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Mercury dynamics in the Rocky Mountain, Colorado, Snowpack

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Gaseous Elemental Mercury (GEM) was monitored at the Niwot Ridge (NWT) longterm ecological research (LTER) site (Colorado, USA, 40° N) from interstitial air extracted from the snowpack at depths ranging from the snow surface to 10 cm above the soil. A highly dynamic cycling of mercury (Hg) in this mid-latitude snowpack was observed. Patterns were driven by both GEM production in surface snow and GEM destruction in the deeper snowpack layers. Thorough mixing and vertical transport processes were observed through the snowpack. GEM was photochemically produced near the snow-air interface leading to enhanced GEM levels in interstitial air of surface snow of up to 8 ng m⁻³. During low wind periods, GEM in surface snow layers remained significantly above ambient air levels at night as well, which may indicate a potential weak GEM production over night. Analysis of vertical GEM gradients in the snowpack show that surface GEM enhancements efficiently propagated down the snowpack, with a temporal lag in peak GEM levels observed with increasing depth. Downward diffusion was responsible for much of these patterns, although vertical advection also contributed to vertical redistribution. Destruction of GEM in the lower snowpack layers was attributed to dark oxidation of GEM. Analysis of vertical GEM/CO₂ flux ratios indicated that this GEM destruction occurred in the snow and not in the underlying soil. The strong, diurnal patterns of photochemical GEM production at the surface ultimately lead to re-emission losses of deposited Hg back to the atmosphere. The NWT data show that highest of GEM production and emission occur shortly after fresh snowfall, indicating that fresh snow possibly resupplies photoreducible Hg to the snowpack.

1 Introduction

Various natural and anthropogenic sources emit mercury (Hg) to the atmosphere, either as gaseous elemental Hg (GEM, Hg°) or as reactive, divalent Hg species (Hg(II)). Due to its long lifetime, GEM can be transported over long distances in the atmosphere

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(Selin et al., 2007). Atmospheric GEM can directly deposit to surfaces (Zhang et al., 2009, and references therein), or it can undergo chemical reactions and subsequently deposit as divalent Hg(II) (Schroeder and Munthe, 1998). Deposition of atmospheric Hg is the main source of Hg contamination in remote ecosystems (e.g. Fitzgerald et ₅ al., 1998); however, deposited Hq may also re-volatilize back to the atmosphere as GEM from both land (Ericksen et al., 2005) and water surfaces (Kuss et al., 2011). The global biogeochemical cycle of Hg is hence highly complex and involves multiple exchange processes between natural reservoirs (such as soils, snow and ice, and water) and the atmosphere (Lindberg et al., 2007).

Among natural Hg reservoirs, the role of the cryosphere (i.e. snow- and ice-covered surfaces) is important as it represents a highly dynamic system situated between the atmosphere and the subniveal (covered by the snowpack) ecosystems (Dominé and Shepson, 2002). A recent review from Durnford and Dastoor (2011) concluded that no study has yet simulated the behavior of Hq in the cryosphere near its full complexity. and that it is crucial to develop models based on physical and chemical processes to simulate re-volatilization processes from the cryosphere, particularly in regards to future changes in climate. Snowpacks act as Hg storage reservoir for atmospheric Hg, but an important fraction of Hg that is deposited onto snow surfaces also is readily emitted back to the atmosphere (Steffen et al., 2002; Dommergue et al., 2003a; Sommar et al., 2007; Johnson et al., 2008; Faïn et al., 2011). This snowpack chemistry is important as seasonal snowpacks are often considered a pollution source for ecosystems because meltwater contains considerable amounts of atmospheric pollutants, including Hg. Further, Hg that enters the meltwater may be converted to highly toxic methylmercury that is subject to bioaccumulation through the aquatic food chain (Lockhart and Evans, 2000; Douglas et al., 2012). It is hence important to understand the physical and chemical processes that control the ultimate fate of Hg in snowpacks.

While some of the Hg deposited onto the snowpack is rapidly re-emitted (Durnford and Dastoor, 2011), quantification of the precise fractions revolatilized is still hotly debated. For example in the Arctic, some studies have suggested that net deposition **BGD**

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associated with springtime Atmospheric Mercury Depletion Events (AMDEs; Steffen et al., 2008) is low or insignificant because of strong re-emission processes (St. Louis et al., 2005, 2007; Kirk et al., 2006; Hedgecock et al., 2008) and that there is no firm evidence that AMDEs exert a significant influence on Hg concentrations in the Arctic Ocean (Outridge et al., 2008). However, other studies have concluded that AMDEs lead to net annual losses of atmospheric GEM (Steffen et al., 2005) and that a substantial fraction of deposited Hg accumulates in snow (Hirdman et al., 2009). While many studies investigating the behavior of Hg in snowpacks have focused on polar latitudes, snow Hg dynamics in mid-latitude snowpacks are also important, particularly as they are generally closer to sources of Hg emission and areas of high population density. Further, different environmental conditions in temperate latitude snowpacks are expected to impact the behavior of snow Hg – such as, for example, effects of forest canopies and subniveal soil (Nelson et al., 2008; Poulain et al., 2007). Consequently, results from polar studies may not be directly applicable to mid-latitude snowpacks.

We conducted extensive Hg sampling in a temperate-latitude snowpack and the lower atmosphere at Niwot Ridge (NWT), a Long-Term Ecological Research (LTER) site located in the Rocky Mountains, Colorado, USA. We continuously sampled GEM, ozone, and CO₂ at six different depths in the seasonal snowpack plus in the atmosphere using a fully automated, continuous snow-gradient sampling system. In addition, physical properties of the snowpack (e.g. density, temperature), meteorological data, and total Hg content of the snow using pit sampling through the season, were investigated. The main goals of this study were to improve our understanding of Hg(II)/GEM redox conversions within the snowpack and to assess how such conversions ultimately affect Hg loads of alpine snowpacks during snowpack accumulation and snowmelt.

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2.1 Study site

This experiment was conducted from 2 February to 5 May 2009, and from 24 November 2011 to 10 May 2012, in a forest clearing near tree line at the high-elevation Soddie site at the NWT-LTER ($40^{\circ}03'$ N, $105^{\circ}35'$ W, 3340 m a.s.l). The site has a 10° southwest facing slope (Erickson, 2004) and has an underground laboratory (3 m × 9 m × 2.4 m) with available line power. An adjacent tower (10 m away) is equipped with a suite of meteorological instruments. Snow cover at the Soddie site generally lasts from late October into June, and $\sim 80\%$ of the annual precipitation of ~ 1000 mm falls as snow (Caine, 1995).

