP/MS (e.g. Monperrus *et al.* 2004; Schäfer *et al.* 2010).

Briefly, precise quantities of isotopically labelled Hg species (¹⁹⁹Hg(II); MM²⁰²Hg) will be spiked into hermetic Teflon(R) reactors (triplicate) containing filtered (sterile) and unfiltered lake water with and without suspended matter or biofilms (from natural and/or artificial supports; e.g. glass plates to preserve the biofilm structure; Huguet *et al.* 2010). After 3 days and 1 week of incubation time (20°C), the methylating/demethylating microbial activity is stopped by acidification and both the concentrations and the experimentally modified isotopic compositions of the present Hg species will be analyzed by species-specific isotope-dilution GC-ICP/MS (Schäfer *et al.* 2010). Additional incubations with previously iced samples (transport and conservation) will be performed in the laboratory by adding i) exo-cellular

polymeric substances (EPS) previously extracted (Jorand *et al.*, 1995) and lyophilized from freshly sampled biofilms, ii) biogenerated Fe^{II}-bearing minerals (products of the anaerobic respiration of iron obtained from pure iron reducing strains or/and from IRB enrichments), iii) a nutritive solution (diluted R2A medium; Huguet *et al.* 2010). These assays will focus on the most methylating samples and compared to Hg methylation by pure bacterial strains used as a positive control (e.g. the methylating strain *Desulfobulbus propionicus*). The nutritional conditions in the reactors will be monitored by dissolved organic carbon (DOC) analyses. The samples will be characterized in terms of cell density (SYBR II green numeration), dry matter and TOC/DOC, SRB and IRB (MPN estimation on specific culture medium; Huguet, PhD thesis, 2009).

Mercury methylating/demethylating potential of microbial communities enriched in either SRB, IRB or methanogens from the biofilms, sediment and SS will be evaluated. Furthermore we will apply specific inhibitors of SRB and methanogen activity (e.g. NaMoO₄, bromoethane sulfonate, respectively; e.g. Avramescu *et al.* 2011), in the presence/absence of Fe^{III} in co-cultures, to evaluate the role of each anaerobic metabolic activity in the net Hg methylation. Note that the incubation of SRB with the Hg^{II}, will be done with electron acceptors other than sulfate (or at very low SO₄²⁻ levels) in order to avoid artifacts due to the interaction of Hg^{II} with sulfur (Benoit *et al.*, 2001). All incubations will be performed at 20°C supporting microbial activity during the laboratory experiments and reflecting realistic water temperatures during the summer (up to 15-25°C at the Whapmagoostui-Kuujuarapik Site - Laurion *et al.*, 2010).

Contribution of the partners:

EPOC (partner 6): J. Schäfer: coordination of Hg_{total}, MMHg, Hg(II) analyses, species-specific mono-isotopic spikes (¹⁹⁹Hg(II) and MM²⁰²Hg) and incubation; J. Schäfer and G. Blanc: interpretation and publication of results; supervision of graduate (Master) students and a PhD student in collaboration with LCPME; C. Bossy and L. Dutruch: Hg_{total}, MMHg, Hg(II) analyses in natural and incubated samples.

LCPME (partner 5): coordination of experimentations with biofilms by F. Jorand. Supervision of PhD (MSER grant) and graduate (Master thesis) students for enrichments with iron reducing and sulfate reducing bacteria, Fe^{II} measurements, evaluation of methylation capacity of microbial compartments; interpretation and publication of results. Biofilm characterization and DOC analysis will be realized by the assistance of H. Guilloteau.

Risks: The partners EPOC and LCPME have previously applied, established and adjusted incubation protocols to quantify methylation potentials of biofilms, plankton cells, SS and estuary sediments in equatorial and moderate climate, respectively, within 2 PhD thesis supervised by J. Schäfer, G. Blanc and F. Jorand (Schäfer *et al.*, 2010; Huguet *et al.*, 2010). The main risk may arise from too weak microbial growth on artificial substrata (glass plates) related to arctic conditions. The biofilm supports will be installed for 12 to 24 months to maximize the mass of bacteria collected and iced by the Canadian researchers. Moreover, the collecting of biofilms from natural substrata will be done during the first sampling campaign, providing sufficient material for the optimization and performance of methylation/demethylation experiments, bacteria enrichments/characterization and EPS extraction. Finally, the use of pure bacterial strains isolated from the site (Lab. of Warwick Vincent) or culture collections (banks) will support additional experiments to evaluate potential effects of biofilm extracts on microbial net Hg methylation.

Task 2c - isotopic fractionation during metal (Ni, Hg, Se) bio-accumulation by plants and lichens (C. Cloquet, T. Sterckeman, J. Carignan)

This sub-task aims to better understand interactions between bio-available metals and plants/lichens during bio-accumulation. For that, we will: 1) grow typical sub-arctic plants (e.g. graminaceae) in contact with an artificial solution spiked with metals of interest (e.g. Ni, Hg, Se) of known isotopic composition; 2) put in contact epiphytic lichens (Evernia, Bryoria, Usea, ...) with similar solutions and leave for equilibration. Results from this sub-task will be used for the interpretation of data obtained from tasks 3 and 4.

Metals accumulation in plants and lichens: Metals accumulating in plants may be essential or toxic ones. Some essential metals like Zn or Se become toxic if their contents are higher than needed. Although metals accumulate through roots (e.g. Perriguet et al. 2008; Redjala et al. 2009), atmospheric fall out may also be an efficient way for bio-accumulation (e.g. Smolders 2001). In nature, trace metals often come as a group, depending on both their source and their geochemical affinities and behavior. A multiple contamination may generate antagonist effects for bio-accumulation (Krzmaric et al. 2009). Some plants have hyper-accumulation strategy and stock metals as complexes with carboxylic acids like citrate and malate (Montargès-Pelletier et al. 2008). During the bio-accumulation cycle, from soil to plants, even within plants, metals adsorb, move from one ligand to another and incorporate proteins or vitamins (Lu et al. 2008, 2009). These processes may lead to significant isotopic fractionation (e.g. Cloquet et al. 2008). For example, Fe isotopic variations might be related to accumulation strategies (Guelke et von Blanckenburg, 2007) and translocation processes, as evidence for Zn (Viers et al, 2007, Weiss et al. 2005, Moynier et al. 2008).

Metals bio-accumulation in epiphytic lichens is exclusively through atmospheric depositions. As for plants, metals are "inactivated" by oxalate and carboxylic groups (Sarret et al. 1998). Carignan et al. (2002, 2009) and Cloquet et al. (2006b) argued that no or insignificant isotopic fractionation of Pb, Hg and Zn should occur during bio-accumulation in lichens. However, Cloquet et al. (2009) showed that bio-accumulation processes in lichens might be more complicated than expected.

Metals accumulation experiments and measurements: Plants: selected plants representative of the studied sites (see section 3.3.3 Task 3) will be grown (1-3 months) in the laboratory in contact with trace metals Ni, Hg, Se of known concentration and isotopic compositions. The solution will also comprise usual nutrients (Ca, Mg, P, ...). Once the plants grown enough, they will be separated from the solution, the roots will be rinsed rapidly with distilled water to remove spike solution in excess and they will be freeze-dry. Metals in the remaining solution stock will be analyzed along with roots, stems and shoots of the grown plants. Experiments will be conducted at the LSE in Nancy (collaborator of partner 2) and analyses will be performed at CRPG-Nancy (partner 2). Metals concentrations will be determined in order to verify the mass budget. Isotopic analyses will be done using an on-line gas separator (Se hydride and Hg cold vapor generation) coupled to a MC-ICP-MS, as reported by Carignan and Wen (2007) and Estrade et al. (2009). Concentration and isotopic mass balance will be verified.

Lichens: we have an on-going project (Cloquet-Carignan) on metal bio-accumulation in lichens. Preliminary results suggest kinetic adsorption of Pb, Hg, Se and Zn on lichen *Evernia sp.* is very fast and imply important diffusion of ions through the solution towards lichens. Work in task 2c proposes to analyze the Se and Zn isotopic composition on our samples to check on any isotopic fractionation of these metals during bio-accumulation. Such a bias between the composition of available metals and that of accumulated ones would have important implications for data interpretations, in particular source tracing. The isotopic composition of Hg is already in progress.

Risks: A small or insignificant isotopic fractionation during bio-accumulation in plants would considerably reduce the constraints on accumulation processes. Contrarily, a significant isotopic fractionation during accumulation in lichens would make difficult to track the composition of atmospheric fall out metals in the ecosystems. Our preliminary results on metal bio-accumulation suggest minor isotopic fractionation.

3.3.3 TASK 3 - BIOGEOCHEMICAL CYCLE OF METALS IN PERMAFROST THAW LAKES: INVENTORY OF PHASES, SPECIES AND REACTIONS.

Partner in charge: Oleg Pokrovsky (GET-Toulouse, partner 3)

This task comprises important field work and will be managing the technical part of these missions and the development of operations in the field for sampling and conditioning of samples prior to analyses. The administrative part of the missions (contacts, permits, travel, etc...) will be managed in task 1. Task 3 comprises 4 sub-tasks on the bases of analytical work to do. Interaction between sub-tasks is essential for both sample selection and interpretation of the data.

Field work

(O. Pokrovsky; S. Kirpotin; A. Prokushkin; J. Carignan; R. Pienitz; D. Amouroux; E. Tessier; M. Bueno; F. Jorand; post-docs and PhD students)

We selected a number of sites according to their access, physical and chemical characteristics, strategic locations regarding potential metal atmospheric fall out, permafrost state, the knowledge acquired through other studies... In Canada, we selected 2 sites, one in the sub-arctic region of Hudson Bay (Kuujuarapik) close the tree line at the edge of the boreal forest (N55°15' - sub-arctic climate at these latitude in Eastern Canada). This site is at less than 30 minutes helicopter from the Inuit village where the CEN own and operate a station, equipped with all facilities including a field laboratory. Water from different lakes next to one another has contrasted color (black, brown, beige) testifying of the various limnology and ecosystem regimes (Fig. 6). Also, the water column in many of these lakes is stratified according to dissolved O₂, testifying of an important redox gradient, anoxic at the sediment-water interface and oxic at the water-air interface. The second Canadian site is located on Bylot Island, north of the Baffin Island (N 73° 15') in the continuous permafrost. The ponds (2-5 m water depth) are formed on low-center polygons and in runnels over melting ice wedges (or runnel ponds) at the surface of permafrost terrain. A CEN field station close by the pond location is also available to the team project. Permanent meteorological stations are close by these sites and data will be available. Permafrost thaw lakes from these two sites were studied by CEN researchers, including the ones from partner 1 of this project (e.g. Côté et al. 2010; Laurion et al. 2010; Pienitz et al. 2008; Ellis et al. 2008) into which more detailed information can be found. In Siberia, we selected 1 site in Western Siberia, close to the town Nojabrsk located within the forest-tundra zone on discontinuous permafrost terrain; 1 site in Central Siberia close to Tura settlement within the forest zone developed on continuous 100-300 m thick permafrost and, finally, 1 site in Russian Subarctic zone (Arkhangelsk and Nenetsk regions) within the tundra zone on sporadic and discontinuous permafrost. All materials necessary for studies in remote regions, far from equipped scientific stations (tents, rubber boats with motors, electricity generators,



Figure 6. Thermokarst lakes in the low Arctic, tundra-forest region of Northern Québec (Nunavik) close to Kuujuarapik (from Watanabe et al. 2010).

small field materials, etc...) were acquired during previous missions in Russia and they are available for work within the present project.

Scientific equipment for field work for on-site measurements (conductimeter, oxymeter, pH-meters with electrodes, portable voltammetry, temperature and soil humidity sensors, spectrophotometer and microscope for field work) and for sampling (centrifuge, Ti pressure device for soil solution extraction, drilling device for sampling of soil and ground ice, pressurized frontal filtration apparatus for collection of river suspended matter, UV lamp for dissolved organic matter destruction) are available in partners laboratories. Special efforts will be made for acquiring the equipment necessary for permafrost ice and lake sediment transport, especially in anoxic conditions, between the field site and the laboratory. The cryoconservator (Dewar for transport in dry state, adapted for biological samples and containing an absorbent of liquid nitrogen that allows to keep the samples at -196°C without leaking) has an autonomy of 21 days for volume of 5 L, it conforms to the norms of aerial transport IATA and ICAO and it will serve to transport the samples from the site of study to local infrastructures and respective laboratories of partners. In each site will be collected 1) filtered acidified water (including depth profiles), 2) suspended matter whenever possible, 3) sediment cores, 4) surrounding soils and vegetation. Specific sampling is detailed in sub-task 3b.

Risks: Some of the field expeditions might be delayed because of permits that should be delivered by local authorities in Canada. Up to now, most field work programs of similar project were attributed permits. Our contacts in both Canadian and Russian Institutions will deal for us and we are very confident. A number of samples already in hands of our partners from previous studies might replace some samples planned to collect in the field. Conservation is critical for some analyses we want to perform.

Task 3a - Major and trace element concentrations in lake ecosystems (O. Pokrovsky; L. Shirokova, S. Audry; J. Carignan; R. Pienitz; post-docs; PhD students; partners engineers)

This sub-task is devoted to acquire a solid chemical data base for all the studied thermokarst lakes. In the different samples retrieved from the eco-geosystems a number of major (Si, Al, Fe, Ti, Mn, Ca, Mg, Na, K, P, S, C, N, Cl) and trace elements (alkaline, alkaline earth, rare earth, transition & heavy metals...). Current analytical methods will be used (elemental analyzers, atomic absorption and emission spectrometry, mass spectrometry, ...) available in partner 2 and 3 labs as well as at CNRS National analytical facilities. We estimate that more than 500 samples will be analyzed over the 4 years of the project. Another goal of this sub-task is to determine sedimentation rates in the studied lakes by using tracers like ^{210}Pb and ^{137}Cs (^{14}C if necessary) in order to have a temporal perspective of metal enrichments in the ecosystems. Paleo-ecology data like diatom assemblages will be retrieved from core sediments in order to document the bio-diversity evolution of the lakes in relation to that of metal contents. Dissolved oxygen contents, pH, total suspended solids, dissolved organic carbon (DOC), chlorophyll a, bacterial abundance and temperature along water depth will also be measured. Interpretations will be in terms of chemical fluxes between reservoirs of the ecosystems, including the atmosphere, and variations of these fluxes through time using the lake sediments as archives.

Risks: no major risk is identified here. Possible high uncertainties on sedimentation rates.

Task 3b - Organometal molecules in water and sediments (inorganic/organic-Se cpds, volatile Se (S, Hg) cpds), metals bond to reactive OM, inorganic speciation and bio-availability of metals in soils and sediments by selective leaching - (D. Amouroux; E Tessier; M. Bueno; O. Pokrovsky; C. Cloquet)

Dissolved and Gaseous Inorganic or organic Se speciation: The chemical speciation of Se is a critical prerequisite in assessing selenium environmental reactivity as the bioavailability and toxicity of Se are greatly affected by its chemical forms. In natural environments, selenium can occur in four oxidation states (-II, selenide; 0, elemental selenium; +IV, selenite; +VI, selenate) and in a variety of inorganic and organic compounds. The organically bound Se(-II) compounds include seleno-amino acids and volatile forms dimethylselenide (DMS_e), dimethyldiselenide (DMDS_e).... Typical Se concentrations in natural waters are generally below 1 µg(Se)/L and may be highly variable depending on geochemical background and/or anthropogenic activities. Inorganic species, including selenite Se(IV) and selenate Se(VI), are the major species in natural waters, and therefore selenium speciation is frequently limited to these two species. Other dissolved Se species, operationally-defined as "organic Se" fraction, occur at lower concentrations than Se oxyanions. The low levels of volatile selenium species can be quantified by sensitive analytical techniques like "purge and trap" followed by GC-QICP-MS (Amouroux and Donard, 1997; Amouroux et al., 1998; Pecheyran et al., 1998). Water samples will be collected at most sites.

