Mercury evasion from a boreal peatland determined with advanced REA and chamber methods

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Zusammenfassung

Gasförmiges, elementares Quecksilber (Hg^0) ist die dominierende Form von Hg in der Atmosphäre und steht in ständigem Austausch mit Böden und Wasseroberflächen. In borealen Mooren ist dieser Land-Atmosphären-Austausch von Hg^0 von besonderer Relevanz. - in solch anoxischen Ökosystem bildet sich das hochtoxische Methylquecksilber (MeHg) -, da sich verändernde Depositions- und Emissionsraten den Hg-Pool im Boden beeinflussen. Um natürliche Einflussfaktoren zu bestimmen, welche die Reduktion von Hg(II) zu Hg^0 und damit die Ausgasung fördern, haben wir dynamische Durchflusskammern (DFCs) verwendet. Der Effekt von erhöhter Schwefel- und Stickstoffdeposition sowie veränderten Temperatur- und Feuchtebedingungen auf den Hg^0-Fluss wurden untersucht und typische Flussraten für unser Untersuchungsgebiet quantifiziert. Das boreale Moor liegt etwa 10 Kilometer westlich von Vindeln, in der Provinz Västerbotten in Schweden. Um den ganzjährigen In- und Output von Hg^0 über die Atmosphäre zu quantifizieren, entwickelten wir ein neues Relaxed Eddy Accumulation (REA) System mit zwei Lufteinlässen, nur einem Detektor und einem ausgefeilten, automatischen Kalibrationsmodul. Während den Hg-Messungen wurden meteorologische Parameter, im Wasser gelöstes Hg^0 (DGM) und die Gesamtdeposition von Hg gemessen. Letztere während der Vegetationsperiode 2014. Das Gesamt-Hg im Boden und im Abflussbereich des Moores wurde vorgängig bestimmt und trägt zum besseren Verständnis des Hg-Kreislaufs bei. Hohe Schwefeldepositionen, wie sie in den 80er-Jahren in Schweden üblich waren, führten zu einer Hemmung von Hg-Emissionen. Dies ist mit einer initialen Ausgasung von Hg zu Beginn des Versuches oder mit dem Binden von Hg an Schwefelgruppen und anschliessendem Abtransport im Oberflächenwasser zu erklären. DFC-Messungen im Juli 2014 wurden während Strahlungstagen durchgeführt und zeigten einen deutlichen Tagesgang und eine starke lineare Abhängigkeit von der Temperatur innerhalb und ausserhalb der Kammern. Erste Auswertungen der REA-Daten zeigten eine Spannweite der Monatsmittelwerte zwischen -6 ng m^{-2} h^{-1} im November 2013 und 15 ng m^{-2} h^{-1} im Juni 2014. Hg^0-Emissionen dominierten während des Sommers und Hg^0-Deposition von Spätherbst bis Frühling. Als erste Forschungsgruppe gelang es uns, den Hg^0-Fluss über einem borealen Moor während eines ganzen Jahres zu messen und dabei REA erfolgreich anzuwenden. Des Weiteren konnten wir mit DFC-Messungen Faktoren identifizieren, welche Hg^0-Emissionen hemmen oder begünstigen. Die Ausgasung von Hg^0 in die Atmosphäre scheint die Menge im Abfluss deutlich zu übersteigen und deutet darauf hin, dass das boreale Moor heute nicht nur eine Quelle für MeHg, sondern auch für Gesamt-Hg ist.

Abstract

There is great interest in defining the air-atmosphere exchange of gaseous elemental mercury (Hg^0) from peatlands that may regulate the pool of Hg in peatlands and ultimately the loading of MeHg to surface waters. To test this hypothesis, Teflon and polycarbonate dynamic flux chambers (DFCs) were used to (i) investigate the effect of sulfur and nitrogen addition as well as warming and changed moisture regimes on Hg^0 flux and (ii) to quantify typical diurnal summertime fluxes from a mixed acid peatland system situated near Vindeln in the county of Västerbotten, Sweden. A dual-intake, single analyzer Relaxed Eddy Accumulation (REA) system was developed for long-term, all-year flux monitoring. Meteorological parameters were recorded simultaneously and dissolved gaseous mercury (DGM) concentrations in the peatland water determined on a weekly basis. Wet bulk deposition measurements of Hg during the growing season in 2014 and information about Hg in soil and runoff enhance the understanding of the main pathways of Hg in- and outputs from boreal peatlands.