2.2 Snowpack gradient sampling method

Snowpack gas flux research at the Soddie site was initiated in the winter of 2003/2004. Since then, snowpack studies have been conducted at this site every year (Williams et al., 2009). Seok et al. (2009) provide an extensive description of the snowpack gradient tower (including photographs and diagrams) that is installed for measurements of interstitial snow air (SIA) trace gas concentrations. This same manifold was used during this study for continuous sampling of GEM, ozone and $\rm CO_2$ in SIA and the atmosphere. This multi-level gradient tower is constructed of square aluminum alloy tubing, has 60 cm long cross bars at seven heights above the ground (10, 30, 60, 90, 120, 150, and 245 cm), and was installed at the Soddie site before the onset of the snow accumulation season. The system becomes progressively covered by precipitating snow and thereby facilitates in-situ snowpack gas measurements throughout the snow-covered season without disturbances. The 245 cm inlet remained above the maximum snowpack height during the entire sampling period and air collected from this height thus represents ambient atmospheric concentrations. Each of the seven cross bars supported a pair of sampling inlets, fitted with 25 mm Acrodisc $^{(R)}$

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hydrophobic polytetrafluoroethylene (PTFE) syringe filters (Pall Life Sciences, Ann Arbor, Michigan, USA) to prevent particles from entering the sampling lines. Sampling lines were all made of perfluoroalkoxy (PFA) Teflon[®], inner diameter of 3.9 mm and outer diameter of 6.4 mm (Parker Hannifin, Cleveland, Ohio, USA), with equal lengths of 18 m. All sampling lines were directed to the underground laboratory, which housed the analytical instruments. Sections of the sampling lines outside the laboratory were wrapped in pipe insulation with a self-controlling water pipe heater to maintain line temperatures slightly above 0 °C to prevent water from freezing and clogging sampling lines. The selection of inlets for sampling at a particular height was done through an array of seven solenoid valves. Sampling was conducted by drawing air sequentially from each inlet height for 10 min. Air from the snow inlets at a total sampling rate of 2.51 min⁻¹ was directed to GEM, ozone, and CO₂ analyzers; since the sampling flow was split between two paired inlets at each height, the effective sampling rate per inlet line was 1.251 min⁻¹. The sampling manifold, calibration system, and data acquisition were controlled through an array of digital input/output modules, temperature input components, and LabVIEW software (National Instruments, Austin, Texas, USA).

GEM was determined using a Tekran 2537B vapor phase mercury analyzer. The 2537B instrument collects the air stream on two gold cartridges. GEM is thermally desorbed and detected by cold vapor atomic fluorescence spectrometry at 253.7 nm. Use of dual gold cartridges allows alternate sampling and desorption on two separate sampling traps, resulting in a continuous measurement of GEM. We sampled GEM at 2.5 min time resolution, resulting in four GEM data points per sampling depth interval. To avoid possible artifact related to the transition from one inlet to the next, the first measurement collected at each inlet was excluded, and the two subsequent measurements were averaged to calculate a mean concentration for each 10-min interval. A mass flow meter supplies the 2537B with a sample volume referenced to STP (Standard Temperature and Pressure: 0°C, 1 atm). Set-up, accuracy, and precision of this instrument have been evaluated previously during field comparisons at an urban/industrial site (Ebinghaus et al., 1999) and a remote marine background location

(Schroeder et al., 1995). The analyzer was recalibrated every 25 h using its internal permeation source. Blanks were measured during each internal calibration cycle and were consistently $< 0.01 \text{ ng m}^{-3}$.

CO₂ concentrations were determined with an infrared gas analyzer (IRGA, LI-COR LI-7000, Lincoln, NE, USA). CO₂ concentrations in the snowpack reached beyond the factory-calibrated range of 0–3000 ppm for the LI-7000 instrument. As a result, calibrations above 3000 ppm were necessary and conducted using a 1 % CO₂ standard that was diluted with zero air using a dynamical dilution system. Daily single point CO₂ calibrations (450 ppm) were performed to monitor the drift of the instrument (< 1% drift over entire sampling period). Ozone was monitored using a UV absorption analyzer (Model 49, Thermoenvironmental Corp.). Air was analyzed for ozone and CO₂ every 10 s and averaged for the respective 5 min interval corresponding to GEM measurements.

2.3 Ancillary data

Temperatures at each sampling height were measured using type-E thermocouple wires (Omega Engineering, Inc., Stamford, Connecticut, USA) that were covered by white heat shrink tubing to reduce radiation artifacts. Wind speed, at 6 m above the ground on the meteorological (MET) tower 10 m away, was measured using a 05103-L RM Young Wind Monitor (Campbell Scientific, Logan, Utah, USA). Barometric pressure was measured using a CS105 Vaisala PTB101B Barometer (Campbell Scientific, Logan, Utah, USA), and incoming solar radiation data (spectral range of 305–2200 nm) were collected with an NR-Lite (Kipp and Zonen) sensor.

Readings of snow depth were taken at 1–2 week intervals from calibrated marks on the snow tower. Gaps in the snow depth record were filled by comparing and interpolating the daily snow depth record from the Niwot SNOTEL site, 1.5 km from the Soddie site. An analysis of the linear correlation between concurrent snow-depth data from these two sites resulted in a coefficient of determination, r^2 , of 0.83.

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Snow sampling and total Hg analysis

Two snowpack profiles were sampled for total Hg and analyzed for total Hg (THg, no filtering) in an open, undisturbed area in close vicinity of the Soddie lab. These sampling sites showed similar characteristics, for example in regards to daytime sun exposure and distance from the trees. Snow pits were sampled on 9 March and 27 April 2009, for depth profiles of THg in depth intervals of 25 cm from the surface to the underlying ground. We used 250 ml borosilicate glass bottles previously cleaned at the Desert Research Institute using 5% HNO₃ acid bath and ultrapure water rinsing (18.2 MΩcm) for snow sampling. All snow samples were collected using clean snow sampling procedures; samples were immediately stored in the dark at -20°C until analysis.