Determination of dissolved inorganic and organic Se species: The most suitable and sensitive technique for selenium speciation analysis is liquid chromatographic separation coupled to inductively coupled plasma mass spectrometry (QICP-MS) detection as it is capable of distinguishing different chemical forms without redox pretreatments which secures species conservation. As Se concentration levels to measure in natural waters are very low (ng(Se)/L range), a preconcentration step before sample analysis is also necessary. On-line simultaneous preconcentration of inorganic and organic Se species was developed on porous graphitic carbon stationary phase using heptafluorobutyric acid as injection medium, inducing an enrichment of solutes at the top of the column which allowed large volumes (up to 1 mL) to be injected. Combining these injection conditions and ⁷⁸Se monitoring with QICP-CRC-MS, detection limits between 2 and 8 ng (Se)/L, depending on the species (SeIV, SeVI, SeMet, SeCyst), are obtained (Dauthieu et al. 2006). Because of the extremely low detection limits obtained, the method was successfully applied to freshwater lake samples showing selenate concentration decrease with depth (102 (-1m) to 44 ng/L (-36m)) and at the opposite an increase of selenite concentration with depth (14 (-1m) to 33 ng/L (-36m)). In all analyzed samples the total Se concentration was higher than the sum of SeIV and SeVI, indicative of the contribution of organic dissolved Se. Another selenium containing compound was indeed detected in some samples (-20 to -1 m depth) which chromatographic retention time did not match with the one of available organoselenium standards. Same analytical method can be used for the determination of selenium species in "water extractable" fraction of soils and/or sediments (Tolu et al. 2011, Ponce de Leon et al., 2003). Sampling and analyses will be performed by partner 4.

Determination of dissolved gaseous methylated Se (and Hg) species: For natural freshwater samples, volatile Se species as well as dimethylmercury can be easily purged and trapped in the field, using cryogenic preconcentration technique or adsorption on activated charcoal columns. The water vapor is removed from the gas stream using a moisture trap (-20°C) and the volatile derivatives are trapped at -196°C onto a cryogenic trap or at ambient temperature on activated charcoal adsorbent, respectively. In the laboratory, the field traps are thermodesorbed and analysed using a multi-element analytical method, involving cryogenic trapping, gas chromatography and inductively coupled plasma-mass spectrometry (CT-GC-QICP-MS). This technique allows to perform simultaneous speciation of dissolved volatile organometal(loid) compounds of several trace elements such as Hg and Se (Amouroux et al., 1998, 2000; Tessier et al., 2002). Water samples will be collected in surface and bottom waters among observed redox gradient and diurnal cycle using a gas-tight Go-Flo sampler. A bulk fraction will be directly purged with pure nitrogen gas in the field to collect gaseous species on adsorbent traps, while dissolved non-volatile

species will be stored in PE bottle at 4°C after field filtration (0.45 µm). Gaseous and dissolved samples will be analyzed within 15 days after the field campaign. For soil and sediment samples, the bioavailability of Se will be evaluated through the water soluble fraction (solid/water extraction over 24h at room temperature). Water tested for such extraction will be milli-Q, and waters from studied sites, i.e. from lakes or “melted snow”. Sampling and analyses will be performed by partner 4.

Other metal speciation: For water samples, ultrafiltration (100, 10 and 1 kDa Amicon YM Regenerated cellulose filters installed in a portable stirred ultrafiltration cell “Amicon 8050” having 50 mL volume) and dialysis experiments (1 and 10 kDa membranes) will be performed within one day after sampling (e.g. Pokrovsky et al 2010). Metal speciation in solution will be assessed via computer modeling using available codes (WHAM 6, vMINTEQ) based on results of 0.22 µm and 1 kDa fractions analysis. These preparation, analyses and calculations will be performed by partner 3.

Bio-availability of metals: The bio-availability of metals will be estimated in different ways: 1- for dissolved species, the bio-availability assay will be conducted using purified cultures of cyanobacteria and heterotrophic bacteria separated from the thermokarst lake water column using sterile filtered lake water with added different metal concentration (partner 3); 2- the phyto-availability of metals (Ni, Zn, Hg, Se) in soils (surface active zone) surrounding the studied lakes will be determined using the stable isotope spike equilibration technique as documented by Sterckeman et al. (2009) for Cd for various types of soils. Metals spikes are available at CRPG (partner 2) and in the process of being calibrated. 3- metal concentrations will be determined in vegetation (grass, small trees, berries, ...) surrounding the thaw lakes in order to estimate the flux of metals transferring to vegetation in comparison to the available stock in soils. Interpretations will use results from tasks 2c and 3c. Point 2 and 3 will be performed by partner 2.

Risks: The main risks here are potential technical problems in the field for sampling S-Se-Hg dissolved gas species although partner 4 has a strong experience for such work. Another risk resides in the fact that some species might be in a lower abundance than our detection limits. Information of these ultra low concentrations would be also an information used for assessing metal speciation and potential toxicity.

Task 3c - Isotope tracing in lake ecosystems (O. Pokrovsky; J. Viers; J. Carignan; C. Cloquet; C. France-Lanord; post-docs; PhD students; partners engineers)

This sub-task is devoted to acquire a solid isotopic data base for all the studied thermokarst lakes. In the different samples retrieved from the eco-geosystems a number of metals (Hg, Se, Cu, Zn, Ni, Fe) and important life elements (C, S). Zn, Cu & Fe stable isotope analyses will also be performed in the various size fractions separated from the water samples (100 µm - 10 µm - 1 µm - 0.22 µm - 100 kDa - 1 kDa). We estimate that more than 250 samples will be analyzed over the 4 years of the project. Most samples will be selected according to their chemical composition as documented in sub-task 3ab. The goal here is to document the isotopic composition range of the different eco-geo-reservoirs of the ecosystems. Interpretations will be in terms of "source tracing" and processes by using an elemental and multi isotope proxy approach. On that basis, we will develop strategies to differentiate natural "geogenic" from anthropogenic metals in the ecosystems. The isotopic compositions will be determined using state of the art measurements in partner 2 and 3 laboratories (MC-ICP-MS for metals and gas IRMS for C and S).

Risks: the major risk here is related to the fact that we will be dealing with various sample matrices and be obliged to adapt our chemical treatments before isotopic analyses analyzes. Very high yields are needed to achieve accurate measurements. Our team proved their ability to deal with complex matrices.

Task 3d - Impact of metals on the ecosystem and biodiversity: data synthesis and box/chemodynamic models - (O. Pokrovsky; J. Viers; S. Audry; C. Cloquet; C. France-Lanord; D. Amouroux; M. Bueno; E. Tessier; J. Carignan; W. Vincent; R. Pienitz; I. Laurion)

This sub-task aims to integrate data and their interpretation from sub-tasks 3abc to propose regional and more global chemodynamic models integrating sources-transport/mobility/reactivity-storage of metals in these aquatic systems. Life cycles, including drainage, of these permafrost thaw lakes will be taken into account. We will be estimating the percentage of influx metals that interact with organic matter, that is made bio-available and that bio-accumulate in vegetation. We will relate these estimates to the type of vegetation and available particulate/dissolved organic matter (using C and S isotopes) and bio-diversity in space and time. We will highlight any differences in the behavior of geogenic and anthropogenic metals in the systems by using speciation and isotope data.

Risks: Limit conditions of the models will not be highly constrained if we do not measure enough contrasts in speciation and isotopic compositions between reservoirs. Note, however, that bio-interactions and bio-accumulation of metals (Zn, Cu) and other elements (Mg, Ca) are reactions that usually leads to the highest isotope fractionations measured for these elements (e.g. Viers et al. 2007; Weiss et al. 2005; Cloquet et al. 2008).

3.3.4 TASK 4 - EXPOSURE TO METAL POLLUTION FOR NORTHERN POPULATION.

Partners in charge:

Eric Dewailly (Nasivvik-Québec, affiliated to partner 1)

Jean Carignan (Takuvik-Québec)

In fish and marine mammal eating populations, there are increasing evidences that a high dietary selenium (Se) intake may play a role in offsetting some deleterious effects of methylmercury (MeHg) exposure (Valera et al. 2009; Lemire et al. 2010). Se is an essential element involved in several body functions through selenoproteins expression, including regulation of oxidative stress, and immune and thyroid functions (Reeves and Hoffmann 2009). Selenoproteins have been postulated as the key targets of Hg toxicity; Hg exhibits a very high affinity for selenol groups in the active site of selenoproteins, thereby inhibiting their enzymatic functions. Conversely, high Se intake may restore selenoprotein activities and contribute to mitigate Hg-induced oxidative damage. Selenoproteins may also promote MeHg demethylation and/or bind to inorganic mercury (IHg) or MeHg and reduce its availability for target proteins and organs. Several complexes between Se and IHg or MeHg have been proposed and reviewed by Khan and Wang (2009). Therefore, in human populations exposed to MeHg, higher dietary Se may be required to reach optimal selenoenzymes levels (Khan and Wang 2009).

In aquatic ecosystems, Se-Hg interactions have likewise been suggested. Some studies have reported that the more there is Se in lake biota, the less fish bioaccumulate MeHg. Inverse associations between Se and Hg have frequently been reported in fish tissues, and some authors have suggested that high Se may trigger MeHg demethylation in fish and therefore reduce MeHg toxicity in fish and bioavailability for humans (Yang et al. 2010). In seabirds and seal livers, insoluble Se-HgI crystals have been observed (Ikemoto et al. 2004). Similar Se-HgI crystals have also been observed in beluga livers, however it is not clear whether similar Se-Hg compounds are present in other parts of marine mammals frequently consumed by Inuit populations (skin, blubber and meat), and to what extent such complex would reduce Hg and Se bioavailability for humans.

The ranges of Se status and Hg exposure in Inuit populations are very broad since the traditional marine diet can be exceptionally rich in Se, and may contain high levels of MeHg. In Nunavik adults, blood Se concentrations varies from 118 to 3553 $\mu\text{g/L}$ (mean 356 $\mu\text{g/L}$), and blood Hg, from 0.2 to 240 $\mu\text{g/L}$ (mean 18.3 $\mu\text{g/L}$). Important regional differences are observed (Fig. 7); persons living in the Hudson Strait villages present significantly higher blood Se, followed by those living in Ungava Bay, who present significantly higher Se compared to those from Hudson Bay. The highest blood Hg concentrations were also observed in persons living in the Hudson Strait villages, followed by the Hudson Bay, who had significantly higher Hg than those from the Ungava Bay. The Hudson Strait is an important region for beluga hunting and blood Se concentrations are significantly associated to beluga consumption, particularly muktuk (beluga skin) and dried beluga meat, followed by walrus and mollusc. Conversely, all marine mammals, including seal, and fish and mollusc significantly contribute to blood Hg concentrations (Lemire et al. 2010). These regional blood Se and Hg variations may reflect the different trophic level of the marine traditional foods preferentially consumed, i.e. mollusc, non-predator and predator fish and marine mammals such as seals, walrus and beluga.

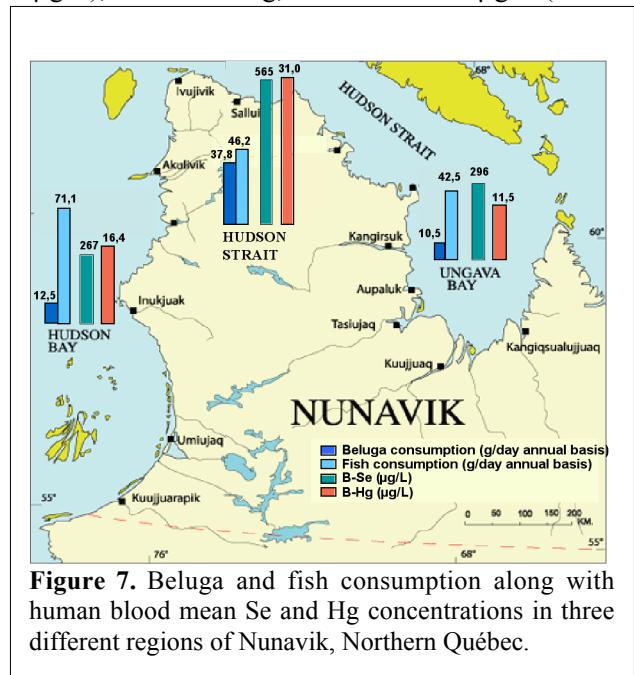


Figure 7. Beluga and fish consumption along with human blood mean Se and Hg concentrations in three different regions of Nunavik, Northern Québec.

Task 4a - Hg and Se concentrations and isotopic compositions in local consumption products (mollusc, fish, beluga) - (M. Lemire, P. Ayotte, E. Dewailly, J. Carignan, C. Cloquet).

This sub-task aims to acquire the first combined Hg-Se isotopic composition on selected country food for Nunavik population (available from a sample bank and collected through visits of villages). In particular, three important parts of beluga will be analyzed (skin, blubber, meat). Samples will be collected and prepared by partner 1 and send to partner 2 for isotopic analyses by multi-collector ICP-MS. Results will be interpreted taking into account the trophic position of animals. The isotopic composition of various parts of a given animal will be linked to our knowledge of bio-accumulation through the different organs and any isotopic variations will be interpreted as possible transfer reactions and reservoir effects. Results from sub-task 4a will be used for data interpretations in sub-task 4b.

Task 4b - Hg and Se isotopic composition in Inuit blood for metal source affiliations - (M. Lemire, P. Ayotte, E. Dewailly, J. Carignan, C. Cloquet).

This sub-task aims to acquire the first combined Hg-Se isotopic composition on selected blood samples from the Nunavik population (available from a sample bank, partner 1). Samples will be prepared by partner 1 and send to partner 2 for isotopic analyses by multi-collector ICP-MS. Results will be interpreted in terms of sources but also in terms of processes of bio-accumulation. Results from sub-task 4a and from

task 3 will be used to isotope source tracing of Hg and Se in blood. Hg-Se isotope relationships will also help to constrain possible links between these two elements (similar pathways, formation of Hg-Se compounds, etc...).

Risks: Task 4 is exploratory and direct relationships the isotopic composition of country food and metals in blood might not be evident. Bias due to unknown reactions or bio-accumulation processes may put noise in the data and result in a difficult interpretation. In any case, our results will be pioneer in the field of metal source tracing in human blood.

3.4. CALENDRIER DES TÂCHES, LIVRABLES ET JALONS

The first year of the project will be devoted to the kick off meeting, the construction of the project web site, the initiation of laboratory experiments and the analyses of some "in-hand" samples such as blood. The project logistics will prepare field work missions in Canada and Russia (coordination with related projects, national and local permits, helicopter transportation, etc...). At the end of the second year, all field work should be finished and data sets for some sub-tasks will be completed. At the end of the third year, all data set will be completed. During the first part of year 3, the mid-term project workshop will be organized in order to present raw data and the first interpretations. Some presentation at international conferences will be done, and the first articles should be published in peer review journals. The last year (#4) will be devoted to data integration and the development of chemodynamic-box model. We will complete the data base with the full set of data and carry on with presenting our work in international conferences and publish scientific articles. At the end of year 4, we will hold the final workshop, integrate results from all tasks and identify perspectives of our project.

