stefan.osterwalder@univ-grenoble-alpes.fr

EDDY MERCURY

martin.jiskra@unibas.ch

features the first eddy covariance flux measurements of Hg^0 over a grassland[1]

Stefan Osterwalder[a,b], Werner Eugster[c], Iris Feigenwinter[c], Martin Jiskra[a]

(a) Environmental Geosciences, University of Basel, Basel, Switzerland; (b) CNRS, IRD, IGE, University Grenoble Alpes, Grenoble, France;
(c) Environmental Systems Science, ETH Zurich, Zurich, Switzerland

Motivation and Objectives

Direct flux studies are crucial to improve our understanding of terrestrial mercury (Hg) cycling and human Hg exposure. However, today it remains unclear whether terrestrial ecosystems are net sinks or sources of atmospheric Hg. Global estimates of the gaseous elemental mercury (Hg^0) flux range between -513 and 1653 Mg a^{-1} (central 25 % of the distribution)[2]. The objectives of the study were to:

1) develop an EC system for Hg^0 flux measurements based on the Lumex RA-915AM fast response Hg^0 analyzer.
2) determine the net ecosystem exchange of Hg^0 over a grassland at the Swiss FluxNet site in Chamau during a 34 day pilot campaign.

Eddy covariance (EC) is the state-of-the-art technique for micrometeorological measurements of energy and greenhouse gas fluxes. In the case of Hg^0, vertical flux is calculated as the covariance between fluctuations in vertical wind velocity and Hg^0 concentration: $F_{Hg0} = \overline{w'\chi'}$, w = vertical wind velocity, χ = Hg^0 density, prime indicates instantaneous fluctuations about the mean, and the overbar denotes a time average.

Conclusions

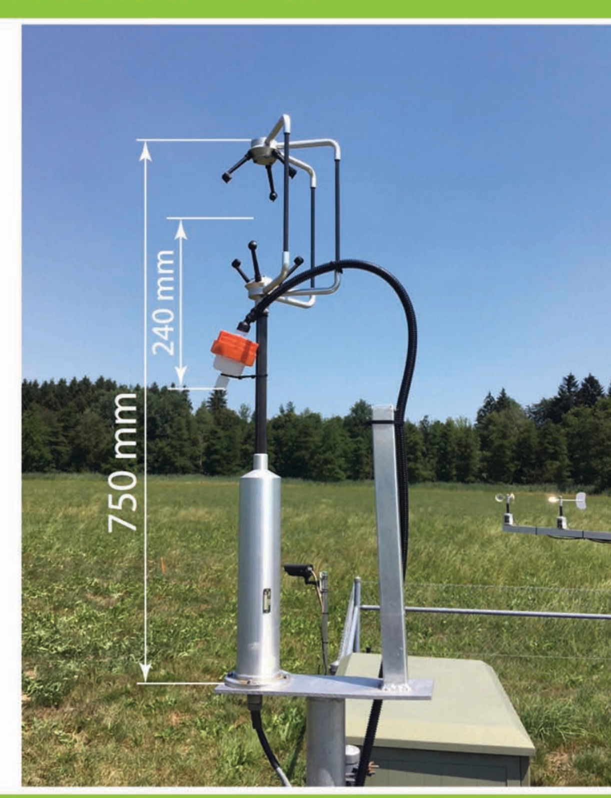
We present the first successful application of the EC method for Hg^0 flux measurements over terrestrial surfaces with background soil Hg concentrations (< 100 ng g^{-1}). Eddy Mercury