Snow samples were analyzed for total THg using a Tekran Model 2600 analyzer (Tekran Inc., Toronto, Canada) according to US EPA method 1631 revision E. Briefly, samples were oxidized with 0.5 % v/v BrCl 24 h before analysis to digest Hg bound to complexes. Excess BrCl was neutralized with pre-purified hydroxylamine hydrochloride. Samples were then automatically mixed with SnCl₂ in a reaction vessel to reduce Hg(II) to GEM. A phase separator and Argon gas were used to load GEM onto two sequential gold traps. After thermal desorption, GEM was detected by atomic fluorescence spectrometry using a Tekran Model 2600 instrument. It was calibrated every day with the NIST SRM-3133 Hg standard (curves with standards of 0, 0.5, 1, 5, 10, 25, and 50 ng I⁻¹ Hg). The detection limit (DL) was re-evaluated every analytical run on a limited set of blanks (usually 3, DL averaging 0.2 ng l⁻¹). During analyses, Ongoing Precision Recovery (OPR; 5 ng I⁻¹) was periodically analysed to check the stability of the system; these measurements showed between 90 % and 118 % recovery. Reagent blanks were measured regularly to assure that the system was clean of contamination. All samples were analyzed in triplicate. THg concentrations reported in this paper are presented as means ±1 standard deviations.

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Vertical and temporal patterns of GEM in the snowpack and the atmosphere

An example of time series data for GEM and CO₂ collected on 1 March from 12:00 p.m. to 01:00 p.m. is illustrated in Fig. 1a. These data show one full sampling cycle through the seven inlets, with measurements starting above the snow surface (sampling height 245 cm, i.e. 83 cm above the snow surface at this time). All GEM data collected in SIA and discussed in this study were combined to evenly-spaced 30 cm depth intervals down from the top of the snowpack; e.g. the 0-30 cm layer contains data when inlets were sampling at that depth range; in the same way we summarized all other depth layers. This representation of data is different from previous publications resulting from the NWT snow tower (Williams et al., 2009) but is appropriate for GEM, a reactive gas experiencing fast production processes in the upper layer of the snowpack (see below).

The GEM concentration in the ambient air above the snowpack (i.e. the 245 cm inlet) shown on Fig. 1a is 1.2 ng m⁻³, GEM levels increased in the upper layer of the snowpack (0-30 cm depth the snow surface), and GEM levels then decreased steadily as the sampling sequence progressed downwards into the snowpack. Corresponding CO₂ concentrations were approximately 389 ppm in ambient air, which then increased with depth to peak concentrations of 3390 ppm in the lowest snowpack layer (i.e. 150–180 cm depth). This example demonstrates the performance and reliability of the measurements; for example, the CO₂ concentration gradient follows patterns that have been well characterized for this alpine snowpack (Liptzin et al., 2009); very similar GEM and CO₂ snowpack profiles were seen in the 2011-2012 data. Please also note that both ambient levels of GEM and CO2 are close to global ambient background concentrations, highlighting that measurements were not subjected to leaks or 25 contamination.

The data from air withdrawn from the snowpack show both concentration enhancements and depletion of GEM compared to ambient air levels during this 70-min sampling cycle. GEM enhancements, as high as 6 ng m⁻³, or equivalent to approximately

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five times ambient air levels, must reflect a source or production of GEM in the snow-pack. Similarly, lower-than-ambient GEM levels in deeper snowpack with levels near the snow-soil interface during this day completely depleted in GEM (i.e. GEM below DL) must be due to removal or destruction of GEM.

In Fig. 1b, we show the time series of GEM concentrations at six levels in the snow and in the atmosphere above the snow surface from 27 to 28 February 2009. Snow-pack height during this period was 154 cm, and consequently all six inlets except the ambient air inlet at 245 cm (black line) reflect SIA GEM levels. During this time period, atmospheric GEM remained relatively stable at ~ 1.2 ng m⁻³. Pronounced enhancements of GEM concentrations were observed within the top 60 cm of the snowpack, and these exhibited strong diel cycles. Diel cycles of GEM enhancements coincide well with the solar irradiation cycle (grey line in Fig. 1b), with maximum GEM enhancements observed at midday. Deeper in the snowpack, particularly close to the soil-snow interface, GEM was always depleted compared to atmospheric values and showed little temporal variability. Figure 1b confirms the depth profile of GEM shown in Fig. 1a, but demonstrates that GEM enhancement near the snow-air interface exhibit strong temporal patterns. GEM concentrations deeper in the snowpack show much smaller temporal variability compared to upper snowpack levels, and these might be related to diffusion from above snow layers (see below).

The GEM patterns in SIA described in Fig. 1 were reproducible through the entire measurement campaign. Figure 2a and b show a summary of all available GEM data collected between 2 February to 5 May 2009 (marked DOY 37 to DOY 122) averaged by hour of the day (Fig. 2a) and by snow depth intervals (30 cm intervals, Fig. 2b).

Figure 2 illustrates that atmospheric GEM concentrations showed little variation during this winter-spring sampling season $(1.3\pm0.1\,\mathrm{ng\,m^{-3}};\,\mathrm{mean}\,\pm\,\mathrm{stdev})$. The ambient GEM levels are in the lower range of values reported from 22 rural sites in the northern hemisphere (i.e. $1.7\pm0.3\,\mathrm{ng\,m^{-3}}$) (Valente et al., 2007), and also lower than the value of $1.6\pm0.2\,\mathrm{ng\,m^{-3}}$ (mean atmospheric total gaseous Hg) collected from 11 sites of the Canadian Atmospheric Mercury Network (CAMNet) between 1995 and 2005

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(Temme et al., 2007). Simultaneous GEM measurements in the Sierra Nevada mountains at 1920 m a.s.l. (Sagehen Station, CA) during spring 2009 showed GEM levels of 1.4 ± 0.2 ng m⁻³ (Faïn et al., 2011), and GEM concentrations observed at the closeby Storm Peak Laboratory in the Rocky Mountains (3200 m a.s.l., CO) during spring of 2008 averaged 1.6 ± 0.3 ng m⁻³ (Faïn et al., 2009). This comparison illustrates the remote and clean-air characteristics of the Niwot Ridge research site.

