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Assessing the trends and effects of environmental parameters on the behavior of mercury in the lower atmosphere over cropped land over four seasons

A. P. Baya and B. van Heyst

School of Engineering, University of Guelph University, Guelph, ON, Canada

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Correspondence to: A. P. Baya (pascalebaya@trentu.ca)

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Abstract

Mercury is released to the atmosphere from natural and anthropogenic sources. Due to its persistence in the atmosphere, mercury is subject to long range transport and is thus a pollutant of global concern. The terrestrial ecosystem is an important atmospheric mercury sink as a significant portion of the mercury emitted can be accumulated on soil surfaces making terrestrial surfaces an important source of previously emitted and deposited mercury. Studying the factors and processes that influence the behavior of mercury from terrestrial sources is thus important for a better understanding of the role of natural ecosystems in the mercury cycling and emission budget.

A one year study (July 2006–August 2007) was conducted at Elora, Ontario, Canada to measure total gaseous mercury (TGM), reactive gaseous mercury (RGM) and particulate bound mercury (Hg^P) as well as TGM fluxes over different ground cover spanning the four seasons typical of a temperate climate zone. TGM concentrations were measured using a mercury vapour analyzer (Tekran 2537A) while RGM and Hg^P were measured with the Tekran 1130/1135 speciation unit coupled to another mercury vapour analyzer. A micrometeorological approach was used for TGM flux determination using a continuous two-level sampling system for TGM concentration gradient measurement above the soil surface and crop canopy. The turbulent transfer coefficients were derived from meteorological parameters measured on site.

A net TGM volatilization ($6.31 \pm 33.98\,ng\,m^{-2}\,h^{-1}$, annual average) to the atmosphere was observed during the study. Average TGM concentrations and TGM fluxes showed significant seasonal differences and distinct diurnal patterns while no trends were observed for Hg^P or RGM. Highest TGM concentrations recorded in late spring and fall were due to meteorological changes such as increases in net radiation and air temperature in spring and lower atmospheric mixing height in fall. Highest TGM fluxes ($18.1\,ng\,m^{-2}\,h^{-1}$, monthly average) were recorded in late spring but also during specific events in winter and fall. The main factors influencing TGM flux were soil moisture content, soil temperature, precipitation events and ground cover. These trends indicate

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that the soil surface could be a significant mercury source in spring and summer seasons but also under specific meteorological conditions in winter or fall.

1 Introduction

Mercury is a priority pollutant due of its ability to accumulate in the food chain in the form of methylmercury, a neurotoxin to living organisms and human beings (Satoh 2000). Mercury is also a global persistent pollutant, as once released, mercury in its elemental form (Hg^0), can remain in the atmosphere for up to 2 years (Mason et al., 1994; Schroeder and Munthe, 1998) and be transported over regional and global distances.

Most of the mercury in the atmosphere (>95%) is in the gaseous form (Iverfeldt and Lindqvist, 1986; Munthe, 1992; Gustin, 2003) and exists in three oxidation sates; 0, +1 and +2. However, in the atmospheric environment, mercury exists predominantly in the elemental form Hg^0 referred to as gaseous elemental mercury (GEM) and in the +2 oxidation state Hg^{2+} referred to as reactive gaseous mercury (RGM) such as $HgCl_2$ or $HgBr_2$ (Schroeder and Munthe, 1998). Total gaseous mercury (TGM) is thus composed of both GEM and RGM. Another important form of mercury in the atmosphere is particulate bound mercury (Hg^P). It is present in the atmosphere either from anthropogenic sources (Schroeder and Munthe, 1998) or from TGM adsorbed onto particle matter (PM) in the atmosphere (Schroeder and Munthe, 1998; Seigneur et al., 2004). Mercury is vertically well mixed in the troposphere and typical TGM concentrations are in the range of 1–4 ng m^{-3} at background sites (Iverfeldt and Lindqvist, 1986; Lin and Pehkonen, 1999). In contrast, RGM and Hg^P concentrations range between 5–70 pg m^{-3} and 7–100 pg m^{-3} respectively (Valente et al., 2007) representing less than 5% of atmospheric mercury.

A significant proportion of the atmospheric Hg accumulates on the soil surface (95%) (Fitzgerald, 1995) making the terrestrial ecosystem the most important atmospheric mercury sink (Fitzgerald, 1995; Mason, Fitzgerald and Morel, 1994). This accumulation

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of Hg is a combination of newly emitted Hg along with previously emitted Hg that cycles between different environmental compartments

In natural terrestrial ecosystems, the behavior and cycle of Hg at the soil and atmosphere interface is believed to be controlled by the soil properties, biological processes, meteorological conditions and atmospheric chemistry and physics. It is thus important not only to understand how Hg behaves over these landscapes but also to try to quantify the contribution of terrestrial land sources to the Hg emission cycle and budget.

Recent technological and analytical developments now enable high time resolution measurements of atmospheric TGM concentrations necessary to determine TGM fluxes using micrometeorological methods (Edwards et al., 2005; Cobbett and van Heyst, 2007; Cobbett et al., 2007; Obrist et al., 2005; Lindberg and Meyers, 1995; Zhang et al., 2001; Poissant et al., 1999) and flux chamber methods (Gustin et al., 1997; Engle et al., 2001). These types of studies attempt to identify the main factors controlling the emissions and deposition of mercury from different surfaces. One shortcoming of these studies, however, is that they are conducted over very short periods of time (a few weeks to a month) thus making it difficult to have a clear understanding of the long-term variability and seasonal behavior of the Hg species and GEM flux.

Longer-term Hg flux measurements from natural background surfaces are needed to better understand the Hg cycle and calculate the mass balance for Hg. In addition, the longer-term studies can provide a more complete picture of the biogeochemical cycle of Hg in the environment including the interactions between environmental parameters (e.g. soil moisture, soil temperature, radiation), chemical factors and surface characteristics (e.g. snow or crop cover).

To address theses issues, a study was conducted in Elora, ON, Canada for 1 year (fall 2006 to summer 2007) measuring TGM flux as well as atmospheric concentrations of TGM, RGM and Hg^P. The main objective was to assess the seasonal behavior of the main Hg species and to quantify the seasonal flux of elemental mercury over different agricultural ground covers.

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2 Methodology

2.1 Site location

The study was conducted from day 305 of 2006 to day 225 of 2007 (1 November 2006 to 13 August 2007) at the Elora Research Station of the University of Guelph, located 7.5 km south of Elora, Ontario (43°39′ N and 80°25′ W) at an elevation of 376 m. While the site is considered rural, there are several cities with industrial areas that may influence the site including the city of Kitchener/Waterloo located 30 km southwest, the city of Stratford situated 75 km southwest and the city of Hamilton, a major industrial area in the region, situated 70 km southeast of the study site.

The experimental site was located on a 6 ha plot on an agricultural research station. The crop rotation consisted of soybeans and corn for the 2006 and 2007 cropping season respectively. The plot was left bare during the winter season with half the plot tilled while the other half was non-tilled.

The soil texture is a silty loam with an average pH of 7.7, organic matter (OM) content of 4.2% dry, and a total carbon content of 2.6% dry. The top soil average mercury concentration during the study period was 0.05±0.006 μg g^{-1} as determined by acid digestion.

2.2 Aerodynamic micrometeorological gradient method

The TGM flux was estimated by measuring the difference in TGM concentrations at two different heights above the soil surface based on the aerodynamic micrometeorological gradient method (Edwards et al., 2005; Cobbett and van Heyst, 2007; Cobbett et al., 2007). The aerodynamic micrometeorological gradient method uses the assumption of Monin-Obukhov (MO) similarity and estimates the flux by:

$$F = -K\frac{\partial C}{\partial z} \approx \frac{u_* \kappa (C_2 - C_1)}{\ln\left[\frac{z_2 - d}{z_1 - d}\right] - \Psi_{h2} + \Psi_{h1}} \quad (1)$$

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where F is the TGM flux (ng m^{-2} h^{-1}), K is the eddy diffusivity (m^2 s^{-1}) and $\partial C/\partial z$ is the concentration gradient of mercury (ng m^{-3}), u_* is the surface friction velocity (m s^{-1}), κ is von Karman's constant (0.4) (unitless), z_2 and z_1 are the upper and lower intake heights respectively (m), d is the zero plane displacement height (m), and Ψ_{h2} and Ψ_{h1} are the integrated stability functions for heat at z_2 and z_1 respectively. As the eddy diffusivity varies with height, surface roughness and atmospheric stability state, it needs to be measured concurrently with the gradient (Edwards et al., 2005).

