Dynamics of gaseos elemental mercury during polar spring and winter

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Abstract

Among pollutants, mercury is a major environmental concern due to its ecological hazard. The mercury can reside in the atmosphere for a long time high, and it is a reason of its global propagation in the Northern Hemisphere and elevated mercury concentrations are reported in the Arctic environment. First time, in 1995, the effect of atmospheric mercury depletion in the troposphere was found at the Canadian station Alert. This phenomenon (called the Atmospheric Mercury Depletion Event - AMDE) is observed during April-June, when the polar sunrise starts till the end of the snowmelt. The same effect was reported for other polar stations situated northerly than 60° N.

Since 2001, the analyzer was placed at Amderma station 69.46°N, 61.41°E, Yugor Peninsula, Nenets Autonomous Region, Russia) distances (ranging from 8.9 to 0.2 km) from the coast of the Kara Sea (see Figure 1). It is necessary to note that such experiment was carried out for the first time during the monitoring in surface layer of the atmosphere at the Russian polar station (Pankratov et al., 2013).

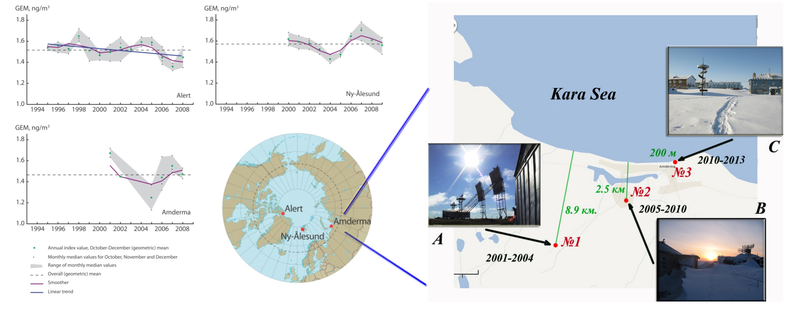

Fig 1. Network of atmospheric mercury monitoring station in the Northern Hemisphere with corresponding to time series of measurements (AMAP, 2011); Geographical locations of the Tekran analyzer for observation period from 2001 to 2013 at the polar station "Amderma".

Atmospheric mercury measurements

Long-term continuous monitoring of gaseous elemental mercury in the surface air at the polar station Amderma using the analyzer Tekran 2537A has been conducted from June 2001 to date. Individual measurements were collected every 30 minutes. It has been shown, that during 11 years of observations the AMDEs were observed every year, from the end of March till early June. For the winter season (Dec-Feb) these events of the atmospheric mercury depletion were registered from 2010 to 2013, which had not been observed before (Fig. 2). A large number of hours during the day, when the concentration of mercury was recorded at level of below 1 ng/m^3, during Dec-Feb. However, the sun declination above the horizon is negative for these seasons, and solar activity is still not enough to trigger the photochemical reactions, but nevertheