Atmospheric mercury at the Zeppelin station

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Rapport
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Statlig program for forurensningsovervåking

Content

1. Summary

The report presents results from three years measurements of atmospheric mercury at the Zeppelin atmospheric research station, Ny-Ålesund, Svalbard, including results from several measurement campaigns, the last two years with international participation.

In the late 90th a new phenomenon was observed at Alert in the Canadian Arctic. After polar sunrise, higher levels of mercury are deposited from the atmosphere than earlier suggested. This phenomenon is caused by the specific chemical and physical conditions that occur in the Arctic during spring. Earlier investigations have shown that ground level ozone (ozone in the lowest part of the atmosphere) is rapidly depleted during this period, due to the formation of elevated concentrations of oxidising radicals in the atmosphere. Apparently, atmospheric mercury is similarly affected. In this case, gaseous elemental mercury (GEM) may be oxidised and converted to reactive gaseous mercury (RGM) and particulate mercury (PM). In total, these have considerably higher deposition velocities than GEM, which leads to an overall enhanced deposition flux of mercury. During such episodes GEM is reduced from about 1.5 ng/m^3 to below 0.2 ng/m^3, whereas a number of measurements of RGM and PM indicate that these species are increasing substantially. RGM and PM are more easily available for biota than GEM, which imply that the deposition flux of mercury in the Arctic is considerable at a time of the year when biota are preparing for peak summertime activity. This may also explain the increased concentrations observed in Arctic biota and sediments

Data from Ny-Ålesund confirm that the atmospheric mercury depletions/deposition episodes (AMDEs) also extend to the Svalbard area. The AMDEs occurred during a three-four months period following polar sunrise and lasted from a few hours to several days. The theory of RGM and PM formation during depletion of GEM in the Arctic, has been strengthened by the results from the present measurements. The concentration of RGM and PM increased as soon as GEM decreased. The transformation to more reactive and short-lived species of Hg is also evident from the increase in concentrations of mercury observed in surface snow from the polar night to the Arctic spring. Some of the snow-bound mercury will probably end up in the runoff when the snow is smelting.

The data is part of the national monitoring programme " Monitoring of long-range transported air and precipitation", and they are also a subject for international programmes such as AMAP (Arctic Monitoring and Assessment Programme), EMEP (European Monitoring and Evaluation Programme), and OSPAR/CAMP (Oslo Paris Commission/Comprehensive Atmospheric Monitoring Programme).

2. Sammendrag

Rapporten presenterer resultater fra tre års målinger av atmosfærisk kvikksølv ved Zeppelinstasjonen, Ny-Ålesund, samt resultater fra flere målekampanjer, hvor det de to siste årene var deltakelse fra flere internasjonale forskningsgrupper.

På slutten av nittitallet ble det oppdaget et helt nytt fenomen ved Alert i det kanadiske høy-Arktis. Etter polar soloppgang blir mer kvikksølv avsatt fra atmosfæren enn hva man tidligere hadde trodd. Dette fenomenet skyldes de helt spesielle kjemiske og fysiske forhold som oppstår i Arktis om våren. Tidligere undersøkelser har vist at troposfærisk (nederste del av atmosfæren) ozon forsvinner på denne tida, på grunn av dannelse av forhøyde konsentrasjoner av oksiderende radikaler i atmosfæren. Tilsynelatende blir atmosfærisk kvikksølv berørt på samme vis. Elementær kvikksølvgass blir oksidert og overført til reaktivt gassfasekvikksølv (RGM) og til kvikksølv på partikler (PM). Disse formene har betydelig høyere avsetningshastighet enn elementært kvikksølv i gassfase, noe som fører til en avsetningstrøm av kvikksølv. Under slike episoder blir konsentrasjonen av elementært kvikksølv i gassfase (GEM) redusert fra omlag 1.5 ng/m^3 til under 0.2 ng/m^3, mens noen målinger av RGM og PM har vist at konsentrasjonene av disse øker betydelig. RGM og PM er lettere tilgjengelig for biota enn GEM, noe som fører til at avsetningshastigheten av kvikksølv er betydelig i Arktis på ei tid av året hvor biota forbereder seg på sommeraktiviteter. Dette kan også forklare de høye konsentrasjonene som er observert i Arktis biota og sedimenter.

Data fra Ny-Ålesund bekrefter at de atmosfæriske nedbryting/avsettingsepisoder (AMDEs) også skjer i Svalbardomådet. AMDE pågikk i en 3-4 måneders periode etter polar soloppgang og varte fra et par timer til flere dager. Teorien om RGM- og PM-dannelse under nedbryting av elementært kvikksølv i Arktis har blitt styrket av resultatene fra dataene presentert i denne rapporten. Konsentrasjoner av RGM og PM økte så snart GEM ble redusert. Overføring til mer reaktive og kortlevde former for kvikksølv sees også klart fra de økte konsentrasjoner av kvikksølv som ble observert i overflatesnø fra polar natt til Arktisk vår (3-4 mnd). Noe av det snøbundne kvikksølvet vil trolig ende opp i avrenninga når snøen smelter.

Dataene inngår i det nasjonale overvåkingsprogrammet "Overvåking av langtransportert forurenset luft og nedbør", og også i flere internasjonale programmer som AMAP (Arctic Monitoring and Assessment Programme), EMEP (European Monitoring and Evaluation Programme), og OSPAR/CAMP (Oslo Paris Commission/Comprehensive Atmospheric Monitoring Programme).

3. Introduction

In the atmosphere mercury exists predominantly in the vapour phase as elemental mercury (Hg°). Hg° is relatively unreactive, has a high volatility and low solubility in natural waters, making it reside in the atmospheric environment for 6-24 months. (Slemr *et al.* 1985; Lindqvist and Rodhe 1985). Once introduced into the atmosphere, Hg° can circulate for long periods of time prior to being transferred to a permanent sink reservoir. Long-range atmospheric transport of Hg°, its transformation to more toxic methyl mercury compounds (Met-Hg), and the substantial bioaccumulation mainly in the aquatic food chain have motivated intensive research on mercury as a pollutant of global concern. Definitions of mercury species mentioned in the text are given in Table 1.

The 1995 discovery of the "springtime atmospheric mercury depletions/deposition events" (AMDEs) at Alert in the Canadian High Arctic (Schroeder *et al*. 1998; 2003) stimulated significant research activities in several nations interested in preventing pollution of polar regions. The last 4 years AMDEs have been measured, not only at Alert but also at other locations in the Arctic: Barrow, Alaska (Lindberg et al. 2001), Ny-Ålesund, Svalbard (*Berg et al.* 2001; Berg 2002); Greenland (Skov et al. 2001), Russia (Steffen and Schroeder 2002); the sub-Arctic (Poissant and Pilote 2001); and in Antarctica (Ebinghaus et al. 2002).

The AMDEs are strongly correlated with ground-level ozone depletion events (Schroeder et al. 1998) which had been discovered 10 years earlier (Barrie *et al.* 1988). The frozen surfaces on the Arctic Ocean contain enriched concentrations of halide ions (Br^-, Cl^-). In the presence of sunlight these halide ions probably will produce halogen atoms (Br· and/or Cl·) and/or highly reactive halogen oxide free radicals (BrO· and/or ClO·). The atmospheric oxidation of elemental mercury (Hg°) to Hg(II) after polar sunrise is believed to involve the halogen atoms and/or the halogen oxide free radicals (Lu et al. 2001; Lindberg et al. 2002; Ariya et al. 2002; Schroeder et al. 2003). During AMDEs, more reactive water-soluble mercury species (RGM, PM) will be produced, which are readily deposited. However, the mechanism for the mercury depletion is not fully understood. Measurements of RGM and PM have shown considerably higher concentrations of these species during AMDEs in the Arctic (Lu et al. 1998; Lindberg et al. 2001; Berg et al. 2003, Steffen and Schroeder 2002; Poissant and Pilote 2001, Ebinghaus et al. 2002). High concentrations of mercury in surface snow (Lu et al. 2000; Berg et al. 2003) indicate that this phenomenon may lead to an overall enhanced deposition flux of mercury in the Arctic.

While the existence of this ecologically important phenomenon in cold environments is now accepted by the scientific community, many uncertainties remain in our understanding of AMDEs (Schroeder *et al.* 2003). The present manscript reports results from three years measurements on AMDE at Zeppelin, Ny-Ålesund in the Norwegian Arctic.

Table 1: Definition of mercury species mentioned in the text.

Abbreviation:	**Full name:**	**Definitions:**
Hg°	Elemental mercury	Elemental mercury (Hg°) in vapour phase
GEM	Gaseous elemental mercury	Elemental mercury (Hg°) in vapour phase measured by a Tekran 2537A
RGM	Reactive gaseous mercury	Oxidized mercury species in vapour phase
PM	Particulate mercury	Oxidized mercury attached to atmospheric particles
Tot. Hg in surface snow	Total mercury in surface snow	All BrCl-oxidizable mercury forms and species in surface snow (elemental, oxidized, particle bound, organo-complexed and some organo-mercurials)
Met-Hg	Methyl mercury	Organo-mercurial compounds: Extremely toxic and easily able to accumulate in aquatic food chains (**not measured in this study**)

4. Experimental

4.1 Sampling location

Experiments were performed within the Ny-Ålesund International Research and Monitoring Facility (78.9^{o}N, 11.9^{o}E) (1a). Ny-Ålesund is situated at the southern shore of Kongsfjorden on the West Coast of Spitzbergen in the Norwegian high Arctic and is partly surrounded by mountains with peaks of 1000-1500 m altitude. It is situated about 15 km from the northern-most Barents Sea. An offshoot of the waning Gulf Current (West Spitzbergen current) causes ice-free conditions along the west coast of Spitzbergen during the entire year. Samples of airborne mercury and mercury in snow were taken at the Global Atmospheric Watch monitoring observatory operated by the Norwegian Institute for Air Research (NILU) at Zeppelinfjellet (474-m a.s.l) (Fig 1b). From the Zeppelin mountain Station (ZS, 78^{o}54’42”N, 11^{o}55’30”E), there is a steep downhill slope to the north towards Ny-Ålesund situated at 2 km distance. South of ZS is also a slope whereas there are higher mountain peaks in the east and west. This channels the local wind into either of the upslope directions, north-northwest and south-southeast (Beine *et al.*, 2001). Situated above the inversion layer, there is minimal influence from local pollution sources in Ny-Ålesund. Air and snow sampling were also carried out downhill at 12-m a.s.l close to the Italian Consiglio Nazionale delle Ricerche (CNR) Base Arctica “*Dirigibile Italia*” (DI) inside the Ny-Ålesund settlement.

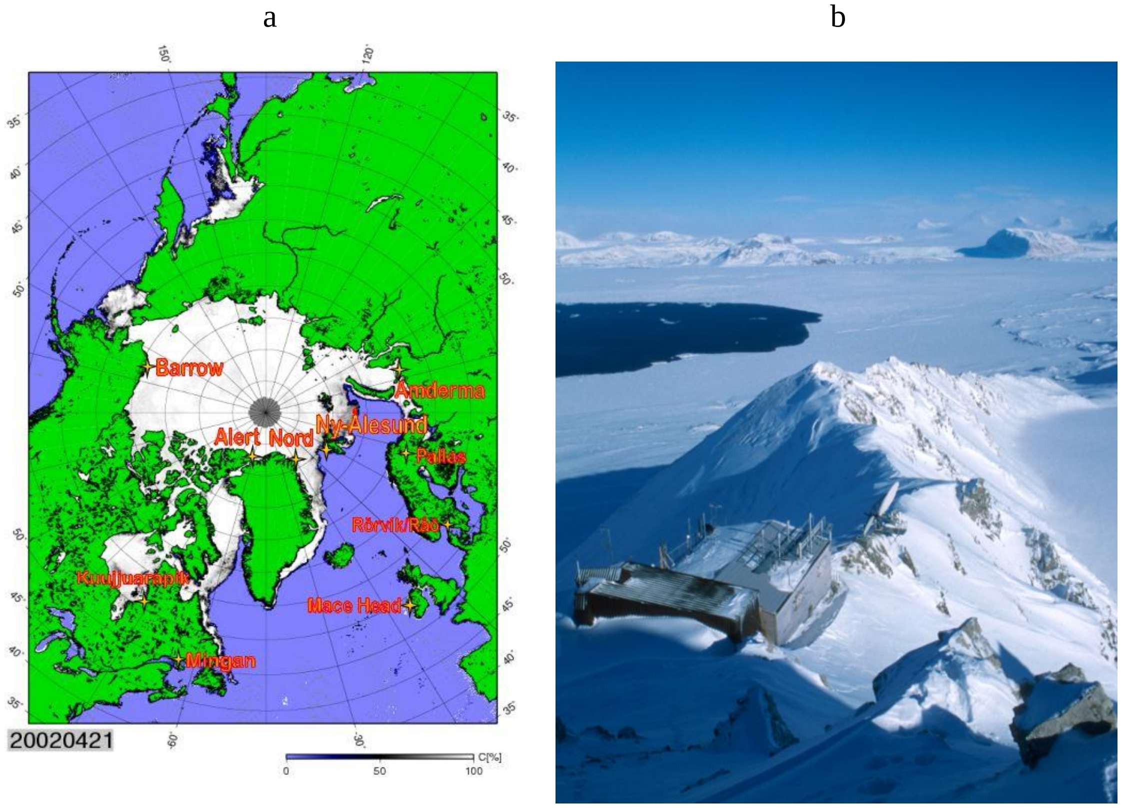

Figure 1a: Some Arctic and sub-Arctic mercury sampling locations including long-time monitoring, and profiles of distribution of winter sea ice. Courtesy of L. Kaleschke (Kaleschke et al., 2001) and 1b: The monitoring station at the Zeppelin Mountain.

4.2 Measurements

4.2.1 Measurement period

Measurements were carried out on routine basis in the period 1. February 2000 to the end of May 2003. Additionally, intensive campaigns were performed in the presence of 24 hours daylight 28. April-15. May 2000; 12. April - 28. April 2001, 17.April - 14 May 2002 and 13. April -10. May 2003.

4.2.2 Gaseous elemental mercury (GEM)

A Tekran Gas Phase Mercury Analyser (Model 2537A; Tekran Inc., Toronto, Canada) was installed at the Zeppelin station in February 2000 for measurements of GEM (Fig. A1). The pre-filtered sample air stream goes through gold cartridges where GEM is collected. GEM is then thermally desorbed and detected by cold vapour atomic fluorescence spectrometry (CVAFS) (l=253.7 nm) (Tekran 1999). Dual gold cartridges allow alternate sampling and desorption, resulting in continuous measurement of GEM on a predefined time base. The sampling time was 30 minutes from 1.2.2000, and decreased to 5 minutes from 1.4.2000. A sampling flow rate of 1.5 l/min was used. The instrument was calibrated daily using an internal permeation source, verified by manual injections every 3 months. A heated sampling line was used to maintain constant temperature throughout the line. The line was mounted ~3 m above the ground on a mast 2 m out of the roof at the Zeppelin station. To reduce the amount of water and/or particles entering the input line, a filter holder containing 2 mm Teflon filter (47 mm diameter) was mounted at the inlet of the sampling line. A recovery of 98% was normally obtained when checking the sampling line for recoveries and leaks.

4.2.3 Reactive gaseous mercury (RGM)

The RGM system has been significantly improved and changed after the first campaign in 2000:

2000: RGM was sampled manually using annular denuders coated with KCl (Fig.A2). The design was attained by modifying a sketch of the denuder employed at Chalmers University of Technology, Gothenburg. The outer tube was 370 mm long with an outer diameter of 21 mm and inner diameter of 17 mm. The inner tube length was 250 mm and the outer diameter 15 mm. An area, about 200 mm long, on the inside of the outer tube and outside of the inner tube, was sand blasted. The rougher surface makes the coating stick better to the denuder walls, and the area is called “the active area”. Air was pulled through the space between the two tubes. During sampling the denuders were placed in a plywood box on the outer wall of the Zeppelin station. The box contained a small oven to keep the temperature inside at approximately 40°C (but was apparently not able to do so). Within the box the denuders were connected vertically to a set of polyethylene tubings. A plastic shield and a Teflon grid at the air inlet protected the denuders from snow and large particles. The sampling flow was approximately 3.5 l/min. During analysis, the denuder was placed in a custom-made denuder oven coupled to a mercury-monitor (Gardis-1A, Lithuania). The Gardis monitor is based on gold amalgamation and atomic absorption spectrometry (AAS) detection (Urba et al. 1995). An aerosol filter positioned between the gas source and the denuders protected the system from particles and water droplets. The introduction period was 15 min and the introduction flow 200 ml/min. During the heating step (500 ºC) RGM is converted to elemental Hg and quantified. The Gardis instrument was operated with zero air during the analysis. Measurements were performed on a daily basis and the sampling time was about 24 hours. Because of the short time available before the campaign, only a few breakthrough tests were performed (two denuders in tandem). No visible breakthrough of RGM was observed. Later, and more thorough, experiments showed however some breakthrough with 24 hours sampling times. Two parallel samples were taken on 29.04, 30.04 and 04.05. All other days only one sample was analysed. A detailed description of sampling and determination of RGM is given in Valdal (2001).