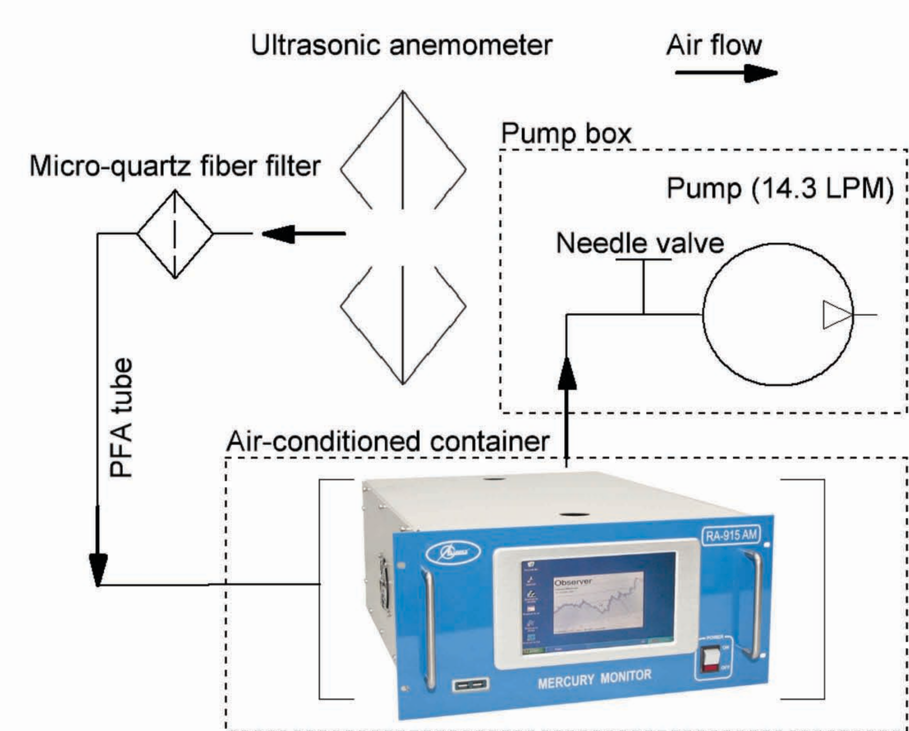
- improves the precision of Hg^0 flux measurements
- facilitates long-term, ecosystem-scale Hg^0 flux measurements
- can be established as standard method for Hg^0 flux measurements over terrestrial ecosystems.
- has the potential to complement air pollution and greenhouse gas flux measurements within the global network of tower sites (FluxNet).

Materials and Methods

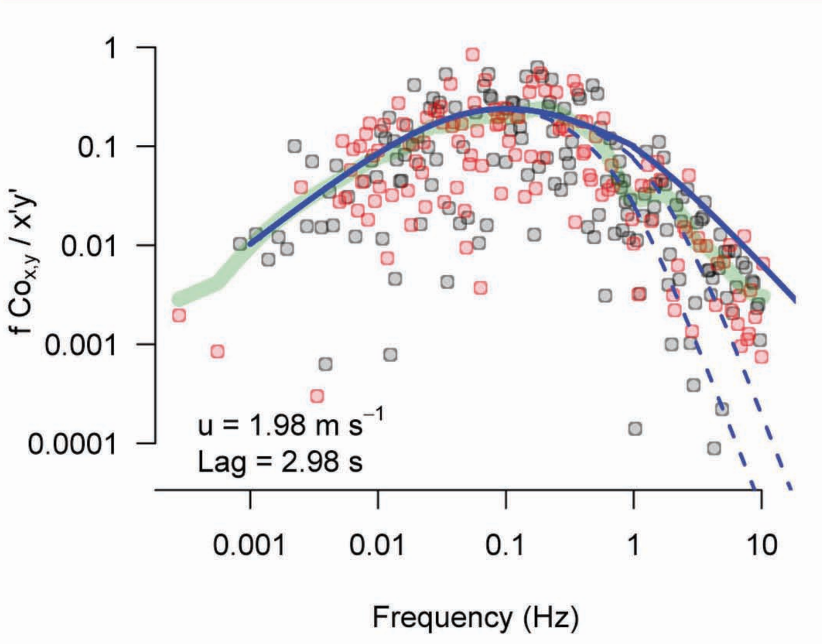
The core of Eddy Mercury is the RA-915AM mercury monitor (Lumex Ltd., St. Petersburg, Russia). The RA-915AM uses atomic absorption spectrometry (AAS) with Zeeman background correction to continuously measure Hg^0 in ambient air[3]. The five steps to calculate the Hg^0 flux include

