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Elemental mercury fluxes over a sub-alpine grassland in Switzerland determined with two micrometeorological methods

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Abstract

The exchange of gaseous elemental mercury (GEM) over a sub-alpine grassland in central Switzerland was measured over a full year. Seasonal and diurnal variability were measured with two micrometeorological techniques: the aerodynamic method and the modified Bowen ratio method. With these two methods mean deposition rates of 4.3 ng m⁻² h⁻¹ and 1.7 ng m⁻² h⁻¹ were calculated throughout the vegetation period. No significant GEM exchange occurred under snow covered conditions. A fair weather period in October 2005 was selected to specifically study diurnal patterns of GEM exchange. During this time vertical day-time GEM gradients averaged 0.01 ng m⁻⁴ and night-time gradients 0.07 ng m⁻⁴, but no clear diurnal pattern of the GEM fluxes was observed. Although the measurement configuration entailed substantial variability, the applied methods agreed well with respect to the direction of the flux and seem appropriate to estimate the magnitude of background GEM exchange rates. Complementary measurements of mercury in precipitation during three rain events revealed...
that dry deposition of GEM would account for 67% of a total annual input of 0.26 g ha\(^{-1}\) and would therefore constitute the major deposition pathway.

Key words: Gaseous mercury, Micrometeorology, Aerodynamic method, Modified Bowen ratio, Background soil

1 Introduction

The 2006 conference on Mercury as a Global Pollutant has highlighted anew the relevance of mercury as an environmental hazard (see Hurley et al. [2006] for the conference declaration). Many research projects have described in detail the long-range transport of elemental mercury and the processes leading to the formation of methylmercury. The latter not only affects the health of humans, wild birds, mammals and fish (IOMC, 2002; Pirrone and Mahaffey, 2005) but might also disturb soil microbial processes at the very bottom of the food chain (Johansson et al., 2001).

In background ecosystems the exchange of elemental mercury is primarily controlled by physicochemical properties of the soil, biological processes in the soil, atmospheric chemistry and meteorological conditions. Depending on these variables mercury might be cycled fairly rapidly between terrestrial surfaces and the atmosphere (Gustin and Lindberg, 2005). However, it remains unclear whether deposited mercury is retained in background soils or whether terrestrial ecosystems are even a source of mercury (Pirrone and Mahaffey, 2005). Moreover, mercury might be taken up by plant leaves or removed through the plant from the soil to the atmosphere (Du and Fang, 1982; Gustin and Lindberg, 2005; Landis et al., 2005; Millhollen et al., 2006a). To address these processes air-surface exchange fluxes of gaseous elemental mercury (GEM) have been measured with various techniques (e.g. Edwards et al., 2005; Gustin et al., 2006; Obrist et al., 2006). One of these widely used techniques are dynamic flux chambers. These are easy to handle and provide results instantly, but affect atmospheric turbulence, temperature and humidity considerably and therefore their application is restricted to short-term measurements (Cobos et al., 2002). On the other hand, micrometeorological techniques allow
spatially averaged measurements without disturbing ambient conditions, but require detailed knowledge of the prevailing micrometeorological situation and the footprint area.

A variety of micrometeorological methods for trace gas flux measurements have been developed (for details see Baldocchi, 2006; Dabberdt et al., 1993; Foken, 2006; Lenschow, 1995). With today’s sensitive analytical instrumentation that allows accurate measurement of background GEM levels of 1.2 to 1.8 ng m\(^{-3}\) (Landis et al., 2005; Pirrone, 2001) most micrometeorological methods are apt to be applied to mercury flux measurements. The eddy covariance (EC) method – the state of the art in turbulent energy, momentum, CO\(_2\) and H\(_2\)O flux measurements – would be straightforward but is not yet practicable for GEM flux measurements as it requires fast response, field deployable sensors that are currently not available for GEM at reasonable costs (laser based systems are being developed and seem promising; Bauer et al., 2002). Alternatively, flux-gradient methods only require a relatively simple setup, which is advantageous for long-term GEM flux measurements. Generally, these methods are based on the theory that the gradient of a scalar quantity is the driving force of the mass or energy flux. Translated to the flux of a trace gas this relationship can be expressed as

\[ F_c = -K_c \frac{\partial c}{\partial z}, \]  

where \( F_c \) is the vertical trace gas flux, \( K_c \) the turbulent exchange coefficient (or eddy diffusivity) and \( \partial c / \partial z \) the concentration gradient of the trace gas in question (Baldocchi, 2006; Dabberdt et al., 1993; Lenschow, 1995). Using the flux-gradient relationship of the Monin-Obukhov similarity theory, fluxes can be estimated by the so-called aerodynamic method and the modified Bowen ratio (MBR). The MBR technique is widely used to estimate air-surface exchange rates of GEM and has the advantage of being independent of empirically derived stability corrections. On the other hand, the aerodynamic method doesn’t require the knowledge of gradients and fluxes of a surrogate scalar.

