

Atmospheric Mercury Fluxes in a Southern Boreal Forest and Wetland

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Received: 18 April 2011 / Accepted: 11 August 2011 / Published online: 1 September 2011
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Abstract Total gaseous mercury (TGM) fluxes from the forest floor and a boreal wetland were measured by a flux chamber technique coupled with an automatic mercury vapour analyser. The fluxes were measured at three sampling sites in southern Finland, 61°14' N, 25°04' E in summer 2007, with additionally in situ TGM concentrations in the air at one of the sites and mercury bulk deposition at another. Most of the flux data were collected during the daytime. At one of the sites, diurnal flux behaviour was studied, and a clear cycle with an afternoon maximum and a night minimum was observed. The highest emissions (up to 3.5 ng m⁻² h⁻¹) were observed at the forest floor site having a moss and grass cover. At the wetland and litter-rich forest floor sites, the emissions were below 1 ng m⁻² h⁻¹ and sometimes negative (down to -1.0 ng m⁻² h⁻¹), indicating mercury uptake. The measured average fluxes in August were 0.9±1.1 and 0.2±0.3 ng m⁻² h⁻¹ for the forest floor sites and wetland sites, respectively. The flux data were compared with the mercury bulk deposition, which proved to be of the same magnitude, but

opposite in sign. At the mossy forest floor site, the extrapolated TGM emissions were 130% of the Hg deposition in August 2007. Comparison with other studies showed that the fluxes in background areas are relatively uniform, regardless of measurement site location and method used. Airborne TGM remained at the background level during the study, with an average value of 1.3±0.2 ng m⁻³; it frequently showed a diurnal cycle pattern.

Keywords Total gaseous mercury · Air–surface exchange · Flux chamber · Deposition

1 Introduction

Unlike other toxic metals, mercury is highly volatile and has low water solubility. Elemental mercury, which is the most abundant species in the atmosphere in background areas, has an atmospheric lifetime of 0.5–2 years (Schroeder and Munthe 1998), resulting in global dispersion of this component. There are several anthropogenic sources for mercury, mainly coal combustion, waste incineration, metal smelting, refining and manufacturing. Not only can mercury be emitted from anthropogenic sources but also from natural surfaces, such as water bodies, soil and vegetation. Thus, gaseous mercury is readily transported from aquatic and terrestrial ecosystems into the atmosphere (Schroeder et al. 1989). The contribution of the Hg emission from soils is important to the

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global Hg cycle (Carpi and Lindberg 1998). To study the fate of mercury that has been emitted into the atmosphere, atmospheric flux measurements are needed.

The Hg flux from, e.g. the soil is influenced by solar radiation (Poissant and Casimir 1998; Bahlmann et al. 2004a), soil and air temperature (Gustin et al. 1997; Poissant and Casimir 1998), soil moisture (Bahlmann et al. 2004b), wind speed (Gustin et al. 1997), ozone (Engle et al. 2005) and possibly even unknown substance(s) in the ambient air (Zhang et al. 2008). The emission rate limiting factors are the abiological and biological formation of Hg^0 (and $(\text{CH}_3)_2\text{Hg}$) in the uppermost soil layers in background areas, and thus, the evaporation rate is probably also strongly influenced by deposited airborne mercury (Schlüter 2000). Given the situation of climate warming and the shorter duration of snow cover in large areas of the boreal forest zone, terrestrial mercury emissions will probably change in the future.

Both flux chambers (Xiao et al. 1991; Carpi and Lindberg 1998; Schroeder et al. 2005; Kuiken et al. 2008a, b) and micrometeorological methods (Kim et al. 1995; Lindberg et al. 1998, 2002; Lee et al. 2000; Poissant et al. 2004; Schroeder et al. 2005) have been widely used in studies of mercury fluxes. At the moment, no standard protocol for flux measurements exists and therefore a wide variety of measurement conditions have been applied (e.g. Eckley et al. 2010). Micrometeorological methods (MM) have relatively large flux footprints and do not interfere with the surface of interest. They are also desirable when the substrate concentration varies greatly over the measurement site, since the flux chamber technique (FC) has a limited footprint. Disadvantages of the MM methods include the demand for a developed infrastructure, especially at a forested site, where towers several tens of metres in height are needed. Often these methods also require an electricity supply and relatively easy access to the measurement site (Rinne 2001). FCs are practical due to their low cost, portability and ease of use. With chamber techniques, the measurement can be carried out on a certain surface instead of a whole ecosystem, and lower emission rates can be detected.

In North America, a vast number of flux experiments from various surfaces have been conducted and published (e.g. Lindberg et al. 1995, 1998, 1999; Gustin et al. 1997; Carpi and Lindberg 1998; Poissant

and Casimir 1998; Edwards et al. 2001; Schroeder et al. 2005; Kuiken et al. 2008a, b). However, on other continents, data are scarce. To our knowledge, background flux data for the Eurasian boreal zone are provided in only a few papers (Schroeder et al. 1989; Xiao et al. 1991; Lindberg et al. 1998).