Table 1. Tasks schedule

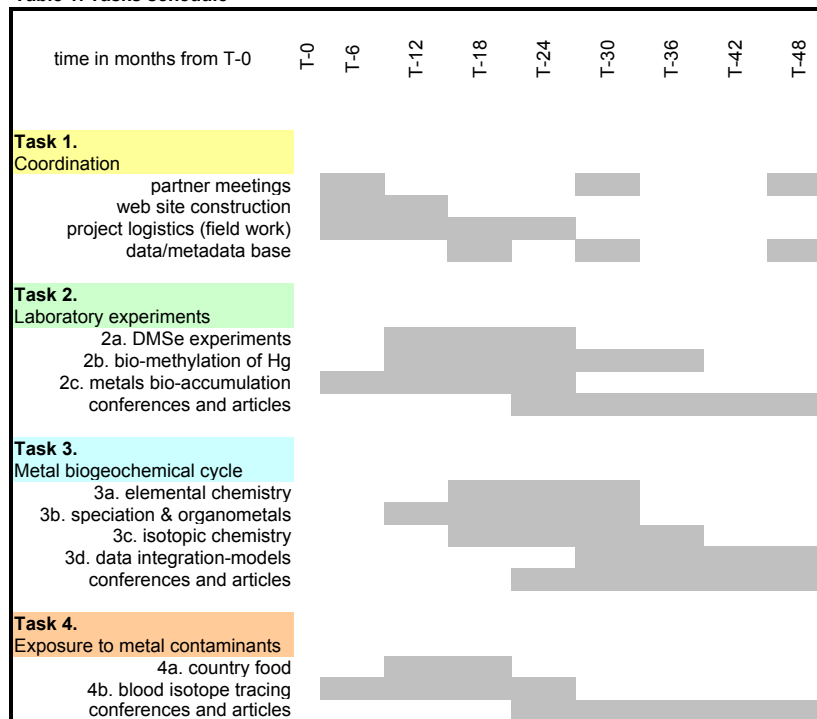


Table 2. Deliverables

time in months from T-0	T-0	T-6	T-12	T-18	T-24	T-30	T-36	T-42	T-48
Task 1. Coordination Responsible for deliverables Jean Carignan		project workshop 1	ANR report project meeting 1 web site metadata on line	first data on line	ANR report project meeting 2 field work done	project workshop 2	ANR report project meeting 3	full data base on-line	ANR report project workshop 3
Task 2. Laboratory experiments Responsible for deliverables Frédéric Jorand					metal bio-accumulation data	MeHg processes data	DMSe processes data	conferences and articles in inter. journals	
Task 3. Metal biogeochemical cycle Responsible for deliverables Oleg Pokrovsky						major-trace element dataset Metal speciation data set	isotope data set	global system models conferences and articles in inter. journals	
Task 4. Exposure to metal contaminants Responsible for deliverables Jean Carignan			country food data set	blood data set		conferences and articles in inter. journals			final data integration with other Tasks

4. STRATÉGIE DE VALORISATION, DE PROTECTION ET D'EXPLOITATION DES RÉSULTATS

The communication of project results will be given through presentations to international conferences such as the European Geophysical Union (EGU), the American Geophysical Union (AGU), the Goldschmidt Conference, Limnology international conferences, etc... as well as to international and national workshops on arctic environments and contaminants and similar topics. The main results of the project will be published in the international peer-reviewed literature and the project data will be made available on the project web site as well as on open access data bases (e.g. Polar Data Catalogue). Parts of our web site will be free of access for both the scientific community and the public at large. Other parts will be of restricted access and specific results and data will be shared within our partners and be protected for at least 2 years to allow time for publication. All publications and conferences from the group will be advised on our web site and available for questions, comments and discussions. Any disagreement or even case of litigation will be treated by the steering committee before publication or presentation.

The project meta data (sites studied, project rationale, objectives, field work, data acquisition, techniques, contacts, partners, ...) will be published rapidly in the Polar Data Catalogue web site (<http://www.polardata.ca/>). This site is free of access and consulted by scientists, governments, regional and local authorities and the general population. It provides many information on projects and partners, according to geographical and topic criteria. Head quarters of Polar Data Catalogue are located at the Centre d'études nordiques (CEN) at Université Laval in Québec city. The coordinator of the Arctic Metals project (Jean Carignan) is a member of the CEN and will have full access.

Finally, we will be organizing meetings with northern authorities and population in Canada to specifically inform them of our results and interpretations and the possible implications for the land management and general public health.

5. DESCRIPTION DU PARTENARIAT

5.1. DESCRIPTION, ADÉQUATION ET COMPLÉMENTARITÉ 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 Péetrographiques 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 environments, 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 ($\delta^{34}\text{S}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, 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 performs 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)

IPREM-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). The IPREM expertises also include collaborative investigations between biogeochemists and microbial ecologists, on the role and impact of metal (Hg, Sn, Cr) and metalloids (Se, Te) on microbiota and in turn the role of micro-organisms in the biotransformations of these elements. One of the main transversal investigation axes concerns the "role of microorganisms on the ecodynamics of metal contaminants". The multidisciplinary approaches developed within the IPREM are based either on field studies (mercury biogeochemistry and microbial communities) and lab-scaled studies with research focused on pure strains of micro-organisms and the study of the metabolic pathways for mercury methylation. 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 ministry (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.

Complementarity and cooperation between partners: The ARCTIC METALS team project comprises a variety of disciplines with a common objective: metal cycle in the environment. From fundamental isotope geochemistry (partners 1, 2) and speciation (partners 3 to 6), to ecosystems/biodiversity (partner 1 and 3) and bio-accumulation and human exposure & health (partner 1 and 2), our team is unique and put together 6 CNRS laboratories along with their international collaborations in Canada and Russia, forming a consortium of more than 30 scientists, engineers and technicians. All partner laboratories are specialized in different but complementary aspects of metals and environmental studies. International collaborators of partner 1 and 3 will give access to field stations and localities for all partners, in particular the SILA network stations in Canada, which is unique and part of the international SCANNET network. Finally, the scientific expertise of partners crosses the fields of chemistry, geology/(isotope)geochemistry, (micro-) biology/(microbial-) ecology, limnology/biodiversity, agronomy, eco-toxicology, health sciences, which is, in our opinion, relevant for an integrated study on metal contaminant in the environment. Our team will also benefit from expert collaborators (listed below) specialized in thermokarst lake ecosystems, chemodynamic models and high arctic lake studies.

Associated international experts :

Isabelle Laurion (INRS-ETE, regular CEN member)

Prof. Laurion is expert in climate change and its influence on lake ecosystems (bacteria, phytoplankton, microzooplankton). Current studies concern the thermokarst lakes and the carbon cycle in these systems. She will be part of the Steering Committee.

Charles Gobeil (INRS-ETE)

Prof. Gobeil is expert in aquatic geochemistry and study early diagenesis and trace element behavior in sediments and interstitial waters. With his team, he works on historical metal contaminant fluxes in lake ecosystems and metals bio-amplification.

Marc Amyot (U. of Montréal)

Prof. Amyot is specialized in metals biogeochemistry. He is active in the Northern Contaminant Program of Ministry of North and Indians affairs: "Production and loss of methylmercury, and its uptake in lake food webs of the High Arctic", namely on photodemethylation of Hg in arctic aquatic systems.

Subcontractors

SARM - CNRS National Facility for Rock and Mineral Analyses, located at CRPG Nancy. Note that the SARM budget for service to other CNRS laboratories is managed directly by INSU and **not by CRPG**.
GEOTOP - Centre de Recherche en géochimie et en géodynamique, université du Québec à Montréal

5.2. QUALIFICATION DU COORDINATEUR DU PROJET

Jean Carignan is now the deputy director of a CNRS laboratory (Takuvik UMI 3376 CNRS-ULaval). He is coordinating the terrestrial part of the scientific program. He has been director of the INSU National Analytical Facility for Rocks and Minerals (SARM) at CRPG (CNRS UPR 2300) for 15 years during which he supervised a team of 15 engineers and technicians. He managed an annual budget of more than 400 keuros and a budget of ~475 KEuro for the renewal of analytical instruments. He was also the French coordinator of a European project: Standards, Measurements & Testing program (~170 KEuro and a MC-ICP-MS for CRPG), involving Spanish, German and British teams; the coordinator of many CNRS-INSU projects (~110 Keuros) and projects supported by ADEME, the French National Agency for the Environment (~360 Keuros); the coordinator of environmental scientific programs supported by the funding of Regional Governments (~ 170 Keuros), including the direction of the geochemistry group of the "zone atelier Moselle" in Lorraine. He was leading the MC-ICP-MS group and recently succeeded in the acquisition of major instrumentations (~620 Keuro) through scientific programs and training. He has (co)-supervised more than 16 Master and 7 PhD students and postdocs and has organized and co-organized international meetings (Geoanalysis International Conference; Spectr'atom; Winters Conference), special sessions and symposia (EUG and EGU meetings) and international workshops (Davos 2001 and Nice 2003 on new stable isotopes). He will benefit from administrative support for project management at Takuvik and CEN.

5.3. QUALIFICATION, RÔLE ET IMPLICATION DES PARTICIPANTS

Partenaire / partner	Nom / Name	Prénom / First name	Emploi actuel / Position	Discipline* / Field of research	Personne.mois** / PM	Rôle/Responsabilité dans le projet / Contribution to the project 4 lignes max
1- Takuvik (UMI 3376) (coordinator)	Carignan	Jean	IRHC CNRS	major-trace elements and isotope geochemistry	28.8	Project coordinator ; coord. Task 4, particip. Task 1 to 4 (sampling, data analyses, interpretation, data management, ...)
	Pienitz,	Reinhard	Prof. ULaval - Takuvik	(paleo-) ecology	7.2	particip. Task 3 (sampling, bio-diversity data, interpretation)
	Vincent	Warwick	Prof. ULaval - Takuvik	limnology	2.4	particip. Task 3 (lake bacteria ecology, data integration and eco-system models)
	Guilmette	Caroline	IE CNRS	analytical geochemistry	11.5	particip. Task 3 (sample conditioning, preparation and analyses)
	-	-	PhD student to be hired -	isotope geochemistry	36	particip. Task 2, 3 (sampling, isotopic analyses, interpretation, chemo-models)

			be hired -	geochemistry		analyses, interpretation, chemo-models)
	Dewailly	Eric	Professor	Public health	4.8	coord. & particip. Task 4 (blood sample management, relations with Inuits, metal exposition studies)
	Ayotte	Pierre	Professor	human toxicology	4.8	particip. Task 4 (blood sample, interpretation, metal exposition studies)
	Lemire	Mélanie	post-doc		4.8	particip. Task 4
2-CRPG (UPR 2300)	Cloquet	Christophe	IR CNRS	isotope geochemistry	14.4	coord. Task 2c; particip. Task 2 to 4 (management of isotopic program, bio-accumulation experiments in plants & lichens, interpretation)
	France-Lanord	Christian	DR CNRS	Carbon geochemistry	4.8	particip. Task 3 (carbon stable isotope analyses and interpretations)
	Sterckeman	Thibault	IR INRA - CNRS FR-EST	agronomy - chemistry	2.4	particip. Task 2 (metal bio-accumulation experiments in plants, interpretation)
	Marie	Barbara	IE CNRS	analytical chemistry	4.8	particip. Task 2 to 4 (Hg and Se contents and sample prep. for isotopic analyses)
	Yeguicheyan	Delphine	IE CNRS	analytical chemistry	4.8	particip. Task 3 (major and trace element analyses)
	Schumacher	Aimeryc	AI CNRS	anal. isotope chemistry	9.6	particip. Task 2 to 4 (metals isotopic analyses)
3- GET (UMR 5563)	Pokrovsky	Oleg	CR1 CNRS	Geochemistry	24	Coord. Task 3; particip. Task 3 (Sampling and analyses Russian lakes)
	Audry	Stephane	Phys. OMP	Geochemistry	14.4	particip. Task 3 (Pore water and sediments analyses)
	Viers	Jerome	Prof	Geochemistry	9.6	particip. Task 3 (isotopes Cu, Zn, Fe analyses)
	Kirpotin	Sergey	Prof (UTomsk)	Geography	24	particip. Task 3 (sampling and coordinating work in W Siberia -Tomsk)
	Prokushkin	Anatoly	CR, Russ. Acad. of Science	Biogeochemistry	14.4	particip. Task 3 (sampling and coordination in Central Siberia)
	Shirokova	Liudmila	CR, Russ. Academy of Science	Microbial ecology	38.4	particip. Task 3 (biological aspects of plankton in lakes)
	-	-	post-doc GET	geochemistry	24	particip. Task 3 (sampling, sample treatment, chemical & isotopic analyses)
	Chupakov	Artem	PhD student at GET	biogeochemistry	18	particip. Task 3 (carbon and metals in constrasting lakes of Siberia)
	Stepanova	Vera	PhD student at GET	biogeochemistry	18	particip. Task 3 (metal and trace elements in peat depositis in Western Siberia)
4- IPREM (UMR 5254)	Amouroux	David	DR CNRS	environmental chemistry	7.2	coord. Task 2a; particip. Task 2, 3 (Se and Hg speciation measurements, Se isotopes and experiments on organomollecule)

	Bueno	Maité	Maitre conf. UPPA	environmental chemistry	9.6	particip. Task 2, 3 (experiments and analyses of organometal molecules)
	Tessier	Emmanuel	IR CNRS to be hired	environmental chemistry	12	particip. Task 2, 3 (sampling, experiments & analyses of organometal molecules)
	Berail	Sylvain	IE CNRS	isotope analyst	4.8	partic. Task 2 (Se isotopic analyses)
	Guyonneaud	Rémy	MC UPPA	microbiologist	4.8	Particip Task 2 (strains culture in Pau)
5- LCPME (UMR 7564)	Jorand	Frédéric	associated professor UHP	Environmental micro-biology	14.4	Coord. Task 2b; particip. Task 2 (field experiment, biofilm incubation and MeHg production)
	Guilloteau	Hélène	IE UHP	micro-biology	8	particip. Task 2 (MeHg and bacteria analyses, DOC analyses)
	Gouhrand	Sébastien	TCN CNRS	analytical chemistry	1	particip. Task 2 Iron measure (ICP-AES), organic acids measure (HPLC)
	-	-	PhD to be hired (MRES grant)	geochemistry & mico-biology	24	task 2b Particip. Task 2b, biofilms incubation, bacterial enrichments, methylation measurement
6- EPOC (UMR 5805)	Schäfer	Jörg	Professor	Geochemistry & Eco-toxicology	12	particip. Task 2 (field experiment, bacteria culture and MeHg production), interpretation and publication of results
	Blanc	Gérard	Professor	Geochemistry	7.2	interpretation and publication of results
	Bossy	Cécile	IE CNRS	Analytical Geochemistry	4.8	particip. Task 2 (MeHg and Hg(II) in bacteria incubations)
	Dutruch	Lionel	IE CNRS	Analytical Geochemistry	4.8	particip. Task 2 (MeHg and Hg(II) in bacteria incubations and natural samples)

* à renseigner uniquement pour les Sciences Humaines et Sociales

** à renseigner par rapport à la durée totale du projet

6. JUSTIFICATION SCIENTIFIQUE DES MOYENS DEMANDÉS

IMPORTANT NOTE: international collaborators were included in the team of partners 1 and 3. These researchers and professors WILL NOT receive in any case money from the ANR. Rather, they will contribute to the project by giving research time, by providing logistics for field work in Canada and Russia and by supporting analytical costs for work in their own laboratories. Details are provided in the related paragraphs below.

6.1. PARTENAIRE 1 / PARTNER 1 : TAKUVIK UMI 3376 CNRS - ULAVAL

- *Personnel / Staff*

Contribution to Task 2 (Laboratory experiments) & **Task 3** (Biogeochemical cycle of metals...)

Full funding of one PhD thesis: **97 k€**

We will be recruiting a PhD candidate in isotope geochemistry. The student will specialize and focus his work on the geochemistry of selenium. He will collaborate with partner 4 (IPREM-Pau) and will be in charge of Se isotopic analyses related to experimental work on Se reduction and production of organic Se molecules. He will be in charge of the analytical work program for all the samples from lakes in Canada and Russia and will collaborate with R. Pienitz (Takuvik) and partner 3 (GET-Toulouse) respectively for sampling and sample selections. The student may have to work on chemical and analytical development to improve the sensitivity of the method, particularly for the analysis of DMSe. Developments, results and interpretations will also be used for Task 4 (Se isotopes in human blood).

Supervisors : Jean Carignan (partner 1), Christophe Cloquet (partner 2)

Collaborators : D. Amouroux (partner 4), O. Pokrovsky (partner 3), R. Pienitz & E. Dewailly (partner 1).

IMPORTANT NOTE:

2 professors from UlaVal in Québec city are official members of the CNRS UMI 3376 Takuvik. They will contribute to the project for a corresponding time/salary of **40.6 k€**.

2 professors and 1 post-doc from ULaval are collaborators of partner 1. They will contribute to the project for a corresponding time/salary of **64.6 k€**.

• *Prestation de service externe / Subcontracting*

Contribution to Task 3 (Biogeochemical cycle of metals...) & **Task 4** (Exposure to metal contaminants...)

- sedimentation rates of lake sediments: ²¹⁰Pb and ¹³⁷Cs in 30 samples: subcontracting to GEOTOP laboratory at Université du Québec à Montréal, Canada: **3 k€**

- major and trace element analyses of water, sediments, soils, vegetation: subcontracting to the CNRS National facility SARM (180 samples, 59 elements/sample at the official CNRS price): **18 k€**

Contribution to Task 1 (Project Coordination)

- production and following of the project web site: **7 k€**

total: **28 k€**

• *Missions / Missions, Travels*

Contribution to Task 1 (Project Coordination)

- Contributions to the organization of 3 project workshops, including travels for keynote speakers and help for students (a average contribution of 7 k€/meeting) : **21 k**

- Project meetings : Travel for meetings between project partners :

in France: (0.2k€ x2/year x5 persons x4 yrs): **8 k€**

international partner meetings (France-Canada-Russia) during international conferences : 2 per year for researchers and PhD students : 8 x 1.5 k€ : **12 k€**

Contribution to Task 3 (Biogeochemical cycle of metals...)