The exchange of Hg^0 from the peatland surface was significantly lower on experimental plots exposed to elevated sulfur deposition. This indicated either earlier Hg evasion or Hg binding to sulfur in organic matter, making Hg less susceptible to volatilization and more prone to transport in runoff.

DFC measurements during cloudless conditions in July 2014 revealed a significant diurnal pattern and a strong linear relationship with air temperature inside and outside the DFC. Preliminary calculations of monthly averaged fluxes measured with REA ranged from -6 (November 2013) to 15 ng m^{-2} h^{-1} (June 2014). Hg^0 fluxes revealed a seasonal pattern over the year with net evasion during growing season and dominating deposition from autumn to spring. We managed to perform the first conditional sampling of Hg^0 flux over a boreal peatland using REA and were able to determine drivers and inhibitors of Hg^0 evasion during short-term DFC measurements. Hg removal via volatilization exceeded the annual export of Hg in streamwater. These two main pathways of Hg output identified the peatland as a net source of Hg.

Keywords: Mercury, gaseous elemental mercury, air-surface gas exchange, micro-meteorological technique, relaxed eddy accumulation, dynamic flux chamber

1. Introduction

Anthropogenic activities have greatly increased emission of mercury (Hg) to the atmosphere, which has resulted in a nearly threefold increase in deposition to the land and ocean compared to preindustrial times (e.g. Lamborg et al. 2014). This also holds for boreal peatlands, where atmospheric deposition has created a store of Hg and especially methylmercury (MeHg) that appears coupled with organic carbon and sulfur accumulation. The “active” soil pool is a potential short- and long-term source of Hg into nearby surface waters (Chen et al., 2012). Since peatlands are considered as zones of high methylation activity and MeHg readily bio-accumulates up the food chain, these landscapes are major mediators for the increased levels of Hg in freshwater fish (St. Louis, et al. 1994, Selvendiran et al., 2008). Besides export in streamwater, gaseous elemental mercury (GEM or Hg^0) volatilization to the atmosphere may be the second main pathway of Hg output from wetlands and could be particularly significant for reducing the present Hg load to fish since the same conditions that promote methylation in wetlands also create volatile species that could evade.

The goal of the project was to test the hypothesis that Hg^0 evasion is an important pathway of Hg removal from boreal peatlands. To understand the biogeochemical processes that could make Hg^0 evasion from peatlands possible we applied dynamic flux chambers (DFCs). We investigated short-term fluctuations of the Hg^0 flux including measurements from experimental plots that had been exposed for 15 years to different combinations of atmospheric sulfur (S) and nitrogen (N) deposition as well as greenhouse treatments simulating climate change (Fritsche et al. 2014). We have pushed the limits of measurement technology by developing a novel Hg-Relaxed Eddy Accumulation (REA) system to quantify the first seasonal land-atmosphere exchange of Hg^0 over a boreal peatland. REA has been widely used to determine land-atmosphere exchange of different trace gases but just a few groups have applied

