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Atmospheric Mercury in Sweden, Northern Finland and Northern Europe

Results from National Monitoring and European Research

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Report Summary

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Atmospheric Mercury in Sweden, Northern Finland and Northern Europe

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Sammanfattning/Summary

Atmospheric mercury concentrations and mercury fluxes measured during the period 1995 to 1999 at the AMAP master station of Pallas, a remote station in Northern Finland, and at Rörvik an EMEP station located on the West Coast of Sweden are reported. The result are discussed and compared with atmospheric mercury data generated within the EU-project, Mercury over Europe (MOE). Total particulate mercury exhibit a strong south to north gradient with the highest concentrations in the south, near source areas in Central Europe. Mercury in precipitation also exhibits a south to north gradient.

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Content

Introduction

Mercury is an atmospheric pollutant with a complex biogeochemical cycle. The atmospheric cycling includes chemical oxidation/reduction in both gaseous and aqueous phases, deposition and re-emission from natural surfaces in addition to emissions from both natural and anthropogenic sources (Schroeder and Munthe, 1998).

In the atmosphere, mercury exists in three different forms; elemental mercury vapour (Hg^0), gaseous divalent compounds (Hg(II)) and associated with particulate matter (Hg(p)). The three different species have different atmospheric behaviour and lifetimes. Hg^0 is stable with a lifetime in the range 0,5 to 2 years and is thus capable of distribution on a global scale. Hg(II) and Hg(p) are more readily deposited on local to regional scales via wet or dry processes.

Long-range transport has been shown to be an important source of mercury in many remote regions (Brosset, 1987; Iverfeldt, 1991; Petersen *et al.*, 1995). These findings were the basis for discussions of international agreements on mercury emission control which led to the signing of a heavy metals protocol for mercury (as well as cadmium and lead) within the framework of the UN-ECE Convention on Long-Range Transboundary Transport of Air Pollutants (UN-ECE, 1998).

In order to derive cost-efficient control strategies for mercury, it is necessary to have quantitative information on emissions, air transport and deposition of mercury. An important part of this information is measurement data of atmospheric mercury species which can be used for source-receptor calculations using regional atmospheric models. Mercury is a part of the EMEP monitoring network in Europe but has until this year been a voluntary contribution. For this reason, information on atmospheric distribution and concentrations of different mercury species is not readily available.

This report describes results from measurements at the AMAP master station of Pallas, a remote station in Northern Finland, and at Rörvik an EMEP station located on the West Coast of Sweden. The location of the two stations is shown in Figure 1. Atmospheric mercury concentrations and mercury fluxes measured during the period 1995 to 1999 are presented. The result will be discussed and compared with atmospheric mercury data generated within the on-going MOE project. The MOE project (Mercury Over Europe) is a research project funded by the Fourth Framework Programme, Environment and Climate, of the European Commission.

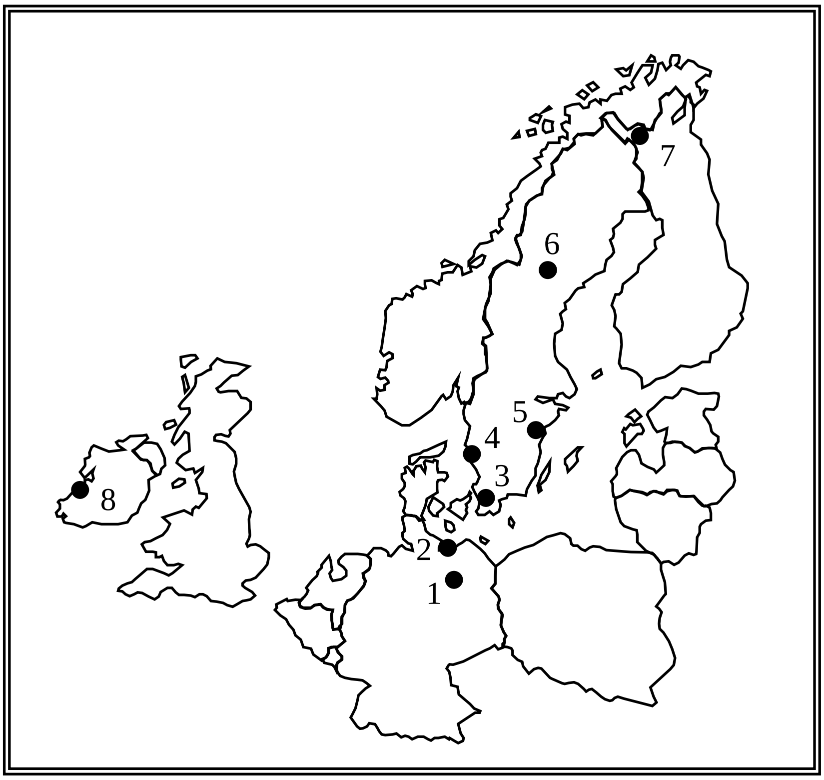

Figure 1. Measurement station map: 1 Neuglobsow, 2 Zingst, 3 Vavihill, 4 Rörvik, 5 Aspvreten, 6 Bredkälen, 7 Pallas and 8 Mace Head.

Sampling and analysis methods

Sampling and analysis of Total Gaseous Mercury (TGM)

The sampling method is based on mercury amalgamation with gold. With the manual Au-trap method, gaseous mercury is sampled by drawing known air volumes through quartz glass tubes containing gold coated quartz glass pieces. The air is pulled through the trap using an air pump and the air volume is measured using a volume meter. The gold traps were analysed at the IVL laboratory by pyrolysis and Cold Vapour Atomic Fluorescence Spectroscopy detection (CVAFS) (Brosset, 1987; Bloom and Fitzgerald, 1988). Samples were collected during 24 h periods with a frequency of 1 to 2 samples per week. The air flow rate was kept at 0.3 – 0.4 L min^{-1} giving a detection limit of 0.01 ng m^{-3} for a 24 h sample time.

Sampling and analysis of Total Particulate Mercury (TPM)

Particles were sampled on Teflon membrane filters with a pore size of 0.45 μm contained in Teflon filter packs. The sampling flow rate is about 10 L min^{-1}. The filters are analysed via acid digestion where the mercury is dissolved as mercury(II). The mercury content of the digestion solution is determined by standard methods (US-EPA-method 1631), i.e. Sn(II) reduction and pre-concentration via Au-amalgamation followed by CVAFS detection. One week average samples were collected with a frequency of 1 to 3 samples per month. The detection limit is 0.1 pg m^{-3}.

During measurement campaigns within the MOE project (Wängberg et al., 2000) an additional method was used to measure TPM at the Rörvik station. A quartz micro-fibre filter (Munktell MK 360), of 7 mm diameter is housed in a quarts glass tube of 140 mm length. The micro-fibre filter is supported by a pure Ni-screen. This device has been developed at IVL following the approach of Julia Lu et al. (1998) and serves as both particulate trap and pyrolyzer for airborne particulate species. The air to be sampled is drawn through the quartz tube at a flow rate of 4-6 L min^{-1}. The Hg content is then analysed via pyrolysis where the trap is heated to 900^{o}C in a stream of argon. In this step, the Hg is reduced to Hg^{0} and subsequently transferred to the gas phase and detected by conventional amalgamation – thermal desorption - CVAFS detection. A 21 h average TPM sample were collected each day starting 12:00 (local time) and ending 9:00 in the morning the following day. The TPM sampling technique allowed a detection limit of 1.0 pg m^{-3} for a 21 h sampling time.

Precipitation sampling and Hg(tot) and MeHg analysis

Precipitation was collected using an open collector, i.e. bulk sampling according to Iverfeldt, 1991a,b; Jensen and Iverfeldt, 1993. The precipitation sampler consists of a borosilicate glass funnel of 8.2 cm diameter and a 500 ml borosilicate glass bottle, which are housed in a polypropylene tube. The precipitation is transferred to the bottle via a capillary tube of 0.4 cm inner diameter. The capillary prevents the sample from evaporation. To preserve the sample the bottles contain 2.5 ml concentrated HCl. The setup is protected from freezing by help of electrical heating. Monthly triplicate samples were collected at each station. The reported values are averages from the three samples.