To capture the extensive meteorological parameters required for the gradient method, the study site was equipped with an instrumented 8.5 m meteorological tower located approximately in the middle of the experimental site with a fetch of more than 250 m in all directions. The meteorological parameters measured included wind speed, wind direction, solar radiation, air temperature, relative humidity, precipitation, soil temperature and soil moisture (Cobbett and van Heyst, 2007).

2.3 Instrumentation and experimental set up

During the experiment, ambient concentrations of the TGM, RGM and Hg^P were continuously measured. TGM concentrations and TGM fluxes were measured using a Tekran 2537A mercury vapor analyzer while the concentrations of RGM and Hg^P were measured using the Tekran 1130 and 1135 speciation units coupled to a second Tekran 2537A mercury vapor analyzer.

The Tekran 2537A analyzer was calibrated automatically every 25 h using its internal Hg permeation source. External calibrations using the Tekran 2505 with manual injections of known concentrations of Hg were performed every 4 months. Based on the calibration procedures, a detection limit of 0.1 ng m^{-3} was expected for the Tekran 2537A.

The Tekran 1130 and 1135 units sampled at a flow rate of 10 l min^{-1} for a period of 2 h. The RGM measurements used KCl coated denuders and were made according to Landis et al. (2002). After sampling, the Tekran 1130 denuder was desorbed (500° C) and flushed. Once completed, the Hg^P collected by the Tekran 1135 on a quartz

filter was then thermally released by a pyrolysis heater (800° C). During the desorption phases, the RGM and Hg^P are converted to GEM which is then sent to the 2537A for analysis.

The sampling inlets were placed at a height of 1.5 m for Hg species concentrations while for the TGM flux, the upper and lower intakes were positioned at 1.20 m and 0.35 m, respectively during most of the study period and adjusted during the cropping season so that the lower intake was 0.35 m above the ground cover.

During TGM flux measurements, ambient air was sampled alternately at the upper and lower intake with a sampling time of 10 min, corresponding to 2 sampling phases of the Tekran 2537A mercury vapor analyzer. This removed any variability or line bias due to the individual cartridges. The air sample was drawn at a rate of 10 l min^{-1} by a Teflon® lined vacuum pump (Model N035, KNF Neuberger). Each intake consisted of 4 inlets to avoid artificial flux due to flow distortion and to increase the spatial extent of the sampling (Edwards et al., 2005). The upper and lower intakes were connected to the Tekran Model 1110 Synchronized Two Port Sampling System to ensure the sampling switching between the 2 intake heights.

3 Results and discussions

The meteorological parameters measured for each season during the study period are summarized in Table 1 and were within the mean values recorded for the region over the past decades. Over the study period, the average air temperature, relative humidity (%RH), net radiation, and wind speed were 9.5±10.96° C (mean ±SD), 74.6±8.06%, 69 W m^{-2} and 9.9±5.90 m s^{-1}, respectively. Summer 2007 was, however, a very dry summer. The annual precipitation for 2007 was 527 mm while the 1971–2000 normal annual rainfall is 770 mm (Environment Canada, 2007).

The mercury species were measured from day 305 in 2006 to day 225 in 2007 (1 November 2006 to 13 August 2007) while the TGM flux was measured up to day 180 (29 June 2007) due to an instrument failure. The average TGM, RGM and Hg^P

concentrations were 1.17±0.51 ng m^{-3}, 15.10±10.02 pg m^{-3} and 16.35±9.54 pg m^{-3} respectively. A detailed breakdown of the mean and standard deviation by month, season and overall study period is given in Table 2 for the current study. Table 3 compares the overall means and ranges of the current study against other published values.

The influence of environmental parameters on Hg species concentrations and TGM flux was investigated by doing multiple regression analyses over the whole study period as well as for the different seasons. The regression coefficient and linear slope were tested for significance using the t-test (p<0.05). Significant results of this regression technique will be further discussed in the subsequent sections.

3.1 TGM concentrations

Monthly means of TGM ranged from 0.8 up to 1.4 ng m^{-3} with the lowest value recorded in July and the highest value recorded in both November and December. The mean monthly TGM concentrations, however, do not display a very consistent behavior from one month to the next. However, the standard deviation for the data tends to be smaller during the fall and winter months with higher variation in the spring and summer months. The exception to this trend is December, which had the highest standard deviation of ±0.86 ng m^{-3}. On a seasonal basis, the TGM concentrations showed some variability with the winter and summer values lower than that for the spring and the fall but the magnitudes of the standard deviations make the differences statistically insignificant and thus the annual TGM mean concentration of 1.17±0.51 ng m^{-3} best describes the TGM behavior. This annual average TGM concentration is lower than that reported by other studies for rural areas (see Table 3) but still within an acceptable range.

The behavior of the TGM concentration on a seasonal average day is given in Fig. 1 and, with the exception of summer, displayed diurnal patterns with highest concentrations recorded at midday and early afternoon when the net radiation and air

temperature were typically highest. The magnitudes of TGM concentrations were highest in the fall followed closely by the spring values and with the winter values typically being less than 1 ng m^{-3} throughout the average day. For the summer, an inverse trend to the other seasons was observed.

Results of the regression analysis indicate that, over the whole study period, net radiation (p=0.032) was the main environmental factor influencing the concentrations of TGM. The average monthly behavior of the TGM concentration versus the monthly average net radiation is depicted in Fig. 2 and illustrates that for the first half of the year, the TGM concentration and net radiation increased in a similar manner. After June, the behavior of the TGM concentrations deviate from that of the net radiation which is consistent with the trends observed in the average day concentrations. In the fall, the TGM concentrations were elevated in comparison to the net radiation levels.

The different behavior of the TGM concentrations in the summer period is attributed mainly to the different meteorological conditions, namely the atmospheric stability, observed in the summer. Figure 3 depicts the seasonal average hourly inverse (Monin Obukhov length scale, m^{-1}) which is an indication of the atmospheric stability. For the winter period, the atmosphere was relatively stable resulting in a reduced mixing height while during the warmer periods of the year, especially in the summer, the boundary layer height was higher and more unstable during the daylight hours resulting in more turbulent mixing and dilution of the pollutants. Thus any increases in TGM concentrations due to the increase in the net radiation in the summer would be difficult to observe as the increased turbulent mixing would quickly transport the TGM away from the surface and thus lower the concentrations near the soil surface during the daytime. At night, when the atmosphere is more stable, a concentration of TGM would build up near the surface as is indicated in Fig. 1.

Other environmental parameters that influenced the concentration of TGM on a seasonal basis included: soil temperature, soil moisture and wind speed and direction. Unfortunately, these parameters did not have a consistent effect across all seasons thus illustrating that the influence of environmental parameters on TGM concentrations

can be seasonally dependent and confounded and should not be assumed constant throughout the year.

As an example, Fig. 4 illustrates the role of wind direction as an important factor influencing TGM concentrations in the atmosphere. High TGM concentrations (>2.0 ng m^{-3}) were recorded mainly when the wind was from the west-southwest (WSW) sector, especially for the fall, where there are suspected industrial sources. These frequent high concentrations from the WSW sector in the fall also explain why the fall season had elevated TGM concentrations above the net radiation as the generation of TGM may not have been from the soil alone.

3.2 RGM and Hg^p concentrations

Monthly values for RGM and Hg^p, given in Table 2, display no clear monthly trend although April had the highest concentrations for both RGM and Hg^p. When aggregated on a seasonal basis, the spring season had the highest concentrations for both RGM and Hg^p due to the elevated levels reported for April. In addition, the average seasonal concentration was higher for Hg^p than for RGM for the fall, winter, and spring whereas the summer experienced higher concentrations of RGM over Hg^p. The observed concentrations of RGM and Hg^p in the current study are consistent with those reported in the literature (see Table 3) albeit the range of the current Hg^p concentrations is larger than that previously observed.

For the current study, RGM and Hg^p concentrations did not exhibit any predictable statistically significant diurnal, monthly or seasonal patterns during the study period nor statistically significant relationships with environmental parameters. The elevated RGM and Hg^p concentrations are believed to be mainly due to agricultural activities occurring in the area and/or the result of polluted air being transported to the site. Higher RGM and Hg^P concentrations were recorded in the spring, typically when the soil is tilled, nutrient amendments added and crops planted and cultivated, as well as in the fall, typically when crops are harvested and soils are ploughed.