- Field work missions from France to Canada, including for partner 1, 3, 4 (as justified in Table below): **45 k€**

Canada							
2 weeks missions, ~ 10 days in the field							
	# mission	# persones	plane tickets/pers	truck rental	local plane/pers	living coasts (2 weeks)/pers	field costs (transportation in helicopter) contribution to total costs
Kuujuarapik	1	4	1200	2660	700	80	7000
sub-total	21740						
facilities/lodging	3261						
TOTAL	25k€						

Total: **86 k€**

IMPORTANT NOTE: Project field work in Canada will be done in conjunction with other field trips organized by Canadian collaborators to share logistic costs. A minimum of 2.7k€ / day is required for helicopter services at Kuujjuarapik and Bylot. The Canadian contribution for a 2*10 days missions in the field is a minimum of **50 k€** for helicopter time flight. Lodging on site will be largely financed by the CEN (a minimum cost will be provided for CNRS researchers and students). The Canadian contribution for a 2*10 days missions in the field is a minimum of **10 k€** for lodging.

• *Autres dépenses de fonctionnement / Other expenses*

Contribution to Task 3 (Biogeochemical cycle of metals...)

- costs for sample preparation for chemical separation for isotopic analyses: pure reagents (acids, solvents, ...) and lab small materials (pipettes, ion exchange resin, columns and supports, hot plates, ...): **14 k€**

IMPORTANT NOTE: sediment core sampling for the project and analytical costs for our international partners will be covered by Canadian funds:

- costs for corers and related small materials: **5 k€**
- costs for sample preparation, micro-fossil and bacteria analyses: **20 k€**

Contribution to Task 4 (Exposure to metal contaminants...)

IMPORTANT NOTE: our Canadian collaborators will provide all samples needed to task 4, either from a sample bank or by sampling during visits of Inuit villages. A total of ~80 samples are expected for an estimated related cost (contribution to bank management and field sampling) of **10 k€**.

6.2. PARTENAIRE 2 / PARTNER 2 : CRPG UPR 2300 CNRS

• *Autres dépenses de fonctionnement / Other expenses*

note: costs for analyzes comprise all reagents and fluids/gazes, reference material controls, replicate samples when necessary.

Contribution to Task 2 (Laboratory experiments)

- analytical costs for sub-task 2a: 30 samples for Se isotopes - **3k€**
- equipment to grow plants in the laboratory (boxes, lamps, ...) for task 2c - **1.5 k€**
- major-trace element analyses including (Ni, Hg, Zn, Se) for task 2c: 40 samples - **4 k€**
- analytical costs for sub-task 2c: 20 samples (Ni, Hg, Zn), 40 samples (Se) - **10 k€**

Contribution to Task 3 (Biogeochemical cycle of metals...)

- analytical costs for sub-task 3b: 18 samples (isotope dilution Zn, Ni, Hg, Se) - **3.6 k€**
- analytical costs for sub-task 3c: 85 samples for Se & Hg isotopes - **17 k€**
50 samples for C and S isotopes - **7.5 k€**

Contribution to Task 4 (Exposure to metal contaminants...)

- analytical costs for sub-task 4a: 20 samples for Se & Hg isotopes - **4 k€**
- analytical costs for sub-task 4b: 60 samples for Se & Hg isotopes - **12 k€**

Total: **62.6 k€**

6.3. PARTENAIRE 3 / PARTNER 3 : GET UMR 5563 CNRS - UPS

- *Personnel / Staff*

Contribution to Task 3 (Biogeochemical cycle of metals...)

Full funding of a 2 year post-doc: **98 k€**

Postdoctoral Research Associate profile: (2 years) This person will be in charge of main sampling (Russia and Canada), and of analytical and experimental efforts in Toulouse. His/her work aims at quantifying the main environmental factors that control i) trace metals elements mobilization from soils and sediments towards the water column of thermokarst lakes, ii) TE cycling during phytoplankton and bacterioplankton activity; iii) experimental modeling of metal isotope fractionation (Cu, Zn and Fe) during heterotrophic bacteria consumption of organo-mineral colloids in the lake water column.

Supervisors : Oleg Pokrovsky (partner 3), Jérôme Viers (partner 3)

Collaborators : D. Amouroux (partner 4), Jean Carignan & Reinhard Pienitz (partner 1).

IMPORTANT NOTE:

1 professors and 2 researchers from UTomsk and the Russian Acad. of Science will contribute to the project for a corresponding time/salary of **427 k€**.

- *Missions / Missions, Travels*

Contribution to Task 3 (Biogeochemical cycle of metals...)

- Contribution to field work missions (20 days) from France to Russia (Krasnoyarsk, Tomsk, Norilsk).

plane tickets: 2 missions x 3 pers. : 6x1.5 k€ - **9 k€**

cargo excess for field equipment: 1 k€/mission - **2 k€**

local transportation on site*: 1 k€/mission - **2 k€**

travel expenses (lodging, food)*: 2missionx3pers.x25€x20days - **2 k€**

Total: **15 k€**

***IMPORTANT NOTE:** some expenses in the field will be covered by our Russian collaborators through the European Associated Laboratory (LEAGE) and GDRI CAR-WET-SIB (Russian funds). Funds for most of the logistics and part of lodging will be covered by our Russian collaborators (**10 k€** for the 2 field missions). At least 2 additional field missions will be needed for sampling in Russia that will be covered by our Russian collaborators: **20 k€**.

- *Autres dépenses de fonctionnement / Other expenses*

Contribution to Task 3 (Biogeochemical cycle of metals...)

- Field work equipment (<4 k€ each)

Cryoconservator for transport of plankton and organic matter samples: - **2.5 k€**

- Sampling devices for lake sediments: - 2.5 k€
- Small materials for sampling
 - 1000 mL PTFE flacons for evaporation of lake water for isotopic analysis, filter units, membranes, dialysis bags, electrodes, maintenance of filtration and sampling systems: - 8 k€
- Analyses
 - 300 samples for major-trace - 6 k€
 - 120 samples for isotopic analyses (Cu, Zn, Fe) - 16 k€
 - Use of clean room facilities (50 €/day x 40d x 4yrs) - 6 k€

Total: 41 k€

IMPORTANT NOTE: No ANR money will be used for laboratory expenses in Russia

6.4. PARTENAIRE 4 / PARTNER 4 : IPREM UMR 5254 CNRS - UPPA

- *Personnel / Staff*

Contribution to Task 2 (Laboratory experiments) & **Task 3** (Biogeochemical cycle of metals...)

Full funding for Research Engineer (12 months): 50.2 k€

The Engineer will be responsible for all the high level experimental and analytical aspects connected to Se biovolatilization and isotopic fractionation experiments (Task 2a), field and analytical work following sampling campaigns (Task 3b), as well as deriving transformation potential and gaseous fluxes from the data obtained. The candidate must have a Ph.D. degree in environmental chemistry with strong backgrounds in speciation analytical methods and tedious field work. The candidate should have experience in multidisciplinary projects and provide good scientific exchanges between chemists and microbiologisty at the IPREM, as well as tight collaboration with other partners during field and lab experiments.

- *Missions / Missions, Travels*

Contribution to Task 2 (Laboratory experiments) and **Task 3** (Biogeochemical cycle of metals...)

- International and national conferences (1 national, 2 internationals, 2 pers) - 5 k€

- *Autres dépenses de fonctionnement / Other expenses*

Note: costs for analyzes comprise instruments maintenance costs, all reagents and fluids, analytical GC and LC columns, reference material controls, replicate analysis when necessary.

Contribution to Task 2 (Laboratory experiments)

- Analytical costs for sub-task 2a:
 - 72 samples for Se speciation by GC-QICPMS - 5 k€
 - 72 samples for Se speciation by LC-QICPMS - 5 k€
 - 36 samples for Se isotopic speciation by GC-MCICPMS - 7 k€
- Elemental analyses QICP-MS (total Se): 72 aqueous samples - 1 k€
- Equipment to strains culture in the laboratory - 1.5 k€

Contribution to Task 3 (Biogeochemical cycle of metals...)

- Analytical costs for sub-task 3c:
 - 80 samples for volatile Se & Hg species by GC-QICPMS - **5.5 k€**
 - 80 samples for dissolved Se species by LC-QICPMS - **5.5 k€**
 - 30 samples for water extractable Se by LC-QICPMS - **2 k€**
- Elemental analyses QICP-MS (total Se):
 - 110 aqueous samples - **1.5 k€**
 - 30 mineralized solid samples - **0.9 k€**

Total: **34.9 k€**

6.5. PARTENAIRE 5 / PARTNER 5 : LCPME UMR 7564 CNRS - NANCY UNIVERSITÉ

• *Missions / Missions, Travels*

Contribution to Task 2 (Laboratory experiments)

- International and national conferences (1 national, 2 internationals, 1 or 2 pers) - **3 k€**
- Total: **3k€**

• *Autres dépenses de fonctionnement / Other expenses*

Contribution to Task 2 (Laboratory experiments)

- teflon bottles for batch incubation before Hg analyses (100×20€ / bottle) - **2 k€**
- equipped Lap top computer - **2.2 k€**
- small lab materials (filters, butyl caps and materials for anaeroby conditioning, needles and seringes, glassware, reagents, cultures, fluorochroms, N₂ fluids, ...) - **7.5 k€**
- Gratifications for Masters (×2) - **5 k€**

Total: **16.7 k€**

6.6. PARTENAIRE 6 / PARTNER 6 : EPOC UMR 5805 CNRS - U. BORDEAUX1

• *Missions / Missions, Travels*

- National and international conferences (2 national, 2 international, 1 to 2 pers) **3 k€**
- Total: **3k€**

• *Dépenses justifiées sur une procédure de facturation interne*

Contribution to Task 2 (Laboratory experiments)

- 180 analyses of isotopically-labelled Hg species in incubation batches by GC-ICP/MS **7 k€**
(gases, cones, solvants, ultrapure acids, derivatization reagents, reference materials, isotopically labelled Hg species – MMHg and Hg(II)-, labware, flasks, etc.)
- 20 analyses of dissolved and particulate Hg species in natural samples **1 k€**
(water, biofilms, sediments)

Total: **8 k€**

• *Autres dépenses de fonctionnement / Other expenses*

- Indemnities Master students (×2) **5.3 k€**

Total: **5.3 k€**

7. ANNEXES / ANNEXES

7.1. RÉFÉRENCES BIBLIOGRAPHIQUES / REFERENCES

This list comprises the references mentioned throughout the proposal, including the "State of the Art section". Partners authors and co-authors are identified in bold.

- Acia [ed.]. 2005. Arctic Climate Impact Assessment. Cambridge University Press.
- Amouroux, D.**, O.F.X. Donard (1997); Evasion of selenium to the atmosphere via biomethylation processes in the Gironde estuary, France. *Marine Chemistry*, 58, 173-188.
- Amouroux, D.**, **E. Tessier**, C. Pécheyran, O.F.X. Donard (1998); Sampling and probing volatile metal(loid) compounds in natural waters by in-situ purge and cryogenic trapping followed by gas chromatography and inductively coupled plasma mass spectrometry (P-CT-GC-ICP/MS). *Analytica Chimica Acta*, 377, 241-254.
- Amouroux, D.**; Wasserman, JC; **Tessier, E.**, et al. (1999). Elemental mercury in the atmosphere of a tropical Amazonian forest (French Guiana). *Environ. Sci. Technology* 33, 3044-3048.
- Amouroux, D.**, C. Pécheyran, O.F.X. Donard (2000); Formation of volatile selenium species in synthetic seawater under light and dark experimental conditions. *Applied Organometallic Chemistry*, 14, 236-244.
- Amouroux, D.**, P.S. Liss, **E. Tessier**, M. Hamren-Larsson, O.F.X. Donard (2001); Role of oceans as biogenic sources of selenium. *Earth and Planetary Science Letters*, 189, 277-283.
- Amouroux, D.**, G. Roberts, S. Rapsomanikis, M.O. Andreae (2002); Emission of biogenic gases (CH₄, N₂O, DMS) from near-shore and shelf waters of the north-western Black Sea. *Estuarine, Coastal and Shelf Science*, 54, 575-587.
- Acharyya, S.K., Lahiri, S., Raymahashay, B.C. and Bhowmik, A. (2000) Arsenic toxicity of ground water in parts of Bengal basin in India and Bangladesh - the role of Quaternary stratigraphy and Holocene sea level fluctuation. *Environ. Geol.*, v. 39, pp. 1127-1136.
- Avramescu M.-L., Yumvihoze E., Hintelmann H., Ridal J. (2011). Biogeochemical factors influencing net mercury methylation in contaminated freshwater sediments from the St. Lawrence River in Cornwall, Ontario, Canada. *Science of the Total Environment* 409, 968-78.
- Benoit J.M., Gilmour C.C., Mason R.P., A. Heyes (1999). Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. *Environmental Science and Technology* 33, 951-957.
- Baron S., Lavoie, M., Ploquin A., **Carignan J.**, Pulido, M., De Beaulieu, J.L. (2005) Record of metal workshops in peat deposits: history and environmental impact on the Mont-Lozère massif, France. *Environ. Sci. Technol.* 39, pp. 5131-5140.
- Bergquist, B.A. and Blum, J.D. (2007)
- Bergquist, B.A., Blum, J.D., (2007). Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* 318, 417-420.
- Blum, J.D. and Bergquist B.A. (2007) Reporting of variations in the natural isotopic composition of mercury. *Anal. Bioanal. Chem.* 388, 353-359.
- Boyd, R; Barnes, SJ; De Caritat, P, et al. (2009). Emissions from the copper-nickel industry on the Kola Peninsula and at Noril'sk, Russia. *Atmospheric Environment* 43, 1474-1480.
- Braune, B.; Outridge, P.; Wilson, S.; Bignert, A.; Riget, F. (2005). Temporal trends. In AMAP Assessment 2002: Heavy Metals in the Arctic; Arctic Monitoring and Assessment Programme: Oslo, Norway,; pp 84-106.

- Bueno, M.**, F. Pannier; Quantitative analysis of volatile selenium metabolites in normal urine by headspace solid phase microextraction gas chromatography–inductively coupled plasma mass spectrometry. *Talanta* (2009), 78, 759-763.
- Camarero, L; Botev, I; Muri, G, et al. (2009). Trace elements in alpine and arctic lake sediments as a record of diffuse atmospheric contamination across Europe. *Freshwater Biology* 54, 2518-2532.
- Campbell, L.M., Norstrom, R.J., Hobson, K.A., Muir, D.C.G., Backus, S., Fisk, A.T. (2005). Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). *Science of the Total Environment* 351–352, 247–263
- Carignan, J.**, Gariépy, C. (1995) Isotopic composition of epiphytic lichens as a tracer of the sources of atmospheric Pb emissions in southern Québec, Canada. *Geochimica et Cosmochimica Acta*.59, No 21, pp. 4427-4433.
- Carignan, J.**, Wen H. (2007) Scaling NIST SRM 3149 for Se isotope analysis and isotopic variations of natural samples. *Chemical Geology* 242, 347-350.
- Carignan, J.**, Hillaire-Marcel, C., De Vernal, A. (2008) Arctic vs North Atlantic water mass exchanges in Fram Strait from Pb isotopes in sediments. *Can. J. Earth Sci.* 45, 1253-1263.
- Carignan J, Cloquet C.** (2009). The isotopic composition of atmospheric zinc. *Geochimica et Cosmochimica Acta* 73, A192-A192.
- Carignan, J.**, Estrade, N., Sonke, J.E., Donard, O.F.X. (2009) Odd isotope deficits in atmospheric mercury measured in lichens. *Environ. Sci. Techn.* 43, 5660-5664.
- Carignan, J.**, Simonetti, A., Gariépy, C. (2002) Dispersal of atmospheric lead in northeastern North America as recorded by epiphytic lichens. *Atmospheric Environment* 36, pp.3759-3766.
- Couillard, Y; Courcelles, M; Cattaneo, A, et al. (2004). A test of the integrity of metal records in sediment cores based on the documented history of metal contamination in Lac Dufault (Quebec, Canada). *Journal of Paleolimnology* 32, 149-162.
- Cloquet, C.**, De Muynck, D., Signoret, J, et al. (2009). Urban/Peri-Urban Aerosol Survey by Determination of the Concentration and Isotopic Composition of Pb Collected by Transplanted Lichen *Hypogymnia physodes*. *Environ. Sci. Techn.* 43, 623-629.
- Cloquet, C., Carignan J.**, Lehmann, M.F., Vanhaecke F. (2008) Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: A review. *Anal. Bioanal. Chemistry* 390, 451-463.
- Cloquet, C., Carignan, J.**, Libourel, G., Sterckeman, T., Perdrix, E. (2006) Tracing source pollution in soils using cadmium and lead isotopes. *Environ. Sci. Techn.* 40, 2525-2530.
- Cloquet, C., Carignan J.**, Libourel, G. (2006b) Isotopic composition of Zn and Pb atmospheric depositions in an urban/peri-urban area of northeastern France. *Environ. Sci. Techn.* 40, 6594-6600.
- Compeau G., Bartha, R. (1985). Sulfate reducing bacteria: principal methylators of Hg in anoxic estuarine sediments. *Applied and Environmental Microbiology* 50, 498-502.
- Côté, G., Pienitz, R., Velle, G. & Wang, X. (2010). Impact of Geese on the Limnology of Lakes and Ponds from Bylot Island (Nunavut, Canada). *International Review of Hydrobiology*. 95(2): 105-129.
- Couture, RM; Gobeil, C; Tessier, A. (2010). Arsenic, iron and sulfur co-diagenesis in lake sediments. *Geochimica et Cosmochimica Acta* 74, 1238-1255.
- de Carita, P., Reimann, C., et al. (1996). Stream water geochemistry from selected catchments on the Kola peninsula (NW Russia) in neighbouring areas of Finland and Norway: 1: element levels and sources. *Aquatic geochemistry* 2, 149-168.
- Dauthieu, M., **M. Bueno**, J.Darrouzes, N. Gilon & M. Potin-Gautier (2006). Evaluation of porous graphitic carbon as HPLC stationary phase for simultaneous preconcentration and separation of organic and inorganic selenium species in "clean" water systems. *Journal of Chromatography A*, 1114, 34-39.

- Dewailly E**, Levesque B, Duchesne J, Dumas P, Scheuhammer A, Gariépy C, et al. (2000) Lead shot as a source of lead poisoning in the Canadian Arctic. *Epidemiology*;11(4):S146.
- Dewailly, E., Ayotte, P.**, Pereg, D., Dery, S. et al. (2007). Exposure to environmental contaminants in Nunavik: metals. Institut National de la Santé Publique du Québec report. Nunavik regional board of health and social services. 13 pages.
- Dietz, R.; Riget, F. F.; Boertmann, D.; Sonne, C.; Olsen, M. T.; Fjeldså, J.; Falk, K.; Kirkegaard, M.; Egevang, C.; Asmund, G.; Wille, F.; Møller, S. (2006). Time trends of mercury in feathers of west Greenland birds of prey during 1851-2003. *Environ. Sci. Technol.*, 40, 5911-5916.
- Ellis, A.S., Johnson, T.M., Herbel, M.J., Bullen, T.D., (2003). Stable isotope fractionation of selenium by natural microbial consortia. *Chemical Geology* 195, 119–129.
- Ellis, C.J., Rochefort, L., Gauthier, G. & **Pienitz, R.** (2008). Paleocological evidence for transitions between contrasting landforms in a polygon-patterned high arctic wetland. *Arctic, Antarctic and Alpine Research* 40(4): 624-637.
- Estrade N., **J. Carignan, F. Jorand**, O.F.X. Donard (2008) Hg isotope fractionation during abiotic reduction by the hydroxysulfate green rust 2. European Geosciences Union General Assembly 2008, Vienna, Austria, 13 – 18 avril.
- Estrade, N., **Carignan, J.**, Sonke, J.E., Donard, O.F.X. (2009) Hg isotope fractionation during liquid-vapor evaporation experiments. *Geochim. Cosmochim. Acta.* 73, 2693-2711. doi: 10.1016/j.gca.2009.01.024
- Estrade, N., **Carignan, J.**, Sonke, J.E., Donard, O.F.X. (2010) Measuring Hg isotopes in bio-geo-environmental reference materials. *Geostan. Geoanal. Res.* 34, 79-87.
- Estrade, N., **Carignan, J.**, Donard, O.F.X. Tracing and quantifying anthropogenic mercury sources in soils of Northern France using isotopic signatures. in press in *Environ. Sci. Techn.*
- Evans, MS; Muir, D; Lockhart, WL, et al. (2005). Persistent organic pollutants and metals in the freshwater biota of the Canadian Subarctic and Arctic: An overview. *Science of the Total Environment* 351, 94-147.
- Feyte, S. (2008). Analyse géochimique des sédiments de mares de thermokarst de la région de Kuujuarapik-Whapmagoostui. Internal report of Institut National de la Recherche Scientifique Centre Eau, Terre et Environnement. 30 p.
- Fontaine J, **Dewailly E**, Benedetti JL, et al. (2008) Re-evaluation of blood mercury, lead and cadmium concentrations in the Inuit population of Nunavik (Quebec): a cross-sectional study. *Environmental Health* 7., article 25.
- Foucher D. and Hintelmann H. (2006) High-precision measurement of mercury isotope ratios in sediments using cold-vapor generation multi-collector inductively coupled plasma mass spectrometry. *Anal. Bioanal. Chem.* 384, 1470– 1478.
- Foucher, D. Ogrinc, N, Hintelmann, H. (2009) Tracing Mercury Contamination from the Idrija Mining Region (Slovenia) to the Gulf of Trieste Using Hg Isotope Ratio Measurements. *Environmental Science and Technology* 43, 33-39.
- Gantner, N; Hintelmann, H; Zheng, W, et al. (2009). Variations in Stable Isotope Fractionation of Hg in Food Webs of Arctic Lakes. *Environ. Science and Technology* 43, 9148-9154.
- Ghosh S., Xu Y. F., Humayun M. and Odom L. (2008) Mass-independent fractionation of mercury isotopes in the environment. *Geochem. Geophys. Geosyst.* 9.
- Gehrke, G.E., Blum, J.D., Marvin-DiPasquale, M. (2010). Sources of mercury to San Francisco Bay surface sediment as revealed by mercury stable isotopes. *Geochimica et Cosmochimica Acta* 75, 691–705.
- Gehrke, G.E., Blum, J.D., Slotton, D.G., Greenfield, B.K. (2011). Mercury isotopes link mercury in San

- Francisco Bay forage fish to surface sediments. *Environ. Sci. Technol.*, dx.doi.org/10.1021/es103053y.
- Gobeil, C.; Macdonald, R.W.; Smith, J.N. (1999). Mercury profiles in sediments of the Arctic Ocean basins. *Environmental Science and Technology* 33, 4194-4198.
- Gobeil, C., Macdonald, R.W., Smith, J.N. and Beaudin, L. (2001). Atlantic water flow pathways revealed by lead contamination in Arctic basin sediments. *Science* 293, 1301-1304.
- Guelke, M. and Von Blanckenburg, F., 2007. Fractionation of stable iron isotopes in higher plants. *Environ. Sci. Technol.* 41, 1896-1901.
- Hare, A.; Stern, G. A.; Macdonald, R. W.; Kuzyk, Z. Z.; Wang, F. (2008). Contemporary and preindustrial mass budgets of mercury in the Hudson Bay marine system: The role of sediment recycling. *Sci. Total Environ.*, 406, 190–204.
- Hinkel, K. M., Eisner, W. R., Bockheim, J. G., Nelson, F. E., Peterson, K. M., and Dai, X. (2003). Spatial extent, age, and carbon stocks in drained thaw lake basins on the Barrow Peninsula, Alaska, Arct. *Antarct. Alp. Res.*, 35, 291–300.
- Huguet L., Castelle S., **Schäfer J., Blanc G.**, Maury-Brachet R., Reynouard C., **Jorand F.** (2010). Mercury methylation rates of biofilm and plankton microorganisms from a hydroelectric reservoir in French Guiana. *Science of the Total Environment*, 408, 1338 – 1348.
- Ikemoto T, Kunito T, Tanaka H, Baba N, Miyazaki N, Tanabe S. (2004) Detoxification mechanism of heavy metals in marine mammals and seabirds: interaction of selenium with mercury, silver, copper, zinc, and cadmium in liver. *Arch Environ Contam Toxicol.*;47(3):402-13.
- Johansen, P; Mulvad, G; Pedersen, HS, et al. (2007). Human accumulation of mercury in Greenland. *Science of the total environment* 377, 173-178.
- Johnson, T.M., (2004). A review of mass-dependent fractionation of selenium isotopes and implications for other heavy stable isotopes. *Chemical Geology* 204, 201–214.
- Johnson, T.M., Bullen, T.D., (2003). Selenium isotope fractionation during reduction by Fe(II)–Fe(III) hydroxide-sulfate (green rust). *Geochimica et Cosmochimica Acta* 67, 413–419.
- Johnson, T.M., Herbel, M.J., Bullen, T.D., Zawislanski, P.T., (1999). Selenium isotope ratios as indicators of selenium sources and oxyanion reduction. *Geochimica et Cosmochimica Acta* 63, 2775–2783.
- Jorand F.**, F. Zartarian, F. Thomas, J.-C. Block, J.Y. Bottero, G. Villemin, V. Urbain and J. Manem (1995) Chemical and structural (2D) linkage between bacteria within activated sludge flocs. *Wat. Res.*, **29**, 1639–1647.
- Kashulina, G; Reimann, C. (2001). Sulphur in the Arctic environment (2): results of multi-medium regional mapping. *Environmental Pollution* 116, 337-350.
- Kashulina, G; Reimann, C; Banks, D (2003) Sulphur in the Arctic environment (3): environmental impact. *Environmental Pollution* 124, 151-171.
- Khan MAK, Wang FY. (2009). Mercury-selenium compounds and their toxicological significance: towards a molecular understanding of mercury-selenium antagonism. *Environ Toxicol Chem* 28(8): 1567-1577.
- Kritee K., Blum J. D., Johnson M. W., Bergquist B. A. and Barkay T. (2007) Mercury stable isotope fractionation during reduction of Hg(II) to Hg(0) by mercury resistant microorganisms. *Environ. Sci. Tech.* 41, 1889–1895.
- Krznaric, E., Wevers, J. H. L., Cloquet, C., Vangronsveld, J., Vanhaecke, F., and Colpaert, J. V., Zn pollution counteracts Cd toxicity in metal-tolerant ectomycorrhizal fungi and their host plant, *Pinus sylvestris*. *Environ. Microbiol.* 12, 2133-2141.
- Landers, D.H., Ford, J., Gubala, C., Monetti, M., Lasorsa, B.K., Matinson, J., (1995). Mercury in vegetation and lake sediments from the U.S. Arctic. *Water, Air, and Soil Pollution* 80, 591-601.

- Laperriere, L., M. A. Fallu, S. Hausmann, **R. Pienitz**, and D. Muir. 2008. Paleolimnological evidence of mining and demographic impacts on Lac Dauriat, schefferville (subarctic Quebec, Canada). *Journal of Paleolimnology* 40: 309-324.
- Laurion I., Vincent W.F.**, MacIntyre S., Retamal L., Dupont C., Francus P., **Pienitz R.** (2010). Variability in greenhouse gas emissions from permafrost thaw ponds. *Limnol. Oceanograph.* 55, 115-33.
- Lemire M.**, Fillion M, Frenette B, Mayer A, Philibert A, Passos CJS, et al. (2010). Selenium and Mercury in the Brazilian Amazon: Opposing Influences on Age-Related Cataracts. *Environ Health Perspect* 118(11): 1584-1589.
- Lemire M.**, Proust F, Ferland A, Dery S, **Dewailly E.** (2010). Selenium – a key element in Nunavik traditional diet. ArcticNet Annual Scientific Meeting, Ottawa – Canada, Dec 14-17. (article in preparation)
- Lockhart, W.L., Stern, G.A., Wagemann, R., Hunt, R.V., Metner, D.A., Delaronde, J., Dunn, B., Stewart, R.E.A., Hyatt, C.K., Harwood, L., Mount, K., (2005). Concentrations and trends of mercury in tissues of beluga whales (*Delphinapterus leucas*) from the Canadian Arctic from 1981 to 2002. *Science of the Total Environment* 351-352, 391-412.
- Lofts, S., P. M. Chapman, R. Dwyer, M. J. McLaughlin, I. Schoeters, S. C. Sheppard, W. J. Adams, B. J. Alloway, P. M. C. Antunes, P. G. C. Campbell, B. Davies, F. Degryse, W. De Vries, K. J. Farley, R. G. Garrett, A. Green, B. J. Groenenberg, B. Hale, M. Harrass, W. H. Hendershot, A. Keller, R. Lanno, T. Liang, W. X. Liu, Y. B. Ma, C. Menzie, S. W. Moolenaar, W. Piatkiewicz, C. Reimann, J. S. Rieuwerts, R. C. Santore, S. Sauve, G. Schuetze, C. Schlegel, J. Skeaff, E. Smolders, S. Tao, J. Wilkins, and F. J. Zhao. 2007. Critical loads of metals and other trace elements to terrestrial environments. *Environmental Science & Technology* 41: 6326-6331.
- Lu, L.-L., S.-K. Tian, X.-E. Yang, X.-C. Wang, P. Brown, T.-Q. Li & Z.-L. He. (2008). Enhanced root-to-shoot translocation of cadmium in the hyperaccumulating ecotype of *Sedum alfredii*. *Journal of Experimental Botany*, 59, 3203-3213.
- Lu, L.-L., S.-k. Tian, X.-e. Yang, T.-q. Li & Z.-l. He. 2009. Cadmium uptake and xylem loading are active processes in the hyperaccumulator *Sedum alfredii*. *Journal of Plant Physiology*, 166, 579-587.
- Lucotte, M., A. Mucci, C. Hillaire-Marcel, P. Pichet, and A. Grondin. 1995. Anthropogenic Mercury Enrichment in Remote Lakes of Northern Quebec (Canada). *Water Air and Soil Pollution* 80: 467-476.
- Marin L, Lhomme J, **Carignan J.** (2003) GFAAS determination of selenium after separation with thiol cotton in lichens and plants: the importance of adding a mineral matrix before decomposition. *Talanta* 61, pp. 119-125.
- Michelutti, N., Simonetti, A., Briner, J.P., Funder, S., Creaser, R.A., Wolfe, A.P. (2009). Temporal trends of pollution Pb and other metals in east-central Baffin Island inferred from lake sediment geochemistry. *Science of the Total Environment* 407, 5653–5662.
- Montarges-Pelletier, E., Chardot, V., Echevarria, G., Michot, L. J., Bauer, A., and Morel, J. L., 2008. Identification of nickel chelators in three hyperaccumulating plants: An X-ray spectroscopic study. *Phytochemistry* 69, 1695-1709.
- Moynier, F., Pichat, S., Pons, M.-L., Fike, D., Balter, V., and Albarède, F., 2009. Isotopic fractionation and transport mechanisms of Zn in plants. *Chemical Geology* 267, 125-130.
- Muir, D.C.G., Wang, X., Yang, F., Nguyen, N., Jackson, T.A., Evans, M.S., Douglas, M., Köck, G., Lamoureux, S., **Pienitz, R.**, Smol, J.P., **Vincent, W.F.** & Dastooro, A. (2009). Spatial Trends and Historical Deposition of Mercury in Eastern and Northern Canada Inferred from Lake Sediment Cores. *Environmental Science & Technology* 43: 4802–4809.

