Author's response on "First eddy covariance flux measurements of gaseous elemental mercury (Hg^0) over a grassland" *by S. Osterwalder et al.*

Line numbers refer to the track-changes manuscript version below. Changes made in the manuscript are given in *italics*.

Comment 1 from the **Referee 1**: The paper "First eddy covariance flux measurement of gaseous elemental mercury over a grassland" should be accepted for publication in AMT.
The paper title should be modified to be something like: An improved method for eddy..... The word first should be deleted.
Author's response: We deleted "Hg(0)" from the title: *"First eddy covariance flux measurements of gaseous elemental mercury over a grassland"*. However, we suggest to keep "first" in the title in order to emphasize that we indeed conducted the first eddy covariance measurements of the Hg(0) flux over a low-Hg level soil (< 100 ng Hg g^{-1} topsoil [0-10 cm]).

Comment 2: Line 9 change "crucial to improve" to "important to for understanding"
Response: We changed that accordingly: *…are important to improve our understanding of global Hg cycling und ultimately…*

Comment 3: Line 16 remove "the first successful"
Response: We removed "successful": *we present the first eddy covariance NEE measurements of Hg^0…*

Comment 4: Line 21 and 22 which should be that...please fix this throughout your document.
Response: We replaced "which" by "that" wherever necessary throughout the manuscript.

Comment 5: Line 27 should start as "This system has the potential"
Response: Done.

Comment 6: Line 33 about is not very scientific change to approximately or~
Response: We now use "approximately".

Comment 7: The authors should mention the fact that Hg(II) dry deposition is important to consider and the limitations associated with only measuring GOM *(should most likely be GEM)*.
Response: We now address Hg(II) dry deposition in the introduction by adding the following statement (L49 – L53): *Dry deposition of Hg(II) is difficult to measure and its contribution to total Hg deposition remains uncertain (Gustin et al., 2013; Jaffe et al., 2014; Miller et al., 2018, Lyman et al., 2019). Hg stable isotope fingerprints identified Hg(0) as the dominant deposition pathway to terrestrial surfaces.*

Comment 8 - 13: Orthography.
Response: We changed the manuscript according to the Referee's suggestions

Comment 14: Line 258 which is a further should be that is an improvement

Response: Done.

Comment 15: Line 262 get rid of however.

Response: Done.

Comment 16: Page 10 has a number of which that should be that

Response: We changed which to that where suitable.

Comment 17: Line 367 comma needed after directions

Response: We added the comma after "detections".

Comment 18: Line 467 comma before but

Response: We added the comma before but.

Comment 19: Line 472 this sentence is really awkward I suggest you delete it

Response: We followed the Referee's suggestion and deleted the sentence

Comment 20: Line 502 would be better if it was "This study demonstrated an application of"

Response: We changed the sentence as suggested.

Comment 1 from the **Referee 2**:

This manuscript is very interesting and presented a very promising methodology significantly improved the Hg(0) flux measurement. Accurate measure Hg(0) flux has been a challenging issue over decades due to the limitations of available methods. As I read this paper, I had an impression that paper proposed a very promising trail work to significantly advance Hg(0) flux measurement. Overall, I support the publication of this manuscript on journal AMT.

Line 14 to 15. The statistical estimate... (50% cut-off). Move this sentence to the present line 18. The field campaign based detection limit should be described in the context of the campaign

Author's response: We moved the sentence to line 18 as suggested.

Comment 2: Line 18, 24 in the abstract and throughout the manuscript (section 3.3), replace "re-emission" with "emission" in general. "Emission" represented the measured results better.

Response: We agree with the Referee and replaced "re-emission" with the more general term "emission".

Comment 3: Line 176-181. Three auto-calibration strategies were performed through the course of field campaign. It seems that frequent auto calibration relaxed the baseline drifting (Fig.2d), and the authors do used same data processing steps to detrend the time-series data. So which measurement routine is better for achieving high quality data? Meanwhile, increased calibration frequency resulted a significant loss of online data, linear interpolation is mentioned to fill the gap before flux calculation: (1) will this increase the uncertainty compared to a less frequency of calibration, in terms of different proportion of

high-frequency data gap filling? (2) the methodology of gap filling of high frequency data was not easy to understand in the present manuscript.

Response: The Referee addresses an important issue: how to find an optimum between long continuous measurements with infrequent quality control of the drift of the instrument away from the calibration target vs. frequent calibration at the expense of losses in the time series due to gaps. We provided a detailed response to this comment in the interactive discussion (see AC2 "Response to Referee 2" published on January 24, 2020).

We have made changes in Section 3.2.1 (L 334 – 340) to explain the gap filling of high frequency data in a more comprehensible way: *With the example data shown in Figure 2e we produced an artificial dataset with gaps that correspond the 4-minute recalibration scheme used during the period shown in Figure 2f. This led to a loss in Hg^0 flux in the order of 12 %. Although nonzero, this should be considered a robust finding given the general understanding that EC flux measurements are accurate to within 10 – 20 % even with higher-quality instrumentation (Aubinet et al., 2012). It is however clear that in order to obtain higher quality EC fluxes than what we can present here it is required to improve the long-term stability of the instrument (Sect. 3.4), whereas improving the gap-filling strategy is not expected to contribute significant new insights into Hg^0 flux calculations.*

We further added a statement regarding instrument drift in L 342: *Removal of any drift also reduces the variance of a signal and hence the flux covariance of interest. Thus, knowledge about the stability of an instrument over which no drift correction is required, becomes important.*

For upcoming Hg^0 flux measurement campaigns, using an improved the *Eddy Mercury* system, we recommend to focus on reducing data gaps. We have added a sentence to Section 3.4 (L 491): *The length of data gaps mainly caused by system calibrations should be reduced to the point where discussions about gap filling methods and detrending procedures can be considered obsolete.*

Comment 4: Line 439, replace dial flux cycle with diel flux pattern.

Response: Done.

First eddy covariance flux measurements of gaseous elemental mercury ~~(Hg^0)~~ over a grassland

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Abstract. Direct measurements of the net ecosystem exchange (NEE) of gaseous elemental mercury (Hg^0) are ~~crucial~~important to improve ~~the~~our understanding of global Hg cycling a~~n~~nd ultimately human and wildlife Hg exposure. The lack of long-term, ecosystem-scale measurements causes large uncertainties in Hg^0 flux estimates. Today, it remains unclear whether terrestrial ecosystems are net sinks or sources of atmospheric Hg^0. Here, we show a detailed validation ~~of the eddy covariance technique for~~ of direct Hg^0 flux measurements ~~(*Eddy Mercury*)~~ based on the eddy covariance technique (*Eddy Mercury*) using a Lumex mercury monitor RA-915AM. The flux detection limit derived from a zero-flux experiment in the laboratory was 0.22 ng m^{-2} h^{-1} (maximum) with a 50 % cut-off at 0.074 ng m^{-2} h^{-1}. ~~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). We present the first successful~~We present the first eddy covariance NEE measurements of Hg^0 over a low-Hg level soil (41–75 ng Hg g^{-1} topsoil [0-10 cm]), ~~made~~conducted in summer 2018 at a managed grassland at the Swiss FluxNet site in Chamau, Switzerland (CH-Cha). The statistical estimate of the Hg^0 flux detection limit under outdoor conditions at the site was 5.9 ng m^{-2} h^{-1} (50 % cut-off). We measured a net summertime ~~re-~~emission over a period of 34 days with a median Hg^0 flux of 2.5 ng m^{-2} h^{-1} (-0.6 to 7.4 ng m^{-2} h^{-1}, range between 25th and 75th percentiles). We observed a distinct diel cycle with higher median daytime fluxes (8.4 ng m^{-2} h^{-1}) than nighttime fluxes (1.0 ng m^{-2} h^{-1}). Drought stress during the measurement campaign in summer 2018 induced partial stomata closure of vegetation ~~which~~. Partial stomata closure led to a midday depression in CO_2 uptake, ~~which~~that did not recover during the afternoon. ~~Thus, t~~The median ~~cumulative net~~ CO_2 flux~~, indicating a small CO_2 uptake over the 34 day period,~~ ~~uptake~~ was only 248 % of the ~~net~~ median CO_2 flux~~uptake~~ measured during the same period in the previous year 2017. We suggest that partial stomata closure dampened also Hg^0 uptake by vegetation, resulting in a NEE of Hg^0 dominated by soil ~~re-~~emission. Finally, we give suggestions to further improve the precision and handling of the *Eddy Mercury* system in order to assure its suitability for long-term NEE measurements of Hg^0 over natural background surfaces with low soil Hg concentrations (< 100 ng g^{-1}). With these improvements, ~~The system, improved in the suggested way,~~ *Eddy Mercury* has the potential to be integrated in global networks of micrometeorological tower sites (FluxNet) and to provide the long-term observations on terrestrial atmosphere Hg^0 exchange necessary to validate regional and global mercury models.