Analyses of total mercury and methyl mercury in the precipitation samples were made at the accredited laboratory of IVL. The total mercury content was determined by first treating the sample with bromine monochloride and analysing using the US-EPA-method 1631. The detection limit is 0.05 ng/L. Analysis of methyl mercury involves a preliminary step where a volatile derivative, ethyl metylmercury, is generated. The ethyl methylmercury is then purged of the solution and separated on GC column followed by reduction to Hg via pyrolysis and CVAFS detection The method is well documented in the literature (Bloom, 1989; Bloom et al., 1995). The detection limit is 0.05 ng/L.

Results

TGM concentrations

The TGM concentration levels measured at Pallas and Rörvik are very similar. Typical time series of TGM data from the two stations are shown in Figure 2 and 3. The data is from 1997 but can be taken to represent the overall feature of the period 1996 to 1999. Individual 24 h average TGM vary in a rather narrow range between 1-2 ng m^{-3} with few outliers. As is shown in Table 1 the annual average concentration for the period studied is between 1.3 to 1.5 ng m^{-3}.

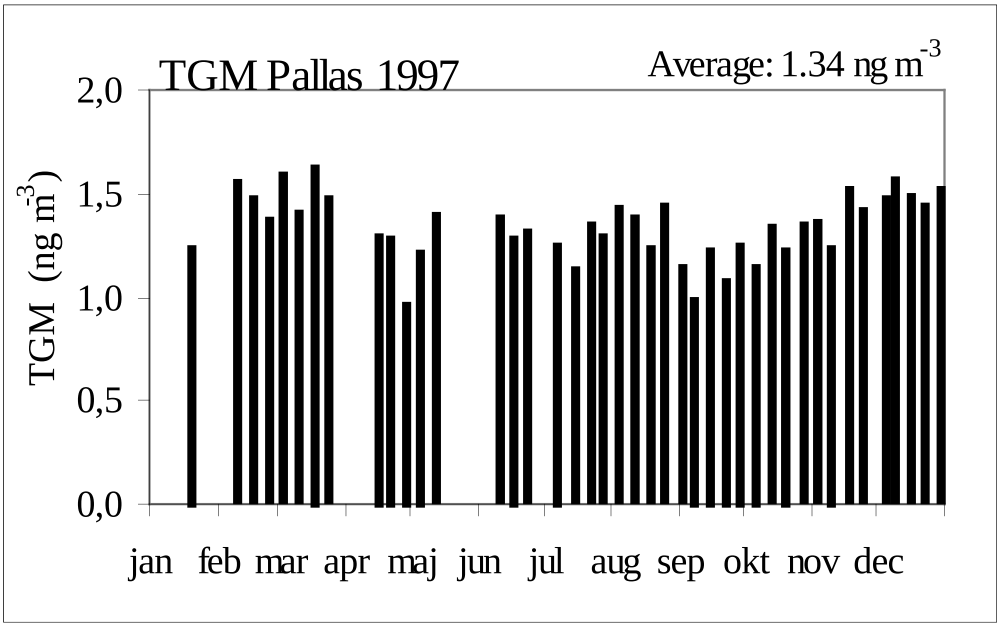

Figure 2. Total gaseous mercury (TGM) at Pallas, 1997.

