MERCURY AND METHYL MERCURY WITHIN THE TUNDRA SNOWPACKS AT KUUJJUARAPIK, QUÉBEC (CANADA)

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1. Introduction

Early after the polar sunrise, BrO radicals are formed in the northern atmosphere when the photolysis of bromide or dibromomethane occurs in presence of ozone (O_3). These BrO react with atmospheric Hg^0, generating Hg^{+1} and Hg^{2+} species which are rapidly deposited onto snow surface. Atmospheric Hg^0 and O_3 concentrations are then reduced below 1 ng m^{-3} and 10 ppbv respectively. These so-known mercury depletion events (MDEs) should represent a potential contamination for northern ecosystems.

The aim of this study is to improve knowledge about the Hg biogeochemical cycle in sub-arctic ecosystems (Tundra of the Hudson Bay) and determine the possible impacts of MDEs for local communities. These works combine (1) a **chemical approach**, to measure ozone (O_3) and total gaseous mercury (TGM) air concentrations in addition to total mercury (THg) and methyl mercury (MeHg) snow concentrations and (2) a **microbiological approach** to study snow microbial populations.

Two field campaign were conducted at Whapmagoostui-Kuujjuarapik. The first investigation was done in March 2004, to investigate the impact of cold weathers and MDEs for THg and MeHg snow concentrations. The second field works were done in April 2005 in order to follow THg and MeHg snow concentrations during snowmelt.

2. Methods

2.1 Site description. Whapmagoostui-Kuujjuarapik (55˚N, 78˚O), is a village of 15.3 km^2 located on the east coast of Hudson Bay at the mouth of the Great Whale River (Figure 1). A research station (Centre d'Études Nordiques; CEN de l'Université Laval) is available year-round and provides some laboratory facilities for scientists. Atmospheric TGM and O_3 concentrations are measured continuously since 1999 by Poissant.

2.2 Sampling strategy

In March 2004, surface snow samples (10 cm) were collected three times a day near the CEN (Figure 1) in order to study the THg and MeHg diurnal cycle. A spatial distribution for THg and MeHg have also be conducted. Snow samples were collected at 4 different sites (S1, S2, S3 and CEN). In April 2005, surface snow (10 cm) and snowmelt water samples were collected over a three weeks period at three different stations (CEN, RIV and BH; see Figure 1). Analyses for THg, MeHg and microbiology were realized. Snow samples were also collected for sulphate (SO_4^{2-}), Cl^- and pH analyses for both field campaign.

2.3. THg and MeHg. THg in surface snow was measured at Environment Canada (Montréal, Canada) using preconcentration of Hg^0 on a gold trap followed by its detection using atomic fluorescence. The sample was prepared by dissociating Hg complexes with BrCl and reducing Hg^{2+} to Hg^0 with $SnCl_2$. A detection limit of 54 pg L^{-1} (3 times the standard deviation) was achieved. MeHg in snow was quantified by using gas chromatograph-atomic fluorescence spectrometry following a solid-phase extraction on sulfide columns and an acidic-potassium bromide elusion (Cai *et al.*,1996). Calibration standards, blanks and MeHg spikes were analyzed with each batch of samples. Recoveries were similar to that found by other researchers and averaged 82% with blank samples containing no detectable MeHg. The detection limit for MeHg was found to be less than 20 pg L^{-1}.

2.4. Bacteria isolation. Snowmelt was filtered on 0.22 µm filters. Retrieved microorganisms and debris were then suspended into 10 ml of sterile snowmelt. This suspension was inoculated into 4 different bacterial growth media: R2A and TCA agars for total heterotrophic counts and Postgate C and E media (Postgate, 1984) for sulphate-reducing bacteria (SRB). Incubations were done at 4 and 20°C.

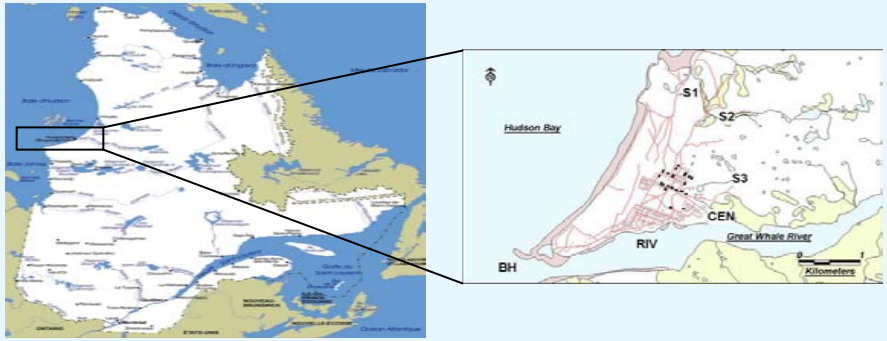

Figure 1. Location of Whapmagoostui-Kuujjuarapik (Québec, Canada). The different sampling stations (S1, S2, S3, CEN, RIV and BH) are identified.

