ASSIMILATION PATTERNS OF GEOCHEMICAL TRACERS AND METAL ACCUMULATION IN BOREAL TREE SPECIES IN THE AREA OF THE HORNE SMELTER (ROUYN-NORANDA)

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In addition to naturally occurring metals, large quantities of airborne, heavy and potentially toxic metals are deposited on the Canadian boreal forest every year, especially in regions surrounding point sources of pollutants such as smelters. Therefore relevant questions for populations living close to these point sources can be raised: How much of these metals are accumulated in the environment? How much metals does a standing forest contain? How much will return to the forest soils? What processes are involved? A dendrogeochemical approach, combining stable isotope, nutrient and heavy metal analyses in tree-rings, was applied in the Rouyn-Noranda region in order to distinguish between natural and anthropogenic accumulation of metals in the surrounding environment and to evaluate the impacts of this copper smelter on the boreal forest ecosystem. At proximal site, the abrupt change of +4 permil in carbon isotope ratios right at the smelter onset reflects a reduction of the photosynthetic rate by about 30% (Savard *et al*. 2004) caused by SO_2 emissions. The spatio-temporal investigation of metals in tree rings has also shown that at least a part of metals emitted by the smelter are accumulated in tree rings, usually after a delay of ca 15 years. As an example, concentrations of Cd range between 0.02 to 1.05 ppm for contaminated sites in the wide Rouyn-Noranda region, while they vary from 0.01 and 0.03 ppm for our control site in the Hudson Bay region.

In order to have an integrated view of physiological processes involved in the accumulation of geochemical tracers in tree rings at a specific level along tree stem, we have analysed the isotopic and elemental distribution in different spruce tree compartments. We have established that the difference of carbon isotope ratios ($\delta^{13}C$) in cellulose of black spruce leaves and rings is -3 permil. Nutrient behaviour is inversely linked to carbon isotope assimilation and is characterized by much higher calcium concentrations in leaves (6000 ppm) than in ring wood (800 ppm), whereas heavy metals such as cadmium show similar concentrations in leaves and ring wood (0.35 ppm). Results also show that heavy metal and nutrient concentrations vary along the stem in response to distinct assimilation processes. For instance, lead concentration gradually decrease from 0.27 ppm at ground level to 0.01 ppm at the apex. The carbon assimilation pattern reflects a Rayleigh process indicating the allocation priority for this element in spruce trees.

What do these anthropogenic metals accumulated in different tree compartments represent at the scale of the forest? We have developed appropriate techniques to evaluate the total metal content in woody tissues for the four most important boreal species (*Picea mariana, Abies balsamea, Populus tremuloides* and *Betula papyrifera*) and focussing on two boreal forest sites exposed to contrasting levels of airborne pollutants in the Rouyn region. This quantitative assessment is the first step in the evaluation of the long term return of metals in woody tissues to soils and contributes to the global understanding of metal biogeochemical cycles in the boreal ecosystem. Metal content for single trees is calculated using wood biomass and metal concentrations for different part of tree structure. Demographic data for boreal populations provided by provincial forest services were then used to extend the total metal content to a given surface unit. Results show that broad leaves species (Aspen and Birch) are particularly efficient at absorbing and accumulating metals in their woody tissues. Their metal content at the most contaminated site can reach levels ten times higher than what it is found in conifers. When combining all investigated species at a proximal site, 9 km from the smelter, the potentially toxic metal load (Pb + Cd) exceeds 20 kg / km^2; this level is 13 times higher than what was found at a distant site, 115 km away from the smelter.

The role of bacteria in the mobilization of arsenic from mine impacted sediments.

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Balmer Lake has been a repository for mining-related discharges of two adjacent gold mining operations since 1965. Under stratifying conditions, levels of dissolved As within the water column often become high (~550-650 μg/L). Florin Lake, located several kilometers southwest of Balmer Lake, also has a history of receiving mining-related discharges. None have occurred for decades, however, and no recent problems with elevated levels of dissolved arsenic have been documented. Sediment cores from both lakes were analyzed over 5cm intervals to determine metal(loid) abundance and total bacterial numbers. The diversity of Eubacteria, as well as relevant metal-respiring taxa were determined by denaturing gradient gel electrophoresis of PCR fragments amplified from ribosomal and arsenate reductase genes. Finally, two As-respiring bacteria have been isolated from Balmer Lake. Their ability to transform arsenic has been characterized, and their phylogenetic affiliations determined with respect to their 16S rRNA gene sequences. We present a model based upon the activity of native bacterial populations that helps to explain the seasonal release of soluble As from Balmer Lake sediments.

Redistribution of metals in lake sediments by bacterially mediated oxidation-reduction reactions

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Our overall project objective is to infer the role of microbial activity on the distribution (or redistribution) of metals in lake sediments through simulation experiments. The implications of this work are significant for the interpretation of metal profiles in fresh water sediments as historical records of anthropogenic metal loading. The simulation experiments are novel in design and experimentally test the hypothesis that bacterially mediated redox reactions redistribute metals within the sediment column under natural conditions. A series of microcosm experiments were set up in November 2001 to study the key hypotheses in our lake sediment study based on fresh sediment samples taken by divers in September 2001. The experiments consisted of 10-cm diameter core tubes containing a 1-cm layer of amended sediment, which was then covered with 6 cm of unamended sediment and 4 cm of overlying lake water. The test parameters consisted of four treatments, two temperatures (room temperature and 6^{o}C) and two sampling times. The treatments were 1) one set of cores was unamended, 2) one was amended with ferrihydrite, 3) one with an organic carbon source (Casamino acids), and 4) one set with both organic matter and ferrihydrite. The room temperature cores containing organic matter (and organic matter plus ferrihydrite) reacted very quickly and strong fermentative activity (gas production) was observed. The gas production interfered with the integrity of the cores; therefore the room temperature cores containing organic matter were not sampled. The cores incubated at 6^{o}C were sampled over a time series, once in January 2002 and also in October 2002. The room temperature columns were sampled in January 2002 and also in August 2002. Preliminary results indicated that elevated concentrations of soluble iron in the porewater fraction are observed throughout most of the sediment column when ferrihydrite was added. Also increased concentrations of solid phase iron were observed in the two cm of sediments above the ferrihydrite-amended layer. Additional experiments will be done in order to determine if the effect is due to mobilization and redeposition of iron or to an artifact of the sampling procedure. The addition of organic matter had no effect on either the microbiology or the chemistry of the microcosms, which supports the view that electron acceptors, rather than electron donors, are limiting in these particular sediments in which organic matter is abundant. Although the experiments using unlabelled ferrihydrite have been completed, new experiments have been initiated with ^{57}Fe-labelled ferrihydrite, which will continue with time series sampling through to the spring of 2005. Currently, metal profiles are taken to represent historic loadings, but if experimental evidence shows that microbial activity influences the sediment metal profile, as is theoretically possible, then this will have to be considered in the ERA process. The results will also provide information towards predictive ERA in terms of the kinetics of metal deposition and burial as well as potential changes in bioavailability. As such, the data may be most useful in the hazard identification, exposure and effects assessments portions of ERA both on local as well as larger scale approaches.