The significance of potential pollulated air masses being transported to site is illustrated in Fig. 5 which gives pollution roses for RGM and Hg^P during a significant four day event. The pollution roses indicate that higher RGM and Hg^P concentrations were recorded when the wind was blowing from the western direction which is in the direction of industrial sources.

3.3 TGM flux

Monthly and seasonal TGM flux data are given in Table 2 although, due to technical difficulties with the Tekran 2537A, data for May, July and August were not obtained. Of the months with data, only December showed an average deposition of TGM to the soil surface although November indicated a zero flux. During these two months, winds from the WSW sector with large TGM concentrations were a frequent occurrence and thus the imported atmospheric TGM burden above the soil may have equaled or been greater to that emitted from the surface and hence the resulting zero or net deposition.

Figure 6 gives the seasonal average day behavior of the TGM flux above the substrate (i.e. bare soil, snow, or crop canopy) and illustrates the large fluxes that occurred in the spring and summer during daytime hours. The TGM flux in the fall and winter behaved differently and displayed very little variation throughout the average day.

The average annual TGM flux was $6.31 \pm 33.98\,ng\,m^{-2}\,h^{-1}$, which is a net volatilization to the atmosphere. The average TGM flux obtained is higher than that reported by Cobbett and van Heyst (2007) and Fritsche et al. (2008) but lower than that given by Cobos et al. (2002). These two studies are among the few studies where TGM flux was measured over terrestrial surfaces although the time frame in which the studies were conducted was of shorter duration.

The multiple regression analysis indicated that solar radiation, soil and air temperature and soil moisture content were all significant factors on the TGM flux. Furthermore, precipitation events and ground cover also had strong influences on the TGM flux to the atmosphere. The effects of these parameters will be discussed in greater detail in the following subsections.

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3.3.1 Solar radiation and temperature

Net solar radiation was the main factor influencing TGM fluxes above the various surfaces. Increased TGM volatilization (up to 517 ng m^{-2} h^{-1}) was recorded at moderate soil and air temperatures (>5° C) as a result of high net radiation (up to 300 W m^{-2}). The effect of radiation on TGM fluxes is demonstrated in Fig. 7 where the daily averaged TGM flux is plotted against the daily average net radiation from fall to summer. The increase in volatilization as well as the more pronounced diurnal pattern is evident starting in mid March and into April (days 75 to 100) as well as continuing in June (days 152 to 180). In winter there is reduced volatilization and relatively less variation in the volatilization rate due to reduced net radiation intensity and amplitude suggesting that, during winter, net radiation might not be the most dominant environmental factor influencing the magnitude of the TGM flux.

3.3.2 Soil temperature and moisture content

Figures 8 and 9 display the behavior of the TGM flux against the soil temperature and soil moisture respectively. From Fig. 8, the TGM flux during the fall of 2006 and winter of 2007, was relatively constant although a few episodes occurred with high TGM fluxes despite the reduced net radiation. These events, which typically occurred when the soil temperature reached temperatures below freezing (≤−5° C), recorded hourly TGM fluxes as high as 130 ng m^{-2} h^{-1} suggesting, that under certain conditions (low net radiation in winter), the soil conditions may be more important in controlling the TGM flux. As with the net radiation, from mid March and into April, high daily TGM fluxes corresponded to increasing soil temperatures as the spring thaw was underway. For June, the high TGM fluxes occurred with the warm soil temperatures.

During the winter, the surface soil moisture content was relatively low (<20%) although the deeper soils (>15 cm depth) were relatively moist and unaffected by the drying of the surface (see Fig. 9). The high TGM fluxes observed under the winter time with low soil temperatures may be the result of the deeper soil water freezing and

causing a reduction in the pore space due to the greater volume of ice and thus forcing soil interstitial air from the soil matrix. In addition, Cobbett and van Heyst (2007) suggest that Hg could be liberated from the water molecule as the water changes to solid phase due to the lower solubility of Hg in ice compared to water and thus increasing the concentration of Hg in the soil air spaces. Either or both of these phenomena may have produced the winter time spikes in TGM fluxes.

The behavior of soil moisture (Fig. 9) also supports the idea of the spring thaw greatly affecting the magnitude of the TGM fluxes. One factor that may cause an increase in the TGM flux is, as the surface soil moisture is replenished from values less than 20% to approximately 40% during the spring thaw, air within the soil matrix must be vented to allow the increase in soil moisture to occur. This displaced soil air may directly contribute to the elevated TGM flux (Song and van Heyst, 2005) and may also promote greater aqueous conversion of bound mercury to elemental mercury within the soil matrix where it can be transported to the soil surface and released into the atmosphere.

The high TGM fluxes recorded in June occurred during periods when the soil matrix was drying, especially at the surface. As the soil dries, more room is made for interstitial soil air and less aqueous chemical conversion would occur thus suggesting that a decrease in TGM flux should have occurred if the soil moisture was the only controlling factor. As such, the data indicates that net radiation and soil temperature have more of a controlling influence on the TGM flux during this time period. A TGM flux spike did occur in June following a major precipitation event as evident by the increase in surface moisture content.

3.3.3 Ground cover

Low TGM fluxes were observed in late winter (January and February – see Table 2) when the ground was covered with snow. The influence of snow cover is illustrated in Fig. 10 where low TGM flux was recorded when the ground was covered with snow. The reduced TGM flux is due to the reduced air exchange between the soil surface

and the atmosphere. Furthermore, the snow cover (up to 18 cm recorded) may have reduced TGM volatilization to the atmosphere by preventing light penetration (already of lower intensity in winter) thus tempering the effect on the Hg volatilization rate.

Figure 10 again illustrates the effect of the spring thaw and the resulting TGM flux spike that occurs after the snow cover melts.

Crop covers also affect the soil moisture content by increasing evapotranspiration and modulating the surface soil temperature thus influencing the TGM flux as shown in Fig. 10. Furthermore, crop cover could be expected to have the same effect as snow cover in controlling the amount of light reaching the soil and thus the soil temperature.

3.3.4 Precipitation events

Figure 9 shows that the TGM flux peaks with each episode of increase in soil moisture as a result of rain (in summer mainly) or snow melting (late winter) while Fig. 10 shows the TGM flux with precipitation events and ground cover. In summer the soil moisture decreased to below 30% at 30 cm depth (day 7.169). The next precipitation event (10 mm) resulted in TGM flux up to 60 ng m^{-2} h^{-1} indicating that increase in TGM fluxes as a response to increasing soil moisture is greater when the soil moisture before the precipitation event is lower (days 7.170–7.172). This can be explained by an increasing volume of air the soil pore spaces in as the soil moisture decreases thus resulting in a greater volume of air being expelled when water penetrates the soil and fills the pore spaces during a precipitation event. Similar observations were made by Song and van Heyst (2005) in a study conducted in the lab where greatest volatilization was recorded after precipitation on dry soil.

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4 Conclusions

The average TGM, RGM and Hg^P concentrations measured during the study over agricultural land were 1.17±0.51 ng m^{-3}, 15.10±10.02 pg m^{-3} and 16.35±9.54 pg m^{-3} while the average annual TGM flux was 6.31±33.98 ng m^{-2} h^{-1}.

The measurement of Hg species and TGM flux over four consecutive seasons demonstrates that different behaviors occurred for TGM concentrations and TGM flux to the atmosphere while RGM and Hg^p were not greatly affected by the changing seasons.

Net radiation and air temperature proved to be the main environmental factor influencing TGM concentrations and fluxes, which exhibited clear seasonal and diurnal trends. The influence of soil conditions namely soil temperature and soil moisture content was demonstrated during numerous episodes where positive fluxes were recorded as a result of increasing soil moisture after precipitation events or snow melting. The wind direction had a strong influence on all the Hg species concentrations by presumably bringing polluted air to the site.

It should be pointed out that even if the main factors controlling the Hg species and TGM flux to the atmosphere have been identified above, no strong direct correlation was observed when analyzing the response of the different mercury species to the controlling environmental parameters. This lack of correlation suggests that the environmental parameters have a more combined effect rather than separate independent effects on the Hg species and behavior at the soil and air interface. This is well demonstrated in summer when lower TGM concentrations were recorded compared to fall and spring despite high radiation and air temperature due to an unstable atmosphere and more mixing. Similarly, a net deposition for December was observed while there were episodes later in winter when high TGM fluxes were recorded due to the combined effect of decreasing soil temperature and soil water freezing.