In this work we describe the first year-long measurement of GEM fluxes above uncontaminated, sub-alpine grassland. With these measurements we intend to compare the aerodynamic and MBR methods and evaluate their suitability for GEM flux measurements.
Additionally we attempt to record the seasonal and diurnal variability of the GEM exchange and to capture any events that would eventually enhance or reduce GEM fluxes, e.g. during or after intensive rain, upon snow fall and during snow melt or after grass cuts.

2 Experimental

2.1 Methodology

The similarity theory by Monin and Obukhov (1954) relates vertical gradients and fluxes in a way that also allows to compute GEM fluxes from GEM gradient measurements. Accordingly, if $K_c$ is substituted in equation (1) the turbulent GEM flux calculated by the aerodynamic method becomes

$$F_{GEM} = \frac{k \cdot u_* \cdot z \cdot \partial \xi_{GEM} / \partial z}{\Phi_h(z/L)}$$

(2)

where $k$ denotes the von Karman constant (0.4), $u_*$ the friction velocity, $\Phi_h(z/L)$ the universal temperature profile, $L$ the Monin-Obukhov length and $\partial \xi_{GEM} / \partial z$ the vertical GEM gradient. The dimensionless Monin-Obukhov stability parameter $z/L$ is used to characterise atmospheric stratification. Dyer (1974) parameterised the universal function $\Phi_h$ as $(1-16z/L)^{-0.5}$ for unstable, $(1+5z/L)$ for stable and 1 for neutral conditions. Using this parameterisation in equation (2) $F_{GEM}$ is obtained as a function of the measured GEM concentration gradient and atmospheric stability. More details about this technique and its underlying assumptions are described in Edwards et al. (2005).

For determination of the turbulent GEM flux by the MBR method the measurement of a surrogate scalar, i.e. sensible heat or a second trace gas, is required. In our application we used CO$_2$ as a surrogate, since its concentration can be easily determined and as its flux is less constrained by solar radiation than the flux of sensible heat (Meyers et al., 1996). By measuring gradients of GEM and CO$_2$ the GEM flux is calculated as

$$F_{GEM} = F_{CO_2} \cdot \frac{\Delta c_{GEM}}{\Delta c_{CO_2}}$$

(3)
where the $F_{CO2}$ flux is obtained directly by eddy covariance (Baldocchi, 2006; Dabberdt et al., 1993; Meyers et al., 1996). An elaboration of the method is given by Lindberg and Meyers (2001) and Meyers et al. (1996).

Both flux-gradient techniques are limited in their application. First, the determined fluxes are the result of a spatially averaged signal that require an adequate footprint. This footprint depends on the prevailing atmospheric conditions, site heterogeneity and the measurement height (Foken, 2006; Lenschow, 1995). A brief description of the fetch at our field site is given in the following section. Second, the assumptions of the applied micrometeorological methods necessitate gradient measurements above the canopy, although fetch requirements are greater and gradients are smaller (Lenschow, 1995). The latter issue poses an additional challenge in our study, as atmospheric GEM concentrations are already extremely low. Third, the methods assume fully developed turbulent conditions, which is adequate for day-time and less so for night-time conditions. Finally, regarding the MBR method, it is assumed that the transport processes as well as the sinks and sources of the investigated trace gas and the surrogate scalar are equal (Dabberdt et al., 1993).

2.2 Site description

We chose the sub-alpine grassland at Fruebuel in central Switzerland at an elevation of 1000 m a.s.l. as location for our GEM flux measurements (47°6’47”N, 8°32’16”E). This undulating plateau, which is a research site of ETH Zurich (Eugster and Zeeman, 2006), is used for hey production with 2 to 3 cuts per year and cattle grazing. The temperate continental climate yields an average annual temperature of 7°C with a mean precipitation of 1200 mm per year (Dipner-Gerber et al., 2004). In the centre of the 9 ha large field ETH Zurich operates a micrometeorological tower that was also used for our flux measurements. The site which is bordered by a birch alley in the south-west and a raised-bog in the northeast, consists of Cambisols in different water influenced varieties. In the proximity to the micrometeorological tower the soil is 1.3 m deep with a bulk density of 1.28 g cm$^{-3}$ (A-horizon). The top soil layer has an organic carbon content of 18.4 mg g$^{-1}$ and a pH of 4.5 (Roth, 2006). A total mercury
concentration ($H_{g_{tot}}$) of 100.8 ±14.5 ng g$^{-1}$ was measured in the A-horizon. Soil solution was sampled three times during the measurement campaign and $H_{g_{tot}}$ concentrations of 3.5 ±0.75 ng l$^{-1}$ were determined at the Swedish Environmental Research Institute IVL, Gothenburg. The dominant species of the pasture include *Alopecurus pratensis*, *Lolium perenne*, *Lolium multiflorum*, *Dactylis glomerata*, *Heracleum sphondylium*, *Rumex acetosa*, and *Rumex alpinus*.