1 Introduction

Mercury (Hg) is a top priority environmental pollutant that is transported through the atmosphere as gaseous elemental Hg^0 (> 95 % of total atmospheric Hg). Anthropogenic Hg emissions into the atmosphere exceed natural emissions by a factor of ~~about~~ five, approximately (Outridge et al., 2018). Atmospheric Hg has a lifetime of 8–13 months, allowing for long-range transport before being deposited back onto the Earth surface also at remote locations far from pollution sources (Saiz-Lopez et al., 2018). Once deposited, Hg can be transformed into methylmercury ~~which~~that can bioaccumulate in the freshwater and marine food webs, thereby posing a threat for human and ecosystem health (Watras et al., 1998; Fitzgerald et al., 2007; Mason et al., 2012; Braune et al., 2015). Atmospheric Hg deposition to terrestrial surfaces occurs predominantly as Hg^0 dry deposition through stomatal uptake by vegetation or as wet or dry deposition after oxidation in the atmosphere to more soluble reactive mercury (Hg(II)) (Lindberg et al., 2007; Driscoll et al., 2013; Jiskra et al., 2018). Wet deposition of Hg(II) via rain and snowfall is relatively well quantified by Hg deposition networks such as the National Atmospheric Deposition Program (NADP), the European Monitoring and Evaluation Programme (EMEP) and the Asia Pacific Mercury Monitoring Network (APMMN). Dry deposition of ~~Hg^0 has been~~Hg(II) is difficult to measure and its contribution to total Hg deposition remains uncertain (Gustin et al., 2013; Jaffe et al., 2014; Miller et al., 2018, Lyman et al., 2019). Hg stable isotope fingerprints identified Hg^0 as the ~~dominating Hg~~dominant deposition pathway ~~over vegetated~~to terrestrial surfaces ~~based on Hg stable isotope fingerprinting.~~. Dry deposition of Hg^0 ~~though stomatal~~through vegetation uptake contributes 65–90 % of the total Hg ~~deposition~~ deposited to soils (Demers et al. 2007; Jiskra et al., 2015; Enrico et al., 2016; Zhang et al., 2016; Zheng et al., 2016; Obrist et al., 2017). However, Hg^0 dry deposition remains poorly constrained due to the lack of long-term monitoring networks (Obrist et al., 2018). Reduction of Hg(II) in terrestrial surface pools and subsequent ~~re~~ emission of Hg^0 back to the atmosphere prolongs the cycling of anthropogenic Hg emissions in the environment and can thereby delay the effects of curbing primary anthropogenic emissions on human Hg exposure (Zhu et al., 2016; Wang et al., 2016; Obrist et al., 2018). ~~The net~~Net ecosystem exchange (NEE) of Hg^0, the ~~sum~~ balance between ~~of~~ Hg^0 dry deposition and ~~the re~~ emission from foliage and soils, represents a major factor in how fast the environment will recover from anthropogenic Hg pollution. On a global scale, estimates of the terrestrial NEE of Hg^0 remain uncertain. In the most recent global mercury assessment, soil ~~re~~ emission estimates were lowered to 1000 Mg a^{-1} (UNEP, 2019) relative to 2200 Mg a^{-1} in the 2013 assessment (UNEP, 2013), however the associated uncertainties remain large. A recent review of 132 direct flux measurement studies revealed a NEE Hg^0 flux between -513 and 1653 Mg a^{-1} (range of 37.5th and 62.5th percentiles, the central 25 % of the distribution) (Agnan et al. 2016). The database predominantly contains Hg^0 flux measurements performed with dynamic flux chambers (85 % of all studies) that are ideal for short-term, mechanistic studies but less suitable for quantitative flux estimations, especially over vegetated surfaces (Gustin et al., 1999; Eckley et al., 2016; Osterwalder et al., 2018). Year-round NEE measurements of Hg^0 at the landscape scale are compelling to reduce measurement uncertainties. However, there are only four year-round whole-ecosystem Hg^0 flux studies published, all using micrometeorological ~~(MM)~~ techniques, including the modified Bowen-ratio and aerodynamic gradient methods (Fritsche et al., 2008a; Castro and Moore, 2016; Obrist et al., 2017), and the relaxed eddy accumulation (REA) technique (Osterwalder et al. 2017). These approaches use instruments that do not fulfill the criterion of fast response of the Hg sensor as it is required for eddy covariance (EC) flux measurements. Hence, these are not direct flux measurements and are thus dependent on a number of assumptions. The main difficulty using the modified Bowen-ratio and aerodynamic gradient method is to resolve a significant concentration gradient during turbulent conditions. During calm

conditions, in contrast, it is challenging to determine a significant eddy diffusivity. Further drawbacks are (1) the potentially different sink/source characteristics of the footprint due to the two measurement heights, (2) temporally intermittent sampling between the two sampling inlets, and (3) the fact that transport characteristics are based on reference scalars like heat, water or CO_2 (Businger et al., 1986; Stannard et al., 1997; Edwards et al., 2005, Sommar et al., 2013a). The REA technique (Businger and Oncley, 1990) circumvents most of these difficulties. However, uncertainties in Hg^0 flux calculations are introduced by the determination of the proportionality coefficient (β-value) and system dependent shortcomings such as a biased offset between the updraft and downdraft sampling lines or difficulties in controlling the air flow from the air inlets to the analyzer. Thus, it remains challenging to accurately measure very small concentration differences with REA (typically < 0.1 ng m^{-3}) between updrafts and downdrafts over natural surfaces with low substrate Hg concentrations (Cobos et al., 2002; Bash and Miller, 2008; Sommar et al., 2013b; Osterwalder et al., 2016, Kamp et al., 2018).

The EC technique has been under development since the late 1940s to measure the surface–atmosphere exchange of heat, mass, and momentum in the surface boundary layer, ~~ in~~ the lowest 20–50 m of the atmosphere (Montgomery, 1948; Obukhov 1951; Swinbank 1951). In order to estimate a vertical turbulent flux, the covariance of two concurrently measured variables is calculated, (1) the scalar quantity of interest (in our case Hg^0) and (2) the turbulent fluctuations of the vertical wind velocity, both measured at high temporal resolution. Since the 1990s a new generation of digital three-axis ultrasonic anemometers, infrared gas analyzers and comprehensive software packages have facilitated land–atmosphere exchange measurements of CO_2 and H_2O (McMillen 1988). Today, the EC technique is considered the standard method to determine evapotranspiration and the NEE of energy and trace gases such as CO_2, CH_4, N_2O, O_2, O_3 and volatile organic compounds using high resolution (10–20 Hz), sometimes portable, and generally very reliable equipment (Aubinet et al., 2012).

The first ~~successful~~ application of the EC technique to measure NEE of Hg^0 reported ~~a re-~~an emission flux of 849 ng m^{-2} h^{-1} over contaminated soils (85 mg Hg kg^{-1} dry soil) during a pilot campaign in Nevada, USA (Pierce et al., 2015). The EC system was based on a fast response (25 Hz), field deployable pulsed cavity ring-down spectrometer (CRDS) (Faïn et al., 2010; Pierce et al., 2013). The minimum detection limit of 32 ng m^{-2} h^{-1}~~-~~, however, did not allow Hg^0 flux measurements over soils exhibiting background Hg concentrations (typically < 100 ng Hg g^{-1}; Grigal et al., 2003) (Pierce et al., 2015).

Here, we present the first EC measurements ~~to determine the~~of NEE of Hg^0 over a grassland with typical background soil Hg ~~levels.~~concentrations. Our novel EC system is ~~based on~~makes use of a Lumex mercury monitor RA-915AM (Lumex Ltd., St. Petersburg, Russia) atomic absorption spectrometer with Zeeman background correction, allowing to measure Hg^0 in ambient air at a relatively high sampling frequency of 1 Hz (Sholupov et al., 1995, 2004). Ambient air Hg^0 measurement comparison studies between the more frequently used Tekran® 2537 analyzer (Tekran Inc., Toronto, Canada) and the ~~mercury monitor's precursor, the Lumex RA-915+ mercury analyzer,~~RA-915AM were performed by the European Committee for Standardization's (CEN) Technical Committee 264 "Air Quality" EN 15852 and showed good agreement between the two instruments (Brown et al., 2010). Among other applications, the mercury monitor's precursor, the Lumex RA-~~915AM~~915+ mercury analyzer was successfully deployed in the Global Mercury Observation (GMOS) project at two sites in Russia and Suriname (Sprovieri et al., 2016).

The objective of ~~the~~ this study was to test the performance of the RA-915AM as fast response analyzer and its suitability for EC flux measurements with the goal to reliably measure the NEE of ~~gaseous elemental mercury or~~ Hg^0 ~~(GEM NEE)~~ over terrestrial ecosystems. Hereinafter, the new EC system is referred to as *Eddy Mercury*. We

provide a description of the *Eddy Mercury* ~~sampling~~ system and present the data analysis procedure to calculate the ~~EC~~ NEE flux of Hg^0 ~~flux~~ in detail. We discuss the patterns in the ~~GEM NEE~~NEE of Hg^0 ~~that was~~ measured over a grassland during a 34-day pilot campaign and give suggestions to improve the reliability and precision of the *Eddy Mercury* system for future long-term applications.

2 Material and methods

2.1 Site description and instrumentation

The *Eddy Mercury* system was tested between 20 July and 6 September 2018 at the Swiss FluxNet site Chamau (CH-Cha), located in central Switzerland, about 30 km southwest of Zurich (47° 12′ 36.8″ N, 8° 24′ 37.6″ E; 393 m a. s. l.). In this study, NEE of Hg^0 and CO_2 was measured concurrently with two independent EC systems over the intensively managed grassland ~~which is~~ used for forage production. Details on grassland species composition, harvest, and fertilization practices are described in Zeeman et al. (2010), Merbold et al. (2014) and Fuchs et al. (2018). The tower for long-term EC greenhouse gas measurements was located between two adjacent grassland parcels (Fig. 1a). The northern parcel, ~~(~~measured when up-valley winds prevail~~)~~, was over~~-~~sown with clover in March 2015 and April 2016 to investigate the N_2O emission reduction potential in comparison to the conventionally fertilized grassland of the southern parcel ~~(Fuchs et al., 2018)~~, ~~(~~measured primarily when down-valley winds prevail (Fig. 1b)~~)~~. The soil type is a gleysol–cambisol, with a bulk density of about 1 g cm^{-3}, 30.6 % sand, 47.7 % silt and 21.7 % clay in the top 10 cm (Roth, 2006). ~~The~~ A ttopsoil pH ~~was~~ of 5.3 ~~, which~~was ~~was~~and ~~was~~ determined by adding 25 ml of 0.01 M $CaCl_2$-solution to 10 g dry soil (Labor Ins AG, Kerzers, Switzerland, in 2014). The 24 year (1994-2017) average annual temperature measured at the nearby SwissMetNet surface weather station in Cham (CHZ, 444.5 m a. s. l.) was 10.1 °C and the average annual precipitation was 997 mm.

The *Eddy Mercury* system was mounted ~~about~~ approx~~.~~imately 3 m west of a fully equipped long-term EC tower measuring greenhouse gas exchange (CO_2, N_2O, CH_4, H_2O) and meteorological variables at 2 m height (Fig. 1~~b~~). The CO_2 flux system consisted of a 3D ultrasonic anemometer (Solent R3-50, Gill Instruments, Lymington, UK) and an open-path infrared gas analyzer for CO_2 and H_2O concentrations running at 20 Hz resolution (IRGA, LI-7500, LI-COR Biosciences, Lincoln, NE, USA). From the 20 Hz IRGA measurements, 30 min flux averages were calculated using the LI-COR EddyPro® software. The 30 min CO_2 flux has been ~~are~~ recorded continuously since 2005 (Eugster and Zeeman, 2006; Zeeman et al., 2010). The measured meteorological variables included temperature and relative humidity (Hydroclip S3 sensor, Rotronic AG, Switzerland), net all-wave radiation (CNR1, Kipp &Zonen B.V., Delft, Netherlands), incoming and reflected photosynthetic active radiation (PARlite, Kipp and Zonen, Delft, Netherlands), and precipitation (0.5 m height; tipping bucket rain gauge from LAMBRECHT meteo GmbH, Göttingen, Germany). In addition, soil temperature~~s~~ was~~were~~ recorded at 0.05, 0.1, 0.15, 0.25, 0.4 m depth (T107, Campbell Scientific Inc., Logan, UT, USA).