The aim of this work was to study atmospheric mercury fluxes at a background site and compare the amount of mercury being released and taken up by the forest and wetland surfaces. Since the Nordic countries are highly forested, the fluxes occurring in such background areas are of interest. Air concentrations were measured to ensure background conditions at the site. This work was conducted as a part of a study to calculate the total mercury budget at a forested natural reserve in southern Finland in 2007.

2 Experimental

2.1 Site Description

The study site is located at Lammi in southern Finland (61°14' N, 25°04' E) in the southern boreal zone (Fig. 1). It is a forested (about 66% of the total area) natural reserve with a small headwater lake and some wetland areas (about 21% of the total area). The area is dominated by Norway spruce (*Picea abies*) with some old birch (*Betula* spp.), aspen (*Populus tremula*) and Scots pine (*Pinus sylvestris*) trees occurring among the spruce. The mineral soils in the catchments are predominately Podzols developed in shallow glacial drift (till) deposits (Mäkelä 1995; Starr and Ukonmaanaho 2001). The catchment is part of the UN/ECE ICP-Forests and ICP IM monitoring programme in Finland.

The flux experiments were carried out at three different locations. The first one (here called L1) was located near the lake at the bottom of a small hill, the second one (L2) was on a hillside some 40 m uphill from L1, while the third one (L3) was sited at a small wetland a couple of hundred metres from the other two sites. The total gaseous mercury (TGM) concentration in the air was measured at L1, while the mercury bulk deposition was collected at L3. The L1 plot contained moss (*Sphagnum*), grass and some brushwood and litter. The L2 plot was covered with litter, with some twigs and brushwood. The L3 site



Fig. 1 Location of the study site

consisted of three adjacent plots with (1) mostly moss (*Sphagnum*) and some grass, (2) grass, moss and cranberry and (3) moss and grass with some litter and cranberry. The mean Hg concentration in the soil humus layer was 0.25 mg/kg (dry weight, dw), while in the mineral soil below (0–25 cm), it was 0.03 mg/kg (dw) (data: Finnish Environment Institute).

The experiments were carried out between April and September of 2007, most of them in August. The air temperature during the experiment days varied between 6°C and 26°C, while the ground temperature rose from 0°C in April to 15°C in late summer. There was hardly any precipitation during the experiment days (less than 1 mm in August and 2.8 mm on May 3). The total monthly precipitation in August was 78 mm at a nearby weather station 7 km from the study site. In general, the temperature and rain amount were close to their average values throughout the summer of 2007, according to the statistics of the Finnish Meteorological Institute (FMI).

2.2 Sampling

The first experiment was carried out shortly after the snow melt in April 2007, and the last was in early September, well before the first snowfall. In total, there were eight different experiment days with one to six measurements on each, resulting in 49 separate flux measurements. At L1, experiments were carried out on all 8 days ($N=33$) while at L2 and L3, there were four ($N=8$) and three ($N=8$) experiment days, respectively, due to the logistical difficulties in a forested natural reserve. On each measurement occasion, two to three “replicate” samplings were conducted. These so-called replicates were separate flux measurements performed successively and thus do not represent exactly the same conditions. Generally, the daily experiments consisted of two successive measurements at one or at all three different locations. In late August, to study diurnal variation, the experiments were performed every third hour around the clock. The concentration of TGM in the air was measured for 1 month from 6 August to 6 September.

The sampling system consisted of a Teflon flux chamber connected to a Tekran 2537A mercury vapour analyser. Both Teflon and polycarbonate chamber designs have been widely used in TGM flux measurements (e.g. Carpi and Lindberg 1998; Eckley and Branfireun 2008; Kuiken et al. 2008a, b; Zhang et al. 2008). However, Teflon has been the recommended choice of material in recent comparison studies (Carpi et al. 2007; Eckley et al. 2010). In this study, the dimensions of the flux chamber, made of 0.05-mm-thick fluorinated ethylene propylene, were $60 \times 60 \times 25$ cm ($l \times w \times d$). The relatively large square area of the chamber gives more reliable results for the flux from a chosen surface compared to most typical mercury flux chamber designs (Eckley et al. 2010 and references therein). Additionally, a large enough chamber was indeed needed in this particular study due to the growing low vegetation. The chamber had an external aluminium frame support. A similar method has been previously employed for, e.g. hydrocarbon emissions; a more detailed description can be found in Hellén et al. (2006). At L1 and L2, the chamber was seated on a stainless steel collar set in the ground 4 months before the first measurements started. The collars remained undisturbed during the whole measurement period. A water bath of ultrapure Milli-Q water between the chamber and collar sealed

the system. At L3, no collar was used, since the chamber could easily be pressed into the vegetation surface.

The Tekran mercury analyser collects and analyses samples continuously at 5-min intervals using two gold cartridges in turn. While one cartridge is collecting a sample, the other is being desorbed and the mercury in the sample analysed by atomic fluorescence spectrometry. The analyser collects only total gaseous mercury and not particles, which were removed from the sample flow with a Teflon filter (diameter 47 mm, 0.2 μm pore size). The sample flow rate was 1.5 Lmin^{-1} , and the carrier gas was argon 6.0 (purity 99.9999%). With these parameters, a detection limit of 0.1 ng m^{-3} , a repeatability of 2% and a measurement uncertainty of 10% are achieved. The analyser was calibrated daily at the site with its internal permeation source. This instrument model has been used successfully at a number of locations around the world and has been found to give results comparable to those with other methods (Ebinghaus et al. 1999).

The chamber and analyser were connected with Teflon tubing. The method was almost static, i.e. no ventilation was performed in the chamber, but the sample flow of 1.5 Lmin^{-1} was estimated to mix the air in the chamber effectively. Also, a narrow open Teflon tube connected the chamber with the outside air to avoid the formation of under-pressure. This dilution was taken into account in the flux calculations. A static method such as this excludes the wind effect, which might underestimate the actual flux in normal conditions due to an increased ground-air boundary layer. However, very low fluxes have been reported to present considerable challenges with dynamic chambers using fast turnover times due to (1) comparable blank and flux results and (2) flux values pushing the limits of instrumental detection (Kuiken et al. 2008a). With very low fluxes, the static method is more useful, since the concentration is not diluted in the method. The static method can, however, diminish the concentrations if the closing time is too long. Pumpanen et al. (2004) have shown that for CO_2 , a 10-min closing time gave very good results, whereas the fluxes were underestimated by 10–15% when the closing time was extended to 30 min. Our chamber remained closed for 20 min, so this effect would not cause large errors in the measurements.

The emission rate was determined from the concentration increase in the chamber during a closure. The optimized experiment time of 20 min allows for four 5-min samples and consequently five data points (four samples plus the background value). When the linearity of the concentration increase was poor ($R^2 < 0.8$), the results were rejected. Out of the total of 49 experiments, 13 results were omitted, 12 of which were considered as showing no flux. When a concentration change (i.e. a change greater than 0.1 ng m^{-3} , which is about the absolute MU) was observed, the correlation coefficients were above the limit value in all cases, except in just one out of the total of 49 experiments. The average values for R^2 were 0.95 for L1, 0.93 for L2 and 0.90 for L3.

Hg blanks with the chamber and stainless steel collar were performed in the laboratory. The chamber system was placed on top of a Teflon film, and the Hg concentration inside the chamber was compared to that in the lab air (1.9 ng m^{-3}). No significant difference was found, and therefore, no blank value was subtracted from the flux results. When not in use, the chamber was stored in a plastic bag in the laboratory with a TGM air concentration of less than 3 ng m^{-3} (usually close to ambient, i.e. less than 2 ng m^{-3}).

Air temperature was measured with a Davis Vantage Pro 2 station, while the temperature inside the chamber and the solar radiation over the chamber were measured with a Li-Cor 190 SB sensor. The air temperature was observed to increase in the chambers during the closure. The increase was insignificant ($\Delta T < 2^\circ\text{C}$) in most cases, since there was seldom direct sunlight in the whole plot area, due to cloudy weather and/or the shading of the canopy. The data for solar radiation are not discussed in this article due to instrumental failures.

The deposition samples were collected at L3 with an IVL-type bulk collector (funnel diameter 15 cm) except during the winter months (December to April), when a wide Teflon funnel (100×100 cm) was used for the collection of snow 10 m from the L2 site. For the precipitation amount, data from a nearby FMI station were used. Two samples were collected in parallel on a monthly basis; these were then shipped to the Swedish Environmental Research Institute (IVL) for analysis according to the EMEP manual (EMEP/CCC 2002).

2.3 Calculation of Hg Flux

The Hg flux F was calculated according to Eq. 1:

$$F = \frac{\frac{\Delta c}{A} V}{t} \quad (1)$$

where Δc is the concentration change during the experiment, A is the plot area, V is the flux chamber volume and t is the duration of the experiment. The dilution volume for each data point was taken into account.