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References

Blanchard, P., Froude, F. A., Martin, J. B., Dryfhout-Clark, H., and Woods, J. T.: Four years of continuous total gaseous mercury (TGM) measurements at sites in Ontario, Canada, Atmos. Environ., 36(23), 3735–3743, 2002.

Brosset, C. and Lord, E.: Mercury in precipitation and ambient air a new scenario, Water Air Soil Poll., 56(1), 493–506, 1991.

Cobbett, F. D., Steffen, A., Lawson, G., and Van Heyst, B. J.: GEM Fluxes and Atmospheric Mercury Concentrations (GEM, GRGM and Hg super(p)) in the Canadian Arctic at Alert, Nunavut, Canada (February–June 2005), Atmos. Environ., 41(31), 6527, 2007.

Cobbett, F. D. and Van Heyst, B. J.: Measurements of GEM fluxes and atmospheric mercury concentrations (GEM, RGM and Hgp) from an agricultural field amended with biosolids in Southern Ont., Canada (October 2004–November 2004), Atmos. Environ., 41(11), 2270–2282, 2007.

Cobos, D. R., Baker, J. M., and Nater, E. A.: Conditional sampling for measuring mercury vapor fluxes, Atmos. Environ., 36(27), 4309–4321, 2002.

Ebinghaus, R., Kock, H., and Schmolke, S.: Measurements of atmospheric mercury with high time resolution: Recent applications in environmental research and monitoring, Fresen. J. Anal. Chem., 371(6), 806–815, 2001.

Edwards, G. C., Rasmussen, P. E., Schroeder, W. H., Wallace, D. M., Halfpenny-Mitchell, L., Dias, G. M., Kemp, R. J., and Ausma, S.: Development and evaluation of a sampling system to determine gaseous Mercury fluxes using an aerodynamic micrometeorological gradient method, J. Geophys. Res., 110(10), 1–11, 2005.

Engle, M. A., Gustin, M. S., and Zhang, H.: Quantifying natural source mercury emissions from the Ivanhoe Mining District, north-central Nevada, USA, Atmos. Environ., 35(23), 3987–3997, 2001.
Fitzgerald, W. F.: Is mercury increasing in the atmosphere? The need for an atmospheric mercury network (AMNET), Water Air Soil Poll., 80(1), 245–254, 1995.
Fritsche, J., Obrist, D., Zeeman, M., Conen, F., Eugster, W., and Alewell, C.: Elemental mercury fluxes over a sub-alpine grassland determined with two micrometeorological methods, Atmos. Environ., 42(13), 2922–2933, 2008.
Gustin, M. S., Taylor, G. E., and Taylor, R.: Effect of temperature and air movement on the flux of elemental mercury from substrate to the atmosphere, J. Geophys. Res., 102(D3), 3891–3898, 1997.
Gustin, M. S.: Are mercury emissions from geologic sources significant? A status report, Sci. Total Environ., 304(1–3), 153–167, 2003.
Iverfeldt, Å. and Lindqvist, O.: Atmospheric oxidation of elemental mercury by ozone in the aqueous phase, Atmos. Environ., 20(8), 1567–1573, 1986.
Landis, M. S., Stevens, R. K., Schaedlich, F., and Prestbo, E. M.: Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air, American Chemical Society, Easton, Pa, 2002.
Lin, C. and Pehkonen, S. O.: The chemistry of atmospheric mercury: a review, Atmos. Environ., 33(13), 2067–2079, 1999.
Lindberg, S. E., Kim, K., Meyers, T. P., and Owens, J. G.: Micrometeorological Gradient Approach for Quantifying Air/Surface Exchange of Mercury Vapor: Tests Over Contaminated Soils, American Chemical Society, Easton, Pa, 1995.
Lynam, M. M. and Keeler, G. J.: Automated Speciated Mercury Measurements in Michigan, Environ. Sci. Technol., 39(23), 9253–9262, 2005.
Mason, R. P., Fitzgerald, W. F., and Morel, F. M. M.: The biogeochemical cycling of elemental mercury: anthropogenic influences, Pergamon Press, Oxford, 1994.
Obrist, D., Gustin, M. S., Arnone III, J. A., Johnson, D. W., Schorran, D. E., and Verburg, P. S. J.: Measurements of gaseous elemental mercury fluxes over intact tallgrass prairie monoliths during one full year, Atmos. Environ., 39(5), 957–965, 2005.
Pacyna, E. G. and Pacyna, J. M.: Global Emission of Mercury from Anthropogenic Sources in 1995, Water Air Soil Poll., 137(1), 149–165, 2002.

Poissant, L., Pilote, M., and Casimir, A.: Mercury flux measurements in a naturally enriched area: Correlation with environmental conditions during the Nevada Study and Tests of the Release of Mercury From Soils (STORMS), J. Geophys. Res., 104(D17), 845–858, 1999.
Poissant, L., Pilote, M., Beauvais, C., Constant, P., and Zhang, H.: A year of continuous measurements of three atmospheric mercury species (GEM, RGM and Hgp) in southern Québec, Canada, Atmos. Environ., 39(7), 1275–1287, 2005.
Satoh, H.: Occupational and Environmental Toxicology of Mercury and Its Compounds, Ind. Health, 38(2), 153–164, 2000.
Schroeder, W. H., Anlauf, K. G., Barrie, L. A., Lu, J. Y., Steffen, A., Schneeberger, D. R., and Berg, T.: Arctic springtime depletion of mercury, Nature, 394(6691), 331–332, 1998.
Schroeder, W. H. and Munthe, J.: Atmospheric mercury – An overview, Atmos. Environ., 32(5), 809–822, 1998.
Seigneur, C., Vijayaraghavan, K., Lohman, K., Karamchandani, P., and Scott, C.: Global Source Attribution for Mercury Deposition in the United States, Environ. Sci. Technol., 38(2), 555–569, 2004.
Slemr, F. and Scheel, H. E.: Trends in atmospheric mercury concentrations at the summit of the Wank mountain, Southern Germany, Atmos. Environ., 32(5), 845–853, 1998.
Song, X. and van Heyst, B.: Volatilization of mercury from soils in response to simulated precipitation, Atmos. Environ., 39(39), 7494–7505, 2005.
Valente, R. J., Shea, C., Lynn Humes, K., and Tanner, R. L.: Atmospheric mercury in the Great Smoky Mountains compared to regional and global levels, Atmos. Environ., 41(9), 1861–1873, 2007.
Xiao, Z. F., Munthe, J., Schroeder, W. H., and Lindqvist, O.: Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden, Tellus B, 43(3), 267–279, 1991.
Yatavelli, R. L. N., Fahrni, J. K., Kim, M., Crist, K. C., Vickers, C. D., Winter, S. E., and Connell, D. P.: Mercury, $PM_{2.5}$ and gaseous co-pollutants in the Ohio River Valley region: Preliminary results from the Athens supersite, Atmos. Environ., 40(34), 6650–6665, 2006.

Table 1. Statistical summary of the environmental parameters measured during the study at Elora Research Station, ON (1 November 2006 to 13 August 2007).

Meterological parameter	Units	*n*	Median	Fall 2006 Mean	SD	Min	Max
Air temperature	°C	12577	4.2	5.0	6.56	−21.1	25.4
Relative humidity	(%)	12577	84	81	12.65	29	98
Soil moisture (1 cm depth)	(%)	13110	41.4	40.4	4.92	3.7	47.3
Soil moisture (30 cm depth)	(%)	13110	43.7	43.7	4.21	13.9	54.6
Soil temperature (1 cm depth)	(%)	13110	5.1	5.8	4.69	−6.1	20.1
Soil temperature (30 cm depth)	(%)	13110	6.1	6.8	3.92	−4.5	16.9
Net radiation	($W m^{-2}$)	13110	−4	26	106.6	−107	629
Wind speed	(ms^{-1})	13110	14	15	8.2	2	50
Inverse Monin Obukhov length	(m^{-1})	13110	0.001	−0.005	0.132	−3.0	0.6
Meterological parameter	Units	*n*	Median	Winter 2007 Mean	SD	Min	Max
Air temperature	°C	12511	−5.8	−6.0	7.10	−25.6	17.5
Relative humidity	(%)	12511	83	80	11.38	34	98
Soil moisture (1 cm depth)	(%)	12672	19.2	24.7	11.81	13.3	46.4
Soil moisture (30 cm depth)	(%)	12672	42.4	42.9	2.47	33.3	49.9
Soil temperature (1 cm depth)	(%)	12672	−1.3	−1.3	2.82	−9.0	7.8
Soil temperature (30 cm depth)	(%)	12672	−0.5	−0.5	2.65	−8.0	7.8
Net radiation	($W m^{-2}$)	12672	−7	−8	51.9	−115	347
Win speed	(ms^{-1})	12672	17	17	9.3	2	52
Inverse Monin Obukhov length	(m^{-1})	12672	0.001	−0.005	0.169	−3.0	1.2

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Table 1. Continued.

