Conditional sampling for measuring mercury vapor fluxes

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Received 20 August 2001; accepted 28 May 2002

Abstract

Surface–atmosphere mercury fluxes are difficult to measure accurately. Current techniques include dynamic flux chambers and micrometeorological gradient and aerodynamic approaches, all of which have a number of intrinsic problems associated with them. We have adapted conditional sampling (relaxed eddy accumulation), a micrometeorological technique commonly used to measure other trace gas fluxes, to measure surface–air mercury fluxes. Our initial flux measurement campaign over an agricultural soil consisted of two 1-week measurement periods, and was longer in duration than previously reported mercury flux measurement periods. Fluxes during both measurement periods ranged between 190.5 (evolution) and –91.7 ng m\(^{-2}\) h\(^{-1}\) (deposition) with an average evolution of 9.67 ng m\(^{-2}\) h\(^{-1}\). The data showed significant diurnal trends, weakly correlated with shallow soil temperatures and solar radiation. This initial trial run indicates that conditional sampling has much promise for the accurate quantification of both short and long-term mercury fluxes.

Keywords: Agricultural soil; Emission; Micrometeorology; Relaxed eddy accumulation; Soil–air exchange

1. Introduction

Recently, efforts have been directed at the measurement of surface–atmosphere mercury fluxes, driven in large part by the tendency of methylated mercury to biomagnify in biological systems to potentially toxic levels. Disturbingly, these high bio-concentrations of methylmercury are found not only in urban areas, but also in remote areas, removed from local pollution sources. Gaseous mercury exists predominantly (>95%) in its elemental form (Hg\(^0\)), which is the dominant species of mercury emitted by soil (Kim et al., 1995). Because of its volatile nature and long atmospheric residence time, Hg\(^0\) sources can be widely separated from areas of deposition. Thus, the sources of Hg\(^0\) to otherwise-isolated systems are often difficult to pinpoint.

To determine the fate of atmospheric Hg\(^0\) emissions, as well as estimate the relative contribution of various sources to the atmospheric burden, it is important to accurately quantify Hg\(^0\) fluxes from (potential) sources. These include not only anthropogenic sources, but also soil and water surfaces, and geologic sources (e.g., volcanoes, geothermal areas, and ore deposits). To accurately estimate contributions from non-point, anthropogenic and natural sources, it is necessary to measure diffuse emissions at the field scale. Recently, several attempts have been made to measure Hg\(^0\) fluxes above both altered and background soil surfaces using dynamic chamber methods (Boudala et al., 2000; Carpi and Lindberg, 1998; Ferrara et al., 1997; Gustin et al., 1999a, b; Kim and Lindberg, 1995; Wallschlager et al., 1999). However, there are several limitations associated with chamber methodologies. Chambers alter the environment of the area being studied by decreasing wind speed and turbulence and attenuating radiation. These effects are less pronounced over the short time periods that chamber measurements are often taken.
However, because Hg$^0$ flux is presumably a function of variable environmental factors, accurate estimation of the contribution of a source requires measurement durations on the order of days to weeks. These types of long-term measurements are difficult with chambers. Additionally, chambers cover a relatively small area (often <1 m$^2$), which may not be representative of the entire source area. Thus, if chamber methodologies are used, numerous chambers and mathematical manipulation of results (Kim and Verma, 1991) are required to estimate a field-scale flux. Additionally, when sampling reactive species such as Hg$^0$, great care must be taken when choosing chamber materials, to prevent spurious fluxes (blank effects) resulting from sorption and desorption of Hg$^0$ on the chamber itself (Carpi and Lindberg, 1998).