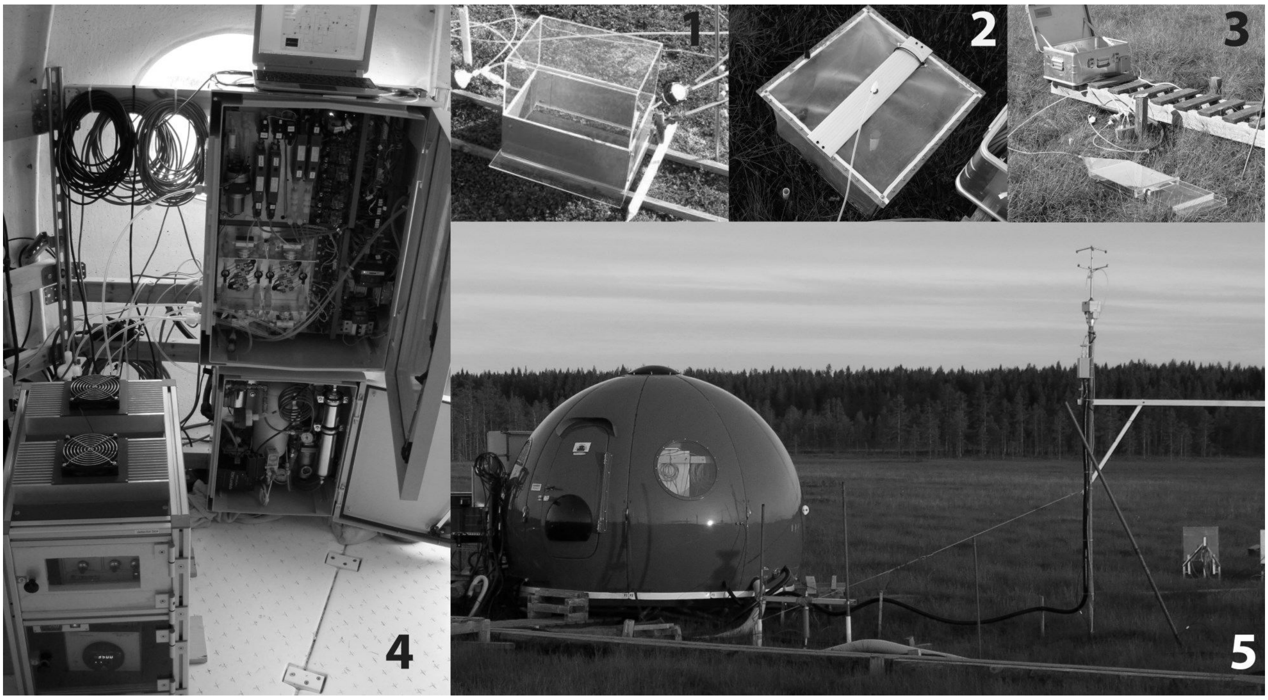

Figure 1-5: Polycarbonate (1, 3) and Teflon chambers (2) applied to measure Hg^0 fluxes on experimental and REA footprint plots. The REA setup (4) was placed in the ICOS-igloo measuring Hg^0 fluxes 3.5 m above the peatland surface (5). Meteorological parameters were logged simultaneously.

REA for measuring Hg^0 fluxes over soils (Cobos, et al., 2002, Olofsson et al., 2005, Sommar et al., 2013a, Zhu et al., 2015a) and forest canopies (Bash and Miller, 2007, 2008 and 2009). Dissolved gaseous mercury (DGM) concentrations in the peatland water combined with total mercury (THg) concentrations in wet bulk deposition have been determined to better interpret evasion and deposition processes relative to catchment stocks.

2. Material and Methods

The mixed acid peatland of Degerö Stormyr, which covers an area of ~6.5 km^2 and is located ~60 km north of Umeå, Sweden, was our study site (see Granberg et al. 2001). Evasion of Hg^0 was measured using a polycarbonate DFC (Fig. 1) on 2 m × 2 m plots, arranged in a random, duplicate 2^3-factorial design with ambient and elevated levels of sulfur (S) and nitrogen (N) as well as ambient and elevated temperatures simulated using a greenhouse cover (GH) (Fritsche et al., 2014). The lower levels of S and N correspond to ambient deposition rates at the site (3 and 2 kg ha^{-1} $year^{-1}$, respectively), while the high levels of 20 kg of S ha^{-1} $year^{-1}$ and 30 kg of N $ha^{-1}year^{-1}$ correspond to maximal deposition levels in southern Sweden during the 1980s. For method intercomparison and to quantify typical all-day summertime fluxes a Teflon and polycarbonate DFC – the latter is described in Lin et al. (2012) - have been applied in July 2014 (Fig 2 and 3). Hg^0 fluxes were alternately measured within the flux source area (footprint) of the REA system in four cardinal directions (N, W, S & E) during two 4x24 hour field campaigns.

