

Name of research institute or organization:

**Institute for Chemical and Bioengineering,
Swiss Federal Institute of Technology, ETH Zurich**

Title of project:

SwissQuick: Emissions and imissions of atmospheric mercury in Switzerland

Project leader and team:

Dr. Christian Bogdal, project leader
Basil Denzler

Project description:

Mercury is emitted in big amounts into the environment. For Switzerland alone estimates lie in the range of 500 – 1000 kg/yr. The most prominent sources in Europe are combustion processes in power plants, cement and steel works. Three forms of mercury are distinguished for atmospheric emissions: gaseous elemental mercury (Hg(0)), gaseous oxidized mercury (Hg(II)) and particle bound mercury (Hg(p)), of which Hg(0) makes up for the biggest share of over 90%. Due to its long residence time, Hg(0) undergoes long-range atmospheric transport [1]. Thus, mercury can occur in regions far away from its initial emission sources.

The first measurement campaign to measure mercury concentrations at Jungfraujoch was conducted in the year 2011/12. Based on the results thereof, a long-term monitoring project started in December 2013 at the High Altitude Research Station Jungfraujoch to improve the understanding of the atmospheric emissions and transport of Hg(0) was continued with interruptions in 2016. Additionally, we were able to start a measurement campaign of Hg(II) and Hg(p). This new data will help us to better understand the transformation and deposition processes of mercury.

A Tekran® 2537X gaseous elemental mercury analyzer is used to measure the concentration of Hg(0) by cold vapor atomic fluorescence spectroscopy (detection limit : 0.1 ng/m³). The instrument provides a high temporal resolution of 5 min and uses an internal permeation source for automated calibration. A Tekran® Model 1130 Oxidized Mercury Speciation Unit in combination with a Particulate Mercury Module 1135 is used to pre-trap any Hg(II) and Hg(p) over a one hour period. A heating system reduces any species to Hg(0), which is then sequentially analyzed by the 2537X as described previously.

In 2017, the results from the 2011 campaign were published [2]. We applied a top-down approach to quantify mercury emissions on the basis of atmospheric mercury measurements. We established the source-receptor relationships for Hg(0), analogous to previous studies on greenhouse gases [3]. By the means of atmospheric inversion we were able to quantify spatially resolved European emissions of 89 ± 14 t/a for Hg(0). Our European emission estimate is 17% higher than the existing bottom-up emission inventories which is within stated uncertainties.

The Hg(0) concentrations measured at Jungfraujoch are comparable to background levels measured worldwide [4]. Hg(II) and Hg(p) species detected in 2017 at Jungfraujoch were found at about the same levels of 10 to 30 pg/m³ throughout the measurement period. Strong peaks in Hg(II) concentration (Figure 1), however, were measured in periods with very low relative humidity (RH) and high ozone (O₃) levels. Our first interpretation points into the direction of stratospheric influence, which brings in air masses that cause Hg(II) levels to rise significantly.

The data set acquired over the new period from 2013 until 2017 will be used in order to establish new and improved top-down emission estimates of mercury for Europe as in our

first publication [2]. Additionally, the data from Jungfraujoch will be combined with measurements of further remote atmospheric monitoring stations.

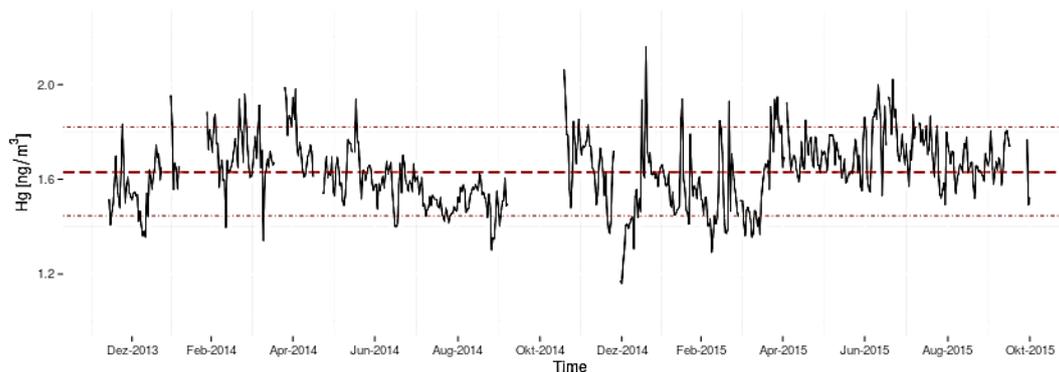


Figure 1. Daily mean $Hg(0)$ concentrations at Jungfraujoch from December 2013 until October 2015 with a median of 1.63 ng/m^3 and percentiles $Q_{0.1}/Q_{0.9}$ of $1.45/1.82 \text{ ng/m}^3$.