3 Results and Discussion

3.1 Forest Floor Emissions

The forest floor fluxes for locations L1 and L2 are given in Fig. 2. The fluxes varied between -1.0 – $3.5 \text{ ng m}^{-2} \text{ h}^{-1}$, being mainly positive, i.e. Hg was emitted from the forest floor. On some occasions (29% of samples), no flux was detected, while a negative flux was observed only rarely (7% of samples). The low flux rates were partially a result of poor light penetration through the forest canopy and frequent cloudy days (see discussion below). In August, when the majority of the experiments were conducted, an average flux of $0.9 \pm 1.2 \text{ ng m}^{-2} \text{ h}^{-1}$ has been calculated from the measured values. Fluxes at L1 were always greater than at L2, with a maximum difference of $1.8 \text{ ng m}^{-2} \text{ h}^{-1}$ during 1 day. This is likely to be due to the different plot vegetations and to differences in solar radiation affecting the chamber plot, since the substrate Hg concentration is expected to be fairly consistent in the study area. The L1 plot was rich in mossy vegetation, while the L2 plot was covered with forest litter and was much dryer than L1. Also, the L1 plot was at the bottom of a slope, while L2 was up on the hillside. Consistent with our study, Kuiken et al. (2008a) reported very low fluxes from a litter-covered forest floor in Tennessee ($37\% < 0.2$ and $19\% < 0.0 \text{ ng m}^{-2} \text{ h}^{-1}$). Xiao et al. (1991) postulated that when the forest soil is covered with litter, any Hg emanating from the soil might be trapped by litter via direct adsorption or via the formation of complexes with humic materials.

In the spring, when the soil temperature was close to zero, the fluxes at L1 were negligible or very small. By early August, the soil temperature had increased,

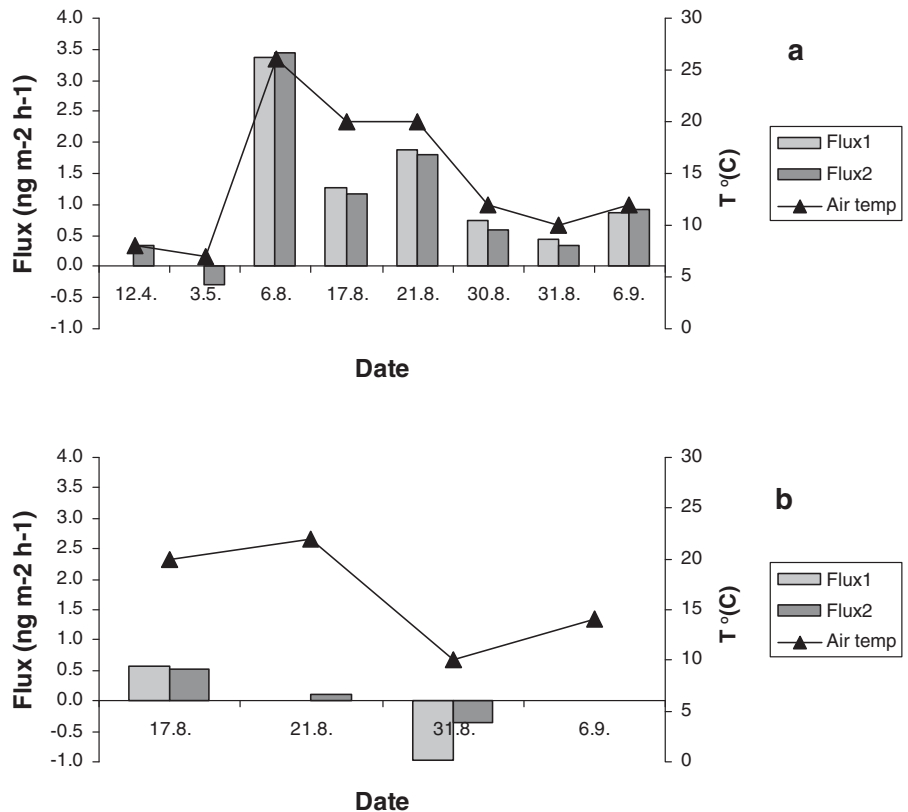
as had also the emissions. Rainless weather or only slight rainfall was recorded before and during the experiments. On 6 September, no exchange of Hg was detected at the L2 site. Mercury deposition from the air to the soil was recorded once at both sites. This occurred on the coldest days: During the negative flux experiments, temperatures were $+6.5^\circ\text{C}$ and $+10^\circ\text{C}$ at L1 and L2, respectively. The average relative deviation of successive flux measurements was 16% at L1.

The correlation between the Hg flux and other parameters (air temperature, soil temperature) was calculated for L1. At the L2 (and L3) plot, there were not enough flux data to make such calculations. The flux pattern was found to follow the air temperature (Figs. 2 and 4); the correlation at L1 is shown in Fig. 3. A linear relationship gave an R^2 value of 0.86, similarly to the exponential relationship. The latter does not accept zero and negative values, resulting in slightly biased data; for this reason, the linear relationship is presented in Fig. 3. An exponential correlation between Hg flux and soil temperature has been found by Lindberg et al. (1995) and Gustin et al. (1997) over contaminated and naturally enriched soils. Gustin et al. (1997) reported a similarity between the Hg^0 vapour pressure curve and the mercury flux curve and concluded that the Hg^0 flux as a function of temperature is strongly influenced by the vapour pressure of Hg^0 .

Gustin et al. (1997) found that the Hg flux is greater when a substrate is indirectly heated by the air than when the substrate itself is directly heated with tape. They therefore suggested that the predominant processes driving the flux of Hg^0 to the atmosphere as a function of temperature are those acting on the soil surface. In our study, the Hg flux correlated more strongly with air temperature ($R^2=0.86$) than with soil temperature ($R^2=0.56$). However, the soil temperature was measured only at a depth of 10 cm; it is expected that the temperature of the top layer of soil was more affected by the air temperature than by the measured soil temperature.