Recent work (Gillis and Miller, 2000; Wallschlager et al., 1999) indicates that the dynamic flux chamber techniques that are commonly used to measure surface/ atmosphere Hg$^0$ exchange are subject to several additional problems. First, there is an apparent relationship between the sample flow rate through the chamber and measured flux rate. Thus, the intercomparison of results from researchers with different measurement protocols is complicated, and more importantly, great uncertainty is introduced into the absolute accuracy of all chamber-derived Hg$^0$ flux measurements. Second, Wallschlager et al. (1999) found a significant correlation between ambient windspeed and flux rate despite the fact that chambers exclude most wind. Subsequently, Gillis and Miller (2000) found that chamber exposure to ambient wind speeds as low as 1 m s$^{-1}$ attenuated the measured flux rates by 60%, increasing to 95% at windspeeds of 3 m s$^{-1}$. These data may explain the results reported by Gustin et al. (1999b) where dynamic flux chambers underestimated surface–atmosphere Hg$^0$ fluxes by a factor of 2-3 relative to micrometeorological techniques.

Micrometeorological flux measurement techniques present an alternative to chamber methods that are not subject to many of the problems described above. First, because micrometeorological methods measure fluxes in the free atmosphere, they are non-destructive and do not appreciably alter the environment over which they are measuring. This allows continuous measurements to be made without fear of the chamber effects mentioned above, which is particularly attractive for long-term, continuous flux measurements. Also, micrometeorological methods have measurement footprints sufficiently large to measure true field-scale fluxes, negating the need for multiple measurement sites and spatial averaging in a given measurement area. These characteristics make micrometeorological techniques an attractive alternative to chamber methods for measuring field-scale surface to air fluxes (Lindberg and Meyers, 2001). Micrometeorological methods are, however, limited by requirements for specific environmental conditions. Inadequate upwind fetch, lack of turbulent mixing (common at night), broken terrain, and point source emissions can all decrease the accuracy and utility of these techniques.

Attempts have been made to measure Hg$^0$ fluxes using several different micrometeorological approaches, including gradient and aerodynamic methods (Gustin et al., 1999a; Kim et al., 1995; Lindberg et al., 1992, 1995; Lindberg and Meyers, 2001; Meyers et al., 1996). The most commonly used and straightforward of these micrometeorological gradient methods is the modified Bowen ratio (MBR) approach. MBR typically requires the measurement of the flux of some trace gas on which eddy covariance can be performed (e.g. CO$_2$, H$_2$O), and the two-height concentration gradient of that same gas and Hg$^0$. Turbulent transport coefficients for the non-Hg$^0$ gas are determined from the scalar fluxes and concentration gradients. Similarity is assumed among the transport coefficients for the various scalars, which are then applied to the measured Hg$^0$ gradient, resulting in an estimation of the flux. Lindberg et al. (1995) and Kim et al. (1995) used MBR to successfully measure Hg$^0$ fluxes over both contaminated and background forest soils. Two groups at the Nevada STORMS project also used MBR to quantify Hg$^0$ fluxes over naturally enriched desert soil (Gustin et al., 1999a; Poissant et al., 1999). Recently, Lindberg and Meyers (2001) developed an automated MBR system, and utilized it to make long-term Hg$^0$ flux measurements in the Florida everglades. While showing considerable promise for reliable and accurate measurement of Hg$^0$ fluxes, the necessity of measuring simultaneous fluxes and concentration gradients of other gases complicates MBR and limits its practicality in some instances.

Another micrometeorological technique that has been utilized to measure fluxes of many other trace gas species is relaxed eddy accumulation or conditional sampling (Businger and Oncley, 1989). This method has been used to measure surface–atmosphere fluxes of volatile herbicides (Pattey et al., 1995), methane, nitrous oxide, and total hydrocarbons (Beverland et al., 1996), various volatile organic carbon compounds (Valentini et al., 1997), CO$_2$ and water vapor (Heilman et al., 1999), and ammonia (Zhu et al., 2000), but never Hg$^0$. Conditional sampling is based on the observation that the flux of any scalar is proportional to the difference in its concentration between upward and downward-moving air parcels (eddies), multiplied by the standard deviation of vertical wind velocity.