The novel REA system was designed with twin inlets at the same level for simultaneous accumulation of up and downdrafts on a pair of gold traps which are then analyzed sequentially on the same detector while another pair of gold traps takes over the accumulation (Fig. 4 and 5). Accurate determination of Hg^0 fluxes has proven difficult

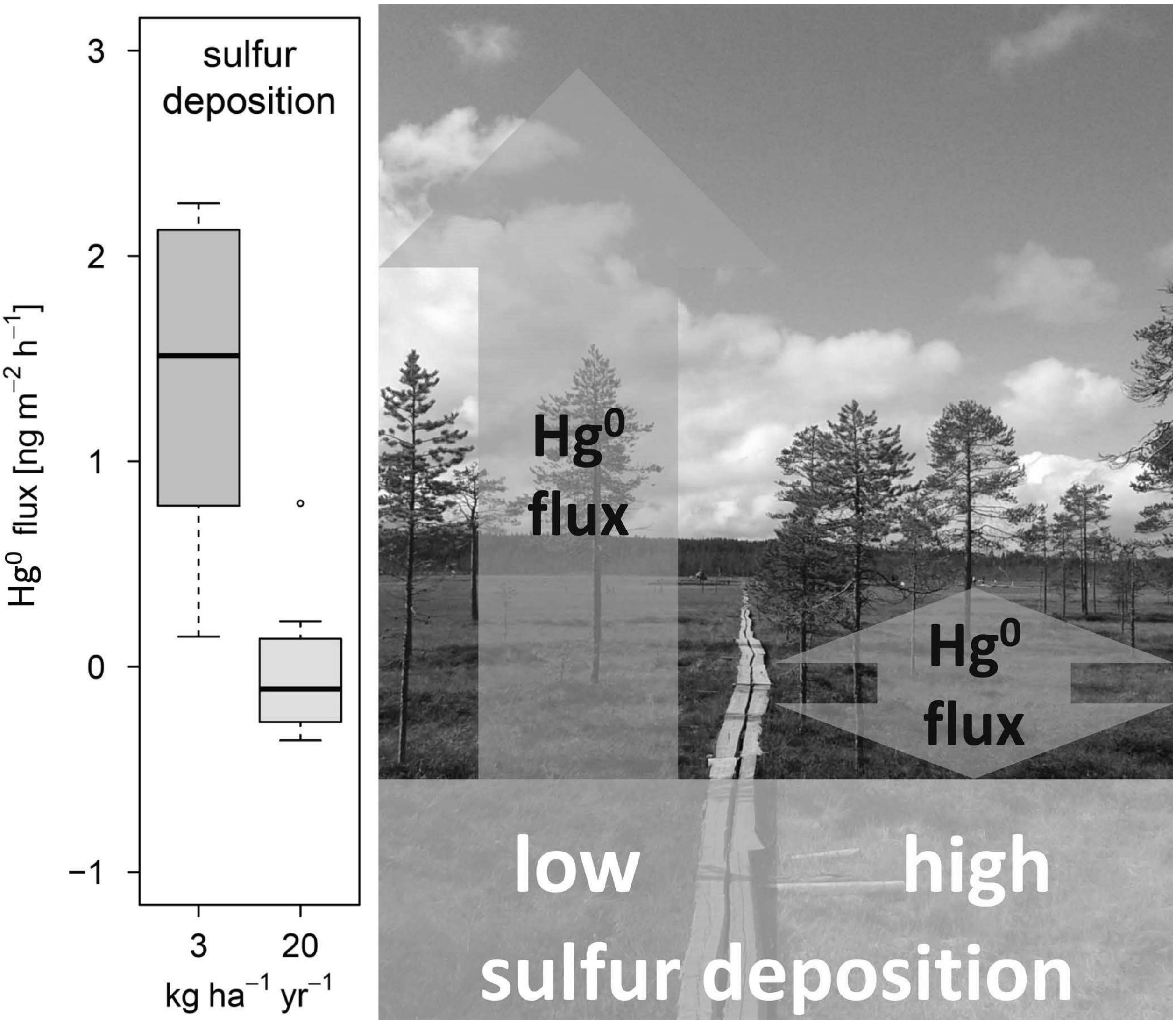

Figure 6: High sulfur deposition led to suppressed Hg^0 evasion. The upper edge of the box indicates the 75th percentile and the lower edge the 25th percentile. Whiskers indicate the 90th and 10th percentiles, while the line within the box marks the median (Fritsche et al., 2014).