The predominant wind direction is south-west to south-south-west, showing a distinct channelled flow as a result of the local, undulating, sub-alpine topography. The largest contributions to the footprint are within approximately 60m of the eddy covariance setup.

2.3 Experimental setup and data analysis

A schematic of our experimental setup is shown in figure 1. In order to determine the GEM fluxes by the micrometeorological methods described above, the GEM concentrations and CO$_2$ mixing ratios were measured at 5 heights above ground. A dual-amalgamation mercury vapour analyser (Tekran 2537A, Tekran, Toronto, Canada) with 5-minute accumulation intervals per cartridge was used to measure atmospheric GEM concentrations; features of this instrument are described in e.g. Lindberg et al. (2000). The CO$_2$ concentrations were analysed with a closed path infrared gas analyser (LI-6262, LI-COR Inc., Lincoln, Nebraska, USA) at a frequency of 1 Hz.

At a distance of about 5 m from the micrometeorological tower the sampling lines were mounted to a separate pole at heights of 0.2 to 1.7 m above ground. The $\frac{1}{4}$”-Teflon$^\text{®}$ sampling lines of 7 m length were run to a 5-port solenoid switch unit to enable sequential sampling of all heights. Downstream of the switch unit the Tekran instrument and the CO$_2$ analyser were connected in series. The internal air pump of the Tekran instrument was operated at a flow rate of 1.5 l min$^{-1}$. To maintain steady flow conditions an auxiliary pump with a flow rate of 6 l min$^{-1}$ was connected to a second port of the switch unit. In this configuration the four lines that were currently not sampled were flushed continuously. Teflon$^\text{®}$ cartridges with 0.45 μm filters were
mounted to the inlet of each line to avoid any particles entering the system. The sampled air was not dried, which necessitated a correction of the calculated fluxes (see below).

With this setup one vertical 5-point concentration profile could be measured every 50 minutes. Sampling was switched every 10 minutes in such a way that a measurement of a line at a lower level was followed by one at a higher level and vice versa. Higher frequencies were not feasible, due to the required analytical pre-concentration of the sampled air.

A suite of ancillary meteorological data (air temperature, net radiation, PAR, humidity, etc.) were recorded by the micrometeorological tower. Carbon dioxide and water vapour fluxes were determined by eddy covariance using a three-dimensional sonic anemometer (Solent R3, Gill Ltd., Lymington, UK) and a LI-7500 open path infrared gas analyser (LI-COR Inc., Lincoln, Nebraska, USA).

After the measurement campaign the logged data were analysed with a self-programmed algorithm using Matlab®. As one of the first data processing steps the GEM and CO₂ gradients were extracted by subtracting the atmospheric concentration trend measured at the top sampling line. This step was considered essential as atmospheric concentrations changed during the course of a measurement cycle of 50 minutes (i.e. 20 minutes for one height pair). GEM exchange rates were then determined according to equations (2) and (3). This was done by calculating the gradients and fluxes of 5 sequential height pairs within the 50-minute intervals (i.e. pairs 0-1, 2-1, 2-3, 4-3 and 0-4 according to figure 1). The median of these 5 values was then calculated to obtain the raw flux. Uncertainty could thus be reduced noticeably. Fluxes determined with the aerodynamic method were then corrected for density fluctuations caused by differences in water vapour content of the air stream (the Tekran instrument measures the GEM concentration relative to moist air). The correction terms of Webb et al. (1980), which are also described in more detail by Lee (2000) were applied. As the Tekran GEM analyser monitors the sampling volume with a mass flow controller, i.e. measures the concentration relative to the sampled air mass, no correction for the sensible heat flux was necessary. Finally the flux data were screened for outliers and values outside the range of the monthly mean ±3 standard
deviations were rejected. All GEM flux data presented in this paper are reported on a mass
basis in ng m$^{-2}$ h$^{-1}$. Fluxes have to be divided by 5 to obtain values in pmol m$^{-2}$ h$^{-1}$.