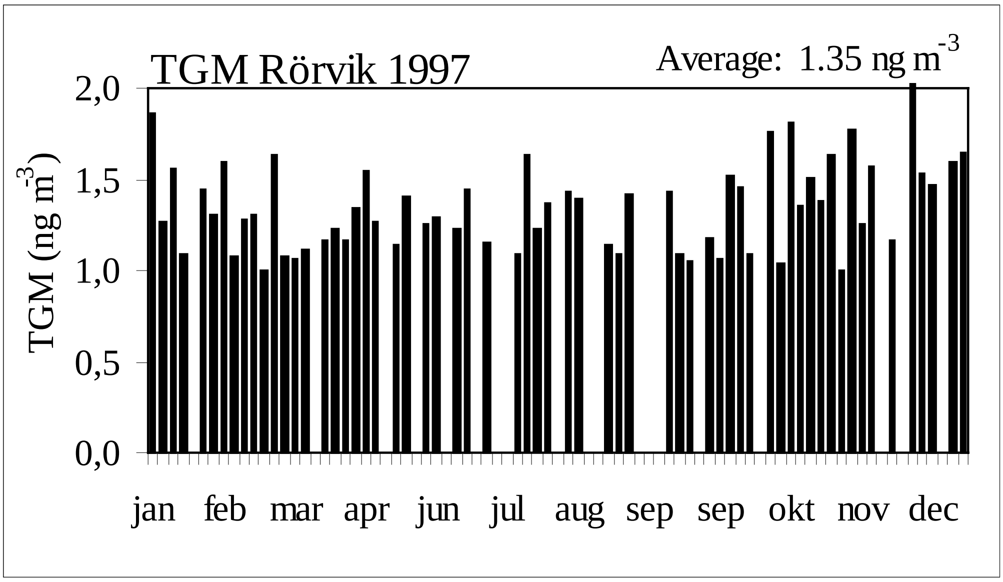

Figure 3. Total Gaseous Mercury (TGM) at Rörvik, 1997.

No pronounced seasonal variation can be found in the TGM data. The relative uniform distribution is reasonable since TGM predominately depends on the relatively stable global/hemispheric background concentration and only occasionally shows higher values, due to influence from major sources.

Table 1. Annual average atmospheric mercury concentrations and deposition fluxes

PALLAS					RÖRVIK			
Year	TGM ng m^{-3}	TPM pg m^{-3}	Deposition Hg(tot) µg m^{-2} y^{-1}	Deposition MeHg µg m^{-2} y^{-1}	TGM ng m^{-3}	TPM pg m^{-3}	Deposition Hg(tot) µg m^{-2} y^{-1}	Deposition MeHg µg m^{-2} y^{-1}
1995	-	-	-	-	1,39	-	8,97	0,090
1996	1,30	1,5	2,12	0,063	1,35	-	8,14	0,060
1997	1,34	1,5	2,52	0,061	1,35	-	6,99	0,084
1998	1,50	1,7	2,50	0,060	1,53	-	4,25	0,029
1999	1,41	1,4	1,91	0,050	1,46	8,7	6,52	0,143

The TGM value from Pallas 1999 may be compared to annual TGM values obtained within the MOE project. Average TGM values from the MOE campaigns measured in 1999 are show in Figure 4 together with the average TGM at Pallas. The stations Neuglobsow to Pallas form a south to north transect, as is shown in Figure 1, starting with the Neuglobsow station 100 km north of Berlin and ending at Pallas, just above the polar circle in Finland. As is shown there is a descending south to north trend in the TGM. This feature also has been observed earlier (Schmolke et al., 1999). The higher values at the German stations reflects the proximity to principal mercury source areas in central Europe.

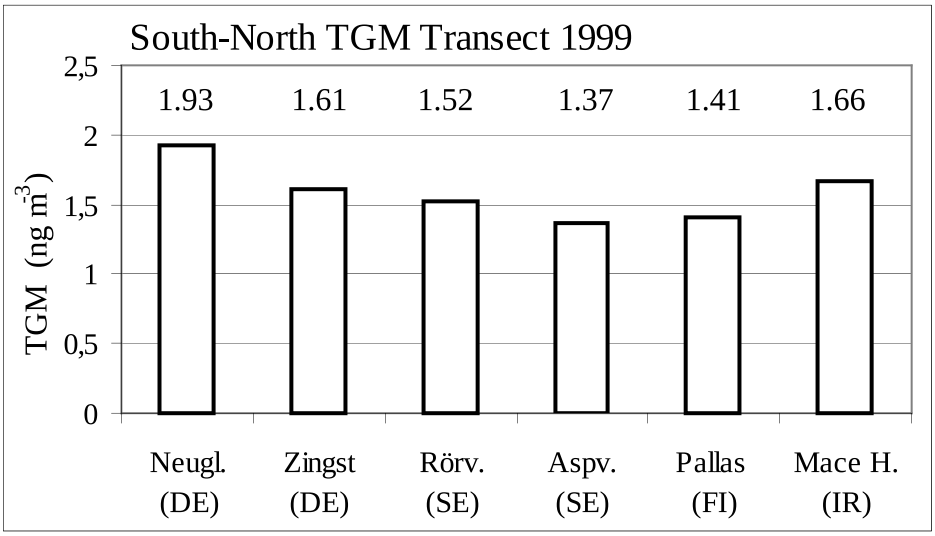

Figure 4. Comparison of average TGM values from 6 European measurement stations during 1999. The MOE data are average values from four MOE campaigns, each of two weeks duration, made in February 99, May 99, July 99 and November 99.