\[
F(\text{ng m}^{-2} \text{h}^{-1}) = B\sigma_w(C_u - C_d),
\]

where \(\sigma_w\) is the standard deviation of vertical wind velocity \(W\) (m h$^{-1}$), \((C_u - C_d)\) is the time averaged difference in concentration between upward and downward moving eddies (ng m$^{-2}$), and \(B\) is a relaxation coefficient determined to be 0.6 ±10% (Beverland et al.,
1996; Businger and Oncley, 1989). Originally thought to be empirical in nature, \( B \) was later derived numerically (Baker et al., 1992; Wyngaard and Moeng, 1992). The numerical derivations of \( B \) rely on the assumption that \( W \) and \( C \) exhibit a joint Gaussian distribution. Experimentally determined values of \( B \) consistently underestimate derived values of \( B \) by approximately 10% across a wide range of trace gases of interest (Baker et al., 1992; Beverland et al., 1996; Businger and Oncley, 1989; Wyngaard and Moeng, 1992), with varying atmospheric stability. Baker et al. (1992) tentatively concluded that this was due to slight non-linearity in the \( c \) versus \( w \) relation, a conclusion supported by later analyses (Katul et al, 1996; Baker, 2000).

Conditional sampling has several advantages over aerodynamic, gradient and MBR techniques. First, conditional sampling requires sampling at only one elevation. Aerodynamic techniques commonly require the measurement of atmospheric \( \text{Hg}^0 \) concentration at four or more elevations, generating a rather large number of samples to be analyzed. This requires either extensive laboratory efforts, or multiple portable \( \text{Hg}^0 \) vapor analyzers. Second, conditional sampling can be used even when conditions limit or prevent measurable fluxes of the ancillary scalars necessary for MBR, with no assumptions made about the similarity of turbulent transport coefficients of different species.

We describe here the first application and testing of conditional sampling to measure \( \text{Hg}^0 \) fluxes. We made measurements over a cornfield during the spring of 2001. Our primary objective was to demonstrate the applicability of conditional sampling for both short and long-term \( \text{Hg}^0 \) flux measurements.

2. Methods

2.1. Site description

\( \text{Hg}^0 \) fluxes were measured at the University of Minnesota’s Rosemount Research and Outreach Center, 24 km south of St. Paul (44°44′N, 93°05′W) during the spring of 2001. The site is characterized by coarse textured glacial outwash overlain by Peoria loess, with the predominant soil classified as Waukegan silt loam. The site has been continuously cropped in corn, soybeans, and alfalfa for at least the past two decades. The flux measurements began shortly after spring planting of corn and ended when the crop was at approximately four-leaf stage. During this time period, the field was mostly bare soil, with up to 30% corn residue coverage.

This site was chosen in part because of a permanent instrument tower that is positioned in the center of a...
17 ha agricultural field with approximately 200 m of fetch in all directions. A full description of the site and instrumentation can be found in Baker et al. (1999). In addition to having ready access to environmental data measured by instrumentation on or near the tower, the availability of AC line power negated the need for a generator. Hg\textsuperscript{0} fluxes were measured continuously at the same site by conditional sampling over two periods: DOY 127–134 and DOY 151–159, 2001.

2.2. Conditional sampling system (Fig. 1)

A three axis sonic anemometer (CSAT-3. Campbell Scientific, Logan, UT) operating at 20 Hz at a height of 1.75 m was used to determine the direction of vertical wind velocity (\( w \)) and to measure \( s_w \). This information was recorded and processed by a datalogger (CR23X, Campbell Scientific). Air was drawn at a constant rate of 3.5 l min\(^{-1}\) through an intake line positioned within 2 cm of the measurement path of the CSAT-3. The sampled air traveled 43.5 cm through 4.8 mm ID Teflon tubing before reaching a high-speed three-way Teflon solenoid valve (648T031, NResearch, West Caldwell, NJ). Based on the relative sign of \( w \) (as measured by the sonic anemometer), the intake sample was routed into one of two separate sample lines by the solenoid valve (Fig. 2), thus producing one sampling line consisting entirely of updrafts and another entirely of downdrafts. To ensure that slight inaccuracies in the leveling of the sonic anemometer did not bias the air sample separation, the solenoid valve was triggered on the mean of \( w \) instead of true zero. The mean \( w \) was recalculated every 10 min to account for changes in prevailing wind direction which, unless the sampling area is perfectly flat, will cause changes in mean \( w \).