2.2 Soil sampling and total mercury analysis

Topsoil samples (0–10 cm) were taken in a circular arrangement around the EC tower (Fig. 1a) using a core drill. The soil samples were transported to the laboratory in sealed plastic bags, and stored in a fridge at 4 °C. The samples were filled into aluminum shells, weighed and dried at 40 °C, until their weight remained constant. The samples were pestled and sieved through a 2 mm mesh to separate the fine earth and the skeleton. The fine earth was ground to powder using a laboratory scale ball mill. To get rid of all potential humidity, the ground samples

were stored in small paper bags in a desiccator and dried again at 40 °C. The 22 topsoil samples were analyzed for total Hg using a DMA-80 Direct Mercury Analyzer (MLS Mikrowellen GmbH, Leutkirch im Allgäu, Germany). Certified Hg standard solution (NIST 3133) was gravimetrically diluted to concentrations of 10 ng g^{-1} to 1000 ng g^{-1} and used for the calibration of the instrument. Repeated measurements of standard reference material (ERM-CC141 loam soil) 90.3 ± 7.8 ng g^{-1} (mean ± SD, n = 3) ~~were in agreement~~agreed with the certified value (83 ± 17 ng g^{-1}).

2.3 Description of the *Eddy Mercury* system

The core of the *Eddy Mercury* ~~apparatus~~ system to measure ~~GEM NEE~~the NEE of Hg^0 is the RA-915AM mercury monitor (Lumex Analytics GmbH, Germany). The RA-915AM uses atomic absorption spectrometry (AAS) with Zeeman background correction to continuously measure Hg^0 in ambient air (Sholupov et al., 2004). The multi-path sample cell of the RA-915AM has an optical path length of 9.6 m and a cell volume of 0.7 L. Baseline corrections (zero drift) ~~are~~were performed automatically by the instrument using Hg-free air at user defined intervals. Span corrections are done using an inbuilt calibration cell that contains Hg^0 vapor. The measurement range ~~can be set~~lies between 0 and 2000 ng m^{-3} and ~~its~~ the instrument detection limit is 0.5 ng m^{-3} according to the analytical specifications by the manufacturer. The air flow rate was increased to 14.3 L min^{-1} by bypassing the instrument pump in order to reduce the residence time in the measurement cell (normal flow: 7 L min^{-1}). For this, a stronger external pump was connected (model MAA-V109-MD, GAST Manufacturing, MI, USA). The instrument was placed in a weatherproof, air-conditioned box (Elcase, Marthalen, Switzerland) to protect the sensitive RA-915AM from rain and reduce temperature fluctuations. A USB-to-RS232 serial data interface was used to establish a one-way communication link from the RA-915AM to the data acquisition computer. The air inlet was mounted 24 cm below the center of the head of the three dimensional (3D) ultrasonic anemometer (Gill R2A, Solent, UK) used for wind vector measurements that was installed 2 m above ground. A micro-quartz fiber filter (Grade MK 360, 47 mm diameter, Ahlstrom–Munksjö, Sweden) was installed in a 47 mm Perfluoralkyl-polymere (PFA) single stage filter assembly (Savillex, Eden Prairie, USA) at the air inlet. The air inlet was connected to the RA-915AM by a 2.8 m intake hose with 11 mm inner diameter (ID) attached to a 0.35 m, 4 mm ID sample intake hose. Both hose segments were unheated, insulated PFA tubing. The median lag time of the turbulent airflow (Reynolds number of > 5000) from the tube inlet to the analyzer was in the order of 1.15 s.

2.4 Eddy covariance flux measurements

The RA-915AM analyzer was configured to measure Hg^0 concentrations at 1 Hz. The Hg^0 concentrations and the 3D wind vectors were measured from 20 July to 6 September 2018 using four different settings of the RA-915AM analyzer with respect to the length of the measurement interval between two auto-calibration cycles (zero and span): (1) 24 hour intervals from 20–26 July 2018; (2) 4 hour intervals from 1–26 August 2018; (3) 1 hour intervals from 27–31 August 2018; (4) 4 minute intervals from 31 August until 6 September 2018. The ultrasonic anemometer had an internal sampling frequency of 1000 Hz~~, which~~that was averaged (8 records of each acoustic sensor pair for each direction) to 20.83 Hz. The 1 Hz RA-915AM data was merged with the ultrasonic anemometer's data stream by oversampling as described in Eugster and Plüss (2010). Data were collected on a Linux-based Raspberry Pi computer equipped with a real-time clock chip and internet access. Because data transfer via the USB port from the embedded Windows 7 system of the RA-915AM was highly unreliable, only the system time stamps were synchronized with the Linux data acquisition system every second via a Windows PowerShell

script. In cases when also this communication failed, an approximate time synchronization was done by polling the RA-915AM timestamp via the Samba file sharing protocol. Thus, in extension of the synchronization method described by Eugster and Plüss (2010) the merging of Hg^0 measurements with wind vector data had to be done offline in a separate data workup step. Fluxes were calculated over 60 minute intervals to account for the low sampling frequency of Hg^0 signals. Thus, under modes (1) and (2) 3600 Hg^0 measurements were used for each 1 hour flux average.

2.5 Eddy covariance Hg^0 flux calculations

Calculation of the ~~GEM~~ NEE of Hg^0 required some modifications of the standard procedure that is established for CO_2 fluxes (e.g. Aubinet et al., 2012). The modifications were done according to the five steps described in detail below.

2.5.1 Preparation of raw Hg^0 measurements

The RA-915AM raw data files provide the following information at 1 Hz resolution: Date and time of measurement, photomultiplier current (arb. unit), air flow rate (L min^{-1}), temperature of analyzed air (°C), temperature of RA-915AM (°C), sample cell pressure (kPa), Hg^0 raw concentration (ng m^{-3}, including all online corrections), status code and status description. The status code (a numerical value) and status description (a text variable) are redundant and provide the necessary information to distinguish ambient air concentration measurements from zero and span calibration measurements. The Hg^0 flux was calculated based on the Hg^0 raw concentration. To account for drift and baseline drift, which both are unavoidable when longer measurement periods are used between calibration events, we proceeded as follows. After a calibration event, the Hg^0 raw concentration was considered to be the best empirical estimate of the true Hg^0 concentration. Until the end of a measurement period (begin of next calibration cycle), in a first step a linear drift correction was applied to bring the Hg^0 raw concentration before the next calibration event to the level of the next calibration result (offset correction). Since visual inspection of the data clearly indicated that there is more drift than a simple linear trend in the data (see examples in Fig. 2), a high-pass filter approach was used to minimize drift and optimize the determination of Hg^0 fluctuations for EC flux measurements (Sect. 2.5.4).

2.5.2 Preparation of the ultrasonic anemometer data

The ultrasonic anemometer data contained the three wind speed components of the wind vector (all in m s^{-1}), the speed of sound (m s^{-1}), and the information sent from the RA-915AM to the data acquisition system via the serial data link. Speed of sound c was converted to virtual sonic temperature $T_v \approx c^2/403$ in Kelvin (Kaimal and Gaynor 1991). The vertical wind speed w was despiked using an iterative 7σ filter that discards w outside the range of the 6 hour mean ± 7 standard deviations.

2.5.3 Merging of ultrasonic anemometer data with Hg^0 time series

After preparation of the two datasets they were merged by accounting for the time difference between the RA-915AM and the Linux data acquisition using the information that could be transferred via the serial link from the RA-915AM to the Linux system (accurate to within 1 second). If no such information was received from the RA-915AM, the time difference between the two systems was determined using a network time drift fallback option specifically added to the Linux system to overcome the problems with serial output from the RA-915AM: during

the field experiment we polled the most recent data record acquired by the RA-915AM every five minutes using the Samba filesharing protocol, and associated that timestamp with the one of the EC system. This (somewhat less accurate) information was then adjusted during periods where both approaches overlapped to determine the time difference required to shift the Hg^0 raw data relative to the ultrasonic anemometer data before merging the two datasets. To ascertain that Hg^0 are lagging the sonic data we added a ≈1.5 s safety margin in the interpretation of the available time synchronization information received either via serial link or Samba filesharing.

2.5.4 Determination of time lag between vertical wind speed and Hg^0 fluctuations

The merged dataset was then divided into 1 hour segments for Hg^0 flux calculations. Within each 1 hour segment the time lag between the two time series was fine-tuned using a cross-correlation procedure to find the best positive or negative correlation within a reasonable time window (0–4 s) around the physically expected time difference (1.15 s physical delay plus 1.5 s safety margin used in step 3). Because considerable non-turbulent drift of the Hg^0 signal was still present after correcting for online calibration (Sect. 2.5.1), we detrended each 1 hour segment using a third-order polynomial fit (Eq. 5) before computing the cross-covariance between the detrended Hg^0 signal and w (Sect. 3.2.1). To account for the different sampling rates of w (20.83 Hz) and Hg^0 (1 Hz), we used simple linear interpolation between individual Hg^0 measurements and to bridge across calibration gaps. After a first automatic run each best estimate for time lag was visually inspected and updated by a narrower search window for each 1 hour segment that narrowed in the search procedure to the most realistic cross-correlation peak (positive or negative). Note that calibration gaps are relevant data gaps with setting 4 (Sect. 2.4) but less problematic with settings 1–3. In all cases, the lack of variance in Hg^0 data during the gaps reduces the computed Hg^0 flux. Thus, our flux estimates are conservative estimates with respect to flux magnitudes.

2.5.5 Computation of Hg^0 EC fluxes

After all data preparations according to Sect. 2.5.1 and Sect. 2.5.4 the Hg^0 flux F_{Hg0} was calculated as the covariance

$$F_{Hg0} = \overline{w'\chi'}, \quad (1)$$

with χ being the calibrated, detrended and linearly gap-filled Hg^0 concentration in ng m^{-3} and w the vertical wind speed. For improved readability F_{Hg0} was converted from ng m^{-2} s^{-1} to ng m^{-2} h^{-1} before reporting. In the notation used here, primes denote short-term deviations from the mean (after detrending according to Sect. 2.5.4) over an averaging period (1 hour) and overbars denote the mean of a variable. Hg^0 flux computations were done using R version 3.5.2 (R Core Team, 2018).

2.6 Determine the Hg^0 flux detection limit

To determine whether a calculated Hg^0 flux is significantly different from a zero-flux we used two approaches: (1) an indoor zero-flux experiment, and (2) a statistical estimate of the flux detection limit following the concept by Eugster and Merbold (2015) ~~which~~that is ~~a further~~an improvement of the concept presented by Eugster et al. (2007). The indoor zero-flux experiment was set up in the laboratory on the two days before installing all equipment in the field. The low turbulence conditions in combination with absence of local Hg^0 sources in the laboratory allowed us to see what fluxes are resulting with the procedure described above when there is no real Hg^0 flux. Such zero-flux experiments ~~however~~ tend to underestimate the flux detection limit under real-world outdoor conditions, where the second approach quantifies the statistical uncertainty of a calculated flux. The flux

(covariance) is the product of the correlation coefficient $r_{w,\chi}$ between w and χ and the square-root of the variances of the two variables (e.g. Eugster and Merbold 2015),

$$\overline{w'\chi'} = r_{w,\chi} \cdot \sqrt{w'^2} \cdot \sqrt{\chi'^2} = r_{w,\chi} \cdot \sigma_w \cdot \sigma_\chi \quad (2)$$

The significance of $r_{w,\chi}$ can be estimated using Student's t test (see Eugster and Merbold 2015) for details. For each 1 hour period we thus computed the value of $r_{w,\chi}$ that is significant at p = 0.05, and multiplied this value with measured σ_w and σ_χ to obtain a more realistic estimate for the flux detection limit. It should be noted that this concept has been brought forward long ago by Wienhold et al. (1996) using a visual empirical approach, whereas Eugster and Merbold (2015) further developed the visual approach to a more objective time series statistical approach to perform the quantification of the flux detection limit. The threshold of significance of $r_{w,\chi}$ can be estimated as

$$r_{w,\chi_p} = \frac{t_p}{\sqrt{n-2+t_p^2}}, \quad (3)$$

where t_p is Student's t value for the significance level p (e.g., 0.05), and n is the auto-correlation corrected number of independent samples in the time series,

$$n \simeq N \frac{1-\rho_1}{1+\rho_1}, \quad (4)$$

where N is the number of samples in a time series, and ρ_1 is the lag 1 auto-correlation coefficient of the scalar product time series $w \cdot \chi$.

2.7 Eddy covariance CO_2 flux calculations and quality control flags

The 30 min CO_2 flux was quantified in the conventional way established in ecosystem studies (see Aubinet et al., 2012) using the Eddy Pro (LI-COR Inc., Lincoln, NE, USA) software (see Fuchs et al., 2018 for specific information related to the Chamau field site). For each 30-minute CO_2 flux interval a flux quality control (QC) flag was determined: 0 (best data quality for detailed investigations), 1 (good data for longer-term studies), and 2 (poor quality), after Mauder and Foken (2004). Since there are no established quality control procedures for Hg^0 fluxes yet, we used the QC information from the CO_2 flux measurement to retain or reject concurrent Hg^0 flux measurements. Thus, we solely present Hg^0 flux measurements with CO_2 flux quality flags < 2. During CO_2 flux processing using the EddyPro software, coordinate rotation for tilt correction, angle of attack correction for wind components, Webb–Pearman–Leuning terms for compensation of density fluctuations (Webb et al., 1980) and analytical corrections for high-pass (Eugster and Senn, 1995; Moncrieff et al., 2004) and low-pass filtering effects (Horst, 1997) were applied. Furthermore, a self-heating correction for the open-path gas analyzer was conducted (Burba et al., 2008) and CO_2 fluxes > 50 µmol m^{-2} s^{-1} and < -50 µmol m^{-2} s^{-1} were discarded.

3 Results and Discussion

3.1 Environmental conditions

In 2018, the annual mean air temperatures in Switzerland reached 6.9 °C, the largest value ever recorded since the onset of meteorological measurements in 1864 (MeteoSchweiz, 2019). This nationwide average temperature was

1.5 °C warmer compared to the average of the normal period of 1981–2010. Total precipitation measured from April to November 2018, was only 69 % of the long-term average (1981–2010). Thus, the period from April to November 2018 was the third driest period ever recorded in Switzerland (MeteoSchweiz, 2019). From the beginning of the growing season until the end of our measurement campaign (April to September 2018), air temperatures at the Cham (CHZ) SwissMetNet surface weather station were elevated by 2.2 °C compared to the long-term average from 1994 to 2017 (15.8 °C) during the same period. Total precipitation from April to September 2018, was only 72 % (467 mm) of the long-term average (648 mm) calculated for the period between 1994 and 2017. These specific conditions reduced CO_2 uptake compared to the same period in 2017 (Sect. 3.3, Fig. 7) and led to lower grassland productivity and yields of only 6.8 t dry matter (DM) ha^{-1} a^{-1} in 2018 compared to an average yield of 12.7 t DM ha^{-1} a^{-1} quantified from 2015 to 2017 (start of the clover experiment). Over the course of the 34-day campaign (20 July 2018, 02:00–24 July 2018, 08:00 and 09 August 2018, 12:00–06 September 2018, 17:00; all times are in Central European Time, CET = UTC+1) sunny conditions prevailed with a mean solar irradiation (Rg) of 310 352 W m^{-2} during daytime (Rg ≥ 5 W m^{-2}) and a mean irradiation of 6069 W m^{-2} at 13:00. The hourly mean air and soil surface temperature ranged from 13.6 °C (06:00) to 24.1 °C (15:00) and from 18.1 °C (08:00) to 21.5 °C (18:00), respectively. The median daytime (Rg ≥ 5 W m^{-2}) and nighttime (Rg < 5 W m^{-2}) wind speed was 0.976 m s^{-1} (range 0.054–5.77 m s^{-1}) and 0.37 m s^{-1} (range 0.065–2.49 m s^{-1}), respectively. The prevailing wind direction during the day was N-NW (474 %) and E-SE (554 %) at night.

3.2 Performance of the *Eddy Mercury* system

3.2.1 High-frequency signal analysis

Two examples of the raw data used to compute fluxes (Eq. 1) are shown in Fig. 2, one from period 1 with 24 hour calibration intervals (Fig. 2a,c,e) and one with frequent calibrations every four minutes (Fig. 2b,d,f). whichthatFrequent calibrations strongly reduceds the instrument drift (Fig. 2d) as compared to the long calibration intervals (Fig. 2c), although at the expense of some loss of variance and flux as will be discussed below. In principle, block-averaging raw data within a sampling interval is the best approach to compute EC fluxes (Aubinet et al. 2012). In case of substantial instrument drift as it is seen with the RA-915AM (Fig. 2c) it is necessary to remove the drift by some adequate procedure. Because of the curvature of the drift of the analyzer a simple linear detrending did not lead to satisfactory results, hence we used a third-order polynomial regression fit,

$$\chi' = \chi + \alpha_0 + \alpha_1 \cdot t + \alpha_2 \cdot t^2 + \alpha_3 \cdot t^3 \,, \quad (5)$$

with t elapsed time within the averaging interval of 1 h. The turbulent Hg^0 fluctuations after this additional detrending led to the time series shown in Fig. 2e and f. Lengthy discussions on possible shortcomings of such a detrending can be found in Lee et al. (2005) and Aubinet et al. (2012) and thus are not repeated here. With the example data shown in Fig. 2e we produced an artificial dataset with gaps that correspond the 4-minute recalibration scheme used during the period shown in Fig. 2f. This led to a loss in Hg^0 flux in the order of 12 %. Although nonzero, this should be considered a robust finding given the general understanding that EC flux measurements are accurate to within 10 – 20 % even with higher-quality instrumentation (Aubinet et al., 2012). It is however clear that in order to To obtain higher quality EC fluxes than what we can present here it is required to improve the long-term stability of the instrument (Sect. 3.4), whereas improving the gap filling strategy is not expected to contribute significant new insights into Hg^0 flux calculations.

Drift of the current version of the *Eddy Mercury* system is substantial (Fig. 3a), an effect that is common with experimental sensor set-ups, but is no longer prevalent with present-day CO_2 sensors. Removal of any drift also reduces the variance of a signal and hence the flux covariance of interest. Thus, knowledge about the stability of an instrument over which no drift correction is required, becomes important. The Allan variance plot (Fig. 3b, see Allan (1966) and Werle et al. (1993)) indicates that the optimum averaging time is ca. 54s. For comparison, a CH_4 analyzer tested by one of the authors (Eugster and Plüss, 2010) shows an optimum average time ~~which~~that is roughly three times as long (ca. 180 s) before the instrument drift starts to dominate the Allan variance. Figure 3b shows that the Allan variance caused by drift at integration times beyond 550 s exceeds the variance associated with turbulence at the 1 second integration time (see blue arrow in Fig. 3b~~),). whereas i~~In a more ideal instrument ~~(see e.g. Eugster and Plüss, 2010)~~ the long-term drift is smaller than the short-term variance of interest for EC measurements (see e.g. Eugster and Plüss, 2010). Despite these findings, Fig. 3 clearly shows the potential and quality of the instrument for Hg^0 flux measurements.

This interpretation is also supported by spectral and cospectral analyses (Fig. 4). Figure 4a shows an example spectrum of Hg^0 measurements obtained over a 1 hour interval. The difference between the red and black lines in Fig. 4a visualizes the effect of polynomial detrending on the power spectrum of Hg^0, ~~which~~that is relatively small and of no real concern. Since the RA-915AM only delivers 1 Hz raw data, we had to oversample this digital Hg^0 signal to match the 20.83 Hz resolution of the ultrasonic anemometer. Spectral densities at high frequencies > 0.5 Hz (the Nyquist frequency of the RA-915AM~~, which~~ is ½ of the sampling frequency) are reflecting the effect of oversampling ~~which in~~. In the case of the RA-915AM, oversampling leads to local minima in spectral densities at 1 Hz and all its harmonic multiples (2, 3, 4, … Hz), ~~which~~that is the result of linear interpolation between measurements. Between these local minima the spectral density ~~obey~~obeys the f^{-1} power law (line "r" in Fig. 4a), ~~which~~that is very close to the inertial subrange slope $f^{-2/3}$ (line "i" in Fig. 4a). A damped signal (first order damping; see Eugster and Senn, 1995) would follow a $f^{-8/3}$ power law (line "d" in Fig. 4a), thus it is obvious that our set-up had an adequate flow rate through the RA-915AM that did not lead to substantial damping of the turbulent Hg^0 fluctuations. With the oversampling used here, the white noise level (blue band "w" in Fig. 4a) is artificially reduced below the level that we would obtain without oversampling.