Meterological parameter	Units	*n*	Median	Mean	SD	Min	Max
			Spring 2007				
Air temperature	°C	13170	10.8	11.4	9.22	−11.0	32.3
Relative humidity	(%)	13170	68	65	20.69	15	97
Soil moisture (1 cm depth)	(%)	4267	39.1	37.2	7.51	14.3	48.9
Soil moisture (30 cm depth)	(%)	4267	45.3	46.3	2.62	21.2	51.3
Soil temperature (1 cm depth)	(%)	13242	11.8	11.6	7.72	−3.5	27.4
Soil temperature (30 cm depth)	(%)	13242	10.5	10.2	6.28	−3.0	27.4
Net radiation	($W m^{-2}$)	13242	10	111	209.3	−116	808
Wind speed	(ms^{-1})	13242	13	14	8.0	2	47
Inverse Monin Obukhov length	m^{-1}	13242	−0.001	−0.007	0.125	−3.0	0.9
			Summer 2007				
Meterological parameter	Units	*n*	Median	Mean	SD	Min	Max
Air temperature	°C	9743	20.1	19.9	5.69	4.4	33.3
Relative humidity	(%)	9743	75	71	19.35	26	97
Soil moisture (1 cm depth)	(%)	5904	20.7	22.1	3.25	13.3	36.7
Soil moisture (30 cm depth)	(%)	5904	30.4	30.8	0.94	27.1	33.1
Soil temperature (1 cm depth)	(%)	9742	18.9	18.7	3.31	7.9	30.7
Soil temperature (30 cm depth)	(%)	9742	17.9	17.7	2.28	12.0	26.7
Net radiation	($W m^{-2}$)	9311	33	147	225.8	−104	912
Wind speed	(ms^{-1})	9742	9	10	5.9	2	34
Inverse Monin Obukhov length	(m^{-1})	9742	0.000	0.002	0.049	−0.1	0.8

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Table 2. Average monthly and seasonal Hg species concentrations and TGM flux measured at Elora Research Station, ON (1 November 2006 to 13 August 2007) over different ground covers.

	Average TGM Conc (ng m^{-3})	SD	Average RGM Cong (pg^{-3})	SD	Average Hg^P Conc (pg^{-3})	SD flux (ng m^{-2} h^{-1})	Average TGM	SD	Ground cover
Month									
November	1.4	0.25	17.2	8.30	22.0	10.59	0.0	9.5	Bare
December	0.4	0.86	10.8	7.24	12.6	7.36	−0.4	9.63	Snow
January	0.9	0.14	17.6	12.37	13.4	8.76	0.5	12.38	Snow
February	0.9	0.14	9.2	5.57	13.8	10.42	1.2	18.12	Snow
March	1.1	0.27					9.2	28.10	Bare
April	1.0	0.34	34.9	24.81	24.5	6.63	18.1	42.87	Bare
May	1.3	0.38	17.4	10.03	19.5	10.29			Corn
June	1.2	0.46	17.9	9.26	17.4	5.20	15.2	59.49	Corn
July	0.8	0.64	13.3	13.58	7.9	7.42			Corn
August	1.1	0.70	10.2	5.28	11.8	5.42			Corn
Seasons									
Fall	1.3	0.53	14.0	8.50	17.3	10.23	−0.1	9.54	Bare/snow
Winter	0.9	0.61	12.5	9.51	13.5	9.67	2.5	21.18	Snow/bare
Spring	1.3	0.63	17.9	4.82	19.5	9.22	19.5	9.22	Bare/corn
Summer	1.1	0.44	13.9	10.88	12.2	2.94	17.0	79.43	Corn
Overall	1.2	0.51	15.1	10.02	16.4	9.54	6.3	33.98	

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Table 3. Published mercury species concentrations and TGM fluxes measured from terrestrial surfaces.

Location	Time of year	Surface	RGM (pg m^{-3})	Hg^{P} (pg m^{-3})	TGM (ng m^{-3})	TGM flux (ng m^{-3} h^{-1})	Reference
Ontario	October–November 2004	Rural	(0–21.7) 2.3	(0–35.2) 3.0	(0.2–42.1) 1.8	(−2.9–3.6) 0.1	Cobbett and van Heyst (2007)
Tennessee	Spring and summer 2004	Rural			1.79		Valente et al. (2007)
Athens, Ohio	July 2004–July 2005	Rural	(0–461.59) 12.45	(0–76.82) 5.29	(0.78–4.38) 1.62	–	Yatavelli et al. (2006)
Quebec	January–December 2003	Rural	3	26	1.65		Poissant et al. (2005)
Michigan	November 2000–May 2001	Rural	(0.19–38.7)		(1.1–4.4)		Lynman and Keeler (2005)
Michigan	July 2000–July 2002	Urban	(0.6–270)	(5.7–60.1)	(2.0–11.8) 4.1		Lynman and Keeler (2005)
Minessota	May–June 2001	Rural				(−91.7–190.5) 9.67	Cobos et al. (2002)
Ireland	1995–2001	Rural	18	8	1.77		Ebinghaus et al. (2001)
Tennessee	1992–1993	Rural	30–163	100	1.93–2.35		Lindberg and Stratton (1998)
Zurich, Switzerland	September 2005–August 2006	Rural			(0.69–2.42) 1.42	(−42–29) −2.9	Fritsche et al. (2008)
Ontario	July 2006–August 2007	Rural	(0.8–124.6) 15.1	(0.4–150.9) 16.4	(0.08–5.97) 1.17	(−342.13–517.19) 6.31	

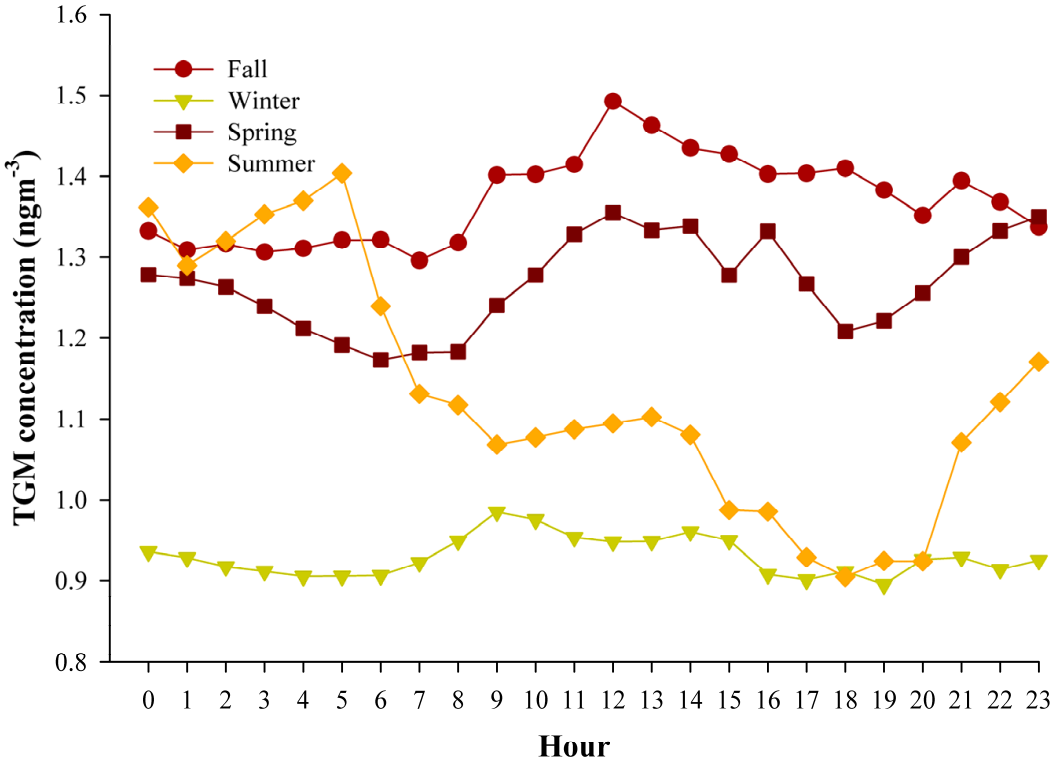

Fig. 1. Seasonal average day behavior of TGM concentrations (ng m^{-3}) measured during the study at Elora Research Station, ON (1 November 2006 to 13 August 2007).