2001: The sampling time was reduced to about 5-6- hours. The sampling flow was changed to approximately 6 l/min.

2002: The denuders were contained in protective housings thermostated to 40^{o}C during sampling. The two sampling systems were identical except that one of the samplers was equipped with Teflon grid inlet. The Gardis monitor was exchanged with a Tekran 2537A Hg Monitor (see 2.2.2). Manual RGM sampling was conducted at ZS in the beginning of the campaign and later moved to DI.

2003: New impactors were used in front of the denuders (sampling cut off for particles was approximately 2.5 μm) (Fig. A4). The sampling flow was approximately 10 l/min (and about 5 l/min with minitraps in the same stream). The sampling time was 2-24 hours. The NILU desorbtion oven was changed to a Lindberg furnace.

4.2.4 Particulate mercury (PM)

Mercury associated with airborne particulate matter was sampled on glass fiber filters (Gelman Type AE, 61635, 142 mm) using two parallel high volume samplers. The sampling flow rate was ~160 l/min which are much lower than normally used for these conventional "Hi-Vol" samplers. The filters were preheated at 450 °C for 8h to reduce the blank content of mercury. Five-day samples were collected each week, with the exception of the field campaign when the filters were changed every day or every second day. Sample treatment and analyses were performed in a clean-room (class 300). The filters were cut into pieces and transferred to Duran glasses. Concentrated HNO_3 (Suprapur, Merck) diluted 1:1 with ultra pure water was added. The glasses were firmly sealed with Teflon coated caps and heated in a pressure boiler at 120ºC for 30 minutes. The samples were cooled to room temperature and 1.5 ml BrCl (2.5% w/w, Merck) was added to 25 ml of the sample for further oxidation/conservation. The samples were analyzed with a modified cold vapour atomic fluorescence spectrometer (CV-AFS) (PS-Analytical, UK) using $SnCl_2$ (Merck) as reduction agent. Calibration was accomplished using standard solutions of 5, 10, 20, 40 and 100 pg/ml, prepared by appropriate dilution of a stock solution (Spex, US). Field blanks in general constituted less than 10% of the mercury concentrations measured in the samples. A detailed description of sampling and determination of PM is given in Sekkesæter (2001).

2003: In addition to high volume samplers, so called mini traps (Fig A3) were also used to measure PM. Two miniature quartz tubes, one with outer diameter of 10 mm, the other with outer diameter of 13 mm, placed one within the other, are held together by a piece of silicon tubing. The conjunction of the tubes holds a filter disk, 10 mm in diameter, cut from a quartz fibre filter sheet (Munktell 360, pore size: 0.3 μm). The filter disk is supported by a nickel screen support (10 mm in diameter). It was possible to sample PM with denuders in front (removing RGM) or without denuders (including some of the RGM) (Fig A4). The sampling flow was approximately 5 l/min when the sampling were carried out with a denuder in front and about 2.5 l/min when no denuders were used. The sampling time was 2-36 hours. A custom-made oven for heating PM-traps to approximately 900 °C was used. This thermal installation consisted of a heating coil shaped into a spiral with a diameter of 13 mm fitting the TPM-trap, a voltage source (transformer), and a time regulator. A fan was positioned at adequate distance underneath the heating wire. Both objects were held in place by a stand of clamps. The box containing the transformer and time regulation was positioned on the floor. The oven could be adjusted to perform heating between one minute and several hours. A Tekran 2537A Hg Monitor was used as detector (see 4.2.2)

4.2.5 Mercury in surface snow

One sample of surface snow was collected approximately once a week in Teflon bottles (250 ml) outside the Zeppelin station. During the campaigns, the snow was collected more frequently. All glass equipment and Teflon bottles used were rinsed in an aqueous BrCl solution (0.5 % w/w, Merck) for at least 24 h before use. The samples were stored in the dark at +5°C for up to 3 months. Before analysis a 25 ml sample aliquot were oxidized with 1.5 ml BrCl (2.5% w/w, Merck) converting stable mercury forms to water-soluble species, which in turn were reduced to Hg° with $SnCl_2$. Analysis was performed using the same CV-AFS procedure as for particulate mercury. Due to some analytical problems the snow sample concentrations from 2003 were all divided by three and only estimated values are given for this year.

5. Results

5.1.1 Gaseous elemental mercury (GEM)

Time series of GEM measured at Zeppelin for the 3 ½ years period February 2000 to May 2003 are presented in Fig. 2. Figures showing each year separately are given in Figure B 1. Concentrations of GEM at Zeppelin were within the range <0.1 - 3 ng/m^3. The annual averages for 2000, 2001 and 2002 were 1.47, 1.56 and 1.59 ng/m^3, respectively. During fall and winter the concentrations of GEM are quite stable at about 1.4-1.5 ng/m^3 at Zeppelin. Several episodic depletions in GEM concentrations, correlating well with the depletions of surface ozone, were seen during the three-month period following polar sunrise (Fig. 3). During such episodes, GEM concentrations could drop from 1.8 ng/m^3 to undetectable levels (<0.1 ng/m^3) within 24 h. Time series of hourly average values for GEM and ground level ozone (O_3), Zeppelin, during spring 2003 are shown in Fig. 3. The insert shows concentrations of GEM versus O_3 at Zeppelin during the same period. A correlation coefficient R^2 =0.84 was observed at Zeppelin during the depletion events.

5.1.2 Reactive gaseous mercury (RGM), Particulate mercury (PM) and total mercury in surface snow

Time series of GEM, RGM, PM and total mercury in surface snow measured during the spring campaign 2003, are presented in Fig. 4. When GEM dropped, RGM levels increased from undetectable concentrations (< 5 pg/m^3) to levels above 200 pg/m^3 during the two major depletion events 21 and 28 April. During the minor event 1-2 May, RGM concentrations were also above 140 pg/m^3. The highest concentration of PM (350 pg/m^3) was observed in the beginning of the first and largest GEM depletion event (19. April). The broken line show results for PM were RGM was not removed from the air stream (no denuder in front of the PM trap). Concentrations of total mercury in surface snow also anti correlates with GEM during the depletion events: concentrations increased from background values to 100 ng/l after GEM events. Seasonal variation of Hg concentrations in snow for the 3-year period 2000-2002 are presented in Fig. 5. Enhanced concentrations of Hg in surface snow are clearly evident throughout the AMDE period. The concentrations vary from a background of about 2 ng/l during the polar night to about 40 ng/l in the Arctic spring. Data on RGM and PM for earlier years are given in Appendix 2.