The diurnal flux variation was studied on 30 and 31 August. Two sequential experiments were performed at an interval of approximately 3 h; these produced 18 flux results (Fig. 4). The highest emission ($0.7 \text{ ng m}^{-2} \text{ h}^{-1}$) occurred at 5 p.m. on 30 August and 11 a.m. on 31 August, when the air temperature was the highest. The soil temperature at a depth of 10 cm did not change during the experiment.

Fig. 2 Forest floor emissions and air temperatures at L1 (a) and L2 (b). Flux 1 and Flux 2 denote sequential measurements. A missing bar indicates no flux



Towards nightfall, the flux decreased, and during the early morning hours (2 and 8 a.m.), the concentration change in the chamber was unclear ($R^2 < 0.8$), and thus, the flux was considered to be negligible. The flux results for which the concentration change correlation was below 0.8 are included in the figure (the hatched bars), but the measurement uncertainty is high for these results. Apart from one data point in the early morning (5 a.m.), which is in the same range as

the daytime fluxes, the diurnal cycle is very clear. Between 4 and 6 a.m., the wind speed decreased to 0 m/s; the lack of wind probably produced an increased concentration of Hg above the soil. It should be noted that sunrise occurred after 6 a.m. at the site. At 11 a.m., there was a large variation between the sequential experiments as a result of temporary solar radiation differences affecting the chamber plot.

Fig. 3 Correlation between Hg flux and air temperature at L1

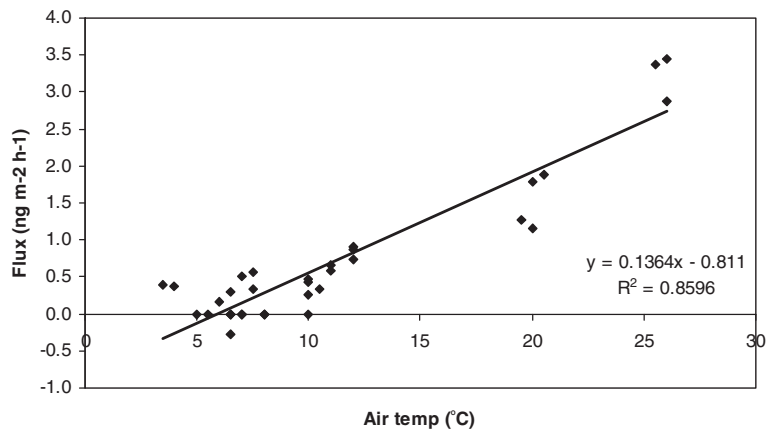
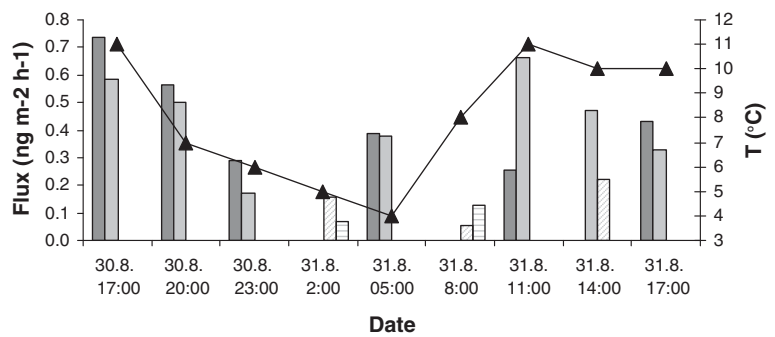


Fig. 4 Twenty-four-hour flux measurements at L1. The bars represent fluxes and the triangles air temperature. The hatched bars are flux results with a high uncertainty

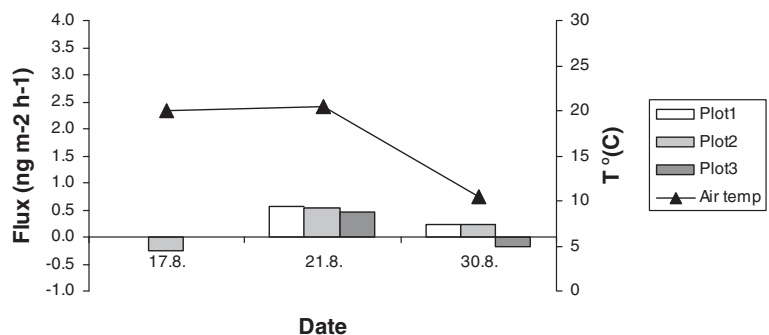


The diel cycle is often associated with diurnal changes in, e.g. temperature and solar radiation (e.g. Poissant and Casimir 1998). Other parameters can also affect this behaviour. Zhang et al. (2008) hypothesized that some unidentified airborne substance(s) in the ambient air, such as ozone or some volatile organic molecules, might be responsible for the cycle. This was studied with contaminated soils held in the dark at a constant temperature in laboratory conditions. In the study, meteorological factors including wind speed were excluded.