The average TGM measured at Mace Head, Ireland is also included in Figure 4. This site is used as a reference for the input of Atlantic air to Northern Europe. The prevailing wind sector at Mace Head is 180^o-300^o, representing clean Atlantic air. Only TGM data associated with this clean wind sector have been used to calculate the average concentration presented in Figure 4. Interestingly, the average TGM value from Mace Head seems to be higher than those in Sweden and at Pallas. The reason for this phenomenon is not known, but could be a result of re-emissions of mercury from the North Atlantic Sea which have been shown to be substantial (Mason *et al*, 1998). Removal processes over land like dry deposition to vegetation or atmospheric conversion to oxidised species may also contribute.

TPM Concentrations

As is clearly seen in Table 1 the TPM concentration at Pallas is very low, with yearly averages in the order of 1.5 pg m^{-3}. Over the period 1996-1999 all TPM values obtained are in a narrow range between 0 – 7.4 pg m^{-3}. The TPM values measured at Rörvik are often as low as one or a few pg m^{-3}, but vary within a much broader range. During the MOE campaign 1999 values between 1 and 40 pg m^{-3} were obtained with an average of 8.7 pg m^{-3}. The TPM values obtained within the MOE project show a pronounced south to north descending geographical distribution as is evident from Figure 5.

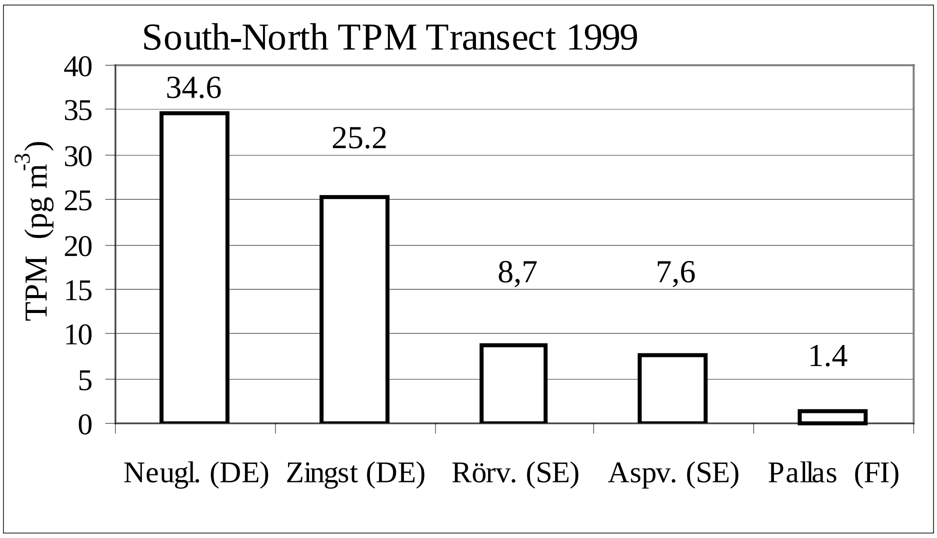

Figure 5. Comparison of average TPM values from 6 European measurement stations during 1999. All data except that from Pallas are from the Moe project.