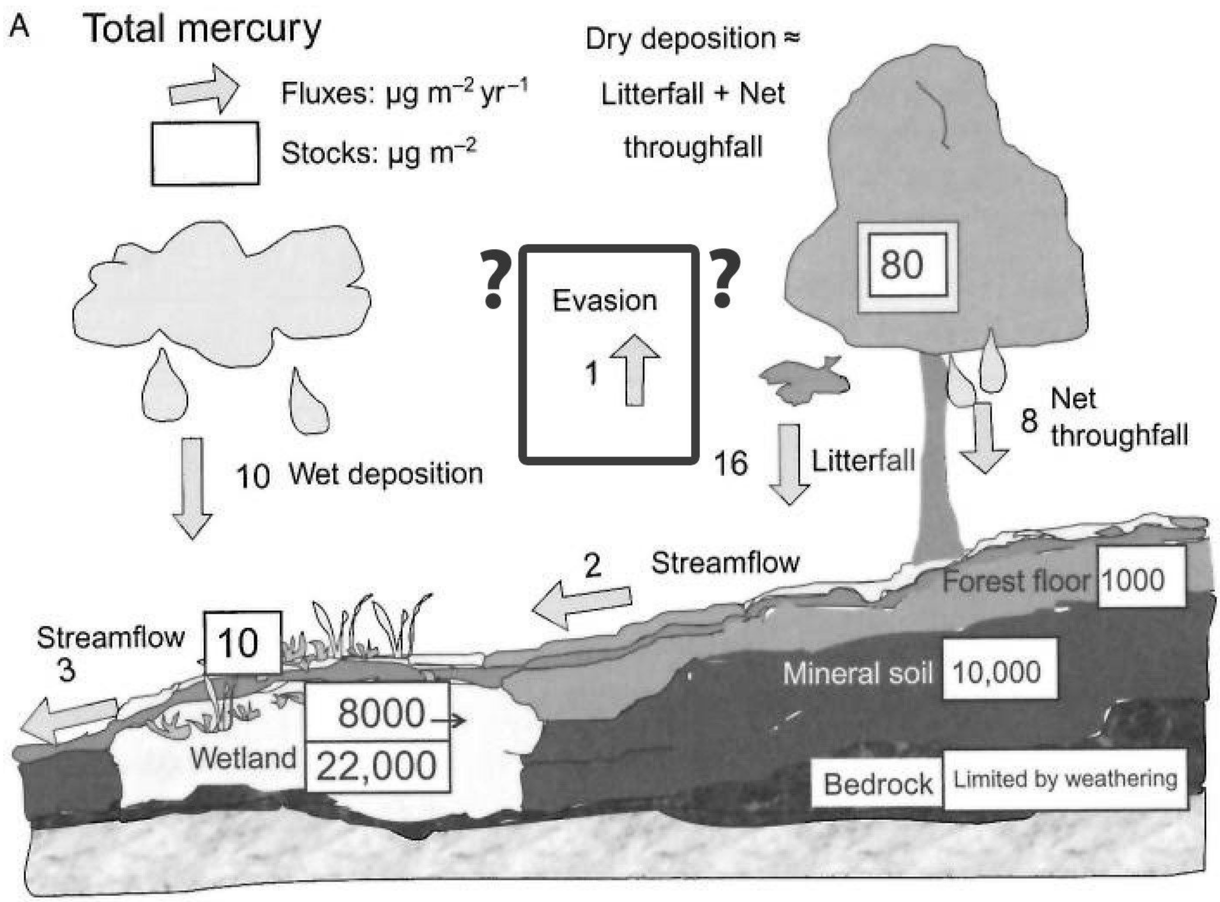

Figure 7: Typical values for stocks and annual fluxes in the northern temperate-boreal landscape for THg after Shanley and Bishop (2012). Long-term measurements of Hg^0 evasion over Degerö Stormyr indicate that the evasion term is underestimated, at least for boreal peatlands.

due to the technical challenges presented by the small concentration differences (< 1 ng m^{-3}) between updrafts and downdrafts. To address this we present a system including a calibration module for periodic quality-control measurements with reference gases. We succeeded in continuously monitoring the Hg^0 flux from June to December, 2013 and from March to July, 2014. Within the same REA footprint plots that were used for DFC measurements, peatland water has been sampled and checked for DGM concentrations. The analysis was performed weekly during the growing season from 18.06 – 09.10.2013 and 02.05 – 17.07.2014. To finally calculate an input-output budget for mercury at Degerö Stormyr a wet bulk deposition survey has been carried out. Every second week from May to August 2014 rain water samples were analyzed to estimate the input of THg from atmospheric deposition.