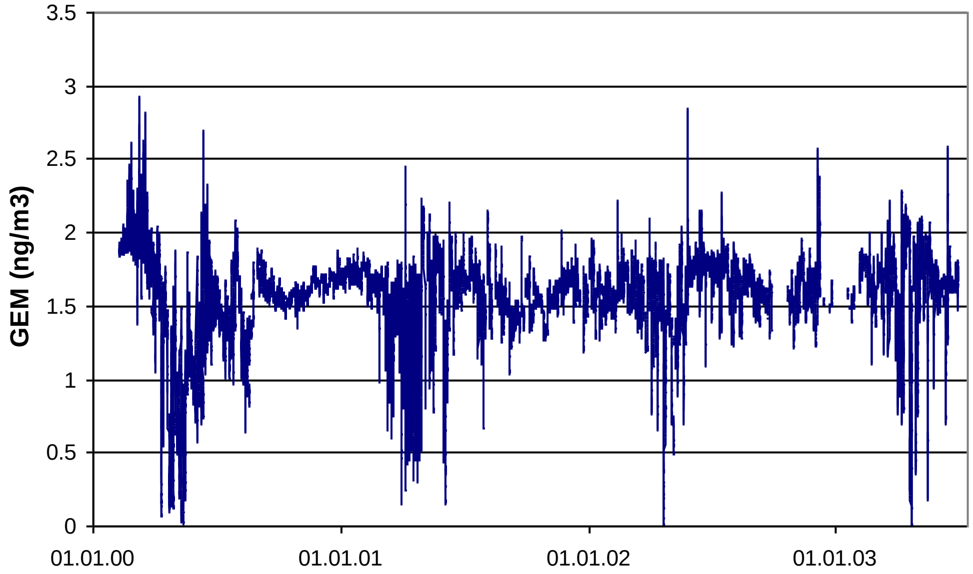

Figure 2: *Time series of hourly average values for GEM, Zeppelin, 2000-2003*

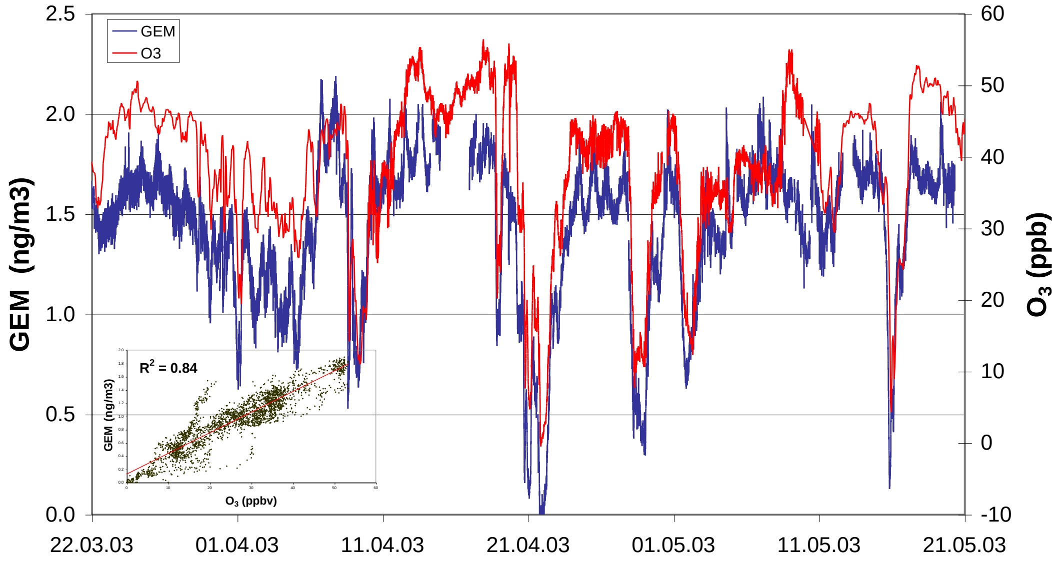

Figure 3: *Time series of hourly average values for GEM (blue) and ground level ozone (red), Zeppelin, during spring 2003. The insert shows concentrations of GEM versus ozone at Zeppelin during the same period (R^2 =0.84 for the correlation at Zeppelin during the depletion events).*

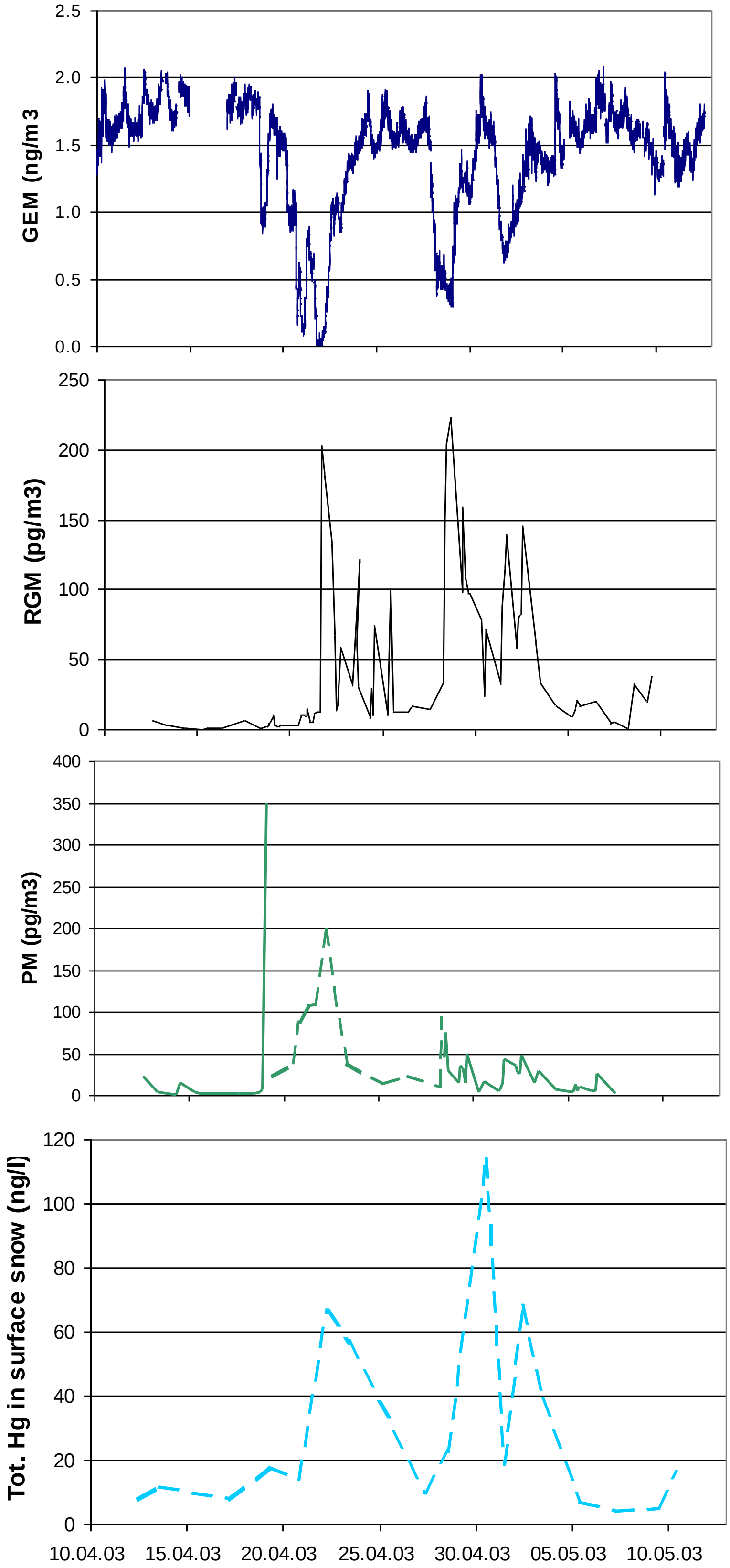

Figure 4: Time series of GEM, RGM, PM and total mercury in surface snow measured during the spring campaign 2003 (campaign period: 13 April -10. May)

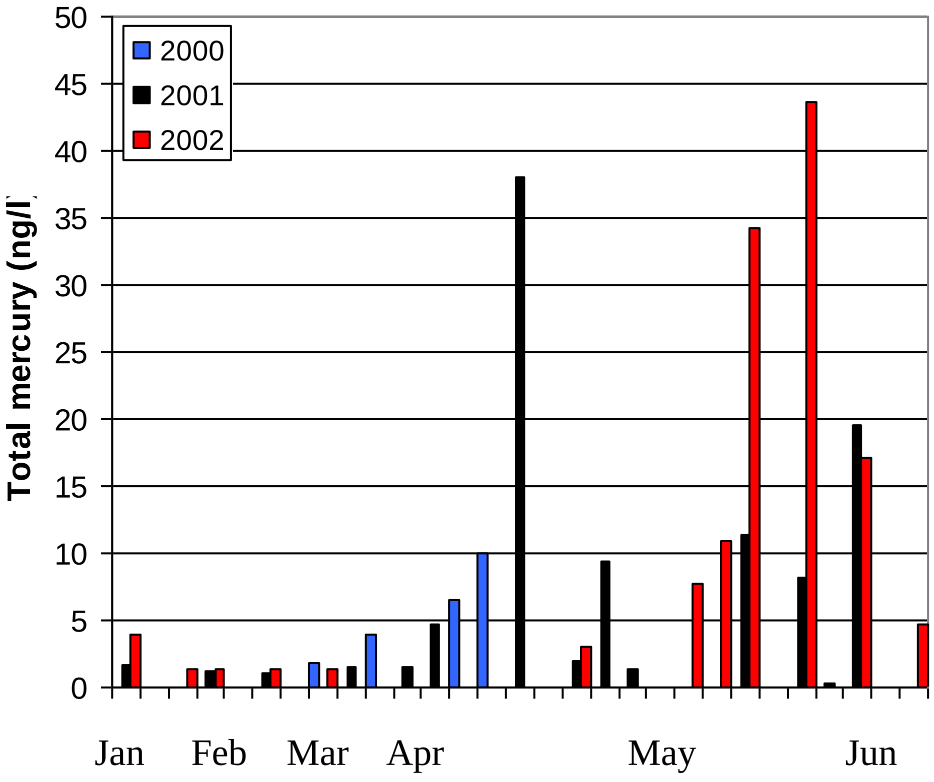

Figure 5: Time series of total mercury in surface snow during 2000-2002

6. Discussion

6.1 Annual means forGEM

The annual means for Zeppelin (1.47-1.59 ng/m^3) are similar to the annual means for Alert (1.54 to 1.60 ng/m^3) reported for the period 1995-1999 (Schroeder et al. 1998, Berg and Hjellbrekke 2001). In contrast, the annual mean for 2000 in Antarctica (1.04 ng/m^3) was significantly lower (Ebinghaus et al. 2001). This is consistent with the fact that most atmospheric Hg emissions to the atmosphere occur in the Northern hemisphere. No trends in the GEM concentrations have been observed at Zeppelin during the measurement period (1995-2002) (Berg et al. 2003b). Manual measurements were carried in 1995-1999.