Figure 2a confirms the pronounced diel concentration cycles of GEM in the snow air in the uppermost snowpack layers. The lowest two snowpack layers, on the other hand, showed little diurnal fluctuation in GEM concentrations. These patterns are also reflected in Fig. 2b by the largest variability of GEM measured in the top snow layers. The most pronounced diurnal cycle, as well as overall highest GEM enhancement, was observed in the top snowpack layer, where GEM concentrations peaked at 01:00 p.m. While diurnal patterns of GEM followed similar diurnal pattern of solar radiation (Fig. 2a), the peak of GEM enhancements was slightly shifted in regards to maximum solar radiation; peak solar radiation occurred at ~ 12:00 a.m., while peak GEM levels in the top 0-30 cm occurred around 01:00 p.m. The diurnal GEM peak was further delayed deeper in the snowpack, e.g. in the layer 30-60 cm below the surface GEM peaked at ~03:00 p.m. These patterns suggest that interstitial air transport processes, which redistribute GEM from the upper snow levels towards deeper snow layers, are involved in determining these patters (see below).

The general features shown in Fig. 2 are summarized below, and underlying reasons are discussed in detail in Sects. 2 and 3. First, from the surface snow to 60 cm depth, GEM in snow interstitial air was consistently enhanced compared to atmospheric levels, both during nights and days. The data from the 60-90 cm depth interval showed a transition where GEM was higher during midday and lower during nights compared to atmospheric values. Below 90 cm depth, we observed that GEM concentrations were consistently below those found in ambient air, independent of daytime or nighttime. At the lowest levels (from 120 cm depth to the snow-soil interface), GEM was found to be rather constant (~0.4 ng m⁻³) during almost the entire campaign, except during two

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events (DOY 49-51, and DOY 60-63), when GEM concentration dropped below the instrument detection limit at this depth.

In Fig. 3, all data measured during the 2009 experiment within the snowpack (between 17-18 individual 10-min measurements per day at each level) are combined 5 in a color contour graph to show in detail the spatial and temporal evolution of GEM in the snowpack. Continuous vertical patterns were obtained by linear interpolation of GEM levels measured from adjacent inlets. Due to changing snowpack height (shown as blue line in the Figure), the depth of the upper snowpack sampling inlet varied from only a few cm to almost 30 cm depth below the snow surface at times. During five periods (gaps in Fig. 3), GEM sampling was interrupted due to other experiments performed and instrument maintenance. This figure visualizes the GEM production in surface snow with its strong diurnal concentration fluctuations and the depletion of GEM in the deeper snowpack.

The behavior of GEM in the snow air as revealed by Figs. 1 to 3 is likely driven by a combination of different processes, including (i) chemical or biological processes leading to destruction and/or production of GEM, (ii) GEM diffusion between snow layers, (iii) natural ventilation, and (iv) advective flow induced by the sampling procedure. While we discuss points (i) to (iii) in the sections below, Fig. 1 suggests that advective flow induced by the sampling procedure is likely too low to significantly impact measurements. GEM levels during consecutive 2.5 min measurements are stable (Fig. 1), including at the surface, indicating that advection of air from different depths or from the atmosphere was minor. Previous snowpack gas studies using this system showed similar results, i.e. there was no evidence of significant sampling induced snowpack ventilation at a total rate of 3.21 min⁻¹ for both NO_x and O₃ measurements (Helmig et al., 2009; Seok et al., 2009).

GEM production in the upper snow layers

In the upper snow layers GEM concentrations were always enhanced relative to levels in the atmosphere above, both during daytime and nighttime throughout the

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measurement campaign. The snow layer right below the surface always exhibited higher GEM as compared to lower snow depths and to ambient air; it is therefore not possible that the enhanced GEM levels originated from diffusion or advection from either above or below. Consequently, the GEM concentration enhancements in the 5 near-surface snow layers must be associated with in-situ production of GEM in the surface snowpack. Depth patterns indicate that GEM production was strongest in the snow near the surface, that GEM production peaked slightly after midday, and that amplitudes of GEM fluctuations were dampened in deeper snow layers and further delayed in their timing. The delay of GEM diurnal maxima in the 30-60 cm and 60-90 cm depth layers suggests that transport plays a determining role in the GEM enhancement in these layers as this time lag would not be expected if in-situ production was the main source of GEM in these layers. Active Hg-related photochemistry has been observed before to depths of ~60 cm or limited to the top ~3 cm depending on the investigated snowpack (Durnford and Dastoor, 2011). We propose that GEM production at the NWT Soddie site mainly occurs in the 0-30 cm depth layer, and that the upper snowpack is the major source of GEM enhancements that was also observed in the deeper snowpack.

In-situ production of GEM is attributed to photoreduction of Hg(II) to GEM, and has been reported to be facilitated by both visible (400-750 nm) (Poulain et al., 2004; Johnson et al., 2008) and ultraviolet-A radiation (320-400 nm) (Poulain et al., 2004; Faïn et al., 2007). Others suggest that photoreduction is enhanced by ultraviolet-B radiation (280-320 nm) (Poulain et al., 2004; Faïn et al., 2007; Dommergue et al., 2007), with 305 to 320 nm being the most important bandwidth (Dommergue et al., 2007). High UV loads at high-altitude sites, particularly in areas of low cloud cover such as in the Rocky Mountains, may particularly favor photochemical reduction of Hq(II). It has been suggested that photoreduction of oxidized Hg(II) in snow is driven by direct photodissociation of mercuric complexes such as chlorocomplexes and hydroxocomplexes (Dommergue et al., 2003b), and that photoreduction may be promoted by reductants (Lalonde et al., 2002, 2003; Dommerque et al., 2007). Such possible reductants of

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oxidized Hg(II) are hydrogen peroxide (H_2O_2) in pH-neutral snow (Lahoutifard et al., 2006), the hydroperoxyl radical (HO_2°) (Dommergue et al., 2003b, 2007), which also could be produced at night (Ferrari et al., 2004b), molecules related to humic acids (Dommergue et al., 2007), and sulphite-based compounds (Munthe et al., 1991; Van Loon et al., 2000). Laboratory investigations by Bartels-Rausch et al. (2011) showed that the presence of benzophenone and of oxalic acid significantly enhances the release of GEM from ice during irradiation, whereas humic acid is less potent to promote the reduction.