As a means to evaluate the quality of the GEM fluxes we also calculated the CO$_2$ fluxes by
the aerodynamic method (equation 2) and compared the results with the CO$_2$ fluxes gained by
eddy covariance. Keeping in mind that the sinks and sources of GEM and CO$_2$ might not be
identical, equal CO$_2$ fluxes would nonetheless imply that the measured GEM fluxes are reliable
(assuming the CO$_2$ fluxes determined by EC to be accurate).

2.4 QA/QC

The mercury vapour analyser was calibrated every 24 hours by means of the internal
mercury permeation source of the Tekran instrument. Additionally, external calibrations were
performed at regular intervals by manually injecting pre-defined volumes of mercury saturated
air from a mercury vapour generation unit (Model 2505, Tekran, Toronto, Canada). Likewise,
the LI-6262 CO$_2$ analyser was calibrated every 2 to 4 weeks by measuring a zero and span gas.
Argon was used as zero gas (relative zero-offset to a N$_2$/O$_2$ gas mixture was 0.4 ppm) and
pressurised air with 451 ppm CO$_2$ as span gas. GEM and CO$_2$ concentrations were corrected
accordingly. In order to exclude any line bias we replaced the particle filters every 2 to 4 weeks
and exchanged the sampling lines for cleaned ones 3 times during the campaign. Additionally
the system was checked for leaks either by measuring mercury-free air generated by a zero air
generator (Model 1100, Tekran, Toronto, Ontario) or constricting the sampling lines temporarily
to generate low pressure within the lines. Teflon$^\text{®}$ parts and tubing were cleaned with ultra pure
HNO$_3$ and deionised water according to an internal standard operating procedure (adapted
from Keeler and Landis, 1994).

3 Results
3.1 Data coverage

Concentration measurements of GEM and CO\textsubscript{2} covered 56% of the period between September 2005 and August 2006. Besides using the instruments at other sites data gaps resulted from maintenance work, failure of instrumentation and invalid measurements within the vegetation or below the snow surface.

To obtain the detection limit of our system we measured GEM and CO\textsubscript{2} concentrations with all sampling lines at 1 m above ground over three days and determined the minimum resolvable gradient (MRG). We defined the MRG as the mean plus 3 standard deviations of the concentration differences measured between the 5 sampling lines (determined according to the calculation of the gradients described in section 2.3). For GEM the MRG was calculated as 0.05 ng m\textsuperscript{-3} and for CO\textsubscript{2} 7.6 ppm. As a large proportion of the measured gradients were around the MRG we set a more relaxed threshold for acceptable values at the mean plus one standard deviation, which translates to 0.02 ng m\textsuperscript{-3} for GEM and 2.5 ppm for CO\textsubscript{2}, keeping the reduced confidence in mind. With this criterion an overall data coverage of 28% for the GEM fluxes and of 32% for the CO\textsubscript{2} fluxes was achieved. Please note that the mean flux values reported in the following sections include data below the MRG (average exchange rates would otherwise be overestimated).

3.2 Seasonal air-surface exchange of GEM

During the measurement campaign the air temperature averaged 6°C and 1150 mm of precipitation were recorded. Between 24.11.2005 and 26.03.2006 the site had a closed snow cover. Figure 3 illustrates the seasonal variation of air temperature and measured atmospheric GEM concentrations. The latter averaged 1.42 ng m\textsuperscript{-3} and ranged from 0.69 ng m\textsuperscript{-3} to 2.42 ng m\textsuperscript{-3} throughout the study period. Lowest concentrations were measured in August 2006 with an average of 1.21±0.08 ng m\textsuperscript{-3} and highest in March 2006 with 1.64±0.18 ng m\textsuperscript{-3}. No association with wind direction could be observed (see figure 2).
A summary of the CO\(_2\) and GEM fluxes is shown in table 1. During the vegetation period (between 26.09. and 23.11.2005 and between 27.03. and 30.08.2006) a mean CO\(_2\) uptake of 4.2 \(\pm\) 10.7 \(\mu\)mol m\(^{-2}\)h\(^{-1}\) was observed with the EC technique and of 6.3 \(\pm\) 19.0 \(\mu\)mol m\(^{-2}\)h\(^{-1}\) with the aerodynamic method. On the other hand, CO\(_2\) emissions of 1.0 \(\mu\)mol m\(^{-2}\)h\(^{-1}\) were recorded during the snow covered season (see figure 3).