1) preparation of the 1 Hz raw Hg^0 concentration measurement
2) preparation of the ultrasonic anemometer data
3) merging ultrasonic data with Hg^0 concentrations
4) time lag calculation between vertical wind speed and Hg^0 fluctuations
5) computation of the NEE of Hg^0

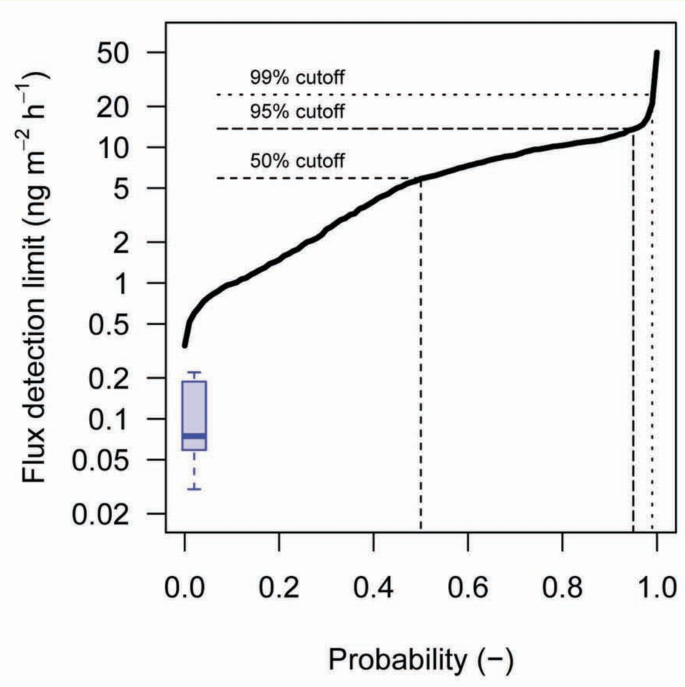




Results 1 - QA/QC

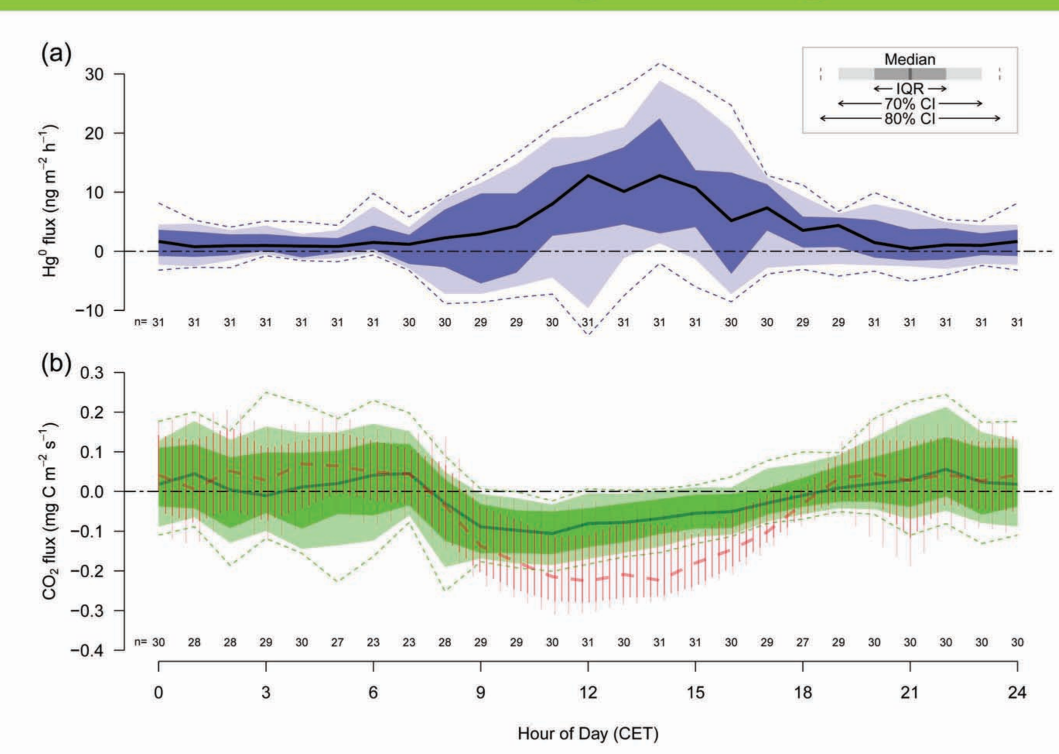


The flux cospectrum of a 1 hour averaged Hg^0 flux shows absolute values of cospectral densities with black symbols denoting positive contributions to ($\overline{w'\chi'}$), and red symbols denoting negative contributions. The light green bold line is a local polynomial regression fit to the data points, whereas the blue line denotes an idealized cospectrum. The two dashed blue lines show damped cospectra with a damping constant of 0.1 and 0.3 s.



Range of the magnitude of measured fluxes during the zero-flux experiment in the lab without Hg^0 sources under very low turbulence conditions (0.22 ng m^{-2} h^{-1} [max] with a 50 % cut-off at 0.074 ng m^{-2} h^{-1}.). The black line shows the theoretical detection limit based on the statistical significance ($p < 0.05$) of the correlation coefficient between vertical wind speed and Hg^0 fluctuations. The statistical estimate of the Hg^0 flux detection limit under real-world outdoor conditions at the site was 5.9 ng m^{-2} h^{-1} (50 % cut-off).

Results 2 - NEE of Hg^0 over grassland



Hourly aggregated diel cycle of (a) Hg^0 fluxes and (b) simultaneously recorded CO_2 fluxes measured in 2018 (green line) and 2017 for the same period (red bold dashed line).

- median NEE of Hg^0: 2.5 ng m^{-2} h^{-1} (-0.6 to 7.4 ng m^{-2} h^{-1}, 25th and 75th percentiles).
- median daytime flux = 8.4 ng m^{-2} h^{-1}; median nighttime fluxe = 1.0 ng m^{-2} h^{-1}
- drought stress induced partial stomata closure leading to a midday depression in CO_2 uptake which did not recover during the afternoon.