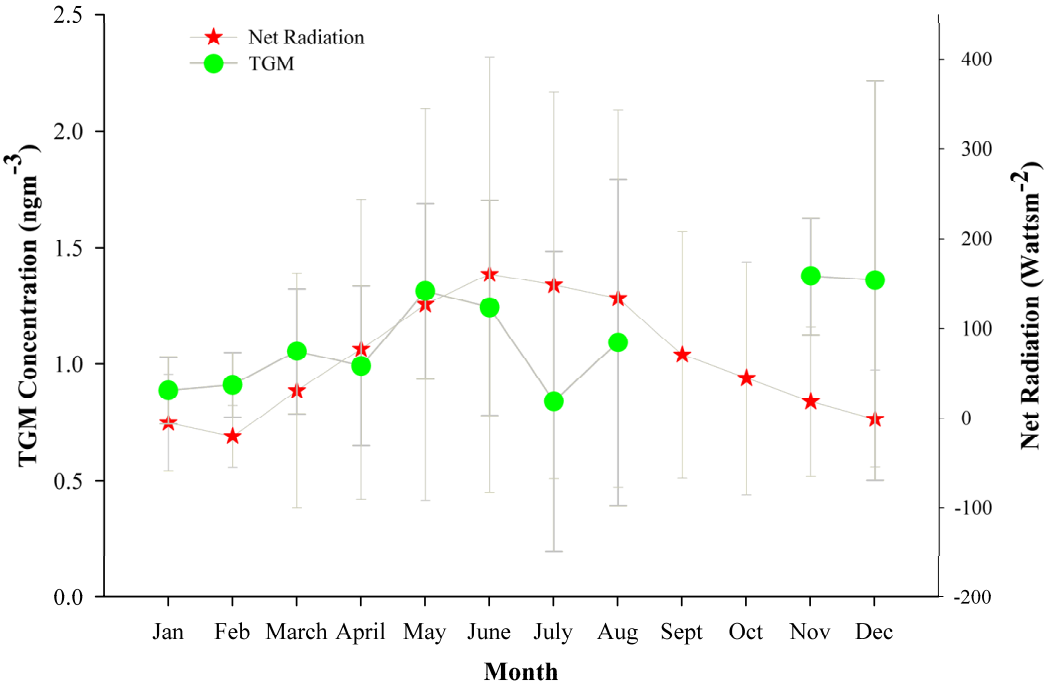

Fig. 2. Average monthly TGM concentrations (ng m^{-3}) and net radiation (watts m^{-2}) measured during the study at Elora Research Station, ON (1 November 2006 to 13 August 2007).

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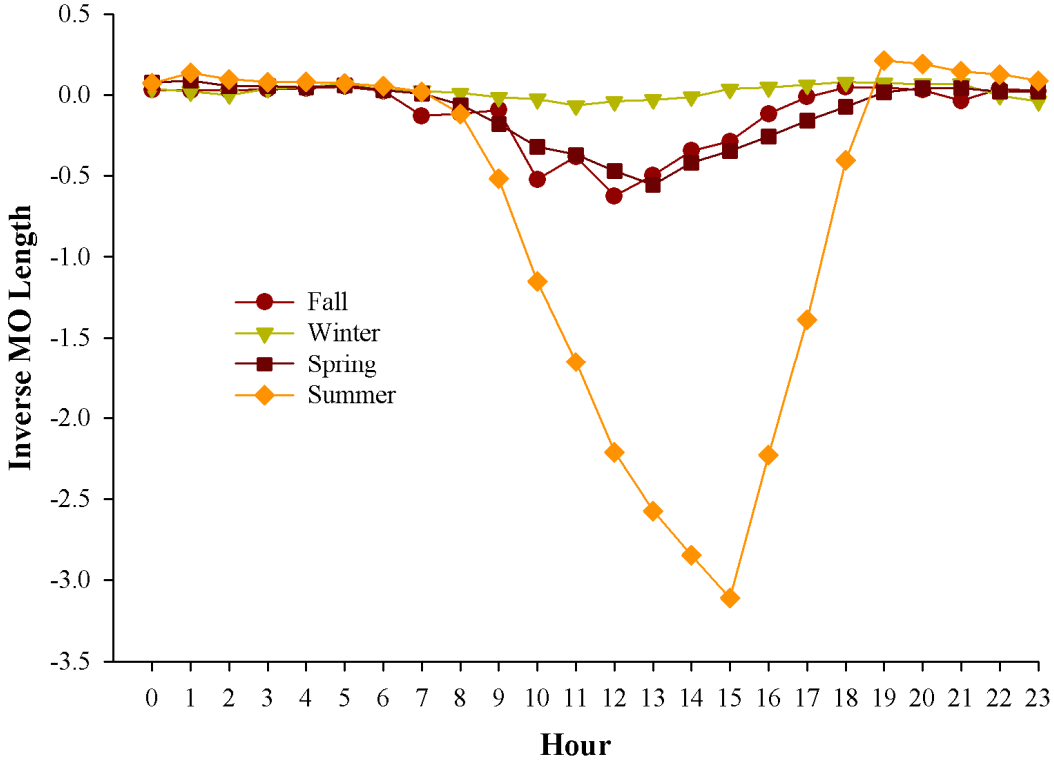

Fig. 3. Seasonal hourly average values for the inverse Monin Obukhov (MO) length (1/L) (m^{-1}) measured from 1 November 2006 to 13 August 2007 measured at Elora Research Station, ON. 1/L>0 indicates stable atmospheric conditions, 1/L=0 indicates neutral atmospheric conditions and 1/L<0, indicates unstable atmospheric conditions.

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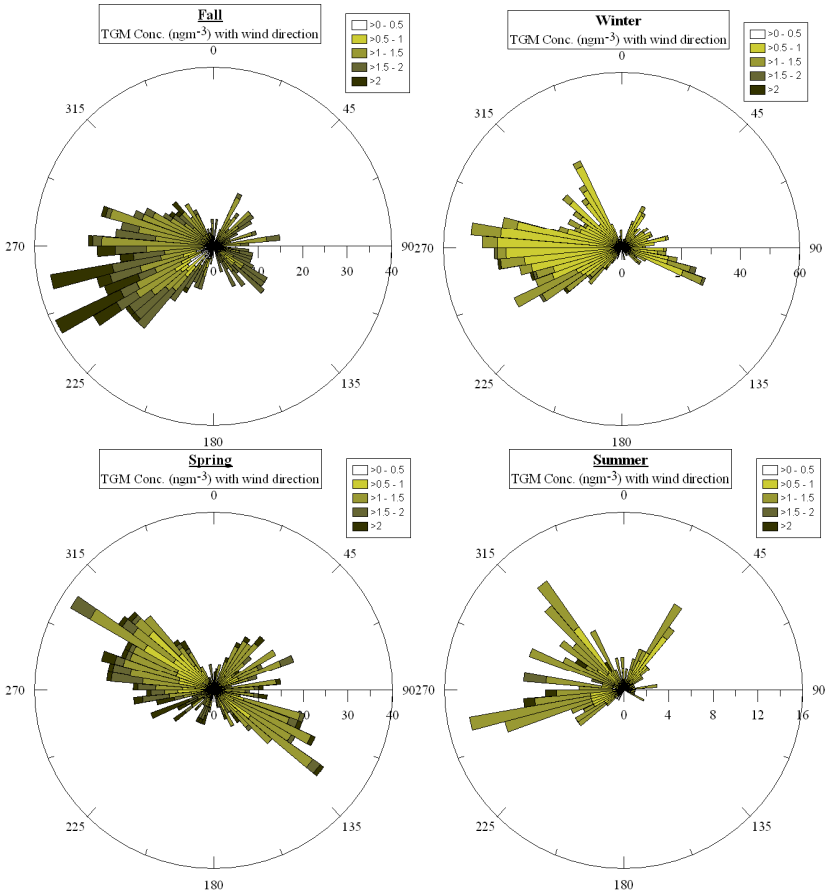

Fig. 4. Pollution roses of TGM concentrations (ng m^{-3}) for each season measured at Elora, ON during the study period (1 November 2006 to 29 July 2007). The concentrations (hourly average) intervals are plotted against the frequency of occurrence on the radius axis.