Mean GEM deposition rates of 4.3 ng m\(^{-2}\)h\(^{-1}\) and 1.7 ng m\(^{-2}\)h\(^{-1}\) were measured during the vegetation period with the aerodynamic and the MBR method, respectively. Fluxes determined by both approaches ranged from –42 to 20 ng m\(^{-2}\)h\(^{-1}\) and from –35 to 34 ng m\(^{-2}\)h\(^{-1}\) respectively. During the snow covered period GEM fluxes were reversed and mean emissions of 0.3 ng m\(^{-2}\)h\(^{-1}\) (range –34 to 29 ng m\(^{-2}\)h\(^{-1}\)) and 0.4 ng m\(^{-2}\)h\(^{-1}\) (range –68 to 82 ng m\(^{-2}\)h\(^{-1}\)) were recorded (see figure 3). Average deposition velocities \((v_d = -\frac{F_{GEM}}{c_{GEM}})\) for the two methods were calculated to be 0.09 cm s\(^{-1}\) and 0.03 cm s\(^{-1}\) for the vegetation period.

In figure 3 one distinct period in May 2006 can be noticed: from the second half of April the aerodynamically determined GEM deposition rate increases progressively from 1 ng m\(^{-2}\)h\(^{-1}\) to 19 ng m\(^{-2}\)h\(^{-1}\) at the end of May and then drops again to 7 ng m\(^{-2}\)h\(^{-1}\). A similar, although less pronounced increase with a maximum of 10 ng m\(^{-2}\)h\(^{-1}\) was identified with the MBR method.

In addition to dry deposition we also measured the total mercury content (Hg\(_{tot}\)) of rain water during three precipitation events between June and September 2006. The mean Hg\(_{tot}\) concentrations of the samples collected over 48 hours each were between 6.1 and 14.0 ng l\(^{-1}\) \((N=6)\).

### 3.3 Diurnal air-surface exchange of GEM

The fair weather period between 6.10.2005 and 16.10.2005 was selected to evaluate the diurnal variability of the measured GEM fluxes. As figure 4 shows the diurnal cycle of air temperature, net radiation and turbulence were steady throughout this time.
Table 2 lists the average fluxes of CO$_2$ and GEM separated by method and time of day, where day-time was defined to last from 9 – 15 hours and night-time from 23 – 5 hours. A mean day-time CO$_2$ deposition rate of 16.8 $\mu$mol m$^{-2}$ h$^{-1}$ and a mean night-time emission flux of 3.8 $\mu$mol m$^{-2}$ h$^{-1}$ was measured with the aerodynamic method; the corresponding rates for the EC method were 14.4 $\mu$mol m$^{-2}$ h$^{-1}$ and 2.7 $\mu$mol m$^{-2}$ h$^{-1}$.

During this fair weather period average day-time GEM gradients of 0.01±0.03 ng m$^{-4}$ and night-time gradients of 0.07±0.05 ng m$^{-4}$ were measured. Figure 5 illustrates the gradients of GEM and CO$_2$. Although the nocturnal profile was pronounced, no stationary diurnal pattern of the GEM fluxes could be observed. The mean exchange rates determined by the aerodynamic and MBR methods were similar with day-time values of −0.8 ng m$^{-2}$ h$^{-1}$ and −0.7 ng m$^{-2}$ h$^{-1}$ respectively, and night-time values of −1.0 ng m$^{-2}$ h$^{-1}$ and −0.9 ng m$^{-2}$ h$^{-1}$ respectively. No correlation of the GEM fluxes with any meteorological variable could be detected.

4 Discussion and Conclusions

4.1 Evaluation of aerodynamic and MBR method

Despite the extremely low GEM fluxes and the low temporal resolution of the measurements the aerodynamic and MBR methods produced comparable results. Our measurements during the fair weather period show that the fluxes agree well, although on few occasions the MBR values are considerably smaller or reversed with respect to the aerodynamic fluxes. The smaller MBR fluxes are primarily the result of very small GEM gradients which diminish the GEM flux. Reversed fluxes on the other hand seem to be due to inconsistent GEM gradients caused by non-stationary turbulence regimes. Over the seasons it has to be noted that during spring and summer 2006 the aerodynamic fluxes were consistently higher than the
fluxes determined by the MBR method. During this period when the grass grew rapidly, one or two lines sampled close above or even within the top of the vegetation, which resulted in enhanced CO$_2$ gradients and diminished GEM fluxes (compare with equation 3).

In general, the MBR technique has the advantage that no stability corrections are required (Lenschow, 1995). The technique therefore seems more robust compared to the aerodynamic method. However, our measurements showed similar variability (see ranges in tables 1 and 2) and suggest that both methods seem appropriate to estimate the magnitude of background GEM fluxes. Applying the aerodynamic approach also to CO$_2$ and considering its good agreement with the fluxes determined by eddy covariance has given us additional confidence in our GEM flux estimates.

4.2 Sources of uncertainty

The GEM gradients were determined with one Tekran instrument by measuring air concentrations in a sequential mode. This configuration entailed substantial variability in the GEM fluxes due to high frequency changes in atmospheric GEM concentration. By calculating 50-minute fluxes from 5 different gradients variability could be reduced considerably. Generally, we believe that only synchronous concentration measurements at two or more heights with effective bias tests could reduce this error further.