Wind data from the sonic anemometer were output to the datalogger 100 ms after wind velocity was measured. This delay combined with other electronic delays in the system produced a total delay of 141 ms between wind measurement and valve closure. The combination of tube length, tube diameter, and flow rate produced a physical delay of 141 ms, matching the electronic delay, thus ensuring proper separation of updrafts and downdrafts (McInnes et al., 1998). After separation, the samples were filtered through 0.7 \( \mu \)m glass fiber particulate filters and routed through 4.8 mm ID Teflon tubing into an environmental enclosure. At the enclosure, the samples entered twin 2 l Teflon reservoir tanks to minimize high-frequency fluctuations in pressure caused by the switching of the sampling valve.

Some conditional sampling systems incorporate the use of dual sample inlets and two-way solenoid valves to separate bulk air into updraft and downdraft samples. With this type of system, one sample line is opened during times of positive \( w \), and the other is opened during times of negative \( w \). With this design, discretization errors arise from the electronic delay between wind measurement and valve actuation. These errors can reduce the measured concentration difference by as much as 40\%, and must be corrected for (Baker et al., 1992). The system design employed in this study was specifically developed to alleviate these errors. One
advantage of a dual-inlet system is that it allows the isolation of a “deadband,” defined as vertical wind velocities at some noise level very near zero that contribute little to vertical mass transport in the atmosphere. When these conditions are detected, both sample inlets are closed. Our system design does not allow the use of a deadband, since air must be sampled into either the updraft or downdraft line at all times.

After separation, the air samples were analyzed for \( \text{Hg}^0 \) by a recently developed, automated atmospheric mercury analyzer (2537A, Tekran, Toronto, Canada). The Tekran analyzer pulls an air sample through one of two pure gold pre-concentration traps which effectively sorbs all mercury from the air sample. The dual trap design allows one trap to be desorbed and analyzed while the other is in the sample stream, thus allowing continuous monitoring of one sample stream. Captured mercury is thermally desorbed from the trap and carried into the detector with high-purity Argon. The detector uses cold vapor atomic fluorescence spectroscopy to generate an analog signal linearly related to the mercury concentration in the detector. This signal is integrated over the course of the desorption cycle, providing a quantitative measure of the amount of mercury that was desorbed from the trap. This, in conjunction with the known flow rate of the sample stream through the trap, yields an average \( \text{Hg}^0 \) concentration for the sample stream, which is output to a laptop computer. The Tekran has a self-calibration routine in which mercury free air, and a permeation source are used to conduct a two-point calibration. A more complete description of the operation of the Tekran 2537A analyzer can be found in Lindberg et al. (2000).

In order to analyze the two separate sample lines (updraft and downdraft), twin 648Ts were plumbed in a four-way valve configuration (Fig. 3). This allowed one sample line to be routed through the Tekran, while the other exited the system through a vacuum pump that was output to a laptop computer. The Tekran has a self-calibration routine in which mercury free air, and a permeation source are used to conduct a two-point calibration. A more complete description of the operation of the Tekran 2537A analyzer can be found in Lindberg et al. (2000).

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2.3. Density corrections

Transport of heat and water vapor gives rise to correlations between air density and vertical velocity that can cause serious errors in flux determinations of other scalars, if they are based on concentration measurements (Webb et al., 1980). In this system, the \( \text{Hg}^0 \) analyzer uses mass flow controllers to maintain constant mass flow, but the air stream is not dried, so the measurement is actually a specific mass content relative to the total moist air. Under these circumstances, corrections for latent heat flux must be made. Corrections for sensible heat flux are unnecessary because the air samples are brought to a common temperature before analysis.

Following the derivation of Webb et al. (1980) the correct \( \text{Hg}^0 \) flux, \( F_{\text{Hg}} \), can be calculated from the raw \( \text{Hg}^0 \) flux measured by our conditional sampling system, \( F' \), and the concurrently measured covariance of vertical windspeed and water vapor density:

\[
F_{\text{Hg}} = F'_{\text{Hg}} + \frac{m_a}{m_v} \frac{\rho \mu w}{\rho \mu w'},
\]

The mole weight ratio of dry air to water, \( m_a/m_v \), is 1.61, while the ratio of mean \( \text{Hg}^0 \) density to mean air density must be determined from the data for each measurement interval.