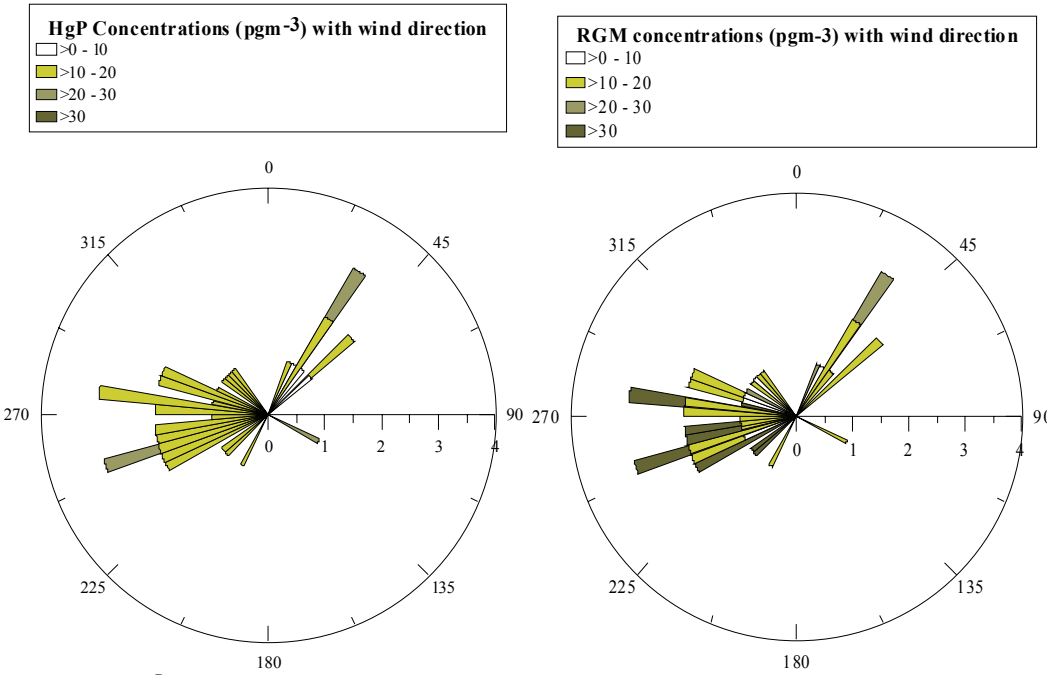

Fig. 5. Hg^P and RGM concentrations range with wind direction for days 175–179 (24 to 28 June 2007) during the study at Elora Research Station, ON showing the influence of wind direction on the Hg species concentration.

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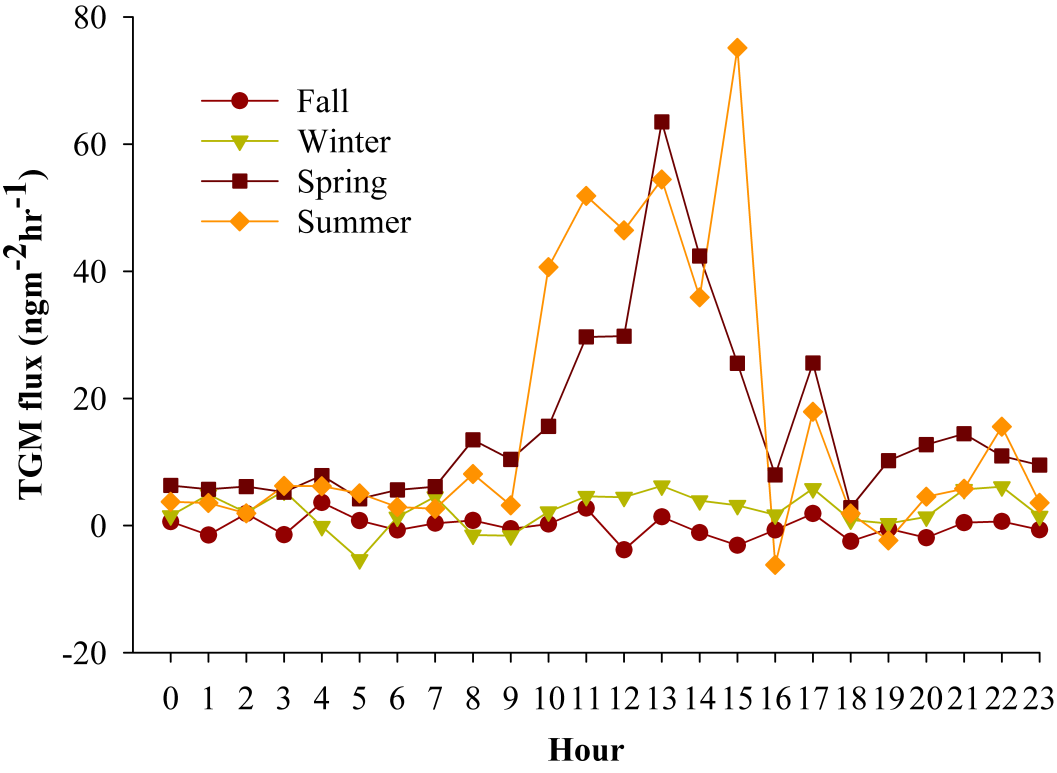

Fig. 6. Seasonal average day behavior of TGM fluxes (ng m^{-2} h^{-1}) measured at Elora Research Station, ON study site (1 November 2006 to 29 June 2007).

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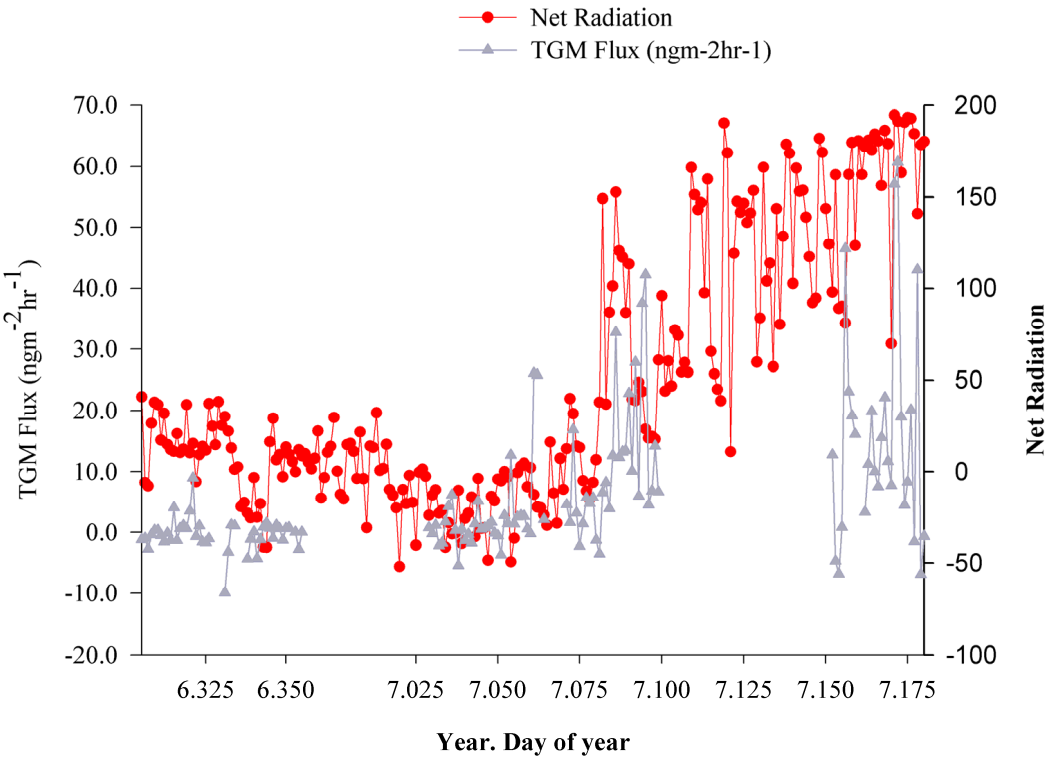

Fig. 7. Daily averages of TGM flux (ng m^{-2} h^{-1}), net radiation (Watts m^{-2}) and relative humidity (% RH) with time (days 305 of 2006 to 180 of 2007) measured at Elora Research Station, ON.