Wind trajectory analysis made within the MOE project clearly show that elevated TPM values, which occasionally are observed at the Swedish sites, are caused by transport from Central Europe. One event, during November 1999, with elevated TPM values at the Neuglobsow, Zingst and Rörvik stations, clearly demonstrates this phenomenon. The TPM data from this period is shown in Figure 6. The TPM concentration at the German sites increases dramatically from relatively low values of about 20 pg m^{-3}, on the 2nd of November, to 74 and 110 pg m^{-3}, respectively, during a 3 days long period. After 4 days the concentrations have reached an intermediate level that lasted for one more day until it eventually decreased further. The same pattern is seen in the Rörvik data, but with about 24 h delay. The TPM values from Aspvreten also seem to be part in this trend although the effect is not as strongly pronounced. Back trajectories calculated for the Rörvik site show that the wind originated from the Atlantic during the 2nd and 3rd of November. During the following days, the wind path changed quite dramatically to Southeast, and simultaneously the TPM at Rörvik increased from 6 to 31 pg m^{-3}. The wind direction remained from the Southeast until the 9th of November when it changed back to westerly winds again. Simultaneously the TPM at Rörvik dropped from 23 to 6 pg m^{-3}. One wind trajectory calculated for Rörvik at the day with the maximum TPM concentration is shown in Figure 7. As is indicated in the Figure, the time needed for transport of air masses between Rörvik and Northeast Europe, a distance of 500 km, is about 24 h. This transport time fits exactly with the time delay in the TPM data as mentioned above.

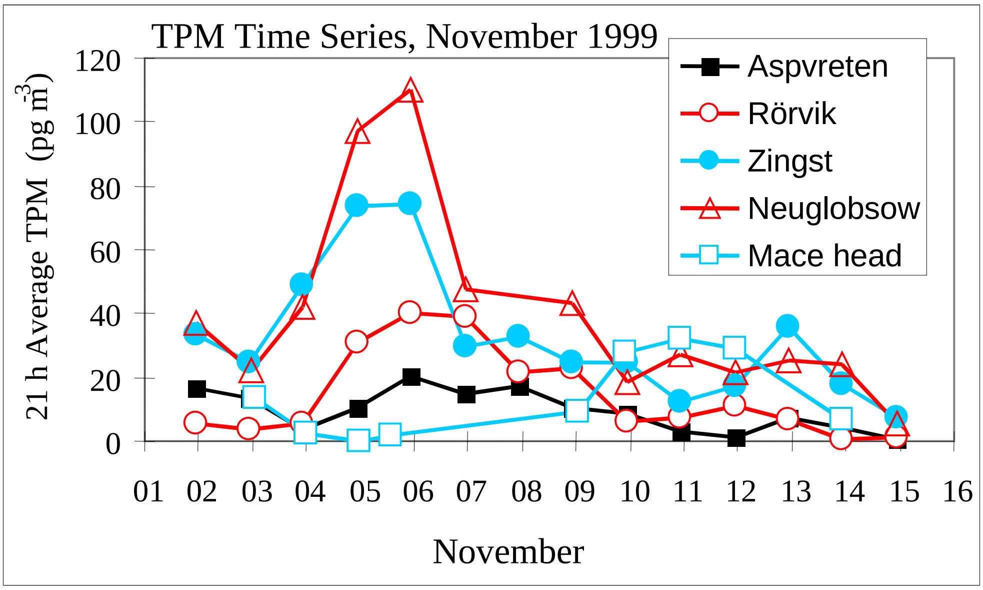

Figure 6. TPM time series from the MOE campaign, 1-15 November 1999.

Elevated TPM values are seldom seen at Pallas and it is reasonable to assume that the large geographical distance between Pallas and source areas in Europe limits air transport of particles. Particles in air masses coming from the south will to the most part be washed out by precipitation or dry deposited before reaching as far north as to the polar circle.