Importantly, mean GEM levels in the top layers of the NWT snowpack remained enhanced above atmospheric background throughout the night (Fig. 2b). Most laboratory and flux chamber experiments (Lalonde et al., 2003; Dommerque et al., 2007) and observations of GEM within the snowpack (Dommerque et al., 2003b; Poulain et al., 2004; St. Louis et al., 2005) indicate that the presence of solar radiation is required for photoreduction and evolution of GEM. The Niwot Ridge data pose the question if the nighttime elevated GEM levels stem from the retention of GEM in the snowpack that was formed during the day, or if there is a possibility that reduction of Hg(II) may also be possible in the dark. This production could be from a continuation of photolyticallyinitiated reactions, i.e. be initiated by a UV-B pulse and continue in the dark for a certain time (Lalonde et al., 2003), or through a reaction requiring no insolation at all (Ferrari et al., 2004b). Numerical simulations of our data using Fick's second law of diffusion indicates that diffusion alone would result in lower GEM levels in the top snow levels (data not shown) at night due to equilibration with ambient air. This diffusion model did not even account for additional mixing in the snowpack such as by advection and convection, consequently it would give a low limit of the gas transport rate inside the snowpack. The modeling results suggest that additional nighttime sources of GEM may be present, and we propose that further studies should focus on nighttime GEM production mechanisms.

To further evaluate the role of environmental parameters, particularly solar radiation, in controlling GEM production in surface snow layers, we investigated in detail a

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20-days period in late winter (from DOY 82 to 102). Figure 4 compares GEM in ambient air (at the 245 cm inlet, or ~80 cm above the snow surface at this time) within the uppermost sampling layer in the snowpack (0-30 cm depth interval). The total snowpack depth was initially stable at ~145 cm from DOY 82 to 85, but increased to ~160 cm from DOY 86 to 88 as a precipitation event occurred during these days. The snowpack depth then remained stable (i.e. 163 ± 4 cm) until DOY 102. Consequently, the inlet sampling the 0-30 cm depth interval changed from the 120 cm to the 150 cm height above ground inlet, which resulted in the sampling depth decreasing from ~25 cm to ~ 10 cm depth from DOY 86 to 88 (Fig. 4, dashed line). Figure 4 also shows wind speed, incoming solar radiation, precipitation amount, and snow temperature.

GEM concentrations in the snow exhibited a diel pattern, with maxima as high as 8 ng m⁻³, which generally occurred about 1 h after the solar irradiation maximum. While GEM in the top snowpack layer was above atmospheric values during most times, including at night, during two nights (DOY 83 and 90) GEM levels dropped to slightly below ambient air levels. The periods of lowest early-morning GEM levels corresponded to periods with high wind speeds. Highest nighttime GEM levels where related to periods with low winds (e.g. DOY 86, 93, or 95). The fact that GEM in surface snow even dropped below ambient air GEM levels during two occasions with high winds (DOY 83 and 90 with wind speeds above $5 \,\mathrm{m\,s}^{-1}$) can possibly be attributed to the mixing with air from deeper in the snowpack with GEM at below-ambient concentrations. The fact that lowest GEM was observed on DOY 83 when the sampling inlet was located deeper, i.e. at 25 cm depth, supports this conclusion. Consequently, in addition to chemical formation and destruction, and diffusive transport, advection from wind pumping influences snowpack GEM levels. This is in agreement with the findings of Seok et al. (2009), who showed that neglecting wind pumping at NWT resulted in considerable underestimation of CO₂ fluxes that were calculated by diffusion theory (36 % on average).

Figure 4 further shows that on three days (DOY 86, 91 and 94) GEM in the 0-30 cm layer increased to even more elevated levels, and that these increases coincided with or occurred shortly after fresh snowfall events. A recent study at Sagehen Basin, a

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high-elevation watershed in the Sierra Nevada mountains in California, showed that wet deposition (precipitating snow) was the major Hg deposition pathway during winter (Faïn et al., 2011). The NWT data suggest that fresh snow provides a new reservoir of photoreducible Hg(II) and that highest surface snow GEM levels are hence linked to the deposition of new snow. Notably, these elevated GEM levels occurred during periods with relatively low solar radiation (as snowfall was related to cloudy conditions), further suggesting that photochemical production of GEM is not radiation-limited at this site. The GEM concentration in the upper snow layer correlates nicely with the precipitation amount observed the same day or on the previous day (Fig. 5). This correlation is progressively lower with increasing number of days after the precipitation occurred, and is finally lost four days after a precipitation event as shown in the regressions that analyze the daytime GEM levels in the 0-30 cm depth layer as a response of fresh snowfall. A similar analysis was conducted on the winter 2011/2012 data. That data record, spanning from earlier to later in the season, however having overall a more intermittent coverage and fewer snow precipitation events for consideration, showed similar tendencies, i.e. elevated SIA GEM levels during and immediately following snow fall events.

These results can be related to previous work conducted by Lalonde et al. (2003) at a mid-latitude Canadian site, which showed a 40 % loss of THg concentrations in the surface snow within 24 h of its deposition. Our data show that re-emission patterns occurred in the top NWT snowpack, confirming the importance to consider photo-induced reduction of Hg(II) in snow and subsequent volatilization in watershed mass balance studies.

3.3 Low GEM levels in the deep snowpack

Figures 1 to 3 show that GEM levels decreased with increasing depth (Fig. 2b) and the consistent occurrence of below ambient GEM concentrations with levels as low as 0.1 ng m⁻³ between DOY 40 and 60 at the lowest inlet located 10 cm above the snow-soil interface. These patterns illustrate that there must be a sink for GEM in the deep

layers of the snowpack throughout the entire measurement campaign. GEM concentration gradients average about $0.02\,\mathrm{ng\,m^{-3}}$ cm⁻¹ in the upper snow layers and become smaller in the deepest snow layers. The GEM gradients imply a vertical transport of GEM from the snowpack layer with its maximum concentration to snowpack layers where concentrations are lowest. Further indication of vertical GEM transport is the temporal delay of peak diurnal GEM concentrations and the decreasing magnitudes of diel patterns with increasing depth. At 135 cm below the snow surface, where GEM concentrations averaged about $0.4\,\mathrm{ng\,m^{-3}}$, diel variability was no longer evident.

There are several possible processes that might drive the GEM depletion in the deeper snowpack. Adsorption of GEM onto ice surfaces could be a possibility, however it has been shown that this process is weak at environmental temperatures (Bartels-Rausch et al., 2008). The adsorption energy of GEM on snow was found to be $\sim 61 \, \text{kJ} \, \text{mol}^{-1}$ (Ferrari et al., 2004a), which is too low to explain depletion of GEM in the deep snow interstitial air. Hence, the low GEM levels in the lower snowpack are evidence for a chemical, physical, or biological sink for GEM located in the snowpack or in the soils underlying the snowpack.