3. Results

3.1 Hg fate in early spring: influence of MDEs

Two MDEs were observed during the March 2004 field campaign (Figure 2A). THg snow concentrations increased from 5 to 15 ng L^{-1} following MDEs (Figure 2B). Snow THg levels were quickly reduced to 2-6 ng L^{-1} after MDEs episodes; over an 11.5 h period, 78% of the THg was lost from the snow (Figure 2B). Photooxidation of $Hg^{2+} \rightarrow Hg^0$ was probably responsible for this THg lost, as snow and air temperature were below the freezing point and high solar radiations were observed (data not shown).

MeHg snow concentrations were not correlated with THg. As MeHg snow concentrations were significantly correlated with Cl^- and SO_4^{2-}, an atmospheric input was suspected. NOAA back trajectories showed that MeHg peaks were associated with air masses from the northern Hudson Bay. Overall, MeHg concentrations was similar at 4 different sampling sites. These results agreed well with St.Louis *et al.* (2005) and Lahoutifard *et al.* (in press).

At the exception of the MDE observed on March 16th, the MeHg concentrations in the samples collected at 8h30 were significantly lower than the concentrations measured in the previous evening. Therefore, unknown reactions should be responsible for nighttimes demethylation activities.

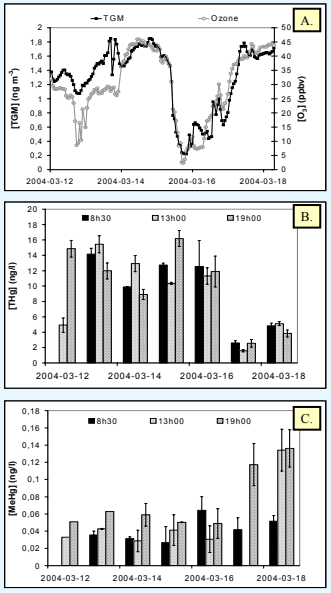

Figure 2. Time series for (A) TGM and O_3 air concentrations, (B) THg snow concentrations and (C) MeHg snow concentrations over a 6 days period at the CEN in March 2004.

3.2. MeHg fate in late spring: influence of microorganisms

A sampling campaign conducted in late spring (April 2005) allowed us to observe that snowfall was not the major contributor for MeHg and THg input into the snowpack (Figure 3A). THg and MeHg snow concentrations increased with time (Figure 3A). Snow sublimation may be responsible for this trend, but the significant relationship observed between MeHg snow concentrations and total heterotrophic counts (Figure 3B) suggests the importance of microorganisms for MeHg production in snow. SRB were also isolated in snow samples (700 UFC L^{-1}). However, their occurrence was not significantly correlated with snow MeHg concentrations.

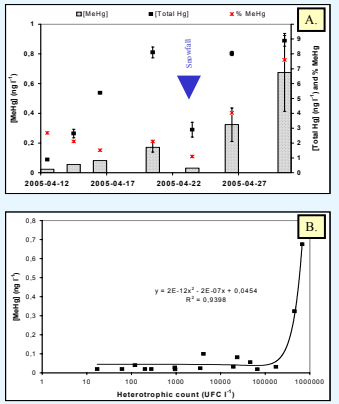

Figure 3. (A) Time series for snow THg and MeHg concentrations measured at the CEN in April 2005. (B) Relationship between snow MeHg concentrations and total heterotrophic counts.

4. Perspectives

Further works are in progress to study the methylation/demethylation activity of the heterotrophic bacteria isolated form the snow samples. These microorganisms will be characterized and molecular biology techniques will be useful to study the microbial populations from the snow samples collected during the 2005 field campaign.

The exact mechanisms responsible for nighttimes demethylation activities observed in March 2004 will need a special attention in our future investigations.

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