Fluxes were corrected for density effects according to section 2.3. The corrected GEM fluxes differed up to 6% relative to the calculated raw fluxes and were thus rather small.

4.3 Atmospheric GEM concentrations

The average GEM concentration of 1.42 ng m$^{-3}$ measured at our grassland site fits well into the global estimated mean of 1.2 to 1.8 ng m$^{-3}$ (Pirrone, 2001). There is no monitoring station in the Alps that measures atmospheric GEM on a continuous basis. However, comparison with concentrations measured at Mace Head in Ireland of 1.55 ng m$^{-3}$ (Kim et al., 2005) and at Pallas, Finnland with 1.34 ng m$^{-3}$ (Kim et al., 2005) implies, that atmospheric GEM is not elevated in
the sub-alpine region of Switzerland, which is dominated by north-westerly winds from France (contrary to Mace Head and Pallas we would expect to measure increased anthropogenic emissions).

4.4 GEM gradients

In order to determine the GEM fluxes of uncontaminated sites with flux-gradient techniques it is of main importance to measure the required concentration profiles accurately. This proved to be very challenging as the measured concentration differences were around the minimum resolvable gradient. The low data coverage has to be partly attributed to these small gradients. However, the concentration profiles in figure 5 and the gradient plot of figure 4 indicate that the applied approach is still feasible, at least under fair weather conditions. Figure 5 illustrates the logarithmic decrease of the CO₂ and GEM concentrations with height, with a clear inversion of the CO₂ profile during the night. The very small day-time GEM gradients suggest that any superficial GEM accumulation from the previous nights was quickly disappearing with increasing turbulence during the day. This is also evident in the diurnal cycle of the GEM gradient shown in figure 4.

Edwards et al. (2005) also applied the aerodynamic approach to measure GEM fluxes above various mercuriferous substrates and reached a gradient resolution of 0.01 ng m⁻³ with a similar setup. Kim et al. (1995) measured GEM gradients of −0.16 to 0.32 ng m⁻³ above forest soils and Lindberg and Meyers (2001) measured GEM over wetland vegetation and determined mean gradients of 0.03 ng m⁻³ with a standard deviation of 0.03 ng m⁻³. In Sweden Lindberg et al. (1998) determined gradients of −0.091 to 0.064 ng m⁻³ over forest soils. The gradients between −0.26 and 0.37 ng m⁻³ measured at our grassland site correspond well with these values, although no details can be given about gradients below our detection limit of ±0.02 ng m⁻³.
4.5 GEM fluxes

Looking at the fluxes over the seasons GEM was deposited in minute amounts during the vegetation period. No exchange occurred during winter when the soil surface was covered with snow (the slight emission rates determined for the snow covered period were not significantly different from zero). Comparison of the available day-time and night-time fluxes of the fair weather period revealed no significant differences — a slight deposition was recorded, independent of time. This is also demonstrated by the plots of $u_*$ and the GEM gradients, where high values of the friction velocity are associated with low GEM gradients and vice versa.

The mean fluxes of $-4.3 \text{ ng m}^{-2} \text{ h}^{-1}$ (aerodynamic) and $-1.7 \text{ ng m}^{-2} \text{ h}^{-1}$ (MBR) determined for our site during the snow free season agree well with previous studies of uncontaminated background sites. For example, Meyers et al. (1996) and Kim et al. (1995) measured GEM fluxes of $6.8 \text{ ng m}^{-2} \text{ h}^{-1}$ and $-2.2$ to $7.5 \text{ ng m}^{-2} \text{ h}^{-1}$ above background forest soils. Cobos et al. (2002) determined average GEM fluxes of $9.7 \text{ ng m}^{-2} \text{ h}^{-1}$ over an agricultural soil with the advanced relaxed eddy accumulation method. In Canada Schroeder et al. (2005) measured exchange rates of $-0.4$ to $2.25 \text{ ng m}^{-2} \text{ h}^{-1}$ over forest soils and of $1.1$ to $2.95 \text{ ng m}^{-2} \text{ h}^{-1}$ over agricultural fields. Poissant and Casimir (1998) used a flux chamber and measured $8.3 \text{ ng m}^{-2} \text{ h}^{-1}$ over a grassy site. Flux chambers were also used by Ericksen et al. (2006) who determined a mean emission rate of $0.9 \pm 0.2 \text{ ng m}^{-2} \text{ h}^{-1}$ from background sites across the USA. Based on the review of previous studies, Gustin et al. (2006) suggests that GEM exchange rates from low mercury containing soils are in the range of $-1$ to $3 \text{ ng m}^{-2} \text{ h}^{-1}$. For comparison, GEM fluxes of 10 to 200 $\text{ ng m}^{-2} \text{ h}^{-1}$ were measured over a soil contaminated with $60 \mu g \text{ g}^{-1}$ of mercury (Lindberg et al., 1995).