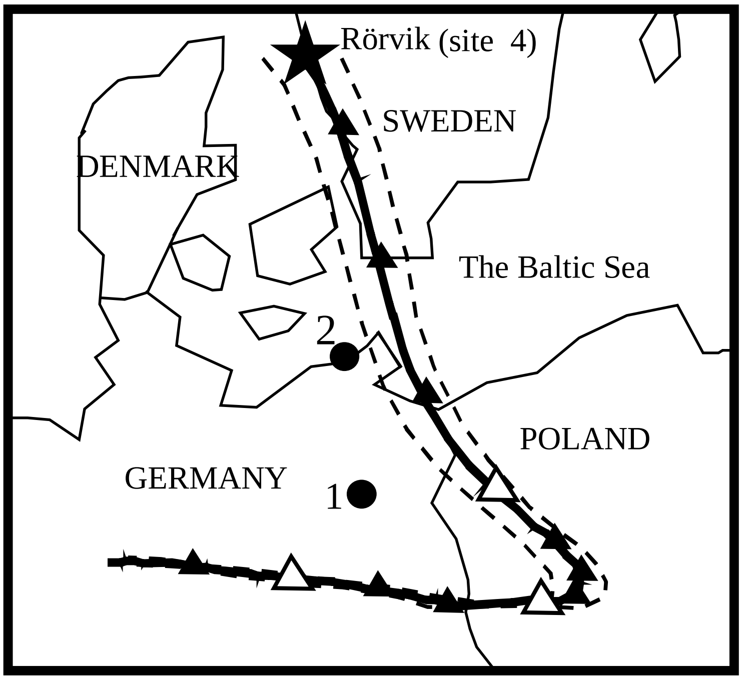

Figure 7. 82 h back trajectories starting at Rörvik 22:00, 5 November 1999. The starting height was 20 m. Filled triangles mark 6 h time intervals and the open triangels mark 24 h intervals. Dotted lines are back trajectories calculated with starting points 37 km west and 37 km east of the Rörvik site.

3.3 Mercury Wet Deposition

Annual wet deposition fluxes of Hg(tot) and MeHg from four Swedish stations and from Pallas are shown in Figure 8 and 9. The Vavihill station is located in District of Skåne in the south of Sweden and Bredkälen in the District of Jämtland in the north as is indicated in Figure 1. The stations in the figures are listed in geographical order from south to north. The deposition fluxes of Hg(tot) show a pronounced geographical trend. Interestingly, the data indicate that Hg(tot) fluxes decreases over the period 1995 to 1999 at some stations. The geographical trend is in accordance with the other mercury data presented above. Concerning MeHg there is no evidence for a temporal decreasing trend, but the general pattern with the highest values found in the south seems to hold.

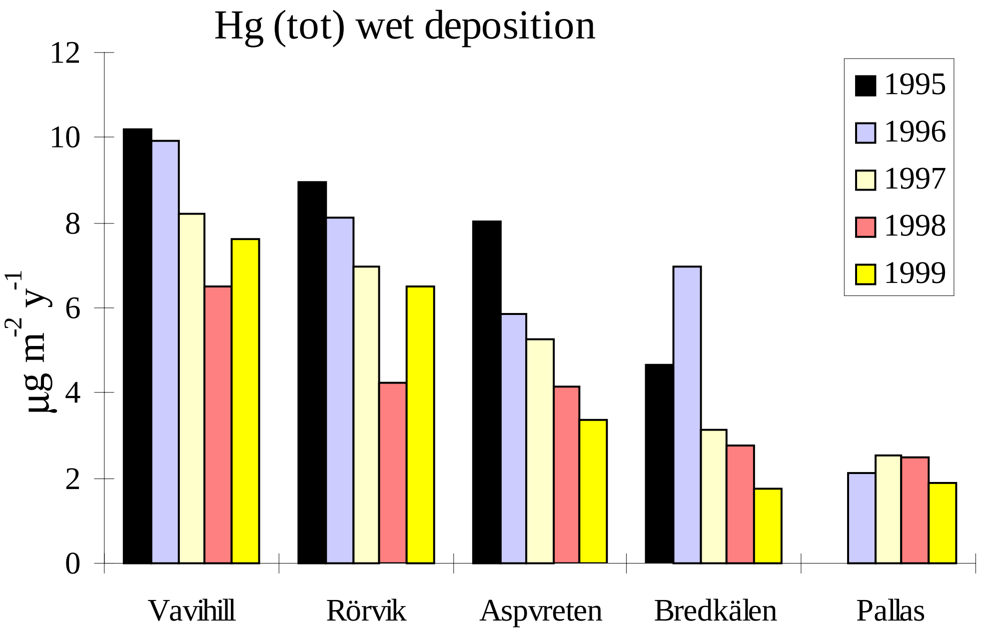

Figure 8. Wet deposition of Hg(tot) at Swedish monitoring sites.