- Monperrus, M., Krupp, E., **Amouroux, D.**, Donard, O.F.X., Rodriguez Martin-Doimeadios, R.C., (2004). Potential and limits of speciated isotope-dilution analysis for metrology and assessing environmental reactivity. *Trends in Analytical Chemistry* 23, 261-272
- O'Loughlin E.J., Kelly S.D., Kemner K.M., Csencsits R., Cook R.E. (2003). Reduction of AgI, AuIII, CuII, and HgII by FeII/FeIII hydroxysulfate green rust. *Chemosphere* 53, 437-446.
- Outridge, P.M., Sanei, H., Stern, G.A., Hamilton, P.B., Goodarzi, F., 2007. Evidence for control of mercury accumulation rates in Canadian high arctic lake sediments by variations of aquatic primary productivity. *Environmental Science and Technology* 41, 5259-5265.
- Outridge, P. M.; Stern, G. A.; Hamilton, P. B.; Percival, J. B.; McNeely, R.; Lockhart, W. L. (2005). Trace metal profiles in the varved sediment of an Arctic lake. *Geochim. Cosmochim. Acta*, 69, 4881-4894.
- Outridge, P. M.; Hobson, K. A.; Savelle, J. M. (2005b). Changes in mercury and cadmium concentrations and the feeding behaviour of beluga (*Delphinapterus leucas*) near Somerset Island, Canada, during the 20th Century. *Sci. Total Environ.*, 350, 106- 118.
- Outridge P. M., Hermanson M. H. and Lockhart W. L. (2002) Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. *Geochim. Cosmochim. Acta* 66, 3521–3531.
- Outridge, P.M., N. Rausch, J.B. Percival, W. Shotyk, R. McNeely (2011) Comparison of mercury and zinc profiles in peat and lake sediment archives with historical changes in emissions from the Flin Flon metal smelter, Manitoba, Canada. *Science of the Total Environment* 409, 548–563
- Pak KR, Bartha R. (1998). Mercury methylation and demethylation in anoxic lake sediments and by strictly anaerobic bacteria. *Appl Environ Microbiol* 64, 1013–7.
- Pal, T; Mukherjee, PK; Sengupta, S, et al. (2002) Arsenic pollution in groundwater of West Bengal, India - An insight into the problem by subsurface sediment analysis. *Gondwana Research* 5, 501-512.
- Pécheyran, C., **D. Amouroux**, O.F.X. Donard (1998); Field determination of volatile selenium species at ultra trace levels in environmental waters by on-line purging, cryofocusing and detection by atomic fluorescence spectroscopy. *Journal of Analytical Atomic Spectrometry*, 13, 615-621.
- Perriguet, J., **T. Sterckeman** & J.-L. Morel. (2008). Effect of rhizosphere and plant-related factors on the cadmium uptake by maize (*Zea mays* L.). *Environmental and Experimental Botany*, 63, 333-341.
- Pienitz, R.**, Doran, P.T., Lamoureux, F. (2008). Origin and geomorphology of lakes in the polar regions, p. 25–41. In W. F. Vincent and J. Laybourn-Parry [eds.], *Polar lakes and rivers—limnology of arctic and antarctic aquatic ecosystems*. Oxford Univ. Press.
- Pokrovsky, O. S., L. S. Shirokova, S. N. Kirpotin, S. Audry, J. Viers**, and B. Dupre (2010) Effect of permafrost thawing on the organic carbon and trace element colloidal speciation and microbial activity in thermokarst lakes of Western Siberia. *Biogeosciences Discuss.*, 7, 8041–8086.
- Ponce de Leon, Claudia A.; DeNicola, Katie; Bayon, Maria Montes, et al. (2003). Sequential extractions of selenium soils from Stewart Lake: Total selenium and speciation measurements with ICP-MS detection. *Journal of Environmental Monitoring* 5, 435-440.
- Redjala, T., **T. Sterckeman** & J.L. Morel. (2009). Cadmium uptake by roots: Contribution of apoplast and of high- and low-affinity membrane transport systems. *Environmental and Experimental Botany*, 67, 235-242.
- Redman A. D., Macalady D. L. and Ahmann D. (2002) Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* 36, 2889–2896.
- Reeves MA, Hoffmann PR. (2009). The human selenoproteome: recent insights into functions and regulation. *Cell Mol Life Sci* 66(15): 2457-2478.
- Reimann, C., D. Banks, and P. De Caritat. 2000. Impacts of airborne contamination on regional soil and water quality: The Kola Peninsula, Russia. *Environmental Science & Technology* 34: 2727-2732.

- Reimann, C., and P. De Caritat. 2000. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. *Environmental Science & Technology* 34: 5084-5091.
- Reimann, C., and P. De Caritat. 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. *Science of the Total Environment* 337: 91-107.
- Reimann, C., and R. G. Garrett. 2005. Geochemical background - concept and reality. *Science of the Total Environment* 350: 12-27.
- Rickard, D. and Morse, J.W. (2005) Acid Volatile Sulfide (AVS). *Marine Chemistry* 97, 141-197.
- Riordan, B., Verbyla, D., and McGuire, A. D. (2006). Shrinking ponds in subarctic Alaska based on 1950–2002 remotely sensed images, *J. Geophys. Res.*, 11, G04002, doi:10.1029/2005JG000150.
- Rosman, K. J. R., W. Chisholm, C. F. Boutron, J. P. Candelone, and S. Hong. (1994). Isotopic Evidence to Account for Changes in the Concentration of Lead in Greenland Snow between 1960 and 1988. *Geochimica Et Cosmochimica Acta* 58: 3265-3269.
- Rosman, K. J. R., W. Chisholm, C. F. Boutron, J. P. et al. (1993). Isotopic evidence for the source of lead in Greenland snows since the late 1960s. *Nature* 362, 333-335.
- Rouxel O, Ludden J.N., Carignan J., Marin L, Fouquet Y. (2002) Natural variations of Se isotopic composition determined by hydride generation multiple collector inductively coupled plasma mass spectrometry. *Geochim. Cosmochim. Acta.*, 66, 18, pp. 3191-3199.
- Salerno, GG; Burton, MR; Oppenheimer, C, et al. (2009). Three-years of SO₂ flux measurements of Mt. Etna using an automated UV scanner array: Comparison with conventional traverses and uncertainties in flux retrieval. *J. Volcanology and Geothermal Research* 183, 76-83.
- Sarret et al. (1998) Mechanisms of lichen resistance to metallic pollution. *Environmental Science & Technology* 32, 3325–3330.
- Schäfer J**, Castelle S, **Blanc G**, Dabrin A, Masson M, Lancelleur L, Bossy C. (2010). Mercury methylation in the sediments of a macrotidal estuary (Gironde Estuary, south-west France). *Estuar Coast Shelf Sci.* 90, 80–92.
- Schäfer, J.**, Castelle, S., **Blanc, G.**, Dabin, A., Masson, M., Lancelleur, L., Bossy, C. (2010). Mercury distribution and methylation potential in sediments of a highly turbid macrotidal estuary (Gironde, France). *Est. Coast. Shelf Sci.*, 90:80-90.
- Schiff, SL; Spoelstra, J; Semkin, RG, et al. (2005). Drought induced pulses of SO₄²⁻ from a Canadian shield wetland: use of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in SO₄²⁻ to determine sources of sulfur. *Applied Geochemistry* 20 Issue: 4, 691-700.
- Shirokova, L. S., Pokrovsky, O. S., Kirpotin, S. N.,** and Dupré, B.: Heterotrophic bacterioplankton in thawed lakes of northern part of Western Siberia controls the CO₂ flux to the atmosphere, *Int. J. Environ. Stud.*, Special Issue “Western Siberia”, 66(N4), 433–445, doi:10.1080/00207230902758071, 2009.
- Shirokova, L. S., Pokrovsky, O. S., Viers, J., Klimov, S. I., Moreva, O. Y., Zabelina, S. A., Vorobieva, T. Y.,** and Dupré, B. (2010). Diurnal variations of trace elements and heterotrophic bacterioplankton concentration in a small boreal lake of the White Sea Basin, *Ann. Limnol. Int. J. 10 Lim.*, 46, 67–75, doi:10.1051/limn/2010011.
- Shoty, W; Zheng, JC; Krachler, M, et al. (2005). Predominance of industrial Pb in recent snow (1994-2004) and ice (1842-1996) from Devon Island, Arctic Canada. *Geophys. Res. Letters* 32, Issue 21, article L21814.
- Simonetti, A., Gariépy, C., **Carignan, J.** (2000a) Pb and Sr isotopic evidence for sources of atmospheric heavy metals and their deposition budgets in northeastern North America. *Geochimica et Cosmochimica Acta* 64(20), pp. 3439-3452.

- Simonetti, A., Gariépy, C., **Carignan, J.** (2000b) Pb and Sr isotopic compositions of snowpack from Québec, Canada: inferences on the sources and deposition budgets of atmospheric heavy metals. *Geochimica et Cosmochimica Acta* 64(1), pp. 5-20.
- Smith, L. C., Y. Sheng, G. M. Macdonald, and L. D. Hinzman. 2005. Disappearing Arctic lakes. *Science* 308: 1429-1429.
- Smith C. N., Kesler S. E., Blum J. D. and Rytuba J. J. (2008) Isotope geochemistry of mercury in source rocks, mineral deposits and spring deposits of the California Coast Ranges, USA. *Earth Planet. Sci. Lett.* 269, 399–407.
- Smolders, E., 2001. Cadmium uptake by plants. *Int J Occup Med Environ Health* 14, 177-83.
- Sterckeman, T.**, F. Douay, D. Baize, H. Fourrier, N. Proix, C. Schwartz, and **J. Carignan**. 2006. Trace element distributions in soils developed in loess deposits from northern France. *European Journal of Soil Science* 57: 392-410.
- Sterckeman, T., Carignan, J.**, Srayeddin, I., Baize, D., **Cloquet, C.** (2009) Availability of soil cadmium using stable and radioactive isotope dilution. *Geoderma* 153, 372-378.
- Sturges, W. T., and L. A. Barrie. 1989. The Use of Stable Lead 206/207 Isotope Ratios and Elemental Composition to Discriminate the Origins of Lead in Aerosols at a Rural Site in Eastern Canada. *Atmospheric Environment* 23: 1645-1657.
- Telmer, K; Bonham-Carter, GF; Kliza, DA, et al. (2004). The atmospheric transport and deposition of smelter emissions: Evidence from the multi-element geochemistry of snow, Quebec, Canada. *Geochimica et Cosmochimica Acta* 68, 2961-2980.
- Tessier, E., D. Amouroux**, G. Abril, E. Lemaire, O.F.X. Donard (2002); Formation and volatilisation of alkyl-iodides and –selenides in macrotidal estuaries. *Biogeochemistry*, 59, 183-206.
- Tolu, J., Le Hécho, I., **Bueno, M.**, Thiry, Y., Potin-Gautier, M. (2011) Selenium speciation analysis at trace level in soils. *Anal. Chim. Acta*, 684, 126-133.
- Urban, N.R., Ernst, K. and Bernasconi, S. (1999) Addition of sulfur to organic matter during early diagenesis of lake sediments. *Geochimica et Cosmochimica Acta* 63, 837-853.
- Valera B, **Dewailly E**, Poirier P. (2009). Environmental Mercury Exposure and Blood Pressure Among Nunavik Inuit Adults. *Hypertension* 54(5): 981-986.
- Van Oostdam, J; Donaldson, SG; Feeley, M, et al. (2005). Human health implications of environmental contaminants in Arctic Canada: A review. *Science of the total environment* 351, SI 165-246.
- Vasyukova, E. V., **Pokrovsky, O. S., Viers, J.**, Oliva, P., Dupré, B., Martin, F., and Candaudap (2010). Trace elements in organic- and iron-rich surficial fluids of the boreal zone: assessing colloidal forms via dialysis and ultrafiltration, *Geochim. Cosmochim. Acta.*, 74, 449–468.
- Viers J.**, Oliva P., Sonke J., Nonell A., Freydier R., Gainville R., Dupré B., 2007. Evidence of Zn isotopic fractionation in a soil-plant-system of a pristine tropical watershed (Nsimi, south Cameroon). *Chem. Geol.* **239**, 124-137.
- Salonen, V.-P., Tuovinen, N., Valpola, S. (2006). History of mine drainage impact on Lake Orija rvi algal communities, SW Finland. *Journal of Paleolimnology* 35: 289–303.
- Weiss, DJ; Mason, TFD; Zhao, FJ, et al. (2005). Isotopic discrimination of zinc in higher plants. *New Phytologist* 165, 703-710.
- Weiss, DJ; Rausch, N; Mason, TFD, et al. (2007). Atmospheric deposition and isotope biogeochemistry of zinc in ombrotrophic peat. *Geochimica et Cosmochimica Acta* 71, 3498-3517.
- Wen, H., **Carignan, J.** (2007) Reviews on Atmospheric Selenium: Emissions, Speciation and Fate. *Atmospheric Environments* 41, 7151-7165.
- Williamson, C. E., J. E. Saros, W. F. Vincent, and J. P. Smol. 2009. Lakes and reservoirs as sentinels, integrators, and regulators of climate change. *Limnology and Oceanography* 54: 2273-2282.

- Yang DY, Ye X, Chen YW, Belzile N. (2010) Inverse relationships between selenium and mercury in tissues of young walleye (*Stizosedion vitreum*) from Canadian boreal lakes. *Sci Total Environ.*;408(7):1676-83.
- Zambardi T., Sonke J. E., Toutain J-P., Sortino F. and Shinohara H. (2008) Mercury emissions and stable isotopic compositions at Vulcano Island (Italy). *Earth Planet. Sci. Lett.* 277, 236–243.
- Zheng W., Foucher D. and Hintelmann H. (2007) Mercury isotope fractionation during volatilization of Hg(0) from solution into the gas phase. *J. Anal. At. Spectrom.* 22, 1097–1104.
- Zimov, S. A., Voropaev, Y. V., Semiletov, I. P., Davidov, S. P., Prosiannikov, S. F., Chapin III, F. S., Chapin, M. C., Trumbore, S., and Tyler, S. (1997) North Siberian lakes: a methane source fueled by Pleistocene carbon, *Science*, 277, 800–802.

Biographies / CV, resume

Partner 1 (Takuvik)

CARIGNAN, Jean

(coordinator of the project)

CNRS Research Engineer (IR HC), BAP B, Section 18, Takuvik (UMI 3376)

Formation and promotions

1992: PhD Univ. Québec à Montréal (UQAM), Centre de Recherche GEOTOP.

"Pb isotope geochemistry: crustal growth and metallogenesis"

1993-94: stage post-doctoral Univ. de Montréal et Carnegie Institution of Washington - DTM

1995: chercheur associé GEOTOP - UQAM et Université McGill.

1996: IR1 CNRS at CRPG. Head of the CNRS-INSU National Rock & Minerals Analytical Facility

2005: habilitation à co-encadrer localement des thèses, INPL

2006-2008: chargé d'enseignement (dispersion des métaux) à la faculté de Pharmacie, UHP.

2008: HDR - habilitation à diriger des recherches, INPL.

2010: IR HC CNRS.

Actual position (since January 2011)

Deputy director Takuvik (UMI 3376), a joint International Research Laboratory between CNRS and University Laval, Québec, Canada.

1996-2010

Head of the CNRS National Facility: Service national d'Analyse des Roches et des Minéraux (SARM –15 engineers & technicians; <http://www.crpq.cnrs-nancy.fr/SARM/index.html>).

Research interests

Development and applications of chemical and isotopic tracers (Pb, Zn, Cd, Se, Hg) to constrain cycles of metals of natural and anthropogenic origin in the rocks-soils-water-atmosphere-vegetation system.

Publications

- 63 articles in rank A international journals;

- citation index: 1151; H-index: 21 (from ISI Web of KnowledgeSM, January 2011)

- 5 selected publications since 2005:

- 1) **Carignan, J.**, Estrade, N., Sonke, J.E., Donard, O.F.X. (2009) Odd isotope deficits in atmospheric mercury measured in lichens. *Environ. Sci. Techn.* 43, 5660-5664.
- 2) Estrade, N., **Carignan, J.**, Sonke, J.E., Donard, O.F.X. (2009) Hg isotope fractionation during liquid vapor evaporation experiments. *Geochim. Cosmochim. Acta.* 73, 2693-2711. doi: 10.1016/j.gca.2009.01.024
- 3) **Carignan, J.**, Wen H. (2007) Scaling NIST SRM 3149 for Se isotope analysis and isotopic variations of natural samples. *Chemical Geology* 242, 347-350.
- 4) Wen, H., **Carignan, J.**, Qiu, Y., Liu S. (2006) Selenium speciation in kerogen from two Chinese selenium deposits: environmental implications. *Environ. Sci. Techn.* 40, 1126-1132.
- 5) Sterckeman, T., Douay, F., Baize, D., Fourrier, H., Proix, N., Schvartz, C., **Carignan, J.** (2006) Trace element distributions in soils developed in loess deposits from northern France. *European Journal of Soil Sciences* 57, 392-410.

Partner 2 (CRPG)

CLOQUET, Christophe

CNRS Research Engineer (IR HC), BAP B, Section 18, CRPG (UPR 2300)

34 ans

Cursus

2010 -	IR2 CNRS au CRPG-UPR2300
2007-2010	CDD CNRS au Centre de Recherches Pétrographiques et Géochimiques (CRPG-UPR 2300) de Vandoeuvre lès Nancy,
2006-2007	Post Doctorat au laboratoire de chimie analytique de Gand, Belgique.
2005-2006	Post Doctorat à l'université du Québec à Montréal (GEOTOP), Canada.
2005	Thèse de Doctorat en Géosciences à l'Institut National Polytechnique de Lorraine (INPL), spécialité géochimie,
2001	Master Géosciences, à l'INPL.
1999	Licence en science de la Terre, option volcanologie, à l'université Blaise Pascal de Clermont-Ferrand.