After having applied an adequate time lag correction to synchronize the detrended Hg^0 signal with vertical wind speed fluctuations w', the cospectra of fluxes that are significantly different from a random pattern are closely agreeing with the theoretical idealized cospectrum for neutral atmospheric stability derived from Kaimal et al. (1972) (see Eugster and Senn, 1995), shown by the solid blue line in Fig. 4b. Some minor signs of damping are seen at higher frequencies where the green spline deviates from the solid blue line (Fig. 4b). The comparison of cospectral densities with theoretical damped cospectra (dashed blue lines in Fig. 4b) clearly confirm the finding from the spectral analysis that the flow rate was high enough in the RA-915AM sample cell to prevent significant damping effects that tend to be a problem with closed-path EC flux measurements.

On occasion of a clear Hg^0 flux ~~which~~that was statistically different from a zero-flux the cross-correlation peak was well defined (Fig. 5a,b). In some occasions with low fluxes relative to the flux detection limit (Sect. 3.2.2) the automatic detection of the cross-correlation peak was not successful. The peak often does not extend very strongly beyond the (expected) noise level, as shown in Fig. 5c. However, when zooming in (Fig. 5d) the peak becomes rather clear, although only marginally above the range of insignificant correlations shown with blue background in Fig. 5. To minimize erroneous peak detections, and thus wrong flux estimates, we fine-tuned the search window

(red band in Fig. 5) for each 1-hour data segment by visually inspecting and selecting the search window within which the local maximum of the absolute correlation coefficient between w and χ was found.

3.2.2 Flux detection limit

The flux detection limit was calculated for each 1 hour flux period (Sect. 2.6). The significance threshold for $r_{w,\chi}$ was calculated for an error probability $p = 0.05$ and the product of this threshold $r_{w,\chi}$ and measured σ_w and σ_χ was determined as the flux detection limit for that specific 1 hour period. Figure 6 shows the probability density function of the flux detection limits from all 1 hour data segments. For comparison, the results from the 14 hour zero-flux experiments in the laboratory are added as a blue boxplot to Fig. 6. This comparison clearly shows that a zero-flux experiment in the laboratory highly overestimate the quality of Hg^0 flux measurements with a median (maximum) flux detection limit of 0.074 (0.22) ng m^{-2} h^{-1}. The more realistic flux detection limits based on statistically significant ($p < 0.05$) correlations are rather in the order of 5.9 (50 % cutoff) to 24 ng m^{-2} h^{-1} (99 % cutoff) with a 95 % cutoff at 13.7 ng m^{-2} h^{-1}. ~~Testing the performance of the *Eddy Mercury* system revealed that~~During the 34 days measurement campaign 49.7 % of the Hg^0 fluxes (363 out of 731 hours) were significantly different from zero.

Using the same approach but in a qualitative way, Pierce et al. (2015) estimated the flux detection limit of their system to be around 32 ng m^{-2} h^{-1}.

3.2.3 Comparison of detection limits for *Eddy Mercury*, gradient-based and REA systems

The *Eddy Mercury* system circumvents major sources of uncertainty compared to gradient-based and REA systems, ~~which~~that are related to assumptions on similarity or equivalence of the eddy diffusivities of the scalar transfer coefficients (sensible heat flux, latent heat flux and trace gases). ~~Testing the performance of the *Eddy Mercury* system revealed that 49.7 % of the Hg^0 fluxes (363 out of 731 hours) were significantly different from zero.~~Generally, land–atmosphere Hg^0 flux measurements using micrometeorological ~~MM~~ methods are scarce and information on detection limits even rarer. For gradient-based systems a minimum resolvable Hg^0 concentrations gradient (MRG) is determined by mounting the sampling lines at the same height for several days (same-air test) and compute the concentration differences between the lines that are used for flux calculations. The MRG threshold is usually defined as the average plus one standard deviation of the concentration difference obtained by the same-air test. Fluxes are considered significant when the Hg^0 concentration difference is above the MRG. Exemplarily, Edwards et al., (2005) derived a flux gradient system-specific MRG of 0.01 ng m^{-3} and a flux detection limit of 1.5 ng m^{-2} h^{-1}. To calculate the flux detection limit of the gradient sampling system, site characteristics and atmospheric conditions have to be considered (see Eq. 8 in Edwards et al., 2005). Fritsche et al. (2008a) derived a MRG of 0.02 ng m^{-3} for their setup. The minimum determinable gradient-based Hg^0 ~~deposition~~ flux was between ~~-~~0.5 and ~~-~~4.6 ng m^{-2} h^{-1} (Fritsche et al., 2008b). Converse et al. (2010) and Zhu et al. (2015b) reported ~~a~~ similar MRG for their gradient-based micrometeorological ~~MM~~ systems of 0.07 and 0.06 ng m^{-3}, respectively. During Hg^0 flux studies over agricultural land in China, 57 and 62 % of the aerodynamic and modified Bowen-ratio measurements were significant (Zhu et al., 2015b). For ~~the only two~~ Hg^0 REA systems, ~~currently applied over terrestrial ecosystems,~~ Zhu et al. (2015b) reported that the absolute precision in the updraft and downdraft Hg^0 concentration difference was concentration ~~(C)~~ dependent at 0.069 ± 0.022 C [ng m^{-3}], while Osterwalder et al. (2017) determined a detection limit of 0.05 and 0.04 ng m^{-3} ~~for both gold cartridge pairs in their system~~. Over wheat canopy, 55 % of the fluxes were significant (Zhu et al., 2015a) while 52 % of the fluxes were significant

over a boreal peatland (Osterwalder et al., 2017). The share of significant Hg^0 fluxes for gradient-based, REA and the *Eddy Mercury*~~EC~~ method~~s~~ is in a similar range ~~(~~~~≈~~of approximately 50 %~~), when applying the statistical significance test for *Eddy Mercury*.~~ . However, the same-air tests applied to determine the detection limit of gradient-based and REA fluxes is more appropriate to compare with our approach to determine the zero-flux in the laboratory. With a median zero-flux of 0.074 ng m^{-2} h^{-1} as measured in the laboratory, the share of significant fluxes measured with *Eddy Mercury* would increase to 99.7 %, which ~~, however,~~ is not realistic for measurements outside the laboratory environment. Generally, the reported mean fluxes derived from gradient-based, REA and *Eddy Mercury* should include data below the detection limit because otherwise the magnitudes of the average exchange rates would be overestimated (see Fritsche et al., 2008a; Osterwalder et al., 2016).

3.3 Net ecosystem exchange of Hg^0 over grassland

The median (interquartile range, IQR) Hg^0 flux measured at the Chamau (CH-Cha) research site using the *Eddy Mercury* system was 2.5 (-0.6 to 7.4) ng m^{-2} h^{-1}. The Hg^0 flux revealed a distinct diel pattern with median (IQR) daytime and nighttime fluxes of 8.4 (1.9 to 15) ng m^{-2} h^{-1} and 1.0 (-0.9 to 3.3) ng m^{-2} h^{-1}, respectively. The minimum hourly median Hg^0 flux (0.5 ng m^{-2} h^{-1}) was detected at 21:00 (Fig 7a). ~~Re-emission~~Emission of Hg^0 reached a maximum between 11:00 and 14:00 (hourly median 10.8 ng m^{-2} h^{-1}). The diel Hg^0 variation corresponded with solar radiation with the highest mean level of irradiance at 13:00 (60~~69~~ W m^{-2}). The flux of CO_2 changed from net emission ~~soil respiration~~ during the night to net uptake by vegetation with sunrise (Fig. 7b). At noon, CO_2 fluxes were 26 % lower compared to the most negative flux occurring between 10:00 and 11:00 (-0.1 mg C m^{-2} s^{-1}). The absence of a midday maximum CO_2 uptake indicates a midday depression due to plant stress by exceptionally hot and dry conditions. The partial closure of their stomata during the warmest period of the day minimizes water loss through transpiration with the consequence of lower CO_2 uptake. Overall the median ~~cumulative~~ CO_2 flux ~~NEE~~ during our measurement campaign in 2018 was only 248 ~~%~~ compared to the same period in 2017 which exhibited average climatic conditions (red dashed line in Fig. 7b). The median CO_2 uptake in 2018 was ~~0.008~~0.031 mg C m^{-2} s^{-1} compared to ~~0.08~~0.127 mg C m^{-2} s^{-1} measured in 2017. We suggest that the increased stomatal resistance of vegetation during the campaign ~~due~~ in response to high drought stress not only led to the above discussed minimized uptake of CO_2, but damped stomatal gas exchange in general~~, thus also~~ including the uptake of Hg^0. Subsequently, soil ~~re~~-emission was the dominating factor driving ~~GEM~~ the NEE of Hg^0 during summer 2018.