6.2 Processes

During fall and winter the concentrations of GEM are quite stable at about 1.4-1.6 ng/m^3 at Zeppelin. Several episodic depletions in GEM concentrations, correlating well with the depletions of ground level ozone (O_3), can be seen during the three-four month period following polar sunrise (Fig. 2 and 3). During such episodes GEM concentrations can drop from the global background to undetectable levels (<0.1 ng/m^3) in less than 24 h. A similar pattern has been observed at several Arctic/Antarctic stations located at similar latitudes (Schroeder *et al.* 1998, Skov *et al*. 2001; Lindberg *et al.* 2002). The AMDEs start at approximately the same time of the year at Alert (82°5’N, 62°3’W), Ny-Ålesund (78°54’N, 11°53E) and Nord at Greenland (81°30'N, 16°40' W). At Barrow (71°19'N, 156°37'W), a more southerly Arctic site, AMDEs start earlier, due to the earlier polar sunrise.

During GEM-depletions (and ground level O_3-depletions), concentrations of RGM and PM increased dramatically, suggesting that GEM is converted to RGM and PM. The daily means of RGM during AMDE were, however, lower than those reported from Barrow, Alaska (Lindberg et al. 2001). Using automatic measurements, Lindberg et al. (2001) established the first evidence of RGM formation during AMDE in February 2000. Prior to Arctic sunrise, RGM remained near detection limit (2 pg/m^3), but increased dramatically after sunrise to levels as high as 900 pg/m^3 (using five min. sampling time) in synchrony with the depletion of GEM. The authors concluded that AMDEs involve rapid in-air oxidation of elemental mercury to a species of RGM by photochemically driven reactions, probably involving the same reactive bromine and chlorine compounds present in ground level ozone destruction. Most of the oxidation does probably take place over frozen surfaces on the Arctic Ocean where there is virtually unlimited supply of the halide ion precursors, leading to the formation of extremely reactive free-radical species (Lu et al. 2001). Thus, elevated mercury levels should also be evident in surface snow on the Arctic Ocean and adjacent areas.

Enhanced concentrations of Hg in surface snow are clearly evident throughout the AMDE period at Zeppelin (Fig. 5). A six-fold increase in the concentrations is seen from winter to spring. Similar background concentrations have also been measured in a previous study at Ny-Ålesund (Berg et al. 2001). The seasonal variation is consistent with the time series shown for the Canadian SHEBA ship which was adrift with the pack ice during 1997-1998 (Lu et al. 2001). The concentrations during spring were as high as 120 ng/l for the SHEBA expedition. The Canadians have also studied the spatial distribution of mercury levels in the snowpack of the Eastern Canadian Arctic and the Hudson Bay region in 1997 (Lu et al. 2001) before any melting occurred (mid-April to mid-May). In the Canadian Island Archipelago and at coastal sites on Hudson Bay, concentrations were generally much higher (25 to 160 ng/l) than those observed at a western site near Tuktoyaktuk (2.2 ng/l), at a sampling site on the eastern shore of Greenland (<2.0 ng/l), and on the southern shore of Winnipeg (1.8 ng/l). The Canadian snowdata are consistent with satellite observations of atmospheric BrO concentrations in the Northern hemisphere (Richter et al. 1998).

The observations seen in the Arctic, constitute direct evidence of a link between sunlight assisted Hg^o oxidation, greatly enhanced atmospheric Hg(II) wet and/or dry deposition, and elevated Hg concentrations in the Arctic snowpack in spring.

6.3 Suggestion for further work

While the existence of this ecologically important phenomenon in cold environments is now accepted by the scientific community, many uncertainties remain in our understanding of AMDEs. A workshop convened in Toronto, Canada, August 2002, brought together 40 scientific experts on this subject from eight countries. Its primary objectives were to share the knowledge pertaining to AMDEs, review and discuss outstanding research questions, examine opportunities for future collaborations, and initiate preliminary planning of prospective studies to fill the existing knowledge gaps. Attendees concluded with a compilation of high priority research questions related to this polar phenomena (Schroeder et al. 2003). Chief among these were:

- What chemical species comprise reactive gaseous mercury?
- What are the sea ice processes leading to the release of photolyzable bromine and chlorine?
- To what extent is the snowpack a sink for reactive gaseous mercury and a source of elemental mercury?
- What is the biotic fate of the deposited mercury?
- What are the climatic variables that control mercury deposition rate

Figure 6 shows our current understanding of Hg cycling in the Arctic Springtime

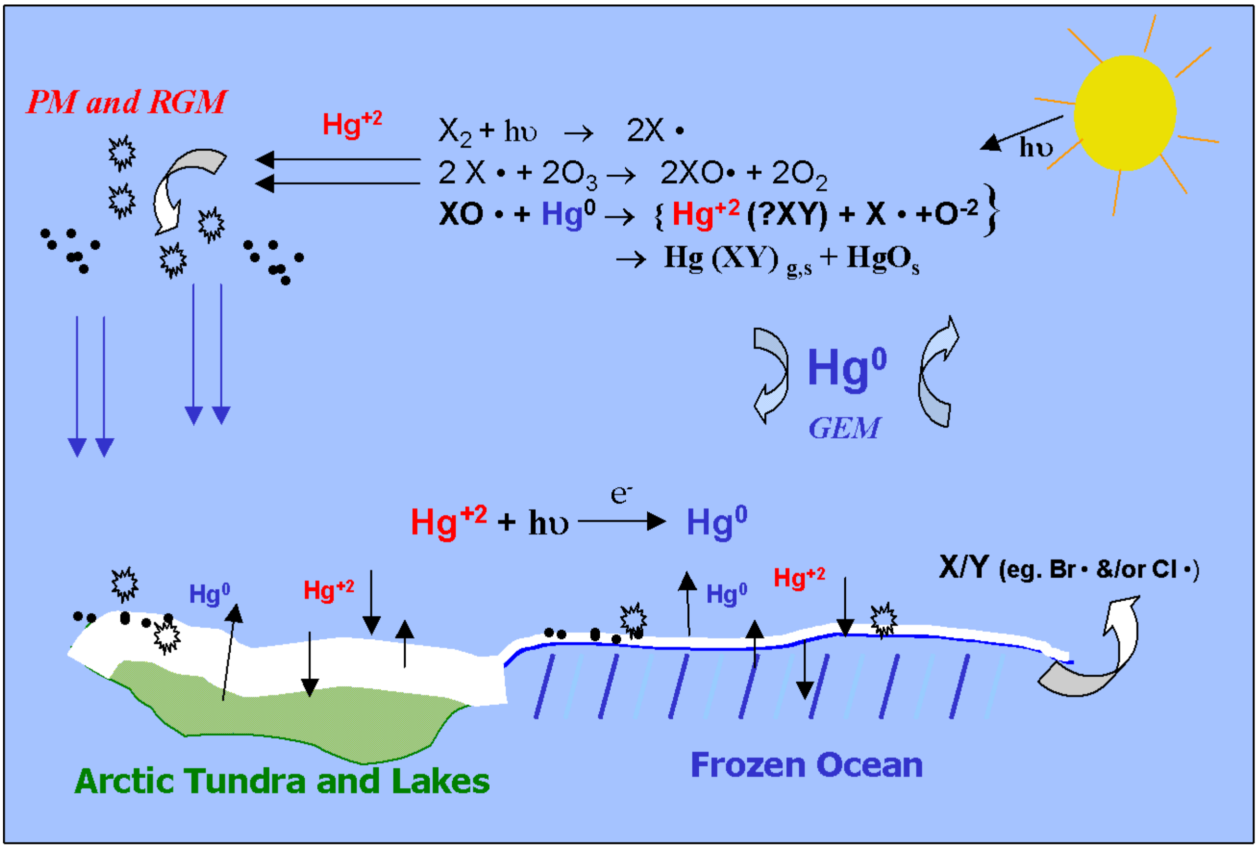

Figure 6: *Current understanding of mercury (Hg) cycling in the Arctic Springtime. Figure kindly provided by A. Steffen, Environment Canada.*