2.4. System testing

To ensure that the conditional sampling system was functioning correctly, water vapor fluxes were measured with the conditional sampling system for 3 days at the same site described above and compared to independently obtained water vapor fluxes. To achieve conditional sampling measurements of water vapor fluxes, the inlet of a closed path infrared gas analyzer (IRGA) (LI-6262, Li Cor, Lincoln, NE) was attached to the exhaust vent of the Tekran analyzer. The air-flow path of the LI-6262 is designed for flow rates as high as
101 min$^{-1}$, so the presence of the IRGA on the outlet of the Tekran had no effect on the air flow through the Tekran analyzer. The IRGA was calibrated immediately prior to use. With the IRGA in place, the conditional sampling system was operated in exactly the same manner as described above. Water vapor fluxes were determined from the product of the standard deviation of vertical wind velocity and the difference in vapor density between updrafts and downdrafts (Eq. (1) modified for water vapor).

$$\text{Flux}(\text{mg m}^{-2}\text{s}^{-1}) = B\sigma_w(C_u - C_d),$$

where $\sigma_w$ is the standard deviation of vertical wind velocity ($W$) (m s$^{-1}$), $(C_u - C_d)$ is the time averaged difference in vapor density between upward and downward moving eddies (mg m$^{-3}$), and $B$ is the relaxation coefficient as described above.

Water vapor fluxes were also simultaneously measured at the same site by permanent instrumentation using eddy covariance, an accepted micrometeorological method for measuring trace gas fluxes (Baldocchi et al., 1988). Fluxes are determined by the covariance between vertical wind velocity and vapor density.

$$\text{Flux}(\text{mg m}^{-2}\text{s}^{-1}) = W\rho_v.$$  (4)

The high-frequency fluctuations in $w$ were measured by a sonic anemometer (CSAT-3 Campbell, Logan, UT) and an open path IRGA (LI-7500, Li Cor, Lincoln, NE). The LI-7500 was calibrated immediately preceding this comparison, and the appropriate coordinate rotations and density corrections were applied to the eddy covariance fluxes.

3. Results and discussion

We measured Hg$^0$ fluxes continuously at the same location from 7 to 14 May and from 31 May to 8 June 2001. Soil/residue mercury concentrations in the measurement footprint ranged from 17.5 to 31.8 ng g$^{-1}$ with
a mean of $24.8 \pm 4.2 \text{ng g}^{-1} (n = 8)$, within the range expected for non-contaminated soils. Atmospheric Hg$^0$ concentrations at a height of 1.75 m from the soil surface averaged 1.47 ng m$^{-3}$ with a range of 1.23–2.65 ng m$^{-3}$ over the course of the measurements (Fig. 5a and b). The flux time series (Figs. 6 and 7), although measured continuously, have several gaps caused primarily by the effects of rain or heavy dew on the ultrasonic transducers of the sonic anemometer. The fluxes measured during both periods ranged from 190.5 (evolution) to $91.7 \text{ng m}^{-2} \text{h}^{-1}$ (deposition). Obvious diurnal trends are present in the data, with the highest emissions occurring near mid-day and fluxes generally fluctuating near zero at night. These trends are consistent with diurnal cycles reported in the literature (Gustin et al., 1999a; Kim et al., 1995; Poissant and Casimir, 1998).

3.1. Density corrections

Eq. (2) was used to calculate the Webb et al. (1980) corrections for density effects due to latent heat flux. The calculated corrections ranged from 0% to 0.01% of the calculated flux and are thus, in this case, trivial. However, it should be noted that the Webb corrections for sensible heat flux are generally greater in magnitude than those for latent heat flux, and may not be trivial for micrometeorological flux measurement systems where samples are not brought to a common temperature before analysis (e.g MBR), or in situations where the deposition velocities are higher.