The Hg^0 flux measured at the CH-Cha site is comparable to Hg^0 fluxes ~~(n = 38)~~ reported for other grassland sites globally (Zhu et al., 2016). A median Hg^0 flux of 0.4 ng m^{-2} h^{-1} and a flux range between -18.7 and 41.5 ng m^{-2} h^{-1} (site-based average fluxes) was reported for nine studies (Poissant and Casimir, 1998; Schroeder et al, 2005; Ericksen et al. 2006; Obrist et al. 2006; Fu et al. 2008a,b; Fritsche et al. 2008a,b; Converse et al. ~~(~~2010). Several studies reported ~~a~~ net ~~re~~ Hg^0 emission ~~of Hg^0~~ during summer. Converse et al. (2010) reported net average Hg^0 ~~re~~-emission of 2.5 ng m^{-2} h^{-1} from a high-elevation wetland meadow in Virginia, USA. Zhang et al. (2001) measured a Hg^0 flux of 7.6 ± 1.7 ng m^{-2} h^{-1} from an open background site in Michigan, USA. The average Hg^0 flux from a grassland in Québec, CA, was 2.95 ± 2.15 ng m^{-2} h^{-1} and a correlation of the diel flux ~~cycle~~pattern with solar radiation was reported (Poissant and Casimir 1998). Average net Hg^0 emission of 1.1 ng m^{-2} h^{-1} was recorded from a pasture in Ontario (Schroeder et al, 2005). The mean Hg^0 flux from four grassland sites in the USA ranged from 0.3–2.5 ng m^{-2} h^{-1} between May 2003 and 2004 (Ericksen et al. 2006). Fu et al. (2008a) reported average Hg^0 fluxes ranging from -1.7 to 13.4 ng m^{-2} h^{-1} from three grasslands in China in August 2006. The ~~Mechanism~~ mechanism driving Hg^0 ~~re~~-emission from grasslands is not fully understood ~~yet~~. Photoreduction has been reported

to enhance Hg^0 emission from ~~the~~ soil~~s~~ and foliage surface and from Hg within foliar tissue (Gustin et al., 2002; Moore and Carpi, 2005; Choi and Holsen, 2009; Yuan et al., 2019). Soil warming has been suggested to promote Hg^0 ~~re~~ emission (Poissant et al., 1999; Zhang et al., 2001; Gustin et al., 2002; Almeida et al., 2009), likely due to increased decomposition of organic material (Fritsche et al., 2008c) and facilitated mass transfer of Hg^0 through the topsoil to the atmosphere (Lin and Pehkonen, 1999). Zhang et al. (2001) reported a strong positive correlation of Hg^0 ~~re emission~~ fluxes with solar radiation and soil temperature. A solar shielding experiment resulted in a 65 % decrease of soil Hg^0 ~~re~~ emission, suggesting that photoreduction is a major factor but also soil temperature cannot be neglected.

Few grassland studies have shown net Hg^0 dry deposition. Fritsche et al. (2008a) reported an average Hg^0 flux of -1.7 ng m^{-2} h^{-1} (modified Bowen-ratio) and -4.3 ng m^{-2} h^{-1} (aerodynamic gradient) during the vegetation period over a sub-alpine grassland at Fruebuel in central Switzerland, 15 km SW of our study site. More summertime Hg^0 fluxes from three Central European grasslands were measured on a campaign basis and average grassland–atmosphere Hg^0 fluxes ranged from -4.3 to 0.3 ng m^{-2} h^{-1}. The highest variability of the fluxes was recorded for the Neustift site in Austria with a range of −76 to 37 ng m^{-2} h^{-1} (Fritsche et al., 2008b). A second full year Hg^0 flux study was performed at an upland meadow in Maryland, USA (Castro and Moore 2016). The hourly mean summertime Hg^0 flux was -1.2 ng m^{-2} h^{-1} and ranged between -224 and 354 ng m^{-2} h^{-1}.

We found that the southern ~~Hg^0~~ source area of our grassland site has a 28 % higher Hg substrate concentration (mean = 59.4 ± 8.4 ng Hg g^{-1}) compared to the northern source area (mean = 46.4 ± 5.1 ng Hg g^{-1}) (Wilcoxon two sample t-test, $p < 0.05$, Fig. 8a). The *Eddy Mercury* system was able to resolve a marginally significant greater daytime (+44 %, $p = 0.0515$) Hg^0 flux (Fig. 8c) and insignificantly greater nighttime Hg^0 flux (+68 %, $p = 0.296$) (Fig. 8b) ~~originating~~ from the southern source area ~~the~~ enriched in Hg ~~enriched~~compared to the northern source area ~~southern source area~~. The proportionality of Hg^0 ~~re~~ emission to soil Hg concentration has been shown across Hg-enriched soils (Eckley et al., 2015; Zhu et al., 2018; Osterwalder et al., 2019~~)~~), but no significant correlation has been observed for low-Hg level background soils (Agnan et al., 2016). There are two possible explanations for the lack of a significant relationship between Hg^0 flux and soil Hg concentration: (i) analytical uncertainty of Hg^0 flux measurements or (ii), at vegetated surfaces~~,~~ ; a masking of Hg^0 ~~re~~ emission by stomatal uptake of Hg^0 ~~which~~that is independent on the soil Hg concentration.

3.4 Suggestions to improve the *Eddy Mercury* system

~~During the pilot campaign and the data analysis we found room for optimization of the *Eddy Mercury* system.~~

Here we propose a number of adjustments that are expected to improve the *Eddy Mercury* system's performance in particular by 1) facilitating data transfer and processing, 2) increasing the measurement frequency and sample air flow through the RA-915AM and 3) achieving more stable temperature conditions in the field. The length of data gaps mainly caused by system calibrations should be reduced to the point where discussions about gap filling methods and detrending procedures can be considered obsolete.

Improve data transfer: The determination of the time lag between the wind speed measurement and the Hg^0 concentration measurement bearded a considerable source of uncertainty and cross-correlation peaks had to be visually verified (Sect. 2.5.4.). In the future, we aim for a real time transfer of raw data to the serial port instead of data transfer via the USB port on the embedded Windows 7 system of the RA-915AM. This will allow a better synchronization between the Hg^0 measurements and the ultrasonic anemometer (Sect. 2.4) and significantly facilitate post-acquisition data treatment.

Increase measurement frequency: The pilot campaign was performed with a measurement frequency of 1 Hz. In the future, we wish to increase the measurement frequency up to 8–15 Hz. Such an increase in measurement frequency is possible through software adaptations of the RA-915AM and will make the oversampling of the Hg^0 signal performed here (Sect. 3.2) redundant and result in better counting statistics.

Increase sample flow rate: During this pilot study we connected a more powerful pump to the RA-915AM and managed to increase the flow rate from standard operation of 7–10 L min^{-1} to 14.3 L min^{-1} resulting in a two times lower residence time in the measurement cell. The lower residence time in the cell reduced the dampening of the signal (Sect. 3.2). However, this high flow led to a reduction in the cell pressure (approx. 700 mbar) ~~which affects~~affecting the detection limit for Hg^0 concentration measurements. In the future, we propose to further reduce the residence time of the air in the measurement cell by increasing the sample air flow by another 30 % to 20 L min^{-1} using an external pump. To account for pressure drop we propose to minimize the constrictions present in the RA-915AM by increasing t~~t~~he internal diameter of the valves and the inlet tubing.

Improve the long-term stability of the instrument: The stability of RA-915AM Hg^0 concentration measurements is temperature dependent (Sect. 3.2). We encountered strong diurnal temperature fluctuations of the instrument during the pilot campaign. We took several measures already during the campaign to increase the temperature stability (e.g. placing the pump outside the temperature controlled analyzer box, isolation of the analyzer box and shading it from direct sunlight). To improve the temperature stability in the future, we suggest to place the RA-915AM in an instrument box that has a better isolation and more powerful temperature control or ideally to place it in a climate controlled instrumental hut. For long-term deployments of the *Eddy Mercury* the sampling hose can be extended to bridge the distance between the air inlet, located close to the sonic anemometer and the instrumental hut where the system is placed. In that case it is important to guarantee a turbulent flow in the tube (Reynolds number of > 3000–3500; Lenschow and Raupach, 1991; Leuning and King, 1992), an adequate refresh rate in the sampling cell and to ensure that the pressure drop in the sampling cell is within the requirements of the instruments (> 600 mbar; pers. communication with Lumex Ltd.).

4 Conclusion

This study demonstrates ~~the first successful~~an application of the EC method for Hg^0 flux measurements over ~~terrestrial surfaces~~a grassland site with low soil Hg concentrations (< 100 ng g^{-1}) ~~with background soil Hg concentrations~~ (< 100 ng g^{-1}). ~~We tested and validated the system at a Central European grassland site.~~ The maximum flux detection limit derived from a zero-flux experiment in the lab was 0.22 ng m^{-2} h^{-1}. The statistical estimate of the flux detection limit under real-world conditions was 5.9 (50 % cutoff) to 13.7 ng m^{-2} h^{-1} (95 % cutoff). The *Eddy Mercury* system overcomes major uncertainties of other micrometeorological methods previously used for Hg^0 flux measurements associated with the intermittent sampling at two different levels (aerodynamic methods) and the stringent sampling and analytical requirements (relaxed eddy accumulation). The *Eddy Mercury* system will considerably facilitate ecosystem-scale Hg^0 flux measurement because it features a fully automated operation, cutting down operation costs for technical maintenance by experienced staff, argon supply and consumables. *Eddy Mercury* bears the potential to be established as a standard micrometeorological method for long-term Hg^0 measurements over grasslands and other terrestrial ecosystems. Such a standardization of measurements is strongly required to obtain comparable data and properly evaluate controlling factors on the net ecosystem exchange of Hg^0 on larger spatial- and temporal scales (Obrist et al., 2018). Ultimately, the *Eddy*

Mercury system could complement air pollution and greenhouse gas measurements within the global network of micrometeorological tower sites (FluxNet) ~~to assessing the impacts of controlling Hg emissions on deposition and re-emission~~ (Baldocchi et al., 2001). The *Eddy Mercury* system also comes at an opportune time to include net ecosystem exchange measurements of Hg^0 in the joint WHO and UN Environment project to "develop a plan for global monitoring of human exposure to and environmental concentration of mercury".

Data availability

Research data will be provided and deposited. A statement Research data can be accesse available here: will be made; DOI: The research data that support the findings of this study will be openly available at https://doi.org/10.3929/ethz-b-000393131

Author contributions

All authors contributed to designing the study, testing the RA-915AM in the laboratory and performing fieldwork. WE analyzed the data. Soil samples were taken by IF and analyzed for total mercury by MJ. IF analyzed the CO_2 flux and meteorological data. SO and MJ coordinated the study. SO, WE and MJ wrote the paper with contributions of IF.

Competing interests

The authors declare that they have no conflict of interest.

