

Dynamics of snow-air mercury exchange at Ny Ålesund during springtime 2011

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Abstract. Continuous time series of flux measurements were carried out in Ny Ålesund, Spitsbergen, during a springtime field campaign from 31 of March to 3 of May, 2011. Flux measurements were integrated with mercury speciation analysis in order to understand the fate of mercury during atmospheric elemental gaseous mercury depletion events (AMDEs). Moreover a methodology for quality assurance of flux measurements is presented. Measurements were made at Gruvebadet, 1 km west from the Ny-Ålesund village (78°55' N, 11°56' E) at an elevation of 18 m above sea level. Ambient concentrations of gaseous elemental mercury, divalent reactive gaseous mercury and particulate phase mercury were semicontinuously measured using an integrated Tekran system. Mercury depletion events were observed during the month of April and were characterized by an incomplete mercury destruction. Indeed Hg⁰ concentration was never below 0.49 ng m⁻³.

Keywords: AMDEs, mercury speciation, elemental mercury fluxes, Arctic

Introduction

Mercury pollution is a concern for the global environment because it can be transformed in methylmercury, a potent neurotoxin that affects human and wildlife development and health. The most abundant form of mercury in the atmosphere, with a global atmospheric mean concentration of about 1.6 ng m⁻³ (Selin, 2009), is elemental mercury (Hg⁰). The oxidation of atmospheric mercury can occur extraordinarily fast, as well-documented Atmospheric Mercury Depletion Events (AMDEs) have been highlighted in both the Arctic troposphere and in Antarctica during springtime (Dommergue et al., 2010; Ebinghaus et al., 2005; Hedgecock et al., 2008; Sprovieri et al., 2002; Sprovieri et al., 2005a; Steffen et al., 2008). During AMDEs Hg⁰ decreases rapidly while divalent mercury (Hg^{II}) spikes (Sprovieri et al., 2005). Hg^{II} is subsequently either deposited to snow and ice surfaces or associated with aerosols (HgP) (Steffen et al., 2008).

Few studies based on Hg⁰ flux measurements in Polar regions are available. Some are based on chambers method (Ferrari et al., 2005; Sommar et al., 2007) and very few on flux-gradient method (Cobbett et al., 2007; Steen et al., 2009). This paper presents a continuous time

series of flux measurements performed at Ny-Ålesund, Svalbard, in an extensive experimental field campaign during the period 31 March – 3 of May 2011. Flux measurements were integrated with mercury speciation analysis in order to understand the fate of mercury during AMDEs. Moreover a methodology for quality assurance of flux measurements is presented.

Materials and Methods

Flux of elemental mercury was measured using a micrometeorological technique, namely the flux-gradient aerodynamic method. It is an indirect method used to measure flux of scalars in the constant flux layer above homogeneous surfaces when a fast response detector to measure the scalar concentration is not available. The aerodynamic method rely on the measurement of the mean vertical gradient of Hg⁰ that is related to Hg⁰ flux by the following equation:

$$F = -K \frac{\partial \bar{C}}{\partial z} \quad (0.1)$$

where F is the elemental mercury (Hg⁰) flux (ng m⁻² s⁻¹), K is the turbulent transfer coefficient, or eddy diffusivity,

($\text{m}^2 \text{s}^{-1}$), and $\overline{\partial C / \partial z}$ is the time averaged vertical gradient of the Hg_0 (ng m^{-4}). The turbulent transfer coefficient is defined by the Monin – Obukhov similarity theory for the surface layer (Monin and Obukhov, 1954). According to similarity theory, under assumptions of stationarity and horizontal homogeneous conditions, vertical gradient of a conservative quantity, when normalized for the appropriate scaling variable, becomes universal function of height z and Obukhov length (L). This function was defined using the formulation of Dyer (1974). The vertical gradient of mercury concentration was measured at 1.7 m and 0.3 m above snow pack using a three-way switching valve and a dedicated Tekran 2537a mercury analyser. The turbulent transfer coefficient was estimated using wind velocity, friction velocity and heat flux estimated through the data measured by a sonic anemometer (model Gill HS-50). Measured fluxes were corrected for the effect on mercury concentration of air density fluctuations due to heat and water vapour fluxes (Webb et al., 1980). Heat and water vapour fluxes were measured using the eddy covariance technique and the open path gas analyser Li-cor 7500. Fluxes of mercury were quality checked using the integral turbulence test and stationarity tests (Foken and Wichura, 1996). Besides these tests we applied a test to evaluate the fulfilment of theoretical requirements of the flux-gradient method. In particular we compared the measured wind profile with the profile predicted by the Monin-Obukhov similarity theory (Monin and Obukhov, 1954). Altogether we discard 16% of the estimated mercury fluxes for bad quality.

Mercury speciation was performed by a Tekran 2537a equipped with 1130 and 1135 speciation units for the determination of Hg_0 , reactive gaseous mercury (HgII), and fine particulate mercury (HgP), respectively (Landis et al., 2002).

Results and Discussion

During the experimental campaign we observed a series of Atmospheric Mercury Depletion Events (AMDEs), that were concentrated in the period 9 – 14 of April, and a short AMDE on the 18th of April was also observed. Flux measurements started the 13th of April at 17:00. Fluxes of gaseous mercury showed on average a little net deposition ($-0.24 \text{ ng m}^{-2} \text{ h}^{-1}$) in the period 13 of April – 2 of May with a maximum net deposition of $-41 \text{ ng m}^{-2} \text{ s}^{-1}$ and a maximum emission of $40 \text{ ng m}^{-2} \text{ h}^{-1}$ measured both the 20th of April (Fig. 1). The average flux value during the time interval 13 – 14 April, when two depletion events occurred, was $-1.02 \text{ ng m}^{-2} \text{ h}^{-1}$, with a maximum of $-9.3 \text{ ng m}^{-2} \text{ h}^{-1}$. Mean flux value during the last AMDE (18th of April) was negative ($-0.14 \text{ ng m}^{-2} \text{ h}^{-1}$) (Fig. 1). An AMDE is considered to occur if the concentration of Hg_0 decreases below 1.0 ng m^{-3} and it is considered to end when the concentration rises to values above 1 ng m^{-3} (Aspmo et al., 2005). The AMDEs occurred in conjunction with changes in wind direction and velocity. The first depletion, for example, was initiated when the wind direction changed from South-East to North-West and a cold air mass with wind speeds above 10 m s^{-1} was received. Since the lifetime of RGM is short (Lindberg et al., 2002) and it will rapidly dry deposit to the snow surface, react and/or adsorb onto particles to form HgP that is then deposited as well, the low content of airborne oxidised mercury observed during the field campaign constitutes an additional evidence for transport. The non-local origin of the AMDEs is suggested also by the values of RGM and HgP (Fig. 2). Indeed HgP was always higher than RGM. Moreover Total Airborne Mercury concentration was on average 48% of the normal mercury atmospheric background suggesting that air masses underwent mercury depletion in the Arctic Basin and then the RGM formed was deposited on the snow pack or included in the particulate matter that was then deposited to the snow surface.