3.2 Wetland Emissions

The fluxes at the three wetland plots are shown in Fig. 5. Here, the surface acted both as a source and as a sink. However, the fluxes were very small (-0.3 – 0.6 $\text{ng m}^{-2} \text{h}^{-1}$), even though the measurement days at the wetland plots were generally warm and sunny. During the closures at the wetland plots, moisture condensed on the chamber walls; the condensed water vapour may have affected the flux results by inhibiting UV penetration into the chamber and absorption of Hg^0 into the condensation droplets. Thus, the wetland results are discussed only briefly here. At the forest floor plots, no condensation occurred.

Fig. 5 Wetland fluxes and air temperatures at L3. Plot 1, plot 2 and plot 3 denote the adjacent experiment plots. A missing bar indicates no flux



The wetland plots differ greatly from those on the forest floor, not only in respect to their vegetation but also by their moisture content. Soil moisture was not measured during the study, but visually it was clear that the forest floor plots were dry soil while the wetland plots were wet. The wet conditions may have inhibited the flux. A similar behaviour in the case of a wet forest canopy has been reported by Lindberg et al. (1998). They suggested that Hg^0 dry deposition to the canopy may be enhanced by the presence of moisture, but that a wet canopy does not necessarily result in net deposition.

During the last measurement day, it rained slightly. Lindberg et al. (1999) discovered that after a heavy rainfall, the mercury emissions increased sharply in a geothermal area in Nevada, USA. In our study, the small rain amount did not change the already wet conditions, and no increased flux was observed.

3.3 Comparison with Other Studies

Fluxes between the air and various surface types have been reported in many North American studies (e.g. Lindberg et al. 1995, 1998, 1999; Gustin et al. 1997; Carpi and Lindberg 1998; Poissant and Casimir 1998; Edwards et al. 2001; Schroeder et al. 2005; Kuiken et

al. 2008a; b). In background areas, studies are still scarce. To our knowledge, mercury flux measurements have been performed in the Eurasian boreal zone only in Sweden (Schroeder et al. 1989; Xiao et al. 1991; Lindberg et al. 1998) prior to our measurements. A comparison of flux results in background areas is presented in Table 1. The spring data from our study with only a few data points at L1 have been excluded from the table.

Our soil results are very similar to the Swedish and Canadian studies (Xiao et al. 1991; Lindberg et al. 1998; Poissant and Casimir 1998; Schroeder et al. 2005), which could be expected due to the similarities in vegetation and latitude. The flux values obtained in the American studies by Kuiken et al. (2008a, b) are also similar to ours. Although the flux depends on the various parameters listed previously, the fluxes are relatively uniform regardless of the measurement site location and measurement method. However, the measurements are mostly conducted during the warm summer period characterized by higher temperatures and high solar radiation. The estimation of annual net fluxes is therefore problematic due to the lack of winter-time measurements.

A comparison of fluxes measured at different wetland locations is given in Table 2. For the wetland, our results are in the low range and similar to studies by Lee et al. (2000) and Schroeder et al. (2005). The areas in the Lindberg et al. (2002) and Poissant et al. (2004) studies were impacted by agricultural, municipal and industrial activities, and thus, higher fluxes at those sites are to be expected. To our knowledge, our mercury flux measurements are the first to be conducted in a Eurasian boreal wetland.

3.4 Emission vs. Wet Deposition

To evaluate the mercury transport at the atmosphere–soil interface, bulk deposition data were compared to the flux results. The monthly Hg deposition in 2007, as monitored by the Finnish Environmental Institute, is shown in Fig. 6.

The bulk deposition in August was 780 ng m^{-2} , which represents a typical deposition amount in late summer. This value was compared to the calculated average monthly Hg flux at the site L1. In August 2007, the average temperature at the nearby weather station was $+16^\circ\text{C}$, while the 30-year average was 14.2°C (FMI statistics). Using the temperature of

Table 1 Comparison of average mercury fluxes between vegetated soil and the air in background areas