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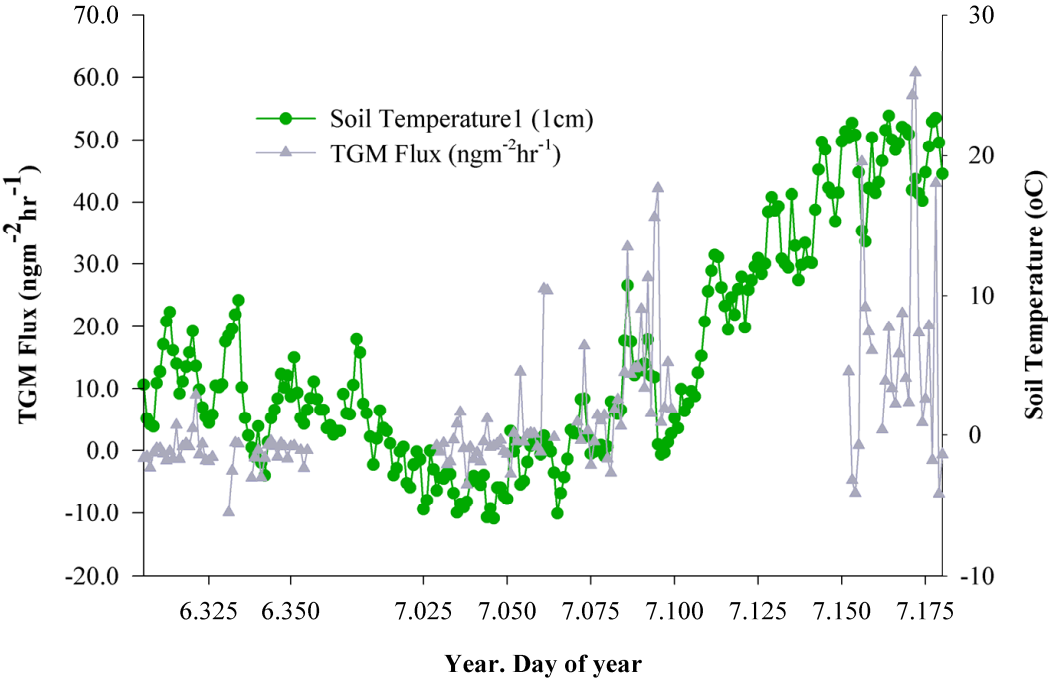

Fig. 8. Daily averages of TGM flux (ng m^{-2} h^{-1}) and soil temperature (° C) with time (days 305 of 2006 to 180 of 2007) measured at Elora Research Station, ON.

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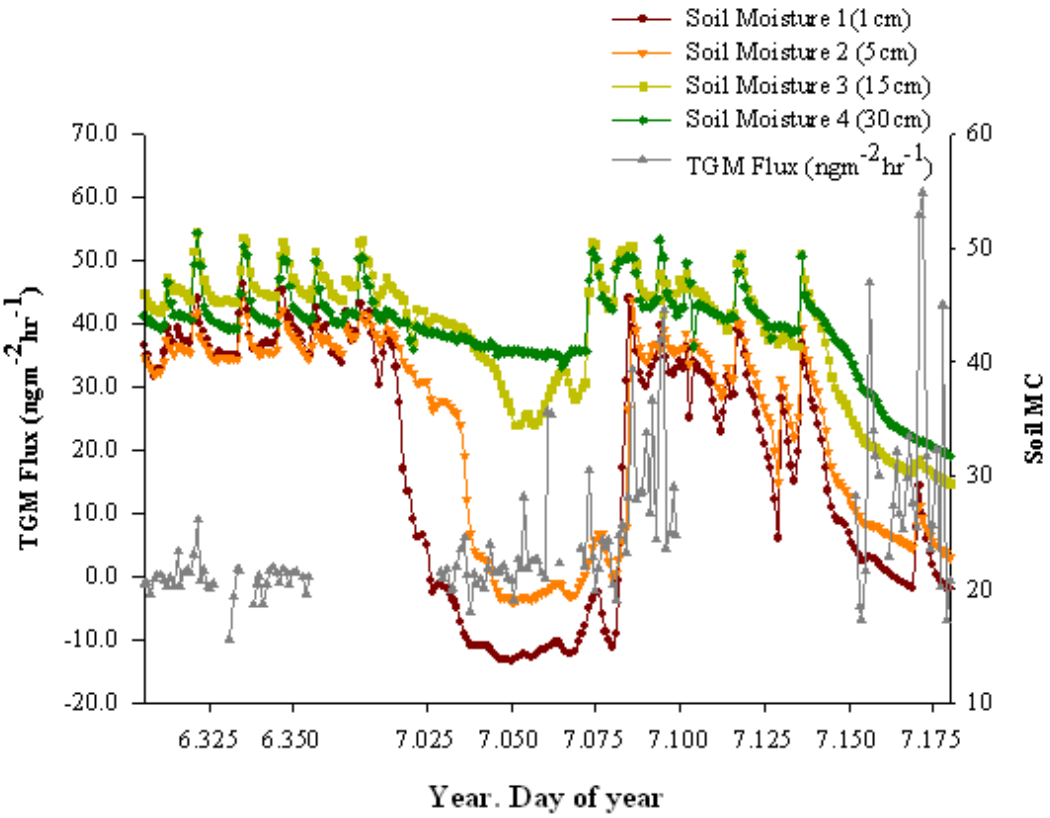

Fig. 9. Daily averages of TGM flux ($ng\,m^{-2}\,h^{-1}$) and soil moisture content (%) with time (days 305 of 2006 to 180 of 2007) measured at Elora Research Station, ON.

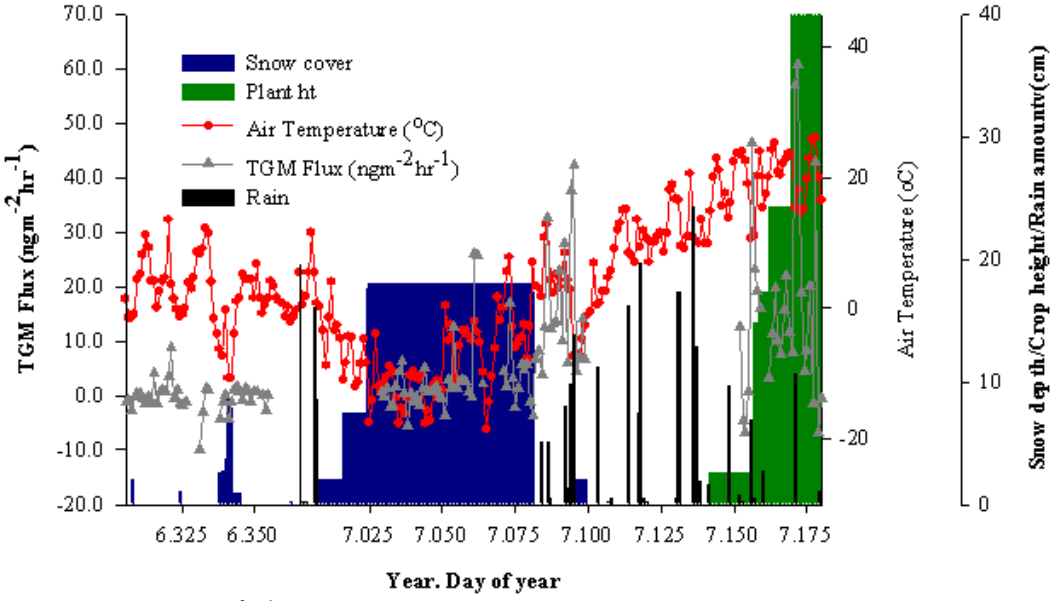

Fig. 10. TGM flux (ng m^{-2} h^{-1}), air temperature (° C), precipitation (mm) and crop cover (cm) with time (days 305 of 2006 to 180 of 2007) measured at Elora Research Station, ON. The days with snow cover and crop cover are highlighted.