7. Conclusions

The data from Ny-Ålesund support the theory that AMDEs is a phenomenon of large geographical scale in Polar Regions. The AMDEs occurred during a three-month period following polar sunrise and lasted from a few hours to several days. The theory of RGM and PM formation during depletion of elemental Hg in the Arctic, has been strengthened by the results from the present campaigns. The concentration of RGM and PM seemed to increase as soon as the elemental Hg concentration decreased. The transformation to more reactive and short-lived species of Hg is also evident from the increase in concentration of Hg observed in surface snow from the polar night to the Arctic spring. Some of the snow-bound mercury is ending up in the runoff when the snow is smelting. The ratio between deposition and re-emission is an important parameter that determines the impact of mercury depletion in the Arctic environment. More research is needed to improve our understanding of this exceptional aspect of environmental mercury cycling.

8. Literature

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Appendix A

Sampling and measurement equipment

Figure A 1: Measurement of GEM and ozone at Zeppelin

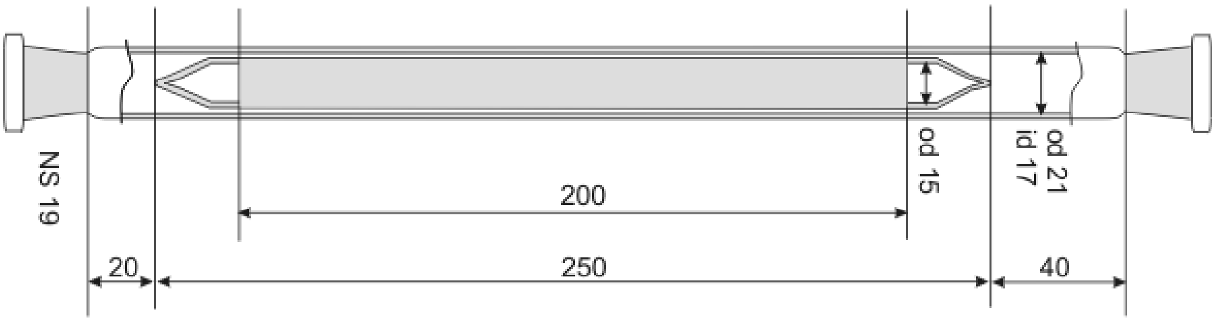

Figure A 2; Denuder for RGM measurements

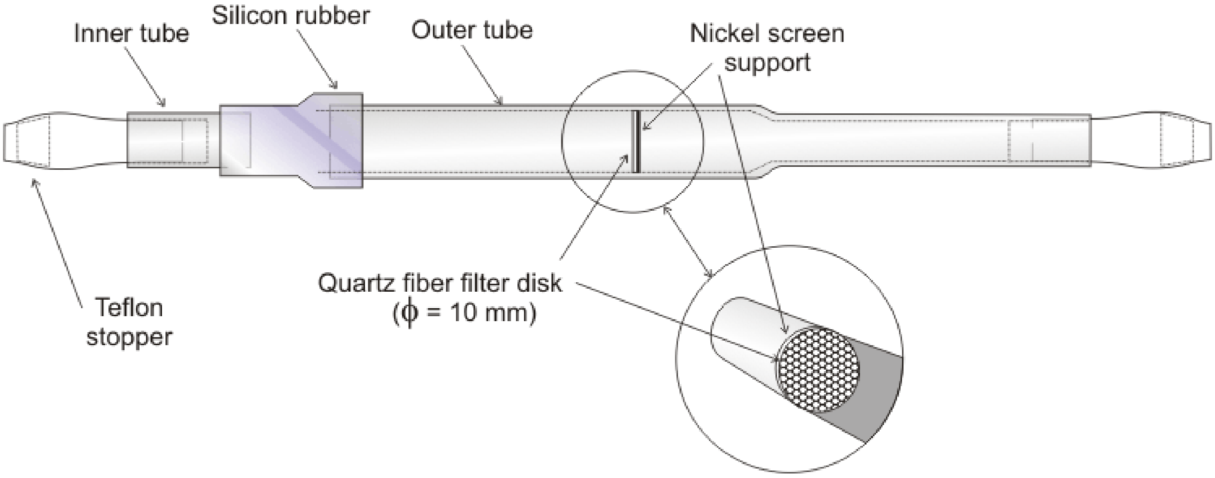

Figure A 3: Minitrap for PM measurements

Figure A 4: Sampling of RGM and PM. Inside long tubes: Denuders for RGM sampling. Inside short tubes (separate and behind long tubes): Minitraps for PM sampling

Appendix B

Results from measurements

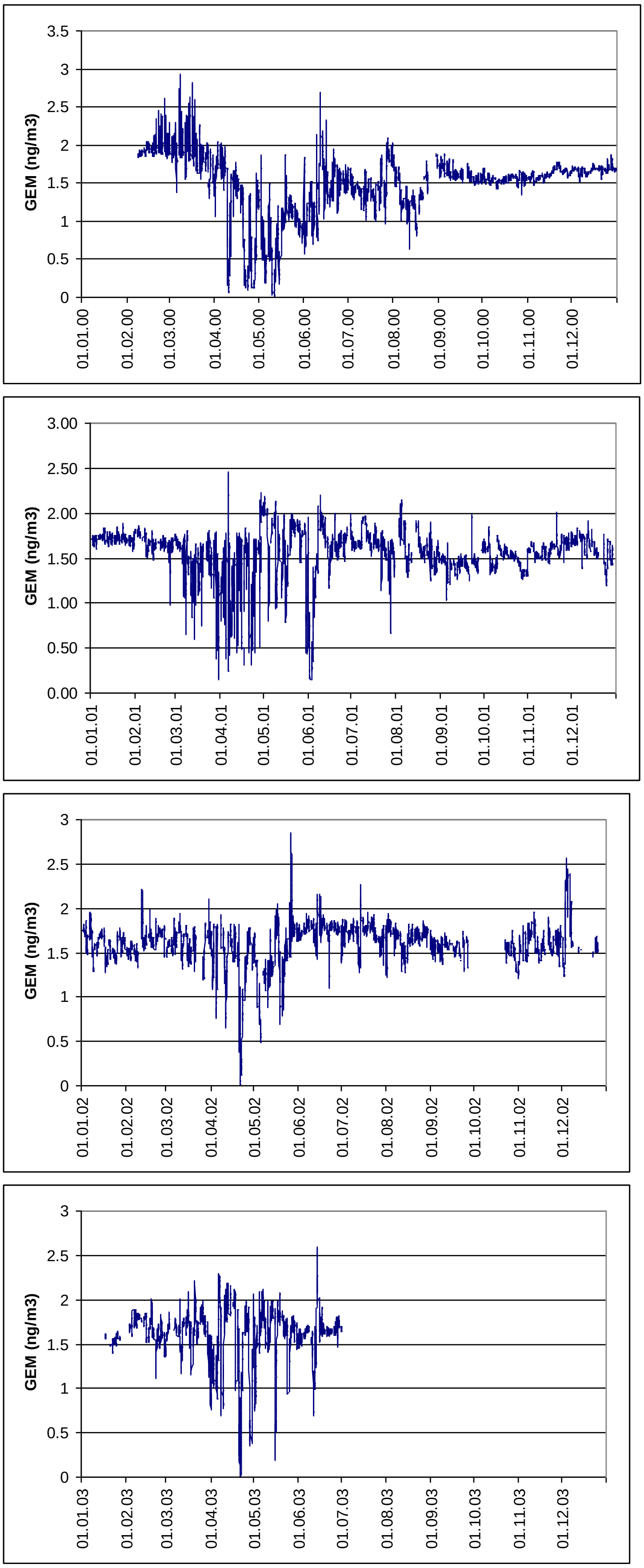

Figure B 1 Time series (hourly) of gaseous elemental mercury (GEM) at Zeppelin 2000, 2001, 2002 and 2003