Measurement site	Method	Time of year	Vegetation/site type	Average (and range of) flux ($\text{ng m}^{-2} \text{ h}^{-1}$)	Air/soil temperature ($^\circ\text{C}$)	Reference
South Sweden	FC	May–June 1988–1989	Coniferous forest	0.3 (–2.0–2.5)	–/10	Xiao et al. 1991
Tennessee, USA (3 sites)	FC	April–August 1995	Deciduous forest	6.98 (2.25–13.94), 2.00 (1.11–2.95), 2.70 (0.98–5.95)	(12–24)	Carpi and Lindberg 1998
Tennessee, USA	MM	September–October 1994	Young pine canopy	18 (–33–86)	16.0–25.9	Lindberg et al. 1998
South Sweden	MM	June 1994	Boreal forest floor	1 (–5.4–4.2)	11.3–16.6	Lindberg et al. 1998
Quebec, Canada	FC	Summer 1995	Rural grassy	2.95 (0.62–8.29)	–	Poissant and Casimir 1998
Nova Scotia, Canada	FC	Summer 1997 and 1999	–	1.1 (–0.4–2.2)	15.6–19.6/14.0–17.5	Schroeder et al. 2005
Tennessee, USA	FC	January–November 2004	Deciduous forest	0.4 (–1.2–3.3)	–5–28/4–22	Kuiken et al. 2008a
Eastern seaboard of the USA	FC	May–June 2005	Different forest types at 6 sites	0.2 (–5.1–2.5)	9–28/10–22	Kuiken et al. 2008b
South Finland	FC	August–September 2007	Coniferous forest	0.9 (–1.0–3.5)	16 (10–26)/11 (9–16)	Our study

FC flux chamber method, MM micrometeorological method

Table 2 Comparison of average mercury fluxes between wetland and the air

Measurement site	Method	Time of year	Vegetation/site type	Average (and range of) flux (ng m ⁻² h ⁻¹)	Air/soil temperature (°C)	Reference
Connecticut, USA	MM	June–July 1997, March–July 1998	Salt marsh	0.46±0.80 (annual estimate)	–	Lee et al. 2000
Florida, USA	MM	April 1996–March 1998	Primarily cattail	17±43 (annual)	–	Lindberg et al. 2002
Quebec, Canada	MM	August–September 2002	Mixed, mainly <i>Scirpus fluviatilis</i>	32.1 (–110–278)	17.3±4.6/19.0±1.5	Poissant et al. 2004
Quebec, Canada	MM	July–August 1999	Dry wetland	0.88 (–1.5–2.40)	–	Schroeder et al. 2005
South Finland	FC	May 2000 August 2007	Wet wetland Mainly moss (<i>Sphagnum</i>) and grass	0.95 (–0.46–7.13) 0.2 (–0.3–0.6)	16 (11–21)/13 (11–15)	Our study

FC flux chamber method, MM micrometeorological method

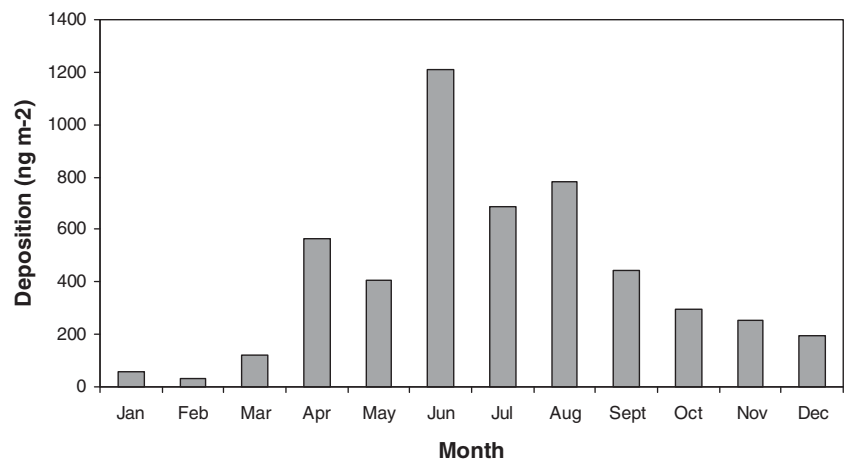
August 2007, an average flux of 1.4 ng m⁻² h⁻¹ is obtained with the correlation equation provided in Fig. 3. This gives a monthly flux of 1,000 ng m⁻², which is close to the amount of Hg deposited by precipitation in August. Calculating the extrapolated emission values for the summer period (May to September 2007) gives emission rates comparable to the bulk deposition during the respective months (the emission found corresponding to 70–150% of the bulk deposition).

As has been shown previously, dry deposition of Hg occurs at the site. Nevertheless, forest floor respiration is an important pathway for Hg transport, and according to our data, it is of the same magnitude as the bulk deposition, but certainly less than the total deposition when calculated from the throughfall and litterfall. In a comparison of the mercury deposition in an open field (bulk), the throughfall and the litterfall in nine catchments in Europe and North America, Munthe et al. (2004) found the lowest in the open field. The increased deposition in throughfall has been attributed to dry deposition of Hg in the canopy; this deposit is washed off by rainfall, with the surface adsorption of reactive gaseous mercury species or deposition of Hg⁰ via stomatal uptake or canopy surface oxidation also possibly being involved. Litterfall fluxes were similar or slightly higher than throughfall in the comparison of Munthe et al. Due to the limited data sets, the fluxes at the hillside site (L2) and wetland sites (L3) are not valid for Hg transport calculations.