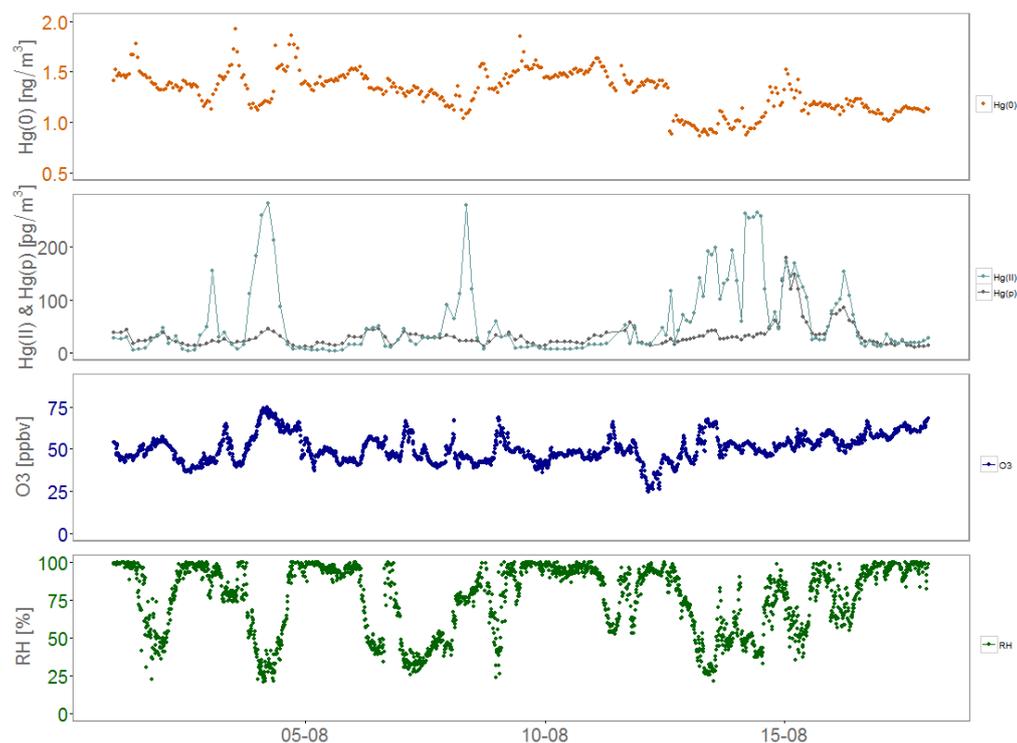


Figure 2. Period with presumable stratospheric influence from top to bottom: $Hg(0)$ concentrations [ng/m^3] in 5-minutes resolution and $Hg(II)$ and $Hg(p)$ concentrations [pg/m^3] in hourly resolution in comparison to Ozone (O_3) concentrations [ppbv] and relative humidity (RH) [%] from 4th of August until 8th August, 2016. The plot show $Hg(II)$ spikes concurring with a drop in RH and high O_3 levels.

Key words:

Mercury, gaseous elemental mercury, long-range transport, air monitoring, trajectory modeling, Lagrangian particle dispersion model

Collaborating partners/networks:

Particle dispersion modeling: Dr. Stephan Henne, EMPA, Dübendorf, Switzerland
Funding: Swiss Federal Office for the Environment (Bundesamt für Umwelt, BAFU)
Measurement devices: Prof. Dr. Ralf Ebinghaus, Dr. Gandrass Jürgen, Helmholtz-Zentrum Geesthacht

Scientific publications and public outreach 2017:

Refereed journal articles and their internet access

- [1] Clarkson, T.W., L. Magos, The toxicology of mercury and its chemical compounds. *Crit. Rev. Toxicol.*, doi: 10.1080/10408440600845619, **36**, 609-662, 2006. <http://dx.doi.org/10.1080/10408440600845619>
- [2] Denzler, B., C. Bogdal, S. Henne, D. Obrist, M. Steinbacher, K. Hungerbühler, Inversion Approach to Validate Mercury Emissions Based on Background Air Monitoring at the High Altitude Research Station Jungfrauoch (3580 m), *Environmental Science & Technology*, **51**, 5, 2846-2853, doi: 10.1021/acs.est.6b05630, 2017. <http://pubs.acs.org/doi/abs/10.1021/acs.est.6b05630>
- [3] Keller, C., M. Hill, M. Vollmer, S. Henne, D. Brunner, S. Reimann, S. O'Doherty, J. Arduini, M. Maione, Z. Ferenczi, L. Haszpra, A. Manning and T. Peter, European emissions of halogenated greenhouse gases inferred from atmospheric measurements, *Environmental Science & Technology*, **46**, 217, doi: 10.1021/es202453j, 2012. <http://pubs.acs.org/doi/abs/10.1021/es202453j>
- [4] Sprovieri, F., N. Pirrone, R. Ebinghaus, H. Kock, A. Dommergue, A review of worldwide atmospheric mercury measurements, *Atmos. Chem. Phys.*, **10**, 8245-8265, doi: 10.5194/acp-10-8245-2010, 2010. <http://www.atmos-chem-phys.net/10/8245/2010/acp-10-8245-2010.html>

Address:

Safety and Environmental Technology Group
ETH Zurich
Vladimir-Prelog-Weg 1
CH-8093 Zürich, Switzerland

Contacts:

Basil Denzler
Tel.: +41 44 633 44 14
e-mail: basil.denzler@chem.ethz.ch
URL: http://www.sust-chem.ethz.ch/people/current_members/denzleba