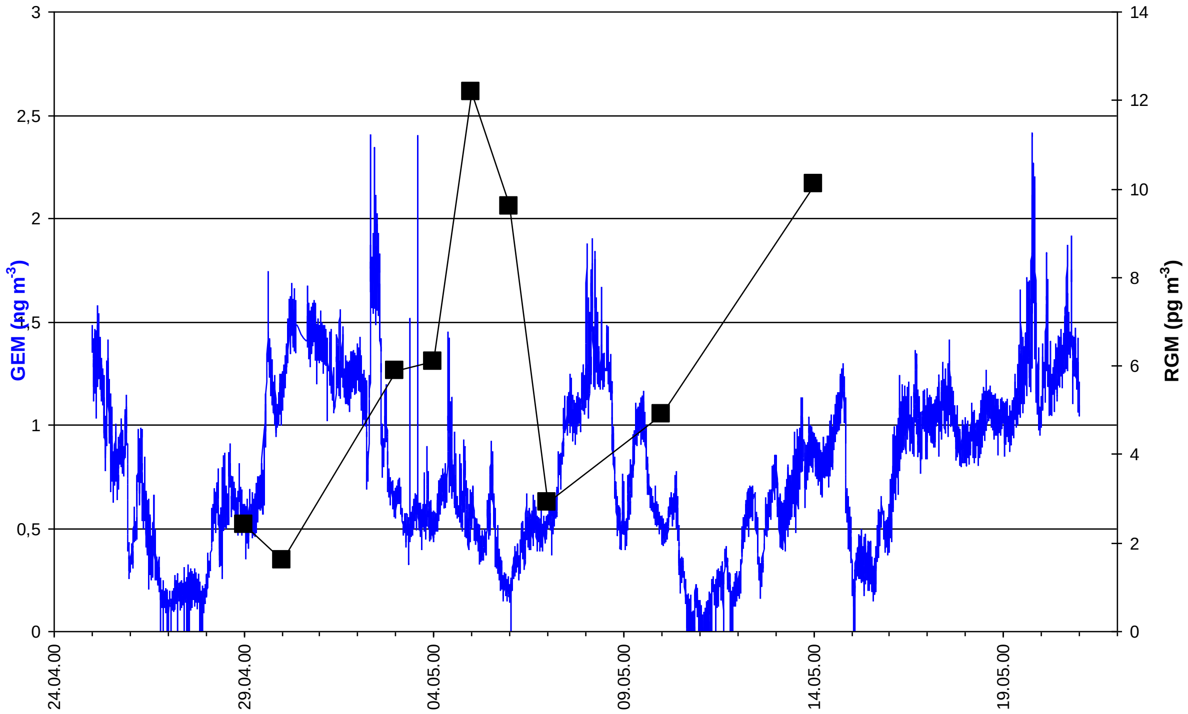

Figure B 2: Time series of GEM (blue) and RGM (black) at Zeppelin during spring 2000

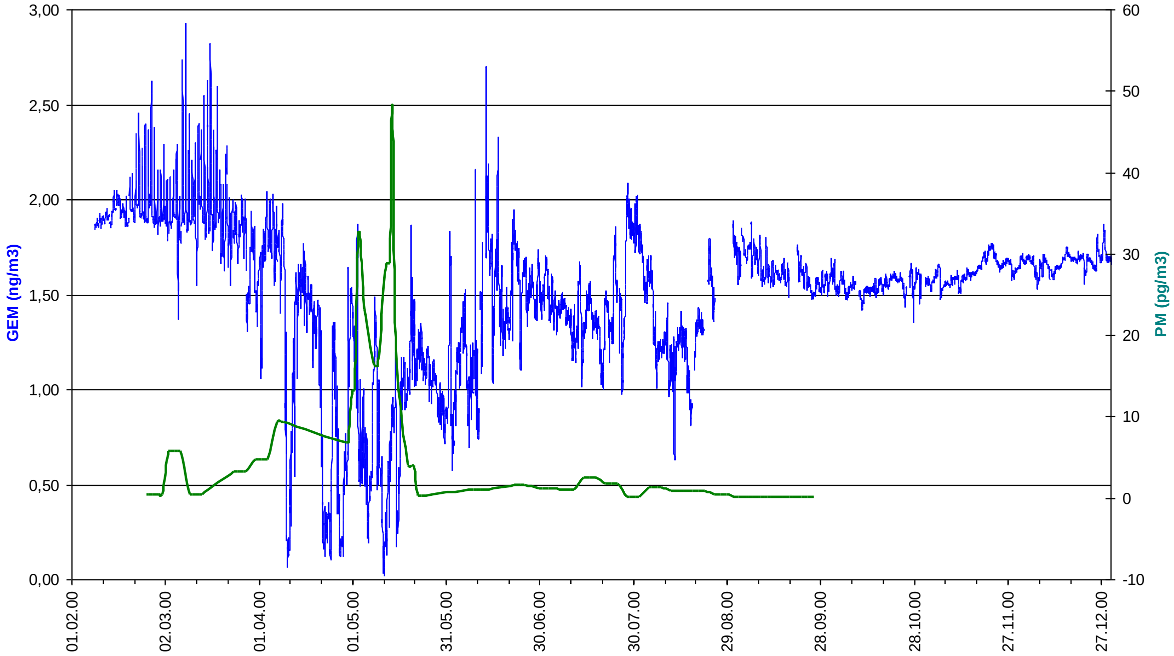

Figure B 3: Time series of GEM (blue) and PM (green) Zeppelin during 2000

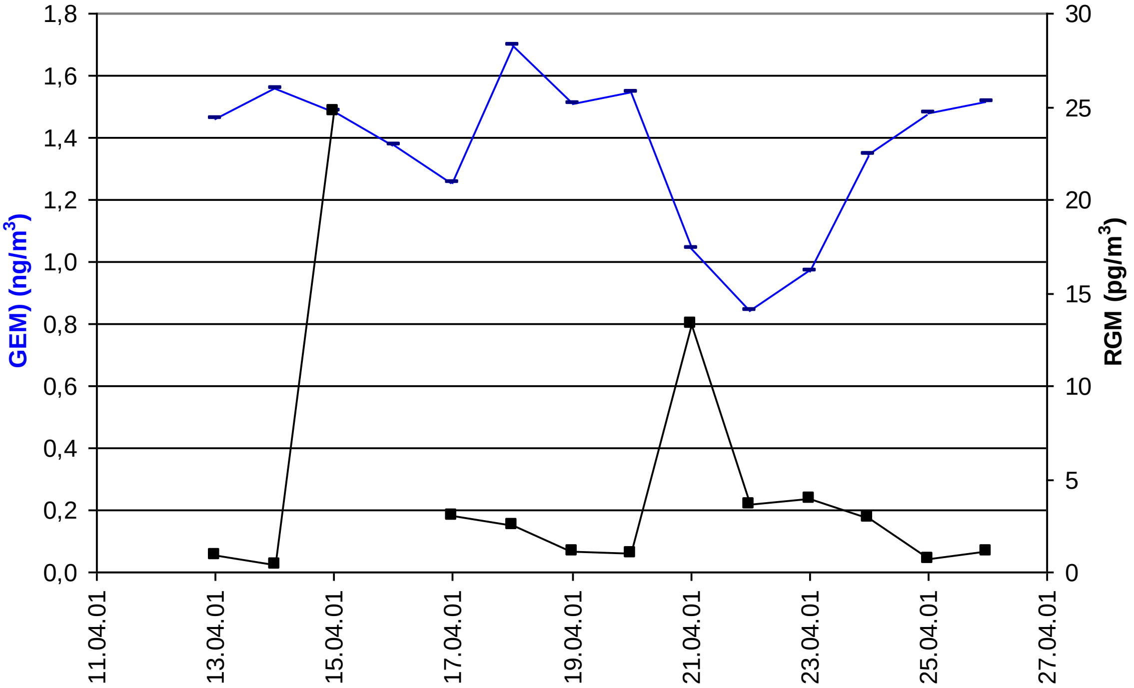

Figure B 4: Time series of GEM (blue)and RGM (black) at Zeppelin during spring 2001