In order to assess if this GEM sink was driven by processes in the lower snowpack layers or by processes occurring in the soil underneath the snow, we investigated in detail the vertical evolution of GEM flux in the snowpack. If soil process were a determining sink, then GEM fluxes through the snow layers above the soil interface would be expected to be constant with height. Consequently, we hypothesize that a decreasing GEM flux from the surface to the bottom of the snowpack would be indicative of a GEM removal mechanism that is located within the snowpack. Conversely, a constant GEM flux through the snowpack would indicate that the snowpack itself is rather inert and that decreasing GEM levels at lower levels are mainly driven by GEM depletion occurring in the underlying soil.

GEM vertical concentration gradients from the multiple inlet measurements allow for calculation of vertical diffusive GEM fluxes through the snowpack using Fick's first law. This approach has been previously applied for CO₂, ozone, and NO_x at NWT, and its

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where $T_0 = 253.16\,\mathrm{K}$, $P_0 = 1013.25\,\mathrm{mbar}$ (STP), T and P are values of temperature and pressure in the snowpack, φ is the snow porosity, τ is the snow tortuosity, and D the diffusion coefficient of the considered gas at STP. It is important to note that the gradient flux approach (Seok et al., 2009) based on Eq. (1) contains approximations, notably due to its 1-D structure which does not accurately represent the spatial heterogeneities of the snowpack. In addition, uncertainties in the snow physics parameters porosity and tortuosity affect the flux calculations.

An elegant way to investigate the changes in GEM fluxes with depth is to normalize GEM gradients to the measured gradients of CO_2 . CO_2 is exclusively released by wintertime respiration processes in the soil underneath the snow (Liptzin et al., 2009). Assuming a constant CO_2 source at the bottom of the snowpack, then changes in CO_2 snowpack gradients are driven by changes in snow physics and wind-induced ventilation. These processes would affect GEM fluxes in the same way, thus the GEM/ CO_2 flux ratio will effectively cancel out uncertainties in the snowpack flux calculation. The GEM/ CO_2 flux ratio, as defined in Eq. (2), is directly related to measured Δ GEM and Δ CO_2 , the gradients in GEM and CO_2 concentrations observed between two defined depths:

$$\frac{F_{\text{GEM}}}{F_{\text{CO}_2}} = \frac{D_{\text{GEM}}}{D_{\text{CO}_2}} \times \frac{\Delta_{\text{GEM}}}{\Delta_{\text{CO}_2}},\tag{2}$$

with D reflecting the diffusivity of both gases, and the ratio of $D_{\rm GEM}/D_{\rm CO_2}$ expected to be constant. Changes in the ratio defined in Eq. (2) with snowpack depth would reflect changes in GEM fluxes that cannot be attributed to snow physics or wind-induced ventilation, and thereby allow to assess GEM chemical sinks (or sources) within the

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snowpack. Figure 6 shows daily averaged $\Delta \text{GEM}/\Delta \text{CO}_2$ ratios calculated for three different depth gradients: inlets 120 to 90 cm, 90 to 60 cm, and 60 to 30 cm, calculated for a 10-day period (DOY 92–102). Note that values reported in Fig. 6 have been all normalized to the ratios observed in the top 30–60 cm layer below the snow surface. Thus, the normalized $\Delta \text{GEM}/\Delta \text{CO}_2$ ratio values are positive (Fig. 6), while the $\Delta \text{GEM}/\Delta \text{CO}_2$ ratios were negative due to opposite directions for GEM and CO₂ fluxes within the snowpack. During this time, the 120 cm inlet was about 40 cm deep. Consequently, the photolytic zone was above the uppermost depth interval considered in this analysis. Soil moisture was constant during this time interval, and thus a relatively constant flux of CO₂ from the soil would be expected during these conditions (Liptzin et al., 2009).

Figure 6 shows clear decreases of the $\Delta \text{GEM}/\Delta \text{CO}_2$ ratio with depth. This pattern is a strong indication that GEM fluxes through the snowpack are not constant with height, and that GEM produced in the upper layer of the snowpack is destroyed within the lower snowpack as it diffuses to lower snowpack depth.

To our knowledge, this analyses shows for the first time evidence of light-independent (dark) destruction of GEM in a mid-latitude snowpack, a process which previously has only been observed in polar snow (Dommergue et al., 2003b, 2012; Ferrari et al., 2004a; Faïn et al., 2008). With more than 70 days of observations (Fig. 3) at our site located further south (40° N), the NWT study demonstrates that this GEM depletion chemistry is more universal and persistent than previously thought.

The GEM loss observed in the SIA in the deeper layers of the NWT snowpack must involve a chemical, physical, or biological sink within the snow. Oxidants leading to GEM destruction in the snowpack are not yet clearly identified. At Summit in Greenland, Faïn et al. (2008) observed a complete depletion of GEM at 200 cm depth during early June, and the authors suggested that the snowpack may act as a dark source of Br₂ which subsequently oxidizes GEM. This mechanism involves dark oxidation of Br⁻ ions by ozone at the surface of the snow crystals as observed by Oum et al. (1998) during laboratory measurements. But it is unclear to what degree bromine species play a role in interior continental snowpacks. Ozone is another potential oxidant for GEM, and

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a wide range of rate constants for the reaction of gas-phase Hg with ozone is reported in the literature. However, it is very unlikely that oxidation of GEM by O_3 proceeds via homogeneous gas-phase reaction; heterogeneous reactions on surfaces are required to induce the collisions necessary to enhance the rate of this reaction by making the formation of the intermediates and products more favorable (Subir et al., 2011). Such heterogeneous reaction conditions may well exist in snowpacks. Ozone in the Niwot Ridge snowpack declines at a fast rate with depth, resulting in less than 10 % of ozone remaining \sim 50 cm below the surface (Bocquet and Helmig, 2007); similar ozone gradients were again observed during this campaign (data not shown). If ozone was the main GEM oxidant, then the upper snowpack layers would exhibit the strongest GEM sink, and GEM loss from ozone would be lower in the deeper snow. The GEM gradients do not point towards this direction, although in theory GEM production could supersede its oxidation rate in the upper snowpack layers.