- partial stomata closure dampened Hg^0 uptake, resulting in net Hg^0 re-emission.
- a previous study[4] showed net Hg^0 dry deposition of -1.7 and -4.3 ng m^{-2} h^{-1} using gradient-based methods during the vegetation period at a grassland 15 km SW of our study site.

Results 3 - Suggested improvements

Eddy Mercury can set a new standard for measuring the net ecosystem exchange of Hg^0 at different terrestrial and aquatic ecosystems. Improvements are suggested towards 1) facilitated data transfer, 2) increased measurement frequency (10 - 20 Hz), 3) higher sampling flow rates (20 L), and 4) more stable temperature conditions during deployment.

References

[1] **Osterwalder, S., Eugster, W., Feigenwinter, I. and Jiskra, M.: Eddy covariance flux measurements of gaseous elemental mercury over a grassland. Atmospheric Measurement Techniques 13, 2057 – 2074, 2020.**

[2] Agnan, Y., Le Dantec, T., Moore, C. W., Edwards, G. C. and Obrist, D.: New constraints on terrestrial surface–atmosphere fluxes of gaseous elemental mercury using a global database, Environ. Sci. Technol. 50, 507 – 524, 2016.

[3] Sholupov, S., Pogarev, S., Ryzhov, V., Mashyanov, N. and Stroganov, A.: Zeeman atomic absorption spectrometer RA-915+ for direct determination of mercury in air and complex matrix samples, Fuel Process. Technol. 85, 473 – 485, 2004.

[4] Fritsche, J., Obrist, D., Zeeman, M. J., Conen, F., Eugster, W. and Alewell, C.: Elemental mercury fluxes over a sub-alpine grassland determined with two micrometeorological methods, Atmos. Environ. 42, 2922 – 2933, 2008.

Acknowledgements

This work was supported by the Freiwillige Akademische Gesellschaft (FAG) Basel and internal funding of the Institute of Agricultural Sciences ETH Zurich and the Department of Environmental Geosciences, University of Basel.