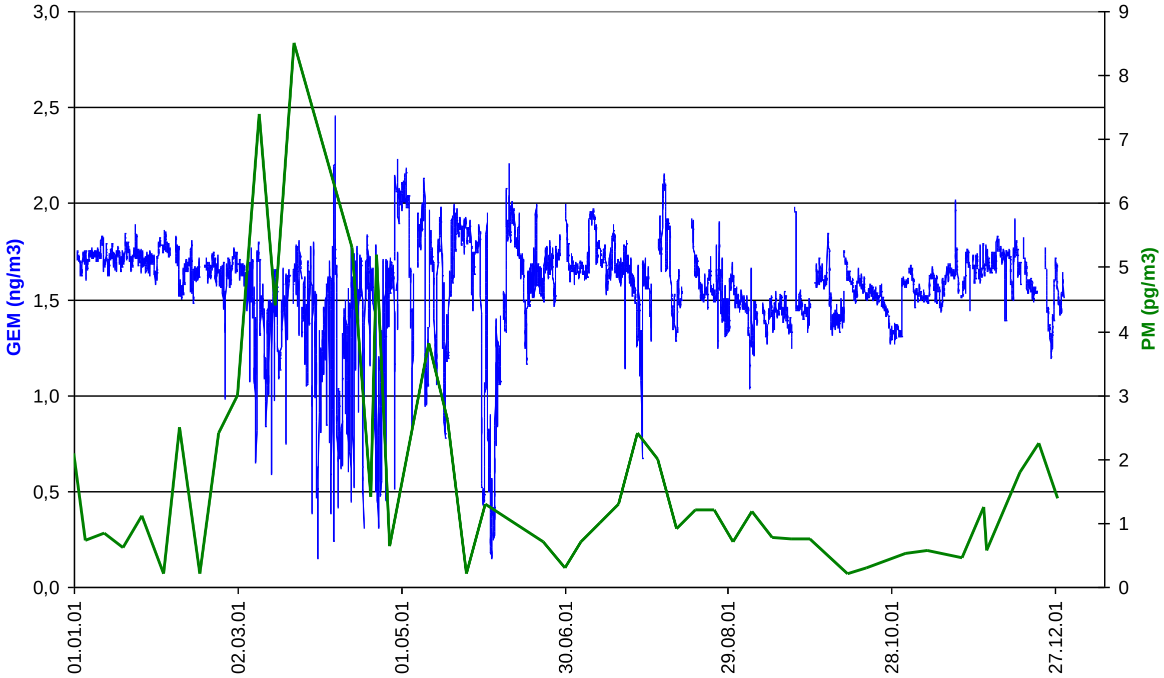

Figure B 5: Time series of GEM (blue) and PM (green) Zeppelin during 2001

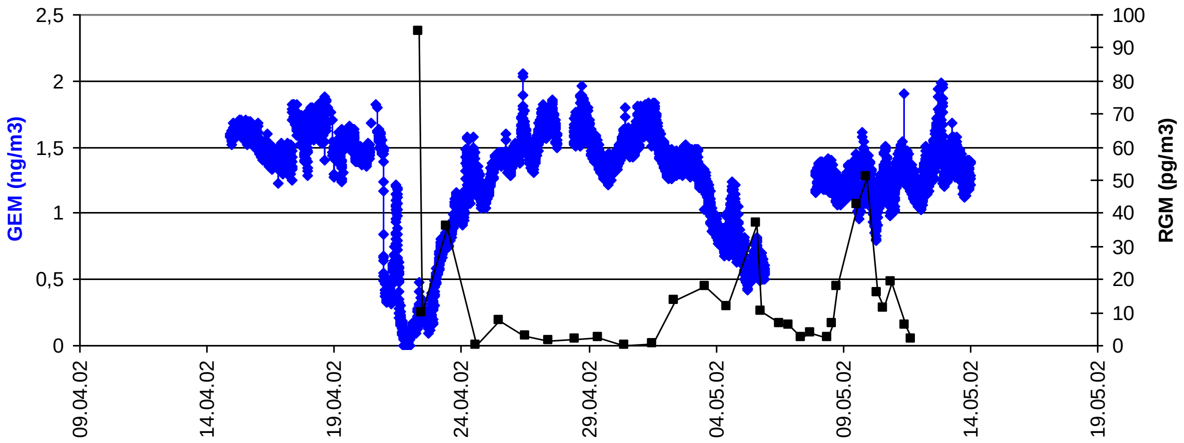

Figure B 6: Time series of GEM and RGM at Zeppelin during spring 2002

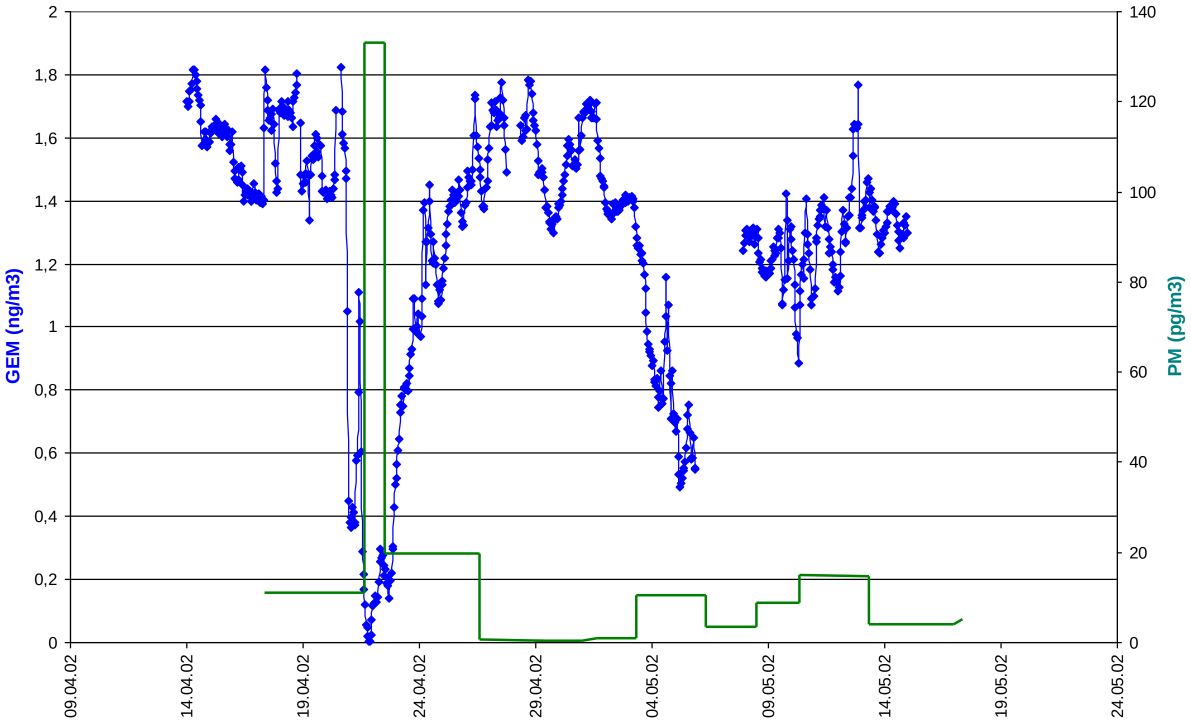

Figure B 7: Time series of GEM and PM at Zeppelin during spring 2002

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STIKKORD		
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REFERAT

Rapporten presenterer resultater fra tre års målinger av atmosfærisk kvikksølv ved Zeppelinstasjonen, Ny-Ålesund, Svalbard. Det er også tatt med resultater fra flere kvikksølvnedbrytingskampanjer som er gjennomført etter polar soloppgang.

TITLE

Atmospheric mercury at the Zeppelin station

ABSTRACT

The report presents results from three eyars measurements of atmospheric mercury at the Zeppelin atmospheric research station, Ny-Ålesund, Svalbard. Results from several mercury depletion campaigns carried out after polar sunrise are also included.

** Kategorier:*	*A*	*Åpen - kan bestilles fra NILU*
	B	*Begrenset distribusjon*
	C	*Kan ikke utleveres*

Statlig program for forurensningsovervåking omfatter overvåking av forurensningsforholdene i luft og nedbør, skog, grunnvann, vassdrag, fjorder og havområder.

Overvåkingsprogrammet dekker langsiktige undersøkelser av:

- overgjødsling av ferskvann og kystområder
- forsuring (sur nedbør)
- ozon (ved bakken og i stratosfæren)
- klimagasser
- miljøgifter

Overvåkingsprogrammet skal gi informasjon om tilstanden og utviklingen av forurensningssituasjonen, og påvise eventuell uheldig utvikling på et tidlig tidspunkt. Programmet skal dekke myndighetenes informasjonsbehov om forurensningsforholdene, registrere virkningen av iverksatte tiltak for å redusere forurensningen, og danne grunnlag for vurdering av nye tiltak. SFT er ansvarlig for gjennomføringen av overvåkingsprogrammet.

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