Several meteorological variables were measured at our site and the data were checked for correlations with the GEM fluxes. However, no significant correlations could be detected. We also screened our flux data for any response to abrupt changes in environmental conditions, e.g. intense showers, rain after longer dry periods and snow melt. None of these events had a visible effect on the GEM flux. Even grass cuts which would imply some GEM emission due to
increases in surface temperature and irradiation had no effect. However, enhanced GEM emission caused by high soil water content or elevated temperatures (as described by Edwards et al., 2001) have been shown in lab experiments with soils from our study site (Fritsche et al., in press). In these experiments we used bare soil samples and flux chambers that generated rather little turbulence. It therefore seems that the GEM flux is strongly influenced by vegetation and atmospheric turbulence.

In section 3.2 we referred to a period in May 2006 with steadily increasing GEM deposition rates (see figure 3). This increase was more pronounced with the aerodynamic method and might be attributed to the fast growing vegetation that removes GEM from the atmosphere. Mercury accumulation in grass has been reported by e.g. Millhollen et al. (2006b).

Summarising our results, uncontaminated grasslands of the temperate sub-alpine climate belt seem to act as a small net sink for atmospheric mercury. This is confirmed by the study of Obrist et al. (2006) who estimated mean GEM deposition rates of 0.2 ng m\(^{-2}\) h\(^{-1}\) at another sub-alpine grassland site in central Switzerland. Net deposition also goes along with the general decrease of air mercury concentrations over Europe since the early 1990’s (Lindberg et al., 2007). It seems that previously deposited mercury is rather stable in soils and does not evaporate in substantial amounts.

Besides dry deposition, the GEM input with precipitation is another important pathway of atmospheric mercury to terrestrial surfaces. We were only able to quantify this input during a few rain events, but the obtained results are in accordance with other studies on wet deposition of atmospheric mercury. The summary of Fitzgerald and Lamborg (2004) for example reports \(\text{Hg}_{\text{tot}}\) concentrations in precipitation between 3 and 23 ng l\(^{-1}\).

If precipitation and dry deposition data are projected to corresponding time scales the ratio of dry to wet deposition and their respective significance could be estimated. Based on our measurements, i.e. a mean \(\text{Hg}_{\text{tot}}\) concentration in precipitation of 7.0 ng l\(^{-1}\) and a mean deposition flux of 2 ng m\(^{-2}\) h\(^{-1}\) (average of both methods over entire period), the annual dry deposition would account for 67% and wet deposition for 33% of a total annual input of
0.26 g ha\(^{-1}\). Thus dry deposition would exceed wet deposition by a factor of 2 and would therefore constitute the major deposition pathway.

5 Acknowledgements

We thank the Swiss National Science Foundation (project numbers: 200020-113327/1 to D. Obrist and C. Alewell; 200021-105949 to W. Eugster and R. A. Werner) for financing this project and would like to express our appreciation to H. Hürlimann, M. Caroni and H. Strohm for their assistance in soil and water analyses, H. Biester for the mercury analysis of our soil samples and R. Vogt as well as C. Ammann for their valuable help in micrometeorological issues.
Figure captions

Figure 1. Schematic of the experimental setup. The tower with the mounted sampling lines is shown on the left, the instrumentation housed in a weather-proof cabinet on the right.

Figure 2. GEM concentration in ng m$^{-3}$ vs. wind direction. Shown are all data points from September 2005 to August 2006 of the sampling line at 1.7 m above ground.

Figure 3. Seasonal trends of air temperature ($T_{\text{air}}$), atmospheric GEM concentration at 1.7 m above ground ($GEM_{\text{air}}$), GEM gradients, friction velocity ($u_*$) as well as the turbulent fluxes of GEM (determined by the aerodynamic and MBR methods) and CO$_2$ (determined by the aerodynamic method and the eddy covariance technique). Time series are low-pass filtered (rectangular filter with fast fourier transform) with a cut-off period of 8 days. Positive GEM and CO$_2$ fluxes indicate emission, negative deposition. White triangles in the GEM flux plot indicate grass cuts.