3. Results and Discussion

Shaded DFC measurements during the summer in 2009 showed emission of Hg^0 to the atmosphere from most of the experimental plots (0.7 ± 0.9 ng m^{-2} h^{-1}). However, Hg^0 exchange rates were significantly lower, occasionally indicating Hg uptake, on plots subjected to S addition at rates of 20 kg ha^{-1} $year^{-1}$ (Fig. 6). Enhanced N deposition and greenhouse treatment had no significant effect on Hg^0 fluxes. We hypothesize that the lower Hg evasion from the sulfur-treated plots is related to either earlier Hg evasion or Hg binding to S in organic matter, making Hg less susceptible to volatilization and more prone to transport in runoff (see Fritsche et al., 2014).

In July 2014 the exchange of Hg^0 from the peatland surface was measured continuously with DFCs during cloudless conditions and averaged 0.6 ± 1.3 ng m^{-2} h^{-1} (preliminary results derived from Teflon DFC measurements). The fluxes showed a diurnal pattern with maximum deposition around 03:30 a.m. and maximum emission around 10:00 a.m and revealed a strong linear relationship with air temperature inside (R^2=0.65, $p < 0.001$) and outside (R^2=0.58, $p < 0.001$) the DFC.
Gustin et al. (2008) reviewed published measurements of soil emission Hg^0 fluxes from background sites which range from -2 to 13 ng m^{-2} h^{-1}. They noted that most of the published data are collected during the summer and in the daytime. Therefore, long-term measurements representing

diel and seasonal variations are requested to improve all-year Hg mass balances. Typical values of inputs and outputs as well as internal THg fluxes and stores have been synthesized for a northern temperate boreal landscape (Fig. 7). The general finding was that Hg export was small relative to inputs and that watershed retention ranges from about 55% to 95% THg (Shanley and Bishop, 2012). In peatlands, retention values might be considerably lower since anoxia, low pH, carbon accumulation, sufficient sulfate availability and low iron concentration favour Hg^{2+} reduction and volatile loss of Hg^0.The absence of a forest canopy also favors Hg^0 volatilization due to increased photo-reduction processes (Garcia et al., 2005).

To demonstrate the REA system performance, we monitored fluxes over two contrasting environments with different turbulence regimes and Hg^0 sink/source characteristics. First, over a heterogeneous urban surface in the center of Basel, Switzerland in February 2012 and second over Degerö Stormyr during snowmelt in May 2012 (Osterwalder et al., in prep.). THg concentrations in the upper 40 cm of the peatland soil averaged at 57 ± 6 ng g^{-1} and represent typical Hg contents in northern Swedish background soils (Åkerblom et al., 2013; Shanley and Bishop, 2012). A preliminary analysis of the all year measurement campaign we conducted, suggests that the actual volatilization was significantly larger than that given in Fig. 7 (red frame). THg wet bulk deposition is estimated at a similar range as in Fig. 7 and regarded as the major Hg input to the peatland ecosystem since no Hg is deposited through litter- or net throughfall. Hg^0 evasion together with export of Hg in stream water (~0.5 ng m^{-2} h^{-1}) defined the peatland to be a net source of Hg to neighboring environments. DGM concentration monitoring indicated that the surface peatland water was supersaturated with Hg^0, which favors Hg^0 emission to the atmosphere, except from measurements in early spring (after snowmelt) and October.
What causes the difference between Hg^0 fluxes measured by enclosure and REA techniques is still debated in the literature. Cobos et al. (2002) suggested that DFCs underestimated the fluxes by a factor of 2-3 since they alter the environment of the area being studied, affecting atmospheric turbulence, temperature and humidity. It is also recommended to incorporate an atmospheric turbulence property such as friction velocity for correcting the DFC-measured flux (Zhu et al., 2015).

4. Conclusion

The Degerö peatland is hydrologically connected to the stream system and plays an important role in Hg and MeHg mobility. We managed to perform the first continuous sampling of Hg^0 flux over a boreal peatland using REA and were able to determine drivers and inhibitors of Hg^0 evasion during short-term DFC measurements. The additional Hg export from Degerö Stormyr via volatilization indicates that the estimated time-span for reduced Hg emissions to translate into lower Hg levels in the soil are too long because up to now the emission of Hg from the peatland surface to the atmosphere has often been underestimated.

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