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# Comparative study of elemental mercury flux measurement techniques over a Fennoscandian boreal peatland

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ABSTRACT

Quantitative estimates of the land-atmosphere exchange of gaseous elemental mercury (GEM) are biased by the measurement technique employed, because no standard method or scale in space and time are agreed upon. Here we present concurrent GEM exchange measurements over a boreal peatland using a novel relaxed eddy accumulation (REA) system, a rectangular Teflon® dynamic flux chamber (DFC) and a DFC designed according to aerodynamic considerations (Aero-DFC). During four consecutive days the DFCs were placed alternately on two measurement plots in every cardinal direction around the REA sampling mast. Spatial heterogeneity in peat surface characteristics (0–34 cm) was identified by measuring total mercury in eight peat cores (57 ± 8 ng $g^{-1}$, average ± SE), vascular plant coverage (32–52%), water table level (4.5–14.1 cm) and dissolved gaseous elemental mercury concentrations (28–51 pg $L^{-1}$) in the peat water. The GEM fluxes measured by the DFCs showed a distinct diel pattern, but no spatial difference in the average fluxes was detected (ANOVA, $\alpha = 0.05$). Even though the correlation between the Teflon® DFC and Aero-DFC was significant ($r = 0.76$, $p < 0.05$) the cumulative flux of the Aero-DFC was a factor of three larger. The average flux of the Aero-DFC (1.9 ng $m^{-2}$ $h^{-1}$) and REA (2 ng $m^{-2}$ $h^{-1}$) were in good agreement. The results indicate that the novel REA design is in agreement for cumulative flux estimates with the Aero-DFC, which incorporates the effect of atmospheric turbulence. The comparison was performed over a fetch with spatially rather homogenous GEM flux dynamics under fairly consistent weather conditions, minimizing the effect of weather influence on the data from the three measurement systems. However, in complex biomes with heterogeneous surface characteristics where there can be large spatial variability in GEM gas exchange, the small footprint of chambers (< 0.2 $m^2$) makes for large coefficients of variation. Thus many chamber measurement replications are needed to establish a credible biome GEM flux estimate, even for a single point in time. Dynamic flux chambers will, however, be able to resolve systematic differences between small scale features, such as experimentally manipulated plots or small scale spatial heterogeneity.

## 1. Introduction

Globally, anthropogenic mercury (Hg) emissions to the atmosphere and its subsequent deposition have increased the storage of this neurotoxic element in peat by a factor of ~4 since pre-industrial times (Amos et al., 2015). The semi-volatile elemental form is produced in organic soils by a suite of reductive (photochemical, microbial, and dark abiotic) processes from the $Hg^{2+}$ pool and can be re-emitted to the atmosphere. The quantification of gaseous elemental mercury (GEM) fluxes from terrestrial environments is important, because the re-emission of GEM to the atmosphere converts the soil bound and rather immobile Hg into a mobile form with potential long-range transport (Selin et al., 2008) subsequent deposition, and accumulation in food chains.

Two main methodologies exist to measure land-atmosphere exchange of GEM: First, dynamic flux chambers (DFCs) representing small-scale spatial measurements which are ideal for comparison studies to understand the influence of individual controlling factors on

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GEM flux (Gustin et al., 1999). The method is based on GEM concentration measurements between the inlet and outlet of the DFC. Up to now DFCs have been used for 85% of GEM flux measurements (Agnan et al., 2016). However, DFC measurements have been criticized because the enclosure disturbs the microclimate by influencing aerodynamics, temperature and the radiation balance (Wallschläger et al., 1999; Gustin et al., 1999). Furthermore, a high variability was observed among DFC studies due to differences in designs, operating procedures, and application protocols (Eckley et al., 2010), as well as a limited spatial representativeness (as reviewed by Agnan et al., 2016).

To overcome the limitation of the DFC measurements, micrometeorological methods (MM) have been developed which allow larger spatial-scale measurements and only marginally modify environmental conditions. They include the relaxed eddy accumulation (REA) method (Cobos et al., 2002; Olofsson et al., 2005; Bash and Miller, 2008; Sommar et al., 2013; Osterwalder et al., 2016; Kamp et al., 2017), the aerodynamic gradient (AGM) methods (e.g. Lindberg et al., 1995; Edwards et al., 2005; Fritsche et al., 2008b; Baya and Van Heyst, 2010), and the modified Bowen ration (MBR) method (e.g. Obrist et al., 2006; Fritsche et al., 2008b; Converse et al., 2010). Field trials of Hg eddy covariance (EC) measurements over background sites revealed no manifest GEM-vertical wind covariance, indicating fluxes were below the method detection limit (Pierce et al., 2015). Comparison studies over Hg-enriched soils have shown that fluxes determined with DFCs were nearly three times lower compared to fluxes derived from AGM and MBR method fluxes (Wallschläger et al., 1999; Gustin et al., 1999; Zhu et al., 2015a). Carpi and Lindberg (1997) found that MM-derived fluxes were generally up to 20% higher than DFC fluxes for sludge-amended soils and Pierce et al. (2015) reported 16% lower fluxes measured with a DFC compared to MBR fluxes. A new type of dynamic flux chamber (Aero-DFC) designed by Lin et al. (2012) accounts for atmospheric surface-layer shear properties by a scaling procedure. Field comparisons indicated that Aero-DFC may bridge the gap in magnitude between DFC- and MM-derived fluxes. Aero-DFC differed less than 10% from AGM and MBR, while the flux derived from a traditional DFC was 42% and 31% lower compared to AGM and MBR (Zhu et al., 2015a).