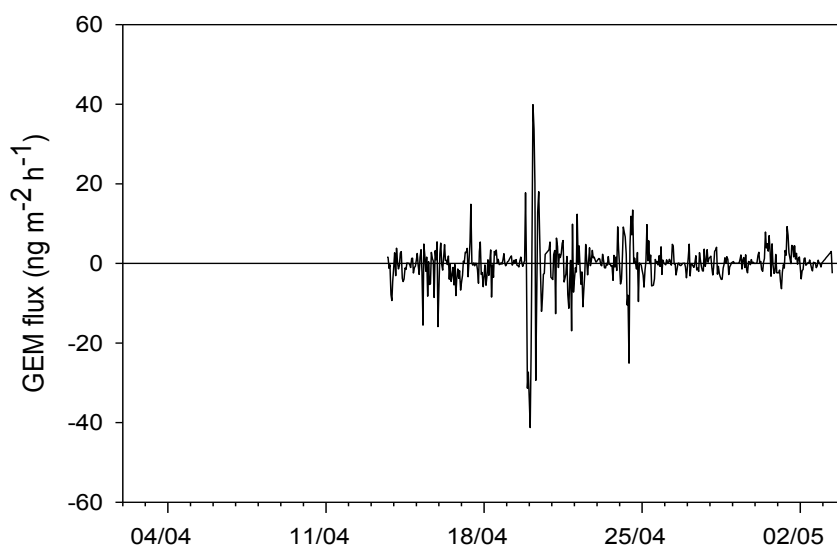


Fig. 1 Hg_0 hourly fluxes

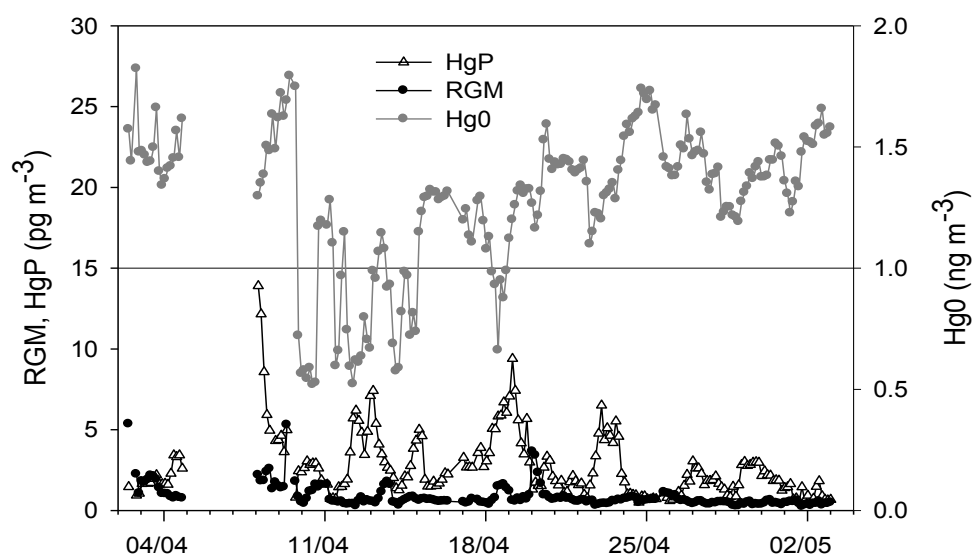


Fig.2 Hg0, HgP and RGM concentrations observed during the sampling campaign

Conclusion

The AMDE dynamics observed in this study confirm the results of the previous experimental campaigns carried out at Ny Ålesund and highlight again that also remote environments are subjected to a process (AMDE) that enhance the mercury deposition in fragile ecosystems. Since the Arctic region climate is undergoing a rapid warming that affect the timing and extent of sea ice and its coverage, the mercury cycling is going to change. Moreover the mercury emission from anthropic activities in Asia will increase in the next years producing an increase of the mercury transported till polar regions. Finally a more robust methodology to measure mercury flux must be defined and implemented in order to produce high quality data that are comparable worldwide. The data quality analysis proposed in this work is a starting point for further improvements of the methodology and of our knowledge on the mercury impact in pristine environments as polar regions.

References

Aspmo K, Gauchard PA, Steffen A, Temme C, Berg T, Bahlmann E, Banic C, Dommergue A, Ebinghaus R, Ferrari C, Pirrone N, Sprovieri F, Wibetoe G. Measurements of atmospheric mercury species during an international study of mercury depletion events at Ny-Alesund, Svalbard, spring 2003. How reproducible are our present methods? *Atmos Environ* 2005; 39:7607-7619.

Cobbett FD, Steffen A, Lawson G, Van Heyst BJ. GEM fluxes and atmospheric mercury concentrations (GEM, RGM and Hgp) in the Canadian Arctic at Alert, Nunavut, Canada (February–June 2005). *Atmos Environ* 2007; 41:6527-6543.