NO shows an upward flux from the soil through the snowpack, implying that biogeochemical processes in the subnival soil are the dominant NO source (Helmig et al., 2009). While diffusing upward, a portion of NO is converted to NO_2 , with ozone being one likely reactant. Interestingly, enhanced NO concentrations in the SIA are co-located with GEM depleted depths. Previous studies have demonstrated that NO_2 is not a potential oxidant for GEM in gas phase. However, destruction of GEM was recently observed at Dome Concordia, Antarctica, both in SIA and 20 cm above the snow surface. These episodes coincided with periods when NO_x emission from the upper photolytic snow layers peaked in late afternoon (A. Dommergue, personal communication, 2012). Although not understood yet and still speculative, these observations suggest to take a closer look at chemical interactions between GEM and NO.

Another interesting aspect of this data is that we did not observe complete GEM depletions as previously reported from SIA measurements at polar latitudes, either above perennial firn in Greenland or Antarctica (Faïn et al., 2008; Dommergue et al., 2012), or above frozen coastal soils at polar latitudes (Ferrari et al., 2004a). At NWT, GEM generally remained close or above 0.4 ng m⁻³ in the deepest snow layers, similarly to

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observations reported during a 4-days study at the sub-arctic location of Kuujjuarapik (Dommergue et al., 2003b). One possible reason for this could be a contribution of GEM emitted from the underlying soils as found by Nelson et al. (2008) who detected upward mobility of isotopically-labeled Hg from soils into overlying snow.

Snowpack temperature is notably different between the NWT snowpack and the polar locations. At NWT, the temperature of the deep snow layer and the soil underneath the snowpack remained relatively stable and close to 0°C during the entire campaign. Such warmer conditions favor quasi-liquid layer chemistry, which consequently could be more important in the warmer NWT snowpack compared to glacial ice caps. It is possible that quasi-liquid layer chemistry promotes GEM oxidation with faster rates of reaction. In addition to more favorable aqueous chemistry, the quasi-liquid layer may also favor the presence of biological processes. The warm NWT snowpack notably supports bacterial, algal, and fungal communities which potentially affect trace gas chemistry (Williams et al., 2009). Interestingly, warm soil temperatures also result in a large thermal gradient at NWT, and a vertical gradient in diurnal growth and shrinking of the quasi-liquid layer around snow grains. A recent study showed that a freezing acidic solution containing nitrite (250 µM) or hydrogen peroxide (2.2 µM) can oxidize dissolved elemental mercury in the dark (O'Concubhair et al., 2012). These authors report laboratory evidences of freeze-induced reaction of dissolved gaseous mercury to form Hg(II) species. Such freezing conditions could exist almost daily in a mid-latitude snowpack given its diurnal cycle of top-bottom thermal gradients.

Although we report for the first time dark oxidation of GEM in a mid-latitude snowpack, there is still a lack of understandings about the GEM oxidation processes observed above and inside the snowpack, and the mechanisms involved within the NWT snowpack remain unclear. More detailed laboratory kinetic studies of GEM oxidation using ice/snow surfaces are thus highly warranted.

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3.4 Does GEM oxidation increase Hg pool stored in snowpacks?

The patterns of GEM dynamics in the NWT snowpack indicate that part of the divalent Hg(II) species deposited to the surface of the snowpack are reduced to GEM, which then is transported both upwards to the atmosphere and downward in the snowpack, where it subsequently is oxidized and potentially stored as divalent Hg(II). One key question is thus if these chemical processes and vertical transport processes affect concentrations of total Hq species in the snowpack? To address this question, two snow pits were sampled at the beginning and at the end of the snow season, on 9 March and 27 April, respectively, for THg determination (Fig. 7). Using snow density profiles carried out in these two pits, we estimate total Hg loads of the snowpack at 4.0 µg m⁻² in early March, and at 5.8 µg m⁻² in late April.

Figure 7 shows depth patterns of THg for the different snow pits. In general, snow Hg concentrations did not show the depth profile that would be expected based on GEM concentrations gradients and diffusion processes; for example, surface snow layers were expected to be depleted in THq due to photoreduction and subsequent losses as GEM, while deeper snow layers are expected to be enriched in THg due to oxidation of GEM and deposition in snowpack as divalent Hq(II). However, the lack of a vertical signal in THg distribution can be explained by a simple calculation. The GEM gradient flux calculations above indicated a flux of approximately 0.05 ng m⁻² h⁻¹ propagating downward from the upper snow layer (averaged value over the entire campaign), decreasing to lower values towards deeper in the snowpack. Assuming that the entire GEM flux is converted and stored as divalent Hg species in deeper snow layers, we would expect an increase of $\sim 60 \, \text{ng m}^{-2}$ of Hg to the snowpack load between 9 March and 27 April. The mass of vertically redistributed of GEM hence is ~ two orders of magnitude smaller compared to the total snowpack Hg loads.

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Gaseous elemental mercury concentrations in the interstitial air in this deep, seasonal, mid-latitude Rocky Mountain alpine snowpack exhibited a highly dynamics cycling. The GEM patterns observed at NWT were complex, involving both production and destruction of GEM within the snowpack, and transport by diffusion and advection driven processes.

Near the snow-air interface, GEM showed distinct diurnal cycles with concentration maxima observed during midday that were associated with solar irradiance. During low wind periods, GEM in surface snow layers remained significantly above ambient air levels not just during daytime, but also at night, which may indicate a potential GEM production in the dark. Further studies should focus on evaluating the mechanisms involved in nighttime GEM production. Interestingly, highest GEM surface production and re-emission occurred after fresh snowfall and possible wet deposition of photoreducible mercury to the snowpack. These results confirm the importance of photo-induced reduction of Hq(II) in snow and subsequent volatilization, and support the notion that snowpacks reduce the effect of atmospheric mercury deposition to watersheds due to re-emission fluxes prior to snowmelt.

In the deep layers of the NWT snowpack, GEM concentrations were consistently below those found in ambient air, independent of daytime or nighttime. At the lowest levels (from 120 cm depth to the snow-soil interface). GEM was found to be rather constant $(\sim 0.4 \, \text{ng m}^{-3} \text{ during almost the entire campaign})$. The analysis of the vertical change of ΔGEM/ΔCO₂ concentration gradient ratios indicated that GEM destruction occurred in the deeper snowpack layers. The chemical or biological mechanisms involved in this destruction remain unclear, and detailed kinetic studies of multiphasic GEM oxidation using snow and ice surfaces are warranted to improve our understanding of such field observations. Specific experiments could also be helpful in linking photochemical cycles of Hg and other compounds (e.g. NO_v) that have been observed at elevated concentrations within the snowpack.