The choice of methods to capture GEM fluxes depends on availability of resources as well as expert knowledge. While DFC measurements are relatively low-cost and require only medium expert knowledge, MM methods and especially the REA method are highly cost intensive and require long-term availability of highly specialized staff. The question remains if DFC measurements can still deliver valuable quantitative GEM flux estimates, where MM methods are not feasible.

Due to the different scales associated, a comparison of DFC (surface area of typically $< 0.1\ m^2$) to MM methods (hundreds to thousands of $m^2$ or more) has to consider the site heterogeneity. The peatland surface within the footprint of an EC system operating at Degerö Stormyr in northern Sweden has previously been defined as a homogeneous mixture of wet lawns and carpet plant communities (Nilsson et al., 2008). Nevertheless, the GEM source strength could be altered by spatial changes in total Hg concentrations in the peat (THg), abundance of vascular plants (VP), water table level (WTL), or dissolved gaseous Hg (DGM) concentration in peatland pore water. Correlations between THg in the soil and GEM fluxes have been found across individual background sites (Nacht and Gustin, 2004; Sigler and Lee, 2006). Higher abundance of vascular plants is expected to contribute more to GEM re-emission due to less Hg sequestration compared to bryophytes (Selvendiran et al., 2008) as well as the capacity of DGM transport by transpiration flow and release of GEM through stomata (Lindberg et al., 2002). Water bodies are defined as net sources of GEM to the atmosphere (Wang et al., 2014). Thus, high water table levels and elevated concentrations of volatile DGM, especially during periods of high surface wind speeds, may promote GEM emissions leading to small scale spatial variability of Hg fluxes to the atmosphere.

The objective of this study was to investigate whether DFC and REA measurements are comparable if small-scale variation in the GEM flux was accounted for by spatial repetition of DFC measurements. As such, the integrated GEM flux over a larger spatial extension upwind of a REA sampling mast at Degerö Stormyr was compared with simultaneous GEM fluxes determined over spatially repeated small footprints using a pair of co-located TDFC and Aero-DFC. We compared and evaluated quantitatively derived GEM fluxes from REA and two different DFC designs, which is a contribution to method standardization. Thus, we present the first method comparison between a Teflon® perfluoroalkoxy (PFA) DFC (TDFC), an Aero-DFC and a dual-inlet, single detector REA system deployed at a pristine peatland catchment site in northern Sweden. Peatlands are hot spots in the landscape for production of highly toxic methylmercury (MeHg) species that in-turn biomagnifies in aquatic food webs. This makes investigations of Hg cycling in such environments of considerable interest (St. Louis et al., 1994; Mitchell et al., 2008; Bergman et al., 2012). GEM land-atmosphere exchange studies conducted over northern peatlands are scarce, but indicated that wetland GEM evasion may seasonally rival the input flux of Hg wet deposition (e.g. Kyllönen et al., 2012; Fritsche et al., 2014; Osterwalder et al., 2016).

## 2. Material and methods

### 2.1. Site description

Measurements were performed continuously between July 8 and 12, 2014 in the center of Degerö Stormyr (2.7 $km^2$), a mixed acid mire system (64°11′N, 19°33′E; 270 m a.s.l.) situated in the Kulbäcksliden domain of the Svartberget long-term experimental research (LTER) facility near Vindeln in the county of Västerbotten, northern Sweden. The surrounding forest is a mixed coniferous forest (*Pinus sylvestris* L. and *Picea abies* L. H. Karst) with minor contribution by birch (*Betula pubescens* Ehrh.). Forested areas in the proximity to the Eddy Covariance and REA flux tower are marked green in Fig. 1a. A LiDAR-derived digital elevation model and aerial photo of the entire catchment can be reviewed in Leach et al. (2016). The average peat depth is between 3 and 4 m. The deepest organic layers correspond to an age of ~8000 years. The peat THg concentrations between 0 and 34 cm measured in autumn 2015 averaged 57 ± 8 (± SE) ng $g^{-1}$. These levels are consistent with the designation of this area as a background site in the boreal zone. Vegetation cover within the REA fetch mainly consists of vascular plants (dominated by *Eriophorum vaginatum* L., *Trichophorum cespitosum* L. Hartm., *Vaccinium oxycoccos* L., *Andromeda polifolia* L., and *Rubus chamaemorus* L., sparsely interspersed with *Carex limosa* L., and *Schezeria palustris* L.) and Sphagnum species (*Sphagnum majus* Russ. C. Jens, *S. lindbergii* Schimp., *S. balticum* Russ. C. Jens, *S. fuscum* Schimp.Klinggr. and *S. rubellum* Wils) (Nilsson et al., 2008; Laine et al., 2012). The 30 year (1981–2010) mean annual precipitation and temperature are 614 mm and +1.8 °C respectively, while the mean temperature in July is +14.7 °C (Ottosson-Löfvenius et al., 2003; Laudon et al., 2013). The dominant wind-direction in summer is northeast (Sagerfors et al., 2008).

### 2.2. Relaxed eddy accumulation technique

The dual-inlet, single detector REA system consists of a USA-1 ultrasonic anemometer (METEK GmbH, Elmshorn, Germany) to measure standard deviation of the vertical wind velocity, two sets of fast-response valves (Model 6128, Bürkert, Ingelfingen, Germany) to sample and separate vertically upward and downward moving air parcels, GEM adsorption cartridges, an atomic fluorescence analytical unit (Tekran Model 2500, Toronto, Canada) as well as a GEM reference gas and Hg zero-air generator unit. The REA design and operation parameters are described in detail by Osterwalder et al. (2016). The vertical GEM flux is calculated over 30 min intervals using:

$$F_{REA} = \beta\sigma_w(\overline{C_u} - \overline{C_d}), \quad (1)$$