Dommergue A, Sprovieri F, Pirrone N, Ebinghaus R,

Brooks S, Courteaud J, Ferrari CP. Overview of mercury measurements in the Antarctic troposphere. *Atmos Chem Phys* 2010; 10:3309-3319.

Dyer AJ. A review of flux-profile relationships. *Boundary-Layer Meteorology* 1974; 42:55-78.

Ebinghaus R, Pirrone N, Lindberg S. 7th International Conference on Mercury as a Global Pollutant. *Atmos Environ* 39, 7449-7450.

Lin, C.J., Pehkonen, S.O., 1999. The chemistry of atmospheric mercury: a review. *Atmos Environ* 2005; 33:2067-2079.

Ferrari C, Padova C, Fain X, Gauchard PA, Dommergue A, Aspmo K, Berg T, Cairns W, Barbante C, Cescon P, Kaleschke L, Richter A, Wittrock F, Boutron C. Atmospheric mercury depletion event study in Ny-Alesund (Svalbard) in spring 2005. Deposition and transformation of Hg in surface snow during springtime. *Sci Total Environ* 2008; 397:167-177.

Foken T, Wichura B. Tools for quality assessment of surface-based flux measurements. *Agricultural and Forest Meteorology* 1996; 78:83-105.

Hedgecock IM, Pirrone N, Sprovieri F. Chasing quicksilver northward: mercury chemistry in the Arctic troposphere. *Environ Chem* 2008; 5:131-134.

Landis MS, Stevens RK, Schaedlich F, Prestbo EM. Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air. *Environ Sci Technol* 2002; 36:3000-3009.

Lindberg SE, Brooks S, Lin CJ, Scott KJ, Landis MS, Stevens RK, Goodsite M, Richter A. Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ Sci Technol* 2002; 36:1245-1256.

Monin A, Obukhov AM. Dimensionless characteristics of

- turbulence in the atmospheric surface layer. *Trans. Geophys. Inst. Akad. Nauk USSR* 1954; 151:163-187.
- Selin NE. Global Biogeochemical Cycling of Mercury: A Review, *Annual Review of Environment and Resources*. Annual Reviews, Palo Alto 2009; pp. 43-63.
- Sommar J, Wangberg I, Berg T, Gardfeldt K, Munthe J, Richter A, Urba A, Wittrock F, Schroder WU. Circumpolar measurements of speciated mercury, ozone and carbon monoxide in the boundary layer of the Arctic Ocean. *Atmos Chem Phys* 2007; 7:151-166.
- Sprovieri F, Pirrone N, Hedgecock IM, Landis MS, Stevens RK. Intensive atmospheric mercury measurements at Terra Nova Bay in Antarctica during November and December 2000. *J Geophys Res-Atmos* 2002; 107.
- Sprovieri F, Pirrone N, Landis MS, Stevens RK. Oxidation of Gaseous Elemental Mercury to Gaseous Divalent Mercury During 2003 Polar Sunrise at Ny-Ålesund. *Environ Sci Technol* 2005; 39:9156-9165.
- Sprovieri F, Pirrone N, Ebinghaus R, Kock H, Dommergue A. A review of worldwide atmospheric mercury measurements. *Atmos Chem Phys* 2010; 10:8245-8265.
- Steen AO, Berg T, Dastoor AP, Durnford DA, Hole LR, Pfaffhuber KA. Dynamic exchange of gaseous elemental mercury during polar night and day. *Atmos Environ* 2009; 43:5604-5610.
- Steffen A, Douglas T, Amyot M, Ariya P, Aspö K, Berg T, Bottenheim J, Brooks S, Cobbett F, Dastoor A, Dommergue A, Ebinghaus R, Ferrari C, Gardfeldt K, Goodsite ME, Lean D, Poulain AJ, Scherz C, Skov H, Sommar J, Temme C. A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow. *Atmos Chem Phys* 2008; 8:1445-1482.
- Webb EK, Pearman GI, Leuning R. Correction of flux measurements for density effects due to heat and water vapor transfer. *Quarterly Journal of the Royal Meteorological Society* 1980;106:85-100.