3.5 Atmospheric Mercury Concentrations

Ambient air concentrations were measured for a 1-month period during the late summer experiment season (between 6 August and 6 September, Fig. 7). The Hg concentration in the air was rather low, with an average value of 1.3 ng m⁻³ and a maximum value of 2.2 ng m⁻³. On most days, a diurnal cycle was observed, with an early morning hour minimum and an afternoon maximum. Similar behaviour has been observed in Canada (Kellerhals et al. 2003), northern Taiwan (Kuo et al. 2006) and Mt. Gongga in China (Fu et al. 2008). Low concentrations (approximately 1.0 ng m⁻³) in the early morning hours of summer have also been detected in Sweden (Schmolke et al. 1999). Kellerhals et al. (2003) stated that the low concentrations resulted from nighttime depletion of

Fig. 6 Monthly Hg deposition at Lammi in 2007 (data: Finnish Environment Institute)



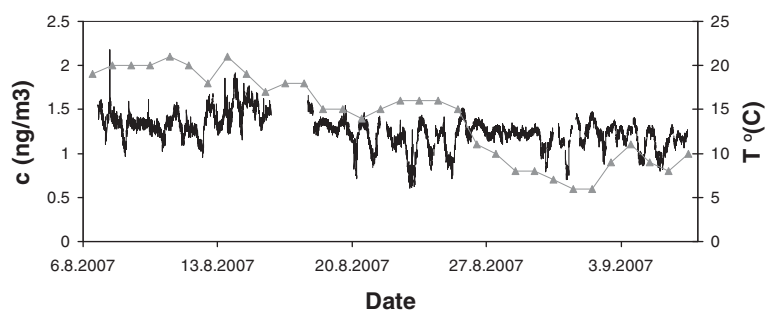
TGM in the lowermost atmosphere, where a shallow TGM-depleted layer is formed underneath the nocturnal inversion layer. Shortly after the sunrise, the nocturnal inversion breaks down, and this air is mixed with undepleted air. This phenomenon might also be happening at our site. Fu et al. (2008) hypothesized that their pattern is due to a strong surface source activated by solar radiation and air temperature at some locations and to wind direction at others. At our measurement site, clean northerly winds with low TGM concentrations were most dominant during the nighttime, but the southerly winds that are expected to carry air from the highly industrialized areas in Europe were almost as frequent. Thus, we conclude that the effect of wind direction is small but existing. The main reasons for the diurnal cycle at our site are believed to be the higher temperature and solar radiation during the day; these increase the surface emission and thus increase the air concentrations, while the nighttime depletion is responsible for the diurnal minimum. During the diurnal experiment, no uptake by the forest floor was detected. However, this does not exclude the possibility that mercury might be

depleted to, e.g. the foliage. In conclusion, no atmospheric pollution sources affecting our flux study were observed.

4 Conclusions

Flux measurements were performed at two diverse forest floor and three adjacent wetland plots in the summer of 2007. Both emission and deposition were observed, although emission was far more frequent during the study. The fluxes at the forest floor sites were in the range -1.0 – 3.5 $\text{ng m}^{-2} \text{h}^{-1}$, with the fluxes at the verdant moss-grown plot always being higher than those at the litter-rich plot. The wetland fluxes were smaller (-0.3 – 0.6 $\text{ng m}^{-2} \text{h}^{-1}$). The diurnal flux was measured at the verdant forest floor site; the flux was found to follow a clear diurnal pattern with a nighttime minimum and a daytime maximum. With the available data, a clear temperature dependence was evident. Since the measurements were limited to summer time, the real net balance is difficult to quantify. The ambient TGM concentration

Fig. 7 TGM concentration (black line) and daily mean temperature (grey line with triangles) at L1 during the late summer measurement campaign



remained at roughly the background level throughout the campaign in late summer.

Forest floor respiration was found to be an important pathway for mercury transport. During August, when the majority of the experiments were performed, the average measured flux was $0.9 \text{ ng m}^{-2} \text{ h}^{-1}$, with the average extrapolated flux being $1.4 \text{ ng m}^{-2} \text{ h}^{-1}$ calculated from the temperature dependence equation. The latter flux value, which we believe represents the real exchange more realistically, is equal to 130% of the mercury deposited by precipitation during the same month.

Although the amount of available flux data has increased during the last decade, data have mainly been forthcoming from North America. Studies in background and contaminated areas, also from other areas than North America, are needed to understand the mercury cycle in the environment. In Finland, 70% of the land use, in total 230,000 km^2 in surface area, is forest, so that emissions from the forest floor affect the total mercury budget greatly, even though the fluxes themselves seem small. Annually, 2–3% of the forests are subject to felling activities (Finnish Forest Research Institute 2007). According to our preliminary data, forestry practises increase mercury fluxes significantly, and Hg has been proven to be effectively transported through different media (Porvari et al. 2003). Only 8% of Finnish forests are protected as the studied site is. Hence, flux studies in forest management areas are of interest. Our future work includes measurements of fluxes in areas affected by forestry practises and includes the employment of micrometeorological methods.

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