3.2. System testing

Time series plots of latent heat (water vapor) fluxes determined by the conditional sampling and eddy covariance systems are shown in Fig. 8a. All systematic biases associated with conditional sampling (improper sample separation, intake tube dispersion) lead to an underestimation of fluxes. If such biases were present, they would manifest themselves as an underestimation of latent heat flux. Surprisingly, the conditional sampling method measured nearly 25% greater latent heat flux than the eddy covariance method. This is possibly caused by eddy covariance under-measurement of the latent heat flux, as has been reported elsewhere.
However, the relatively good agreement between the conditional sampling and eddy covariance-derived latent heat flux data increases confidence that the conditional sampling system is functioning properly.

3.3. Sources of uncertainty

With conditional sampling, where the measurement of slight concentration differences between two samples is fundamental to resolving fluxes, contamination in either

Fig. 5. (a and b) Time series plots of atmospheric mercury concentration. Updraft and downdraft concentrations are plotted separately.

Fig. 6. Time series plots of raw Hg\textsuperscript{0} flux, numerically smoothed Hg\textsuperscript{0} flux, shallow soil temperature, net radiation (Rn), momentum flux, CER, and volumetric water content in and above the agricultural soil for the first measurement period. Soil temperatures were not recorded prior to day 130 due to the removal of thermocouples for field tillage and planting.
or both sample lines would render the system useless. Special precautions were taken to prevent this from occurring. New Teflon tubing was used for the sample lines for both trials. Additionally, before the onset of each trial, both sample lines were situated to pull ambient air from the same point in space. After time centering, the concentration difference was found to be insignificant in both instances.

Because one analyzer was used to measure two separate samples, the concentrations of both samples could not be measured simultaneously (see Fig. 4). While air pulled through the updraft line was being adsorbed onto the gold trap, air pulled through the downdraft line was vented to the atmosphere with no analysis and vice versa. Since simultaneous measurement of both sample lines was not possible, the resulting concentrations were time centered to eliminate the effects of low-frequency changes in ambient Hg\textsuperscript{0} concentration. However, high-frequency changes in ambient Hg\textsuperscript{0} concentration will introduce error into these measurements. Because each sample line was trapped for 10 min, any temporary rise or fall in ambient Hg\textsuperscript{0} concentration of 10 min or less in duration could be particularly problematic if it falls entirely during one trapping period. Such short-term variation in ambient Hg\textsuperscript{0} concentration could be caused by a number of factors including changes in wind direction to and from areas of greater source strength, and mobile Hg\textsuperscript{0} sources such as automobiles. These problems are not unique to conditional sampling. Nearly all published studies where an automated Hg\textsuperscript{0} analyzer was used in conjunction with a dynamic chamber or MBR technique use a similar asynchronous sampling method.

Our Hg\textsuperscript{0} fluxes exhibit a certain amount of noise, for which there are several possible causes. First, lack of turbulence associated with (mainly nighttime) periods of atmospheric inversion, renders this and other micro-meteorological flux techniques ineffective. This is evident in the CO\textsubscript{2} flux data that are measured continuously at the permanent instrument tower near our sampling location. These data are measured by eddy covariance with an open-path infrared gas analyzer. Figs. 6 and 7 show CO\textsubscript{2} exchange rate (CER) plotted with time over our measurement periods. The CER data exhibit scatter similar to the Hg\textsuperscript{0} flux data during periods of low turbulence.

There is also the possibility that advection may transport non-source area air of higher Hg\textsuperscript{0} concentration to the sampling location. Two possible sources at this site are road construction machinery that was being operated nearby (the closest approach of the road to the mast is approximately 350 m), and a large petroleum refinery situated \( \sim 2 \) km from the sampling site. Such “plume effects” have been reported by Kim et al. (1995). Wind direction analysis did not conclusively show plume effects to be present (data not shown), but we have

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Fig. 8. Time series plot of latent heat fluxes measured by conditional sampling system and independently by eddy covariance. The gap in data collected by eddy covariance on day 89 is a result of heavy dew interfering with the IRGA measurements of water vapor.

Fig. 7. Time series plots of raw Hg\textsuperscript{0} flux, numerically smoothed Hg\textsuperscript{0} flux, shallow soil temperature, net radiation (Rn), momentum flux, CER, and volumetric water content in and above the agricultural soil for the second measurement period.
incomplete data on the presence of road construction equipment.