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Figures and captions

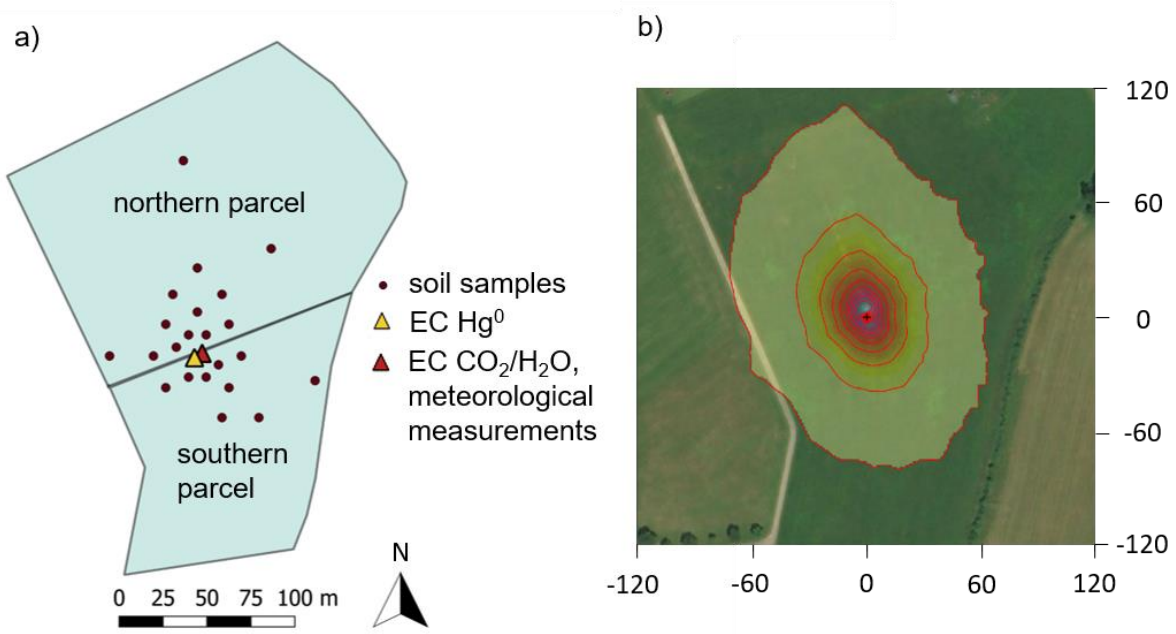

Figure 1: (a) Schematic of the experimental setup at Chamau (CH-Cha) research site with exact location of topsoil samples for total Hg analysis (n = 22) and Eddy covariance (EC) flux measurements of Hg^0, CO_2 and H_2O conducted between 20 July and 6 September 2018. (b) Footprint contour lines of 10 % to 90 % in 10 % steps representing the flux source area during our measurement period. Numbers indicate the distance in meter from the EC station (black cross). The footprint was calculated applying the footprint model presented in Kljun et al. (2015). Figure 1b is a direct output from the online tool: http://footprint.kljun.net/.

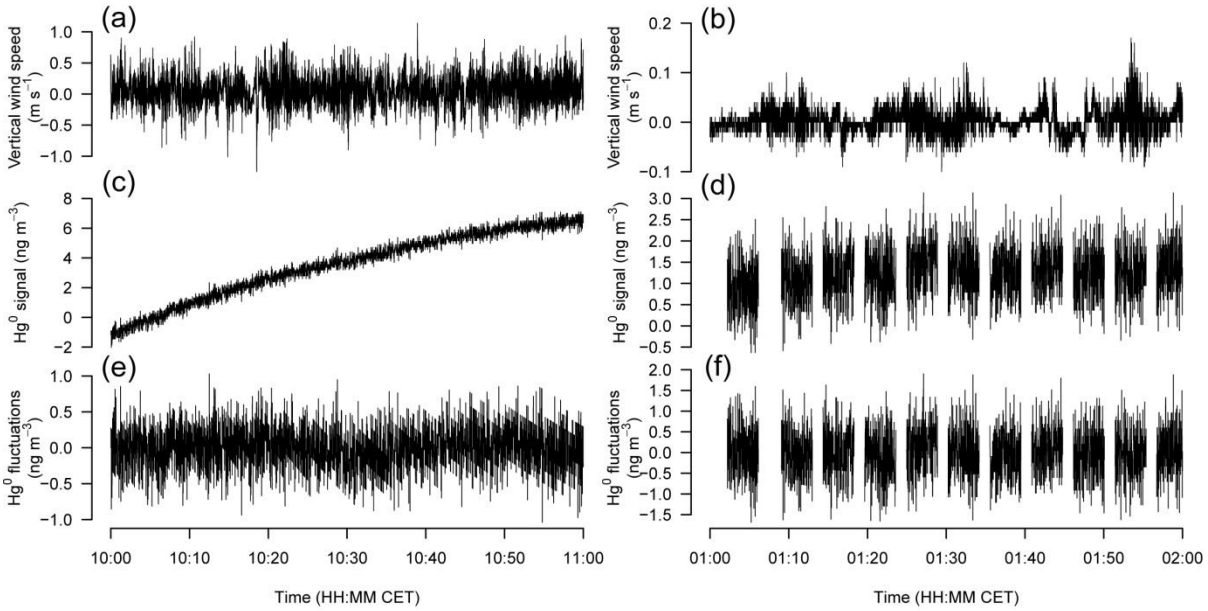

Figure 2: Examples of raw data time series over a 1 hour data segment, (a, c, e) during period 1 with 24 hour calibrations only (21 July 2018, 10:00–11:00), and (b, d, f) during period 4 with 4 min instrument calibration intervals (6 September 2018, 01:00–02:00). Vertical wind speed (a, b) was not detrended. Hg^0 concentrations are shown before (c, d) and after detrending (e, f). While the 4 min calibration intervals clearly reduce the longer-term drift (d) compared to daily calibrations (c), the gaps during calibrations had to be filled by linear interpolation before calculating fluxes.

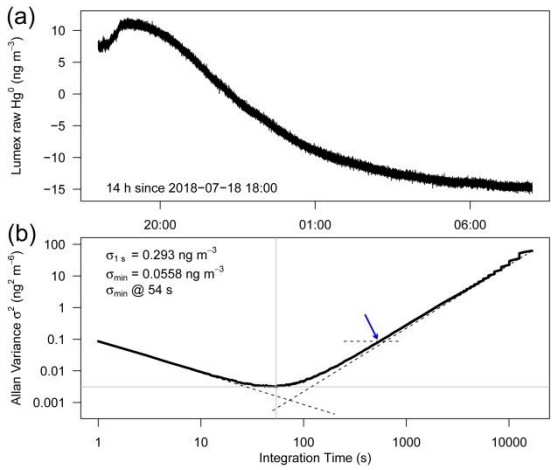

Figure 3: Allan variance plot using 14 h of continuous measurements in the laboratory (zero-flux experiment), starting 18 July 2018, 18:00. (a) Raw time series, (b) Allan variance as a function of integration time.

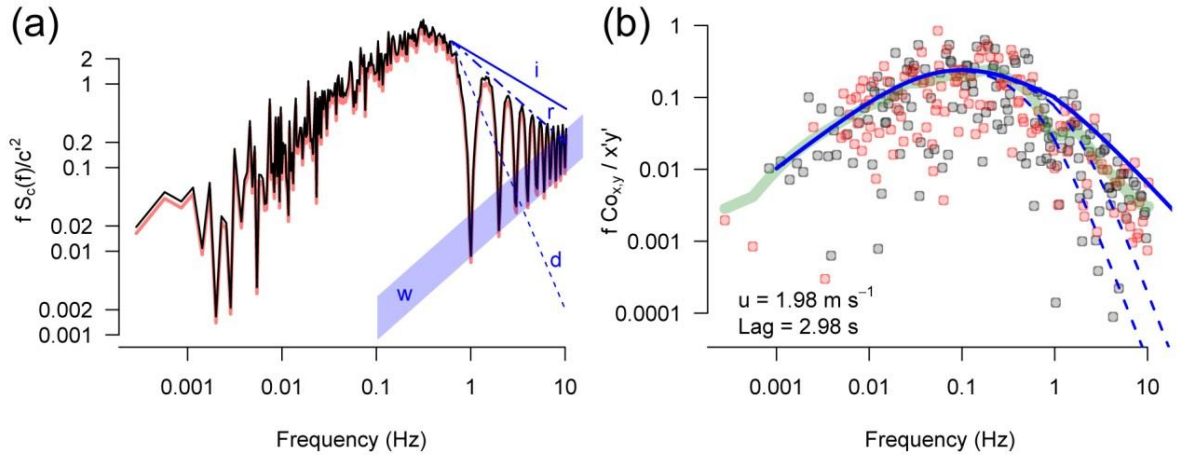

Figure 4: Example spectrum (a) of Hg^0 fluctuation measurements and (b) cospectrum of the 1 hour averaged Hg^0 flux, 31 August 2018 14:00–15:00. The power spectrum (panel a) before (red line) and after detrending (black line) is shown, and the theoretical slopes in the inertial subrange are shown for ideal conditions (i, solid line,$f^{-2/3}$ slope), for a rectangular oversampling at frequencies > 1 Hz (r, broken line, f^{-1} slope), and for a first-order damped spectrum (d, dashed line, $f^{-8/3}$ slope). The approximated white noise level is shown with a color band (w, f^{+1} slope). The flux cospectrum (b) 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.