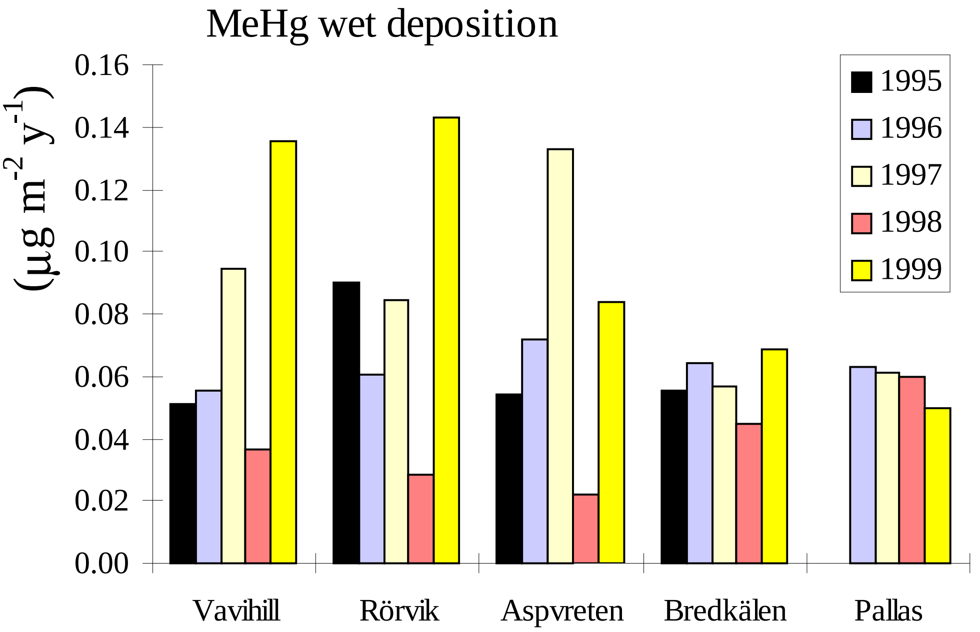

Figure 9. Wet deposition of MeHg at Swedish monitoring sites.

Discussion and conclusions

Atmospheric mercury at northern European monitoring stations consists of contributions from both global background and regional source areas. For Total Gaseous Mercury (TGM), the global component is dominant and influences from anthropogenic sources can only be seen clearly at the German stations Neuglobsow and Zingst and to some extent at the station on the Swedish west coast, Rörvik. The global background of TGM should not be interpreted as a natural background but also contains significant contributions from anthropogenic emissions of TGM as well as re-emissions of previously deposited mercury.

Total Particulate Mercury (TPM) exhibits a strong south to north gradient with higher concentrations near source areas in Central Europe. Annual average concentrations at the northernmost station, Pallas, are 1.5 pg m^{-3} and at Rörvik 8.7 pg m^{-3} *i.e.* nearly a factor of 6 higher at Rörvik. Trajectory analyses of episodes with concentrations at Rörvik reaching >30 pg m^{-3} indicate the main source areas in Central Europe. Due to more efficient wash-out and dry deposition of TPM in compartison to TGM, very little transport occurs to the Pallas station.

Mercury in precipitiation also exhbits a south to north gradient with wet deposition fluxes at Rörvik of 7.0 µg m^{-2} and 2.3 in Pallas (annual averages for 1995 to 1999). This represents an decrease by a factor of 3 when moving from south to north *i.e.* less than the difference for TPM. The wet deposition is also influenced by oxidation of Hg^0 to water soluble species and a smaller difference in gradient is thus expected.

Methylmercury (MeHg) in precipitation varies significantly between years at the stations in southern Sweden. Significant anthropogenic or natural sources of MeHg are not known and further investigations of the atmospheric cycling of this species are needed before the variations in concentrations and deposition fluxes can be explained. The wet deposition of MeHg varies considerably less at Pallas and Bredkälen possibly indicating that the southern stations are influenced by episodes of transport from sources or by the presence of precursors leading to atmospheric formation of MeHg.

Acknowledgments

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The Pallas station is operated by the Finnish Meteorological Institute (FMI). The Mace Head station is operated by the University of Galway, Ireland, and the mercury measurements were made by the GKSS Research Center, Geestacht, Germany. Neuglobsow and Zingst are national monitoring stations operated by the Umweltbundesamt, Germany.

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