3.4. Influences

Many previous soil-atmosphere Hg\textsuperscript{0} flux studies have attempted to derive relationships among measured flux rates and a variety of environmental parameters. Figs. 6 and 7 show plots of the measured Hg\textsuperscript{0} fluxes and several environmental parameters of interest. Correlations are evident among the environmental variables and Hg\textsuperscript{0} fluxes, but regression analysis produced rather weak coefficients of determination. The relatively long duration of the study periods certainly reduced these correlations, since the various environmental parameters all changed over the course of the study (e.g., soil moisture, deep soil temperature, etc.). Additionally, because the environmental parameters that were measured are intrinsically correlated to each other, these data are not of great utility in determining the effects of different environmental factors on Hg\textsuperscript{0} fluxes. Such relationships are best determined with laboratory studies where a single factor can be systematically varied while others are held constant, or with in situ dynamic chambers. Micrometeorological techniques are better suited to provide assessment of the actual magnitude and variability of fluxes (Gustin et al., 1999a).

To reduce the background noise, numerical smoothing was performed on both data sets using a Savitsky-Golay 7-point cubic smoothing technique. These smoothed data (Figs. 6 and 7) allow for a better visual interpretation of the diurnal variations in the data. Correlations between the smoothed data and environmental variables were not determined, as these data have been manipulated. However, visual analysis suggests relationships between the measured efflux and solar radiation/shallow soil temperature.

3.5. Emission estimates

The average emission over each measurement period was 7.6 ng m\textsuperscript{-2} h\textsuperscript{-1} for the first measurement period and 11.5 ng m\textsuperscript{-2} h\textsuperscript{-1} for the second measurement period. When gap filling techniques were applied to the data set, the average effluxes were corrected to 8.4 and 11.2 ng m\textsuperscript{-2} h\textsuperscript{-1} respectively, with an overall average emission during both periods of 9.67 ng m\textsuperscript{-2} h\textsuperscript{-1}. This is higher than the 2.5 ng m\textsuperscript{-2} h\textsuperscript{-1} average reported by Poissant and Casimir (1998) from a rural grassy site, but lower than the 12–45 ng m\textsuperscript{-2} h\textsuperscript{-1} average for open field soil reported by Carpi and Lindberg (1998). Overall, there was net Hg\textsuperscript{0} evolution during both periods totaling 3.3 µg m\textsuperscript{-2}.

To this point, continuous Hg\textsuperscript{0} flux measurement campaigns have been of relatively short duration. Poissant and Casimir (1998) took continuous chamber measurements for 2.5 days over soil, Kim et al. (1995) took micrometeorological point measurements for 5 day periods, and Lindberg and Meyers (2001) routinely took 2–4 day continuous measurements, but no references to continuous measurement campaigns of the duration described in this study were found in the literature. The temporal variability that is apparent in our data would make estimating an accurate long-term Hg\textsuperscript{0} balance difficult for this ecosystem with measurements of even week-long duration. Obviously, these measurements are preliminary, so care must be taken when extrapolating short-term results to estimate annual evolution. To accurately quantify field-scale Hg\textsuperscript{0} fluxes for use in global mercury models it probably is necessary to repeat such measurements periodically throughout the year.

4. Conclusions

In the spring of 2001, we measured field-scale Hg\textsuperscript{0} fluxes using conditional sampling, a widely used micrometeorological flux measurement technique which has not previously been adapted to Hg\textsuperscript{0}. The data collected over two separate week-long periods showed strong diurnal cycles, with mean values that were intermediate between previously reported short-term fluxes from non-forested background soil. Several factors, both environmental and technical, contributed to uncertainty in the measured fluxes. Significant temporal variability present in the measured fluxes confirms the need for longer measurement campaigns than have been undertaken in the past. Accurate quantification of source strength will only be achieved through several long-duration measurement cycles per year. We believe that conditional sampling holds great potential for research of these long-term surface-atmosphere Hg\textsuperscript{0} exchange rates as well as short-term Hg\textsuperscript{0} flux dynamics.

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