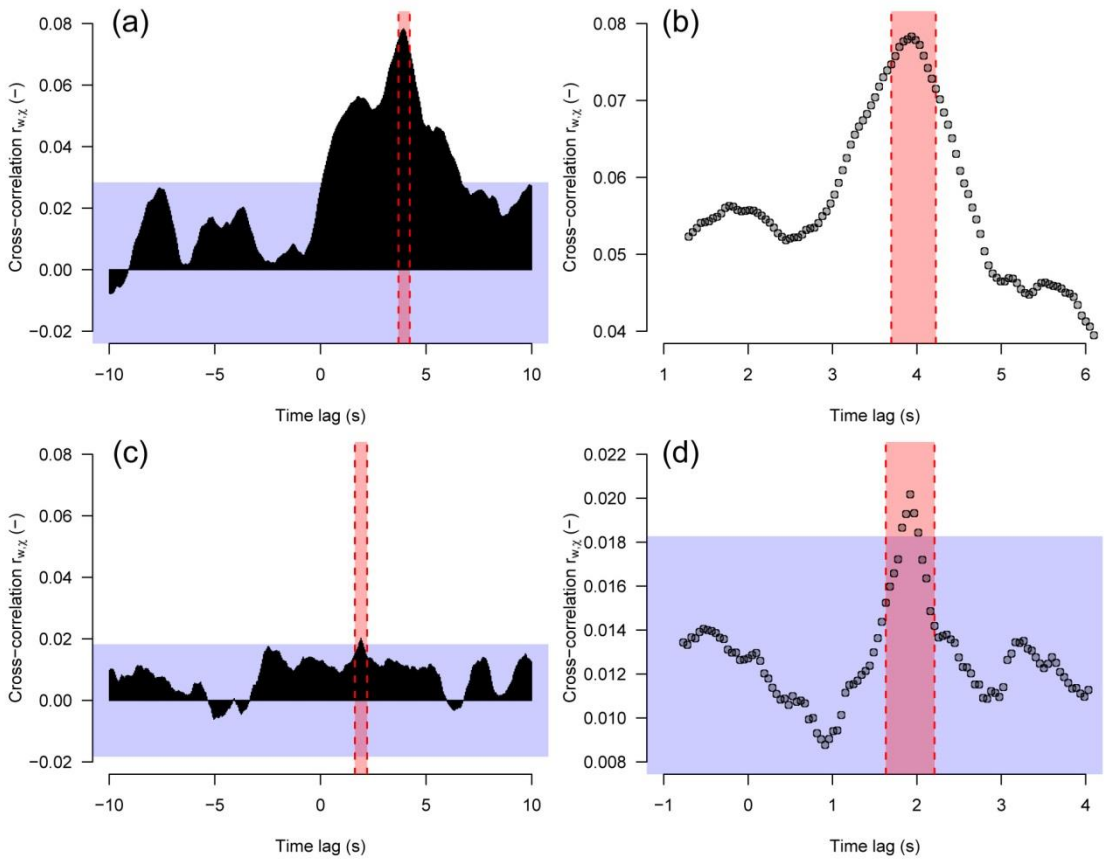

Figure 5: Cross-correlation analysis to determine the time lag between vertical wind speed (w) and Hg^0 time series (χ). (a,b) Example with a clearly positive Hg^0 flux (21 July 2018, 10:00–11:00), and (c,d) with a marginally positive flux (6 September 2018, 01:00–02:00). Panels (a) and (c) show the cross-correlation within a time lag window of ±10 s, and (b,d) zoom in to the search window used in this study (vertical red band). The blue horizontal band shows the range of zero-fluxes (cross-correlation $r_{w,\chi} \neq 0$ with $p \geq 0.05$).

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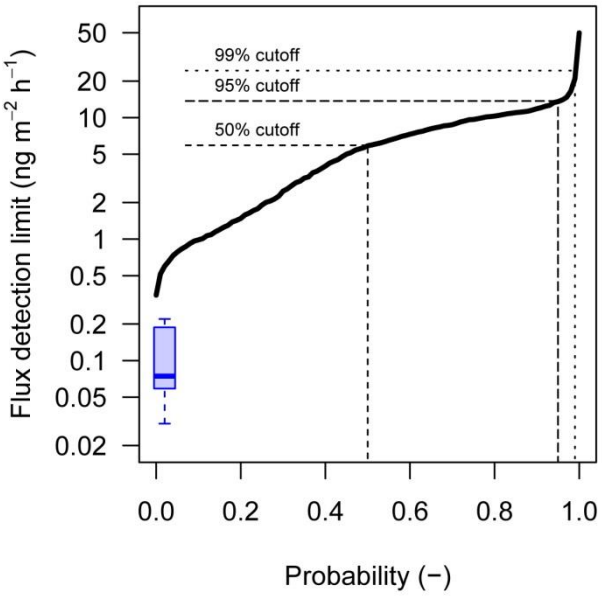


Figure 6: Flux detection limit empirical probability distribution of the magnitude of flux measurements under outdoor conditions (black line). The boxplot insert shows the range of the magnitude of measured fluxes during the zero-flux experiment in the laboratory without Hg^0 sources under very low turbulence conditions. 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.

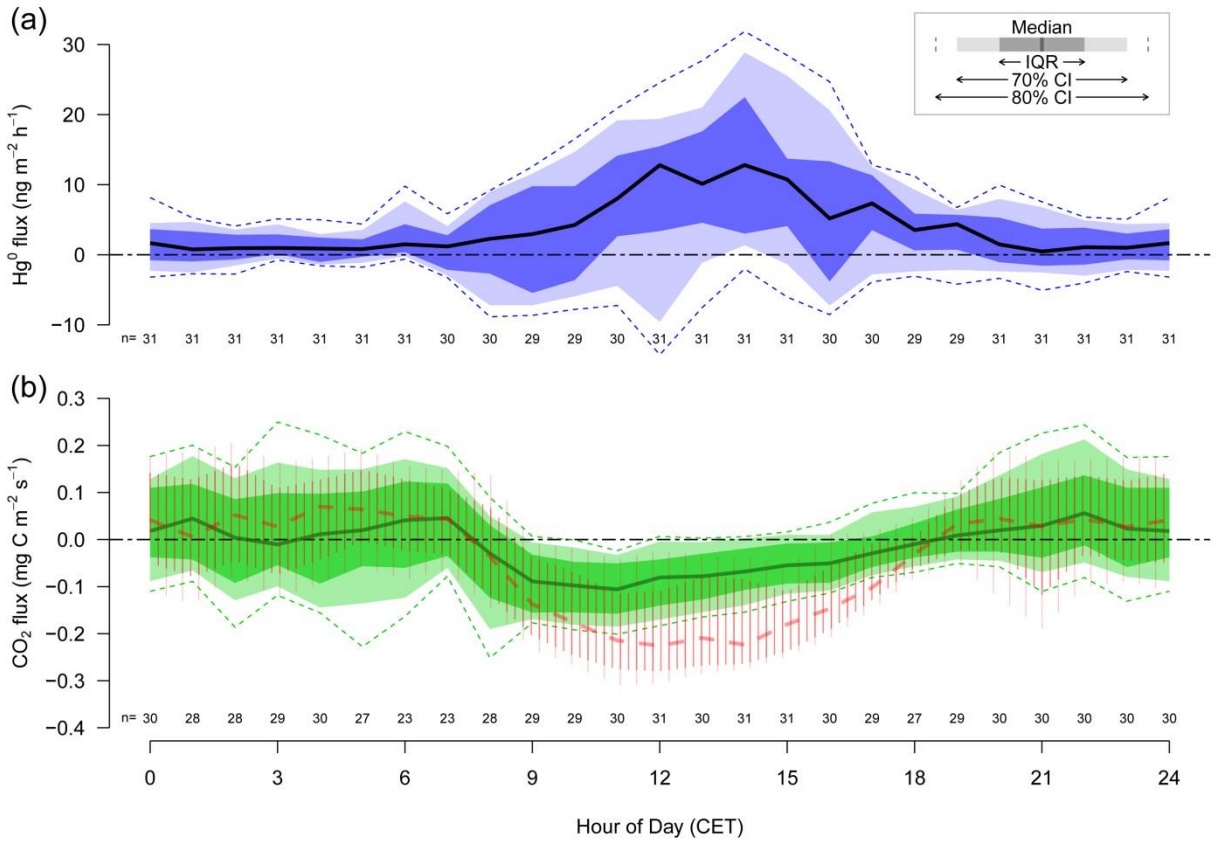
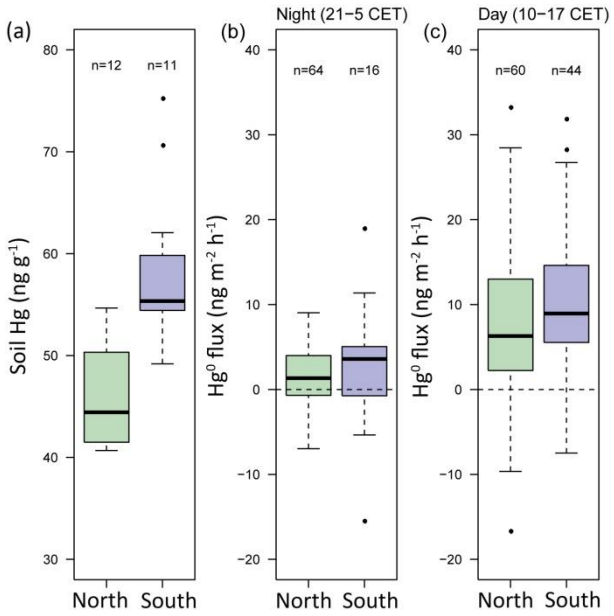


Figure 7: Hourly aggregated diel cycle of (a) Hg^0 fluxes and (b) simultaneously recorded CO_2 fluxes (bold green line) and fluxes measured in 2017 (red bold dashed line) for the same period. Each hour of day represents the quantiles obtained from a three-hour window centered at the respective hour of all technically valid observations. The bold lines represent median flux values. The interquartile range (IQR) is the range of the middle 50 % of the data. The 70 % and 80 % confidence intervals (CI) and the number of measurements per hour (n) are given. The median CO_2 flux in 2017 is displayed (red bold dashed line). The IQR (red vertical lines) and 70 % CI (lightered vertical lines) are indicated.



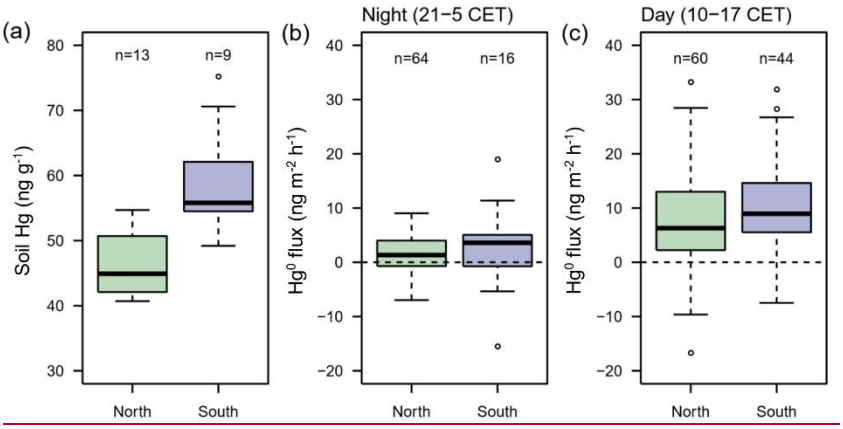


Figure 8: Boxplots display (a) the total topsoil Hg concentration (0–10 cm) in the northern and the southern parcels as well as the Hg^0 flux over the respective parcels (b) during the night (21:00–05:00) and (c) during the day (10:00–17:00).