18 publications dans des revues internationales

citations: 271

H-index:9

Publications significatives

- 1) Christophe **Cloquet**, David De Muynck, Jonathan Signoret and Frank Vanhaecke (2009) - Urban/Peri-urban Aerosol Survey by Determination of the Concentration and Isotopic Composition of Pb Collected by Transplanted Lichen Hypogymnia Physodes. *Environmental Science & Technology*, 43, 623-629 - DOI: 10.1021/es801739p
- 2) Christophe **Cloquet**, Jean Carignan, Moritz F. Lehmann and Frank Vanhaecke (2008) - Variation in the isotopic composition of zinc in the environment and the use of zinc isotopes in Biogeosciences: a review. *Analytical and Bioanalytical Chemistry*. 390, 451-463 - DOI: 10.1007/s00216-007-1635-y
- 3) Christophe **Cloquet**, Jean Carignan, Guy Libourel (2006) - Isotopic composition of Zn and Pb atmospheric depositions in an urban/Peri-urban area of northeastern France. *Environmental Science & Technology*, 40, 6594-6600.
- 4) Christophe **Cloquet**, Jean Carignan, Guy Libourel, Thibault Sterckeman and Espérance Perdrix (2006) -Tracing source pollution in soils using cadmium and lead isotopes. *Environmental Science & Technology*, 40, 2525-2530.
- 5) Christophe **Cloquet**, Jean Carignan and Guy Libourel (2006) -Atmospheric pollutant dispersal around an urban area using trace metal concentrations and Pb isotopic compositions of epiphytic lichens. *Atmospheric environment*, 40, 574-587.

Partner 3 (GET)

CURICULUM VITAE :

Etat civil

Name : Jérôme VIERS

Date of birth : April, 18th 1971

Present position : Professor at the Université Paul Sabatier (Toulouse), leader of the « Environment Soil Erosion » team at the Laboratoire des Mécanismes de Transfert en Géologie (LMTG) – Observatoire Midi Pyrénées (OMP), France

Education

2008 : Professor (Université Paul Sabatier, Toulouse)

2008 : HDR (Université Paul Sabatier, Toulouse)

2000 : Maître de Conférences (Université Paul Sabatier, Toulouse)

1999 : Post-doctoral position (California Institute of Technology) (supervisor: G.J. Wasserburg)

1994-1998, PhD in environmental geochemistry (Université Paul Sabatier, Toulouse) ; PhD topic: Weathering processes and elements transfer in humid tropical environment

1993-1994 : Post Graduate Degree (Géosciences de l'environnement, Université d'Aix-Marseille, major de promotion). "*Water-rock interaction processes within a lateritic system, Goyoum, Cameroun.*" (supervisor: B. Dupré et M. Polvé)

Publications and Conferences

50 refereed publications in international journals,

47 participations to international conferences (abstracts published)

Citation Index 'ISI WEB OF KNOWLEDGE' = 744, H-index = 14

5 Selected articles

Viers J., Roddaz M., Filizola N., Guyot J-L., Sondag F., Brunet P., Zouiten C., Boucayrand C., 2008. Boaventura G.R., Nd and Sr isotopic compositions of suspended sediments from the Solimoes and Madeira Rivers, the two main tributaries of the Amazon River, during one year long hydrological cycle. *Earth Planet. Sc. Lett.* **274**, 511-523.

Poitrasson F., **Viers J.**, Martin F., Braun J-J., 2008. Limited influence of lateritisation process on iron isotopes : example of the lateritic soils from Nsimi, Cameroon. *Chem. Geol.* **253**, 54-63.

Viers J., Oliva P., Sonke J., Nonell A., Freydier R., Gainville R., Dupré B., 2007. Evidence of Zn isotopic fractionation in a soil-plant-system of a pristine tropical watershed (Nsimi, south Cameroon). *Chem. Geol.* **239**, 124-137.

Viers J., Barroux G., Pinelli M., Seyler P., Oliva P., Dupré B., Boaventura G., 2005. The influence of the Amazonian floodplain ecosystems on the trace element dynamics of the Amazon River mainstem (Brazil). *Sci. Total Environ.* **339**, 219-232.

Viers J. and Wasserburg G.J. Behavior of Sm and Nd in a lateritic soil profile. *Geochim. Cosmochim. Acta* **68(9)**, 2043-2054, 2004.

Surname : **POKROVSKY** Name : **Oleg S.**
 Born on **6th July 1972** in Moscow, Russia
Nationality : Russian, French resident
Position : Chargé de Recherche CR1 CNRS (permanent position)
Doctoral degree (PhD, Geochemistry) obtained on 16 december 1994 (Moscow State Univ.)
Habilitation (HDR) obtained on 19.10.2009 (University of Toulouse)

I – GRADUATE EXPERIENCE

December 1994 Doctoral thesis PhD (Geochemistry), equivalent to «Doctor of Philosophy in Geological-Mineralogical sciences »
1989-1994 Student, Faculty of Geology, Moscow State University (Russia)

II – PROFESSIONAL EXPERIENCE

1995-1996 Post Doc, Laboratory of f-elements, Florida State University (USA).
1997-1999 Post Doc, Laboratoire de Géochimie, UPS-CNRS, Toulouse (France)
1999-2002 Junior Researcher (CR2) in Laboratoire de Géochimie, UPS-CNRS, Toulouse
2002 – present CR1 in the LMTG, CNRS, UMR 5563 Toulouse

III – RESEARCH ACTIVITY

Articles published and in press (peer-reviewed international journals) : **80**
 Publications in Russian, English-translated journals : **30**
 Conference proceedings (abstracts published) : **~120**
 ISI Thomson Citation number: **~1360**; HI-factor: **21**

IV. TEACHING and TRAINING ACTIVITY :

Direction and co-direction of doctoral thesis (PhD): 5 theses completed, 6 theses in preparation
 Teaching at the Master level; supervision of Master projects (5 since 2000)

V. ADMINISTRATION OF RESEARCH :

Review of manuscripts in international journals (~30-35/year), organization of section at the International Conferences; Co-director of European Associated Laboratory « Environmental Geochemistry » LEAGE (2006-2013)

VI. SCIENTIFIC PROJECTS :

Since 2000, I participated in more than 40 national and international scientific projects and I coordinated more than 15 projects. Over last 10 years, I organized and conducted more than 20 field expeditions in various parts of Russian Arctic and Subarctic zone in the field of earth surface biogeochemistry

VII. SELECTED PUBLICATIONS :

- POKROVSKY O.S.** and **SCHOTT J.** (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology* **190**, 141-179.
- POKROVSKY O.S.**, **SCHOTT J.** and **DUPRE B.** (2006) Trace elements fractionation and transport in boreal streams and soil solutions of basaltic terrain, Central Siberia. *Geochim. Cosmochim. Acta* **70**, 3239-3260.
- POKROVSKY O.S.**, **VIERS J.**, **EMNOVA E.E.**, **KOMPANTSEVA E.I.**, **FREYDIER R.** (2008) Copper isotope fractionation during its adsorption on soil and aquatic bacteria and metal hydroxides: possible structural control. *Geochim. Cosmochim. Acta* **72**, 1742-1757.
- POKROVSKY O.S.**, **MARTINEZ R.**, **FEURTET-MAZEL A.**, **MORIN S.**, **M. BAUDRIMONT M.**, **DUONG T.**, **COSTE M.** (2010) Experimental study of cadmium interaction with periphytic biofilms. *Applied Geochemistry*, **25**, 418–427.
- POKROVSKY O.S.**, **VIERS J.**, **SHIROKOVA L.S.**, **SHEVCHENKO V.P.**, **FILIPOV A.S.**, **DUPRÉ B.** (2010) Dissolved, suspended, and colloidal fluxes of organic carbon, major and trace elements in Severnaya Dvina River and its tributary. *Chemical Geology*, **273**, 136–149. **Jérôme VIERS** -

Stéphane AUDRY - CURICULUM VITAE :

Name: Stéphane Audry

Date of birth: January 19th 1973

Present position: Physicien-Adjoint (CNAP) at the Laboratoire des Mécanismes et Transferts en Géologie (LMTG)–Observatoire Midi-Pyrénées (OMP), Toulouse (France)

Education

2005-06	Post-doctoral position (Limoges University)
2004-05	Post-doctoral position (Bordeaux 1 University)
1998-03	PhD in environmental biogeochemistry (University Bordeaux 1). <u>PhD thesis topic:</u> Geochemical statement of heavy metal transport in the polluted Lot-Garonne-Gironde fluvial system
1997/98	Post Graduate Degree (French DEA) “Oceanic and Coastal Environments and Paleoenvironments” passed with honours, top student (University Bordeaux 1, France)
1996/97	Master degree “Oceanic Environment Sciences” (University Bordeaux 1, France)
1995/96	Bachelor of Science in Geology passed with honours (University Bordeaux 1, France)
1992/95	French “DEUG” in Earth Sciences passed with honours (University Bordeaux 1, France)

Publications and Conferences

14 refereed publications

29 references in national and international conferences

Citation Index ‘ISI WEB OF KNOWLEDGE’ = 93

5 Selected articles

- 1) Sonke, J.E., Schäfer, J., Chmeleff, J., **Audry, S.**, Blanc, G., Dupré, B. (2010) Sedimentary mercury stable isotope records of atmospheric and riverine pollution from two major European heavy metal refineries. *Chem. Geol.* 279, 90-100.
- 2) **Audry, S.**, Grosbois, C., Bril H., Schäfer J., Kierczak J., Blanc G. (2010) Post-depositional redistribution of trace metals in reservoir sediments of a mining/smelting-impacted watershed (the Lot River, SW France). *Appl. Geochem.*, 25, 778–794.
- 3) Sivry, Y., Riotte, J., Sonke, J.E., **Audry, S.**, Schäfer, J., Viers, J., Blanc, G., Freydier, R. Dupré, B. (2008) Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters. The Riou Mort-Lot River system. *Chem. Geol.* 255, 295-304.
- 4) **Audry, S.**, Blanc, G., Schäfer, J., Guérin, F., Masson, M., Robert, S. (2007) Behavior and budget of Mn, Cd and Cu in a macrotidal estuary: The Gironde estuary (SW France). *Mar. Chem.* 107, 433–448.
- 5) **Audry, S.**, Blanc, G., Schäfer, J., Chaillou, G., Robert, S. (2006) Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, V) in the freshwater reaches of a macrotidal estuary. *Geochim. Cosmochim. Acta* 70, 2264-2282.

Dr. Anatoly S. Prokushkin

CURRICULUM VITAE

V.N. Sukachev Institute of Forest SB RAS, Akademgorodok, Krasnoyarsk 660036, Russia
Tel: +7(3912)494439, Fax: +7(3912)433686, E-mail: prokushkin@ksc.krasn.ru

Personal Information

Citizenship Russian Federation
Marital status married, 2 children
Date of birth July 1, 1972
Place of birth Pervomaysk, Ukraine
Title/Position Dr., Head of Laboratory of biogeochemical cycles in forest ecosystems, the V.N.Sukachev Institute of Forest SB RAS

Education

1999 PhD, plant physiology, Krasnoyarsk State University, Krasnoyarsk, Russia
1995 – 1997 MSc student of Central European University, Department of Environmental sciences and policy, Budapest, Hungary
1994 Diploma with honors, Department of Biology, Krasnoyarsk State University
1989-1994 Student of Biological Department of Krasnoyarsk State University, Krasnoyarsk, Russia.

Field of research

Plant ecology, forest ecosystem dynamics, biogeochemistry, carbon and nitrogen cycles in permafrost affected ecosystems

Professional experience

2008 Head of Laboratory of biogeochemical cycles in forest ecosystems, Institute of Forest SB RAS, Krasnoyarsk, Russia.
1997 – 2008 Assistant, Researcher and Senior Researcher, Institute of Forest SB RAS, Krasnoyarsk, Russia.
1994 – 1997 Research Assistant, Krasnoyarsk State University, Krasnoyarsk, Russia.

Teaching Experience

2000 – 2005 Assistant Professor, Krasnoyarsk State Agricultural University, Krasnoyarsk, Russia.
1994 – 1997 Teaching Assistant, Krasnoyarsk State University, Krasnoyarsk, Russia.

Prokushkin A.S., Kawahigashi M., Tokareva I.V. (2008) Global Warming and Dissolved Organic Carbon Release from Permafrost Soils. In “Permafrost Soils” (Ed. R. Margesin). Series: Soil Biology, Vol. 16, Springer-Verlag. __. 237-250. ISBN: 978-3-540-69370-3.

Prokushkin A.S., Tokareva I. V., Prokushkin S. G., Abaimov A. P. and Guggenberger G. (2008) Fluxes of dissolved organic matter in larch forests in the cryolithozone of Central Siberia. Russian Journal of Ecology, 2008, Vol. 39, No. 3, pp. 151–159.

Prokushkin A.S., Gleixner G., McDowell W.H., Ruehlow S., Schulze E.-D. (2007) Source- and substrate-specific export of dissolved organic matter from permafrost-dominated forested watershed in central Siberia. Global Biogeochemical Cycles, 21 (4): Art. No. GB4003.

Dr. Liudmila S. Shirokova

Institute of Ecological Problems of the North, Naberezhnaya Severnoi Dviny, 23, Arkhnagelsk, Russia
Tel: +7 8182 21 57 50, Fax: ++7 8182 28 76 36, E-mail: Lshirocova@yandex.ru

Personal Information

Citizenship Russian Federation
Marital status married
Date of birth February 9, 1980
Place of birth Arkhangelskaya region, Russia
Title/Position Institute of Ecological Problems of the North, Ural Branch of Russian Acad. of Science

Education

2007 PhD, lake microbiology, Ural Branch of Russian Academy of Science, Syktyvkar, Russia
2004 Master diploma in Biology, Pomorski University, Arkhnagelsk, Russia

Field of research

Lake ecology, microbiology, biogeochemistry, carbon biogeochemical cycle in boreal aquatic ecosystems

Professional experience

2007- 2010: Senior researcher, Laboratory of Freshwater Ecosystems,
Octobre 2007 – Décembre 2007 (3 mois) Post-rouge Université Paul Sabatier (LMTG, Toulouse)
April 2008 – May 2009 (5 months) Invited Associate Researcher at the Observatory Midi Pyrenees,
« Experimental modeling of relationship between trace metals and production/mineralization cycle in boreal lakes »
2004 – 2007 Teaching Assistant, Pomorski State University, Arkhangelsk, Russia.

Publications :

SHIROKOVA L.S., POKROVSKY O.S., KIRPOTIN S.N., DUPRÉ B. (2009) Heterotrophic bacterio-plankton in thawed lakes of northern part of Western Siberia controls the CO₂ flux to the atmosphere. *International Journal of Environmental Studies*, Special Issue "Western Siberia" **66**, N 4, 433-445. DOI: 10.1080/00207230902758071

POKROVSKY O.S., **SHIROKOVA L.S.**, BENEZETH P., SCHOTT J., GOLUBEV S.V. (2009) Effect of organic ligands and heterotrophic bacteria on wollastonite dissolution kinetics. *American Journal of Science*, **309**, 731-772, DOI: 10.2475/08.2009.05.

SHIROKOVA L.S., POKROVSKY O.S., VIERS J., KLIMOV S.I., MOREVA O.YU., ZABELINA S.A., VOROBIEVA T.YA., DUPRE B. (2010) Diurnal variations of trace elements and heterotrophic bacterioplankton concentration in a small boreal lake of the White Sea basin. *Ann. Limnol. - Int. J. Lim.* **46**, 67–75. DOI: 10.1051/limn/2010011.

GONZALEZ A., **SHIROKOVA L.S.**, POKROVSKY O.S., EMNOVA E.E., SANTANA-CASIANO J.M., GONZÁLEZ-DÁVILA M., POKROVSKY G.S. (2010) Adsorption of copper on *Pseudomonas aureofaciens*: protective role of surface exopolysaccharides. *J. Coll. Interface Sci.*, **350**, 305-314. doi.org/10.1016/j.jcis.2010.06.020

POKROVSKY O.S., **SHIROKOVA L.S.**, KIRPOTIN S.N., AUDRY S., VIERS J., DUPRE B. (2011) Effect of permafrost thawing on the organic carbon and metal speciation in thermokarst lakes of Western Siberia. *Biogeosciences*, Special issue *Siberian Arctic Land-Shelf-Atmosphere Interface*, In: *Biogeosciences Discuss.*, **7**, 8041–8086, 2010. doi:10.5194/bgd-7-8041-2010.

