

Name of research institute or organization:

Labor für Radio- und Umweltchemie der Universität Bern und des Paul Scherrer Instituts

Title of project:

Mercury behaviour in the seasonal snow cover
VIVALDI (Variability in Ice, Vegetation, and Lake Deposits — Integrated), within the frame of NCCR Climate

Project leader and team:

PD Dr. Margit Schwikowski
Sarah M. Biner
Manuel Schläppi
Leonhard Tobler
Michael Sigl

Project description:

Mercury (Hg) exists in different forms in our environment and has a very complex geochemistry, summarized in the Hg cycle. Emission sources can be natural (e.g. soils, forests, volcanoes, lakes and open oceans) and anthropogenic (emissions from fossil fuel combustion, waste incineration and mining). Hg is highly toxic and can easily enter the food chain. Elemental Hg has a long residence time in the atmosphere and is globally distributed. The deposition back to the ground is just a matter of time. In order to estimate anthropogenic and natural emission sources in the past, natural archives such as glacier ice cores can be used. However, in the case of Hg, it is not clear if it is fully preserved in snow and ice. Schuster et al. (2002) reported a Hg profile from the Upper Fremont Glacier. The continuity of the Hg profile and the presence of various concentration peaks attributed to volcanic eruptions and anthropogenic activities were interpreted as an indication that Hg is preserved in ice. Another study from Lalonde et al. (2002) presented results that Hg is highly labile in snowpacks and could be rapidly reduced and re-emitted. The aim of this study was therefore to investigate Hg preservation in the seasonal snow cover at the high-alpine research station Jungfrauoch (3450 m a.s.l.).

Snow pit samples and firn cores were collected at the Jungfrauoch in March, April, and June 2007. In addition, surface snow was sampled in August 2007 (Fig. 1). Hg concentrations were determined with cold vapour-atomic fluorescence spectrometry (CV-AFS, MERCUR, Analytik Jena). After melting, all Hg species in the liquid samples were oxidized to Hg^{2+} by adding BrCl -solution. Afterwards the excess of free halogens had to be neutralized with $\text{NH}_2\text{OH}\cdot\text{HCl}$. The dissolved Hg^{2+} in the liquid sample is reduced to Hg^0 with SnCl_2 . Gaseous elemental Hg is purged by Ar from the solution and collected onto a gold trap for preconcentration. After thermal desorption Hg is transported to the fluorescence cell and detected (US EPA, 2001).

Hg concentrations were in the lower ng/L (ppt) range where the analytical limit is reached (limit of determination: 1.2 ng/L). We could show that Hg is preserved in the seasonal snow cover, since the concentration profile observed in March could be recovered in April and June (Fig. 2). Hg fluxes during the overlapping time period showed no significant difference.

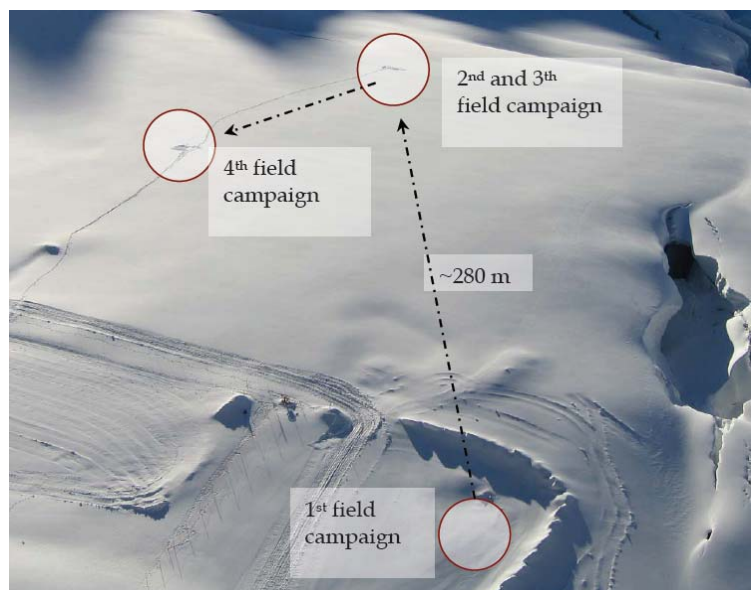


Fig. 1: Photo of the sampling locations at the Jungfrauoch in August (31.08.07). The photo was taken from the Sphinx observatory. In the front the ski piste and traces of the snow cat can be seen.