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Observations of photolytic GEM production in surface snow and GEM destruction in deeper snow layer led us to investigate the possibility for a net transfer of mercury from upper to lower snow layers in the NWT snowpack. Our study shows that transport processes and redox reactions were too small to drive significant vertical redistribution of total Hg in the snowpack. However, further studies should quantify not only total Hg, but various forms of soluble Hq, particle bound Hq (PHq), and bioavailable Hq to assess the importance of such vertical redistribution. While soluble mercury could be reduced more easily, PHg may accumulate in snowpacks and not be subject to photo-reduction and transport.

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Interactive Discussion



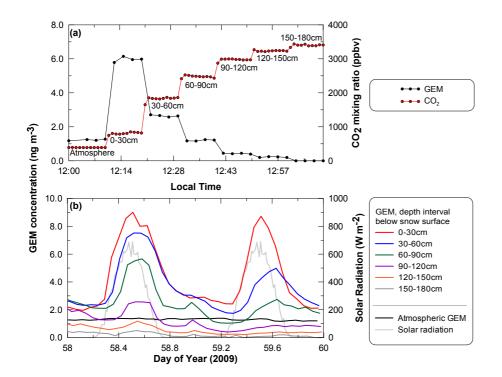


Fig. 1. (a) Time series of GEM and CO₂ concentrations during one sampling cycle from the snowpack gradient sampling tower on 1 March 2009. This 70 min sampling started with 10 min of measurements in ambient air above the snow, and then moved downward in 10 min intervals to six depths in the snowpack. Total snowpack depth at this time was 162 cm. (b) GEM concentrations collected at the six depths in the snowpack and in the atmosphere above the snow (black line) from 27 to 28 February 2009. Snow height was 155 cm during this period. The grey line shows the averaged diurnal solar irradiation cycle from DOY 37-122.

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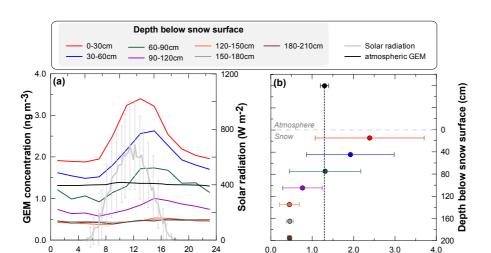


Fig. 2. Snow air GEM data from DOY 37 to 122, 2009, combined into 30 cm depth intervals down from the top of the snowpack. **(a)** Diurnal evolution and averaged incoming solar radiation in the depth profile. **(b)** 24 h-averaged vertical patterns and standard deviation for the respective depth layers. The dashed vertical line shows the mean ambient atmospheric GEM concentration.

GEM concentration (ng m⁻³)

Hour of the day

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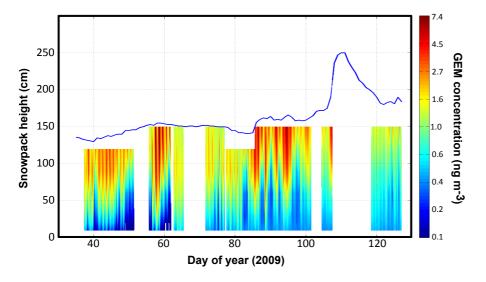


Fig. 3. Color contour plot of GEM in the snowpack. The upper edge (blue line) of the colored area indicates the snowpack height, the x-axis the day of year 2009, and the color log scale shows the mixing ratio of GEM.

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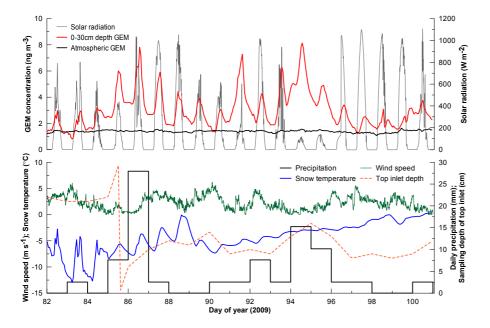


Fig. 4. GEM concentration in the snow interstitial air measured in the 0–30 cm depth top snow layer from day of year 82 to 102 (red line). During this period, the depth of this inlet decreased from 22 cm to 13 cm (dashed orange line). Atmospheric GEM (black line) was stable with an average value of 1.4 ± 0.1 ng m⁻³. Wind speed (green line), solar radiation (grey line), and daily precipitation collected at the Soddie SNOTEL station are also reported.

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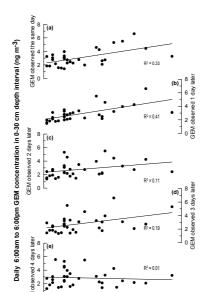


Fig. 5. GEM concentration observed in the upper snowpack layer (0–30 cm depth) from 06:00 a.m. to 06:00 p.m. and averaged daily, as a function of the daily amount of precipitation (in liquid water equivalents) observed the same day **(a)**, a day before **(b)**, two days before **(c)**, three days before **(d)**, and four days before **(e)**. Individual data and their best fit linear regression analysis result from the entire measurement campaign (i.e. from DOY 37 to 128) are plotted.

Daily precipitation (mm)

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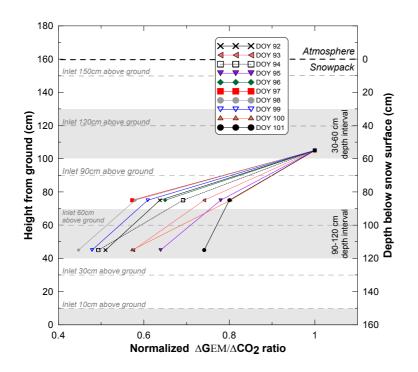


Fig. 6. Evolution of daily $\Delta GEM/\Delta CO_2$ ratio with depth calculated over three inlet intervals: 120-90 cm above ground (i.e representative of 30-60 cm layer below snow surface), 90-60 cm above ground (i.e representative of 60-90 cm layer below snow surface), 60-30 cm above ground (i.e representative of 90-20 cm layer below snow surface) for 10 days (labeled by day of year (DOY)). All ratio values were normalized to the ratio observed in the top 30-60 cm layer below the snow surface.

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