Partner 5 (LCPME)

Frédéric JORAND, 45 ans, Maître de conférences depuis 1998.

Affecté à la Faculté de Pharmacie, Université Henri Poincaré, Nancy 1 et au Laboratoire de Chimie Physique et Microbiologie pour l'Environnement, LCPME UMR 7564 CNRS- Nancy Université.

Biochimiste, Doctorat en Chimie et Microbiologie de l'Eau (1995, Université Nancy 1) sur le thème des agrégats microbiens dans les systèmes de traitements biologiques des eaux.

Titulaire de l'HDR (2008, Université Nancy 1) sur le thème de la bioréactivité des oxydes de fer (survie bactérienne et biominéralisation) et bénéficiaire de la PEDR (2006 – 2009) et PES (2010-2013).

Domaines de recherches actuels :

- Bio-réactivité des espèces du fer,
- Survie bactérienne en milieux oligotrophes,
- Caractérisation des surfaces bactériennes,
- Biofilms microbiens.

Direction et co-direction de 4 thèses d'Université, 10 DEA ou M2R et 2 directions de thèse en cours (soutenances prévues fin 2011-début 2012) concernant les biofilms de circuits de refroidissement et la biominéralisation d'oxydes mixtes FeII-FeIII par des bactéries ferriréductrices.

28 articles à comité de lecture, 35 communications orales dont 20 internationales.

Citations: 563; H-index: 10 (Isi web of knowledge, February 2011)

Participation au jury de 9 thèses (1 comme rapporteur, 4 comme examinateur, 4 comme co-encadrant).

Organisateur de 4 écoles thématiques CNRS sur les biofilms et les surfaces cellulaires.

Membre élu du Conseil de Laboratoire LCPME et du conseil de Faculté (Fac. Pharmacie).

Advisory expert for the Research Networking program « The Functionality of Iron Minerals in Environmental Processes (FIMIN) » (European Coordinator: S. Peiffer), ESF.

Reviewer for international journals (Environmental Science and Technology, Journal of Hazardous Materials, Geochimica Cosmochimica Acta, Water Research, ...).

Selection of 5 Main PAPERS in the last 5 years

- 1) Zegeye A., C. Ruby and **F. Jorand** (2007) Kinetic and thermodynamic analysis during dissimilatory g-FeOOH reduction: formation of green rust 1 and magnetite. *Geomicrobiol. J.* 24, 51 – 64. IF = 2,083.
- 2) **Jorand F.**, A. Zegeye, F. Landry and C. Ruby. Reduction of ferric green rust by *Shewanella putrefaciens* (2007) *Let. Appl. Microbiol.* 45, 515 – 21. IF = 1,440.
- 3) Zegeye A., Huguet L., Abdelmoula M., Carteret C., Mullet M. and **Jorand F.** (2007) Biogenic hydroxysulfate green rust, a potential electron acceptor for SRB activity. *Geochim. Cosmochim. Acta.* 71, 5450 – 62. IF = 3,897.
- 4) Zegeye A., Mustin C. and **Jorand F.** (2010) Bacterial and iron oxide aggregates mediate secondary iron mineral formation: green-rust vs magnetite. *Geobiology* 8, 209–22. IF = 3,596.
- 5) Huguet L., Castelle S., Schäfer J., Blanc G., Maury-Brachet R, Reynouard C., **Jorand F.** (2010) Mercury methylation rates of biofilm and plankton microorganisms from a hydroelectric reservoir in French Guiana. *Science of the Total Environment.* 408, 1338-48. IF = 2,579.

Partner 6 (EPOC)

Dr. Jörg SCHÄFER, 43 years, Professor University Bordeaux 1 (UMR CNRS 5805 EPOC).

PhD in Environmental Geochemistry (1998, University Karlsruhe, Germany),

Habilitation (HDR) in Environmental Biogeochemistry, (2006, University Bordeaux 1, France)

Research interests in trace metal/metalloid geochemistry in aquatic systems: sources, speciation, reactivity, fluxes, bioaccumulation, biotransformation. Coordinator of the project EEL-scope: «Eco-toxicological and Economical Liability of eel exposed to Seasonal and global Change-induced O₂ - depletion and Pollution in Estuaries» (ANR Vulnérabilité, Milieux et Climat, 2008-2010). Co-leader of research projects OR3 et OR4 of P2 GIS-ECOBAG programme; co-leader of several industrial collaborative projects (e.g. SCP-Science, Thermo-Fisher, Suez); leader, co-leader or participant of regional, national and international public research projects: Région Aquitaine, Programme ECOBAG, Agence de l'Eau Adour Garonne LITEAU, ACI-ECCO, EC2CO, CPER (FNS), FEDER, ANR VMC, ANR CES, ANR International, GAGILAU (France – Québec).

50 publications (1 invited) in peer-reviewed journals, books, **7 publications (1 invited)** in journals without peer-review, **122 contributions** to international conferences; **35 invited conferences** (programme restitutions, workshops, seminars, etc.); **32 scientific/technical reports; h-index = 18**

5 selected publications:

- 1) **SCHÄFER J.**, CASTELLE S., BLANC G., DABRIN A., MASSON M., LANCELEUR, L., BOSSY C. (2010). Mercury distribution and methylation potential in sediments of a highly turbid macrotidal estuary (Gironde, France). *Estuarine Coastal and Shelf Science*, 90:80-90.
- 2) Huguet L., Castelle S., **Schäfer J.**, Blanc G., Maury-Brachet R., Reynouard C., Jorand F. (2010). Mercury methylation rates of biofilm and plankton microorganisms from a hydroelectric reservoir in French Guiana. *Science of the Total Environment*, 408, 1338-1348.
- 3) Sonke J.E., **Schäfer J.**, Chmeleff J., Audry S., Blanc G., Dupre B. (2010). Sedimentary mercury stable isotope records of atmospheric and riverine pollution from two European heavy metal refineries. *Chemical Geology*, 279:90-100
- 4) Castelle S, **Schäfer J.**, Blanc G., Dabrin A, Lancelleur L., Masson M. (2009). Seasonal variability of gaseous mercury at the air-water interface of a highly turbid estuary (Gironde Estuary, France). *Marine Chemistry*, 117:42-51.
- 5) **Schäfer J.**, Blanc G., Audry S, Cossa D, Bossy C. (2006) Mercury in the Lot-Garonne River system (France): Sources, fluxes and anthropogenic component. *Applied Geochemistry* 21:515-527.

Supervision: 10 PhD theses (7 finished, 3 ongoing), **6 post-docs**, **22 Master II** and **17 Master I** students; **31 student fellows** (e.g. ERASMUS, IUP, international, etc.)

Distinction for Environmental Research (Umweltpreis) by Sparkasse Karlsruhe (May 1999)

Responsible of Bachelor (1st year) and (Master 1) teaching units, University Bordeaux 1

Member of the pedagogic working groups Socrates/Erasmus and European Master MER

Evaluation of national and regional research programmes (ACI-ECCO, ACI « Jeunes Chercheurs », Région Rhône-Alpes)

Reviewer for 15 different peer-reviewed journals, 2 book projects (Wiley-Blackwell)

Member of the Editorial Board: “Environmental Science and Pollution Research” -ESPR

Scientific leader of 14 oceanographic sampling campaigns,

Member of the French National Commission for the Coastal Research vessels

Member of the Scientific Committee: ‘International Estuarine Biogeochemistry Symposium’ series

Chairman International Estuarine Biogeochemistry Symposium (sessions in 2006, 2008, 2011)

Co-organiser RST 2010, session: Metal Geochemistry and Pollution, nov. 2010, Bordeaux, France

7.2. IMPLICATION DES PERSONNES DANS D'AUTRES CONTRATS / INVOLVEMENT OF PROJECT PARTNERS INTO OTHER GRANTS, CONTRACTS, ETC ...

(Un tableau par partenaire)

Cf. § 5.3.

Mentionner ici les projets en cours de réalisation soit au sein de programmes de l'ANR, soit auprès d'organismes, de fondations, à l'Union Européenne, etc. que ce soit comme coordinateur ou comme partenaire. Pour chacun, donner le nom de l'appel à projets, le titre du projet et le nom du coordinateur.

Part.	Nom de la personne participant au projet / name	Personne . Mois / PM	Intitulé de l'appel à projets, source de financement, montant attribué / Project name, financing institution, grant budget	Titre du projet : Project title	Nom du coordinateur / coordinator name	Date début & Date fin / Start and end dates
N° 1	Jean Carignan	8	GNR FORPRO II 26 k€	Se isotopes and redox tracing	J. Carignan	2009-2010
N°1	Jean Carignan	16	INSU EC2CO 30 k€	BIOMELI metals in lichens	J. Carignan	2009-2010
N°1	Jean Carignan	4	ANR JC 230 k€	MERCY Hg isotopes cycle	J. SONKE	2009-2012
N°1	Jean Carignan	12	INSU LEFE-EVE 35 k€	Pb-Sr-Nd in Fram Strait sediments	L. Reisberg	2009-2011
N°1	Jean Carignan	16	ADEME-Haganis 141 k€	atmospheric Hg-Pb in an urban area	Jean Carignan	2008-2010
N°2	Christian France-Lanord	30	ANR Blanc	CALIMERO	J. Lavé	2009-2013
N°3	O.S. Pokrovsky	10	ANR Contaminants, Ecosystems, Santé	RESUST REcovery assessment of a metal impacted fluvial SYSTEM after remediation of an industrial site	A. Feurtet-Mazel	2009-2011
N°3	O.S. Pokrovsky	10	ANR Captage et stockage du CO2	CO2-FIX In-situ CO2[bio]-mineralization	P. Benezeth	2009-2011

				: a combined experimental and numerical approach		
N°3	O.S Pokrovsky	8	EC2CO Cytrix	PERMAFROS T Erosion et migration des éléments en trace et du carbone organique en contexte de pergélisols : étude de bassins versants sibériens	S. Derenne	2011-2011
N°3	S. Audry	4	EDF	EPONGES Emission et production de gaz à effet de serre	D. Serça, F. Guérin	2009-2011
N°3	S. Audry	4	EC2CO Cytrix	FERANT Les isotopes du fer comme nouvel indicateur de la pression anthropique	F. Poitrasson	2009-2010
N°3	J. Viers	2	EC2CO Cytrix	FERANT Les isotopes du fer comme nouvel indicateur de la pression anthropique	F. Poitrasson	2009-2010
N°3	J. Viers	2	EC2CO Cytrix	PERMAFROS T Erosion et migration des éléments en trace et du carbone organique en contexte de pergélisols : étude de bassins versants sibériens	S. Derenne	2010-2010

N°4	D. AMOUROUX	9.6	ANR CES	RIPOST	P. GONZALEZ	2009-2013
N°4	D. AMOUROUX	9	ANR BLANC	CHIVAS	L. CHAUVAUD	2009-2012
N°4	D. AMOUROUX	9	ANR CES	IDEA	M. MONPERRUS	2008-2011
N°4	D. AMOUROUX	2.4	INSU EC2CO	COMIBOL	D. POINT	2009-2011
N°4	D. AMOUROUX	1.8	ANR JC	MERCY	J. SONKE	2009-2012
N°4	E. TESSIER	3.6	INSU EC2CO	COMIBOL	D. POINT	2009-2011
N°4	E. TESSIER	3.6	INSU EC2CO	PANTANAL	C. BARBIERO	2009-2011
N°4	R. GUYONNEAUD	2.4	INSU EC2CO	COMIBOL	D. POINT	2009-2011
N°4	R. GUYONNEAUD	4.5	ANR CES	IDEA	M. MONPERRUS	2008-2011
N°4	M. BUENO	3.6	INSU EC2CO	PANTANAL	C. BARBIERO	2009-2011
N°5	Frédéric Jorand	12	ANR Blanc 2010, 84 k€ / 450 k€	MOBIOPOR	Fabrice Golfier (LAEGO)	2011-2014
N°5	Frédéric Jorand	8	Convention d'étude (Circuits de refroidissement), EDF R&D-LNHE, 45 k€	Biofilms et amibes	Frédéric Jorand	2009-2011
N°5	Frédéric Jorand	8	ICEEL 10 k€ / 155 k€	HYDROGEN	Michel Panfilov (LEMETA)	2011-2013
N°5	Frédéric Jorand	1,2	ACI-INSU- INTERRVIE / 7,5 k€	Etude par microscopie électrochimique (SECM) de l'altération minérale des systèmes bactéries-silicates	P. Billard/S. Desobry (LIMOS)	2011
N°6	J. Schäfer G. Blanc C. Bossy	22 9 9.6	ANR Vulnérabilité Milieux et Climats (270 K€ ; 48 months)	Eco-toxicological and Economical Liability of eel exposed to	J. SCHÄFER	01/2008-12/2011

				seasonal and global Change-induced O2-depletion and Pollution in Estuaries: Eel-Scope		
N°6	J. Schäfer G. Blanc C. Bossy	5.4 1.8 3.6	ANR CES (45 k€ ; 36 months)	Récupération d'un SYSTème fluvial pollué par les métaux (Cd, Zn) après remédiation d'un site industriel RE-SYST	A. Feurtet-Mazel	10/2009-10/2011
N°6	G. Blanc J. Schäfer C. Bossy L. Dutruch	6 10 8 6	Région Aquitaine GAGILAU (100k€ ; 24 months)	PERIMETRE Pratiques domestiques, perception, présence, transferts et devenir d'Argent comme contaminant métallique émergent parmi d'autres métaux urbains rejetés dans les fleuves et estuaires	J. SCHÄFER	04/2010-04/2013

7.3. LETTERS OF SUPPORT



**UNIVERSITÉ
LAVAL**

CEN : Centre d'études nordiques
Centre for Northern Studies

8 February, 2011

Dr. Jean Carignan
Directeur adjoint
Takuvik Unité Mixte Internationale, CNRS/ULaval
Centre d'études nordiques (CEN)
Université Laval
Québec QC G1V 0A6
Canada

Dear Jean,

This letter is to express our full support and collaboration at CEN in your project entitled “**Arctic metals**” on the fate of metals in the arctic environments and the implications for ecosystem and human system exposure in the circumpolar North.

This project is important and timely. It is of great interest to us and is well integrated with our research themes at CEN, notably our work on permafrost geosystems and ecosystems, and our research axis: evaluation of georisks and ecological risks in the northern environment.

We are delighted to welcome you to work here at Centre d'études nordiques (CEN), within the framework of the joint research unit (UMI) Takuvik, between Université Laval (Canada) and CNRS (France). As a full member of CEN, you will have access to all of our facilities, and in particular to our network of eight Arctic field stations and >70 automated climate stations.

We look forward to collaborating with you on this important project.

Yours sincerely

Warwick F Vincent, PhD, FRSC
Director, Centre for Northern Studies (CEN)
Canada Research Chair in Aquatic Ecosystem Studies

Centre d'études nordiques
(CEN : Centre for Northern Studies)
Québec (Québec)
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Государственное образовательное учреждение
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ИНН 7018012970

03.02.2012 № 98

на № _____ от _____

Letter for supporting the CNRS project Arctic Metals

Dear members of ANR committee,

The project Arctic Metals proposed by many CNRS Laboratory is in total agreement to our own research here in Siberia. Studying the fate of trace elements in wetlands, in particular thermokarst lakes, is critical for our understanding of general biogeochemical cycles of metals. Russia is an important producer of metals and, unfortunately, some may be dispersed in the environment. The Arctic Metals project proposes new approaches to evaluate the contributions of anthropogenic metals to ecosystems in order to document their interactions with organic matter and living organisms. This is an important knowledge for both the scientific community and populations living in these area.

We are working for a number of years with CNRS teams and our collaboration is very successful, by forming students and post-docs and by publishing scientific articles in internationally recognize journals. We will be proud to continue this collaboration with the Arctic Metals project, by providing field facilities and infrastructures as well as our expertise in the field biogeochemistry of wetlands in Siberia.

Best regards,

Vice Rector for International Affairs,
National Research Tomsk State University,
Professor



[Handwritten signature]

Sergey Kirpotin