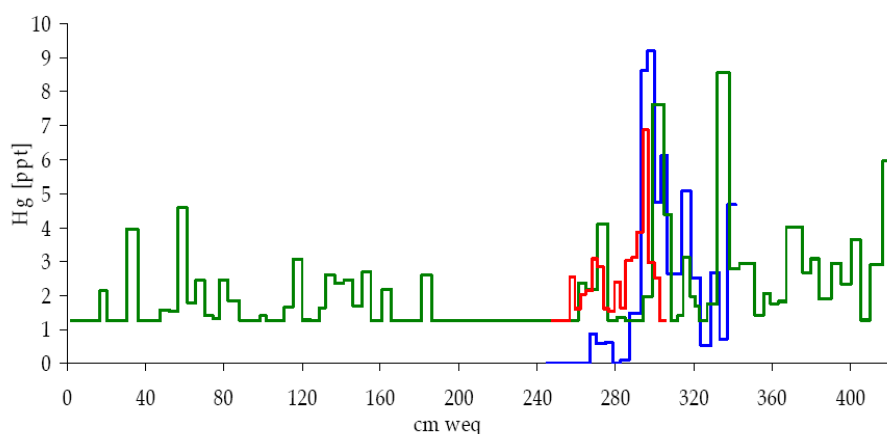


Fig. 2: Hg concentrations in the firn core samples from March (red), April (blue) and June 2007 (green). Concentrations below the limit of determination were replaced by the determination limit. The data set for core April is blank corrected.

A particular loss of Hg was observed in the topmost snow layers during the exceptional conditions in August 2007 with rainfall during the first three days and strong solar irradiation on the last day (Fig. 3). We assume that the Hg is partly percolated with rain and melt water and the other part was re-emitted to the atmosphere due to photoreduction processes. The topmost cm of the surface snow layer showed elevated concentrations of Hg. This was also observed in March, April, and June, but cannot be explained yet.

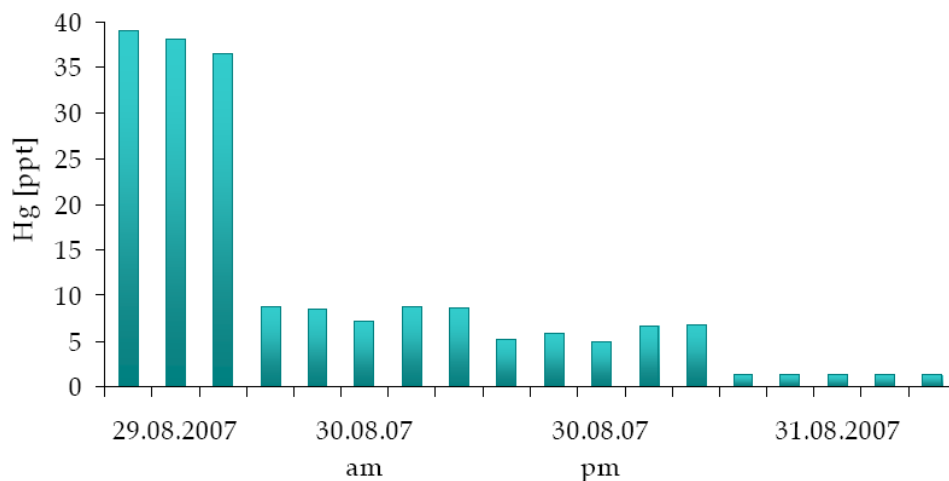


Fig. 3: Hg concentrations of surface snow samples from the Jungfrauoch. Concentrations below the limit of determination (all values for 31.08.07) were replaced by the determination limit.

Within the VIVALDI project the temperature-stable isotope relationship using the well-dated Colle Gnifetti ice core record has been investigated. Stable isotope records from ice cores are widely used to reconstruct past climate conditions especially in polar regions (Johnson et al., 2001), but increasingly also in mid-latitude high-alpine environments (Henderson et al., 2006). Temperature during condensation of water vapour leaves a fingerprint in the isotopic composition of precipitation, which can be used to decipher site temperature, applying methods of linear regression.

For correlation studies we smoothed predictor and predictant with a 5-year moving average to deal with the dating uncertainty within the proxy data. The time period covered by our temporal calibration studies is 1865 to 2003. As suspected correlations were in general highest between climate variables and proxy between 1930 and 2003 indicating a better reliability in dating compared to time periods prior (Fig. 4). Surprisingly correlations between $\delta^{18}\text{O}$ and mean temperature of months when accumulation takes place (e.g. Apr-Sep, Jun-Aug) are quite low. The highest correlations are observed with February temperature at the different climate stations.

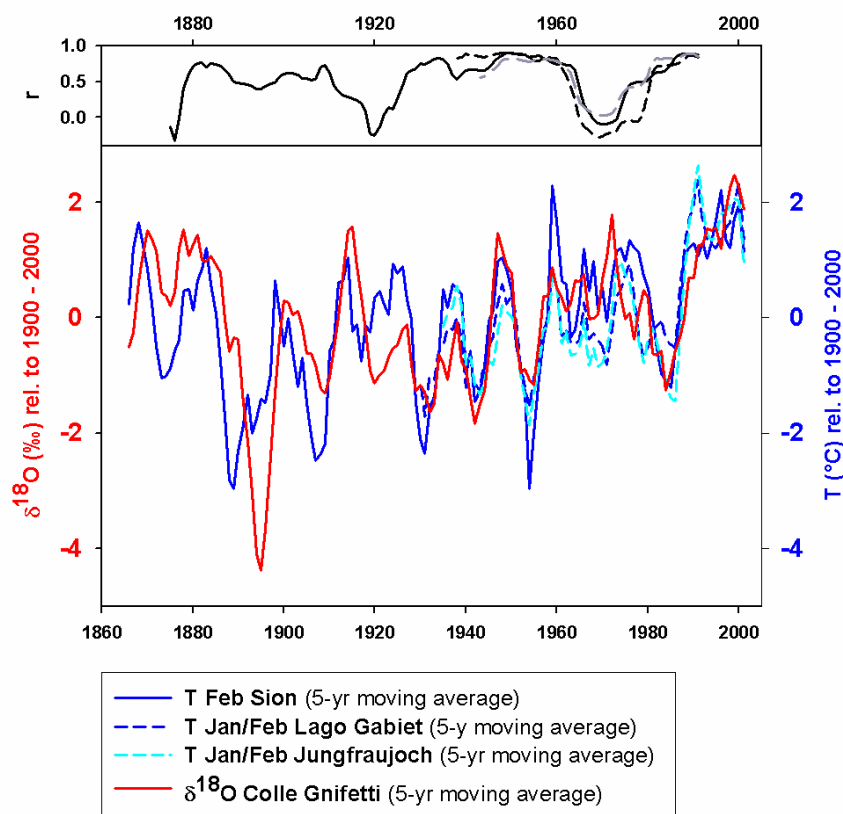


Fig. 4: Comparison between the $\delta^{18}\text{O}$ ice core record (red line) and temperatures anomalies relative to 1901-2000 (meteorological stations Sion, Lago Gabet, and Jungfraujoch).

Acknowledgement

The access to the high-alpine research station Jungfraujoch is highly acknowledged.

References

- Henderson et al., *J. Geophys. Res.*, **111** (2006).
Johnsen et al., *J. Quat. Sci.*, **16** (2001).
Schuster et al., *Environ. Sci. Tech.*, **36**, 2303–2310, (2002).
Lalonde et al., *Environ. Sci. Technol.*, **36**, 174-178 (2002).
United States Environmental Protection Agency (US EPA), Method 1631 (2001).

Internet data bases:

<http://lch.web.psi.ch/>
<http://www.nccr-climate.unibe.ch/>

Collaborating partners/networks:

Markus Leuenberger, KUP, University of Bern.
Martin Grosjean, Heinz Wanner, Geographical Institute, University of Bern.

Scientific publications and public outreach 2007:

Refereed journal articles

T.M. Jenk, S. Szidat, M. Schwikowski, H.W. Gäggeler, L. Wacker, H.-A. Synal, M. Saurer, Microgram level radiocarbon (^{14}C) determination on carbonaceous particles in

ice, Nucl. Instr. Meth. Phys. Res. B **259**, 518-525, doi:10.1016/j.nimb.2007.01.196 (2007).

H. Reithmeier, M.Schwikowski, V.Lazarev, W.Rühm, H.W.Gäggeler, E.Nolte, Increase of ^{129}I in the European environment, *Chimia* **61** (1/2), 283 (2007).

Address:

Paul Scherrer Institut
Labor für Radio- und Umweltchemie
CH-5232 Villigen
Switzerland

Contacts:

Margit Schwikowski
Tel.: +41 56 310 4110
Fax: + 41 56 310 4435
e-mail: margit.schwikowski@psi.ch
URL: <http://lch.web.psi.ch/>