Figure 4. Diurnal variation for the fair weather period in October 2005. Shown are the time series for air temperature ($T_{\text{air}}$), net radiation ($R_n$), atmospheric GEM concentration at 1.7 m above ground ($GEM_{\text{air}}$), friction velocity ($u_*$), GEM gradients as well as the turbulent fluxes of GEM (determined by the aerodynamic and MBR methods) and CO$_2$ (determined by the aerodynamic method and the eddy covariance technique). Flux data are low-pass filtered (rectangular filter with fast fourier transform) with a cut-off period of 5 hours. Positive GEM and CO$_2$ fluxes indicate emission, negative deposition.

Figure 5. GEM and CO$_2$ concentration profiles of the fair weather period in October 2005 separated by day (9 – 15 hours) and night (23 – 5 hours). Dots and error bars represent means and standard errors of the 10-day period. The dashed line shows the approximate height of the vegetation.
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Table 1. Summary of seasonal CO$_2$ and GEM flux data (entire measurement period)

<table>
<thead>
<tr>
<th></th>
<th>Aerodynamic method</th>
<th></th>
<th>EC method</th>
<th></th>
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<tbody>
<tr>
<td><strong>Mean CO$_2$ flux [µmol m$^{-2}$s$^{-1}$]</strong></td>
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<tr>
<td>Entire period$^c$</td>
<td>-2.5 (-86 to 66)$^a$</td>
<td>5111</td>
<td>-2.5 (-55 to 43)$^a$</td>
<td>5345</td>
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<tr>
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<td>-4.2 (-55 to 43)$^a$</td>
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<tr>
<td>Snow covered period$^e$</td>
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<td>1387</td>
<td>1.0$^b$ (-27 to 30)</td>
<td>1334</td>
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<tr>
<td><strong>Mean GEM flux [ng m$^{-2}$h$^{-1}$]</strong></td>
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<td></td>
<td>MBR method</td>
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<tr>
<td>Entire period$^c$</td>
<td>-2.9 (-42 to 29)$^a$</td>
<td>5214</td>
<td>-1.1$^b$ (-68 to 82)$^a$</td>
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<tr>
<td>Vegetation period$^d$</td>
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<td>-1.7 (-35 to 34)$^a$</td>
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<td>Snow covered period$^e$</td>
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<td>1357</td>
<td>0.4$^b$ (-68 to 82)$^a$</td>
<td>957</td>
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</table>

$^a$ range  
$^b$ not significantly different from zero  
$^c$ from 26.09.2005 to 30.08.2006  
$^d$ from 26.09.2005 to 23.11.2005 and from 27.03.2006 to 30.08.2006  
$^e$ from 24.11.2005 to 26.03.2006
Table 2. Summary of diurnal CO$_2$ and GEM flux data (fair weather period of October 2005)

<table>
<thead>
<tr>
<th></th>
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<th>N</th>
<th>EC method</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean CO$_2$ flux [µmol m$^{-2}$ s$^{-1}$]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>day-time$^c$</td>
<td>$-16.8$ ($-46.3$ to $-3.6$)$^a$</td>
<td>66</td>
<td>$-14.4$ ($-27.8$ to $14.7$)$^a$</td>
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</tr>
<tr>
<td>night-time$^d$</td>
<td>$3.8$ ($-0.5$ to $23.3$)$^a$</td>
<td>40</td>
<td>$2.7$ ($-6.5$ to $8.8$)$^a$</td>
<td>23</td>
</tr>
<tr>
<td><strong>Mean GEM flux [ng m$^{-2}$ h$^{-1}$]</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>day-time$^c$</td>
<td>$-0.8$ ($-12.8$ to $9.5$)$^b$</td>
<td>67</td>
<td>$-0.7$ ($-10.5$ to $10.0$)$^a$</td>
<td>69</td>
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<tr>
<td>night-time$^d$</td>
<td>$-1.0$ ($-10.3$ to $1.4$)$^a$</td>
<td>40</td>
<td>$-0.9$ ($-4.0$ to $1.9$)$^a$</td>
<td>32</td>
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</table>

$^a$ range
$^b$ not significantly different from zero
$^c$ from 9 – 15 hours
$^d$ from 23 – 5 hours
Figure 2
Figure 3

- $T_{\text{air}}$ [°C]
- GEM$_{\text{air}}$ [ng m$^{-3}$]
- GEM$_{\text{gradient}}$ [ng m$^{-3}$]
- GEM$_{\text{flux}}$ [ng m$^{-2}$ h$^{-1}$]
- $CO_2$ flux [$\mu$mol m$^{-2}$ h$^{-1}$]

- Snow covered period

- MBR aerodynamic method
- EC aerodynamic method

Legend:
- \( u^* \) [m s$^{-1}$]
Figure 5

![Graph showing GEM$_{air}$ [ng m$^{-3}$] and CO$_2$ [ppm] vs. height [m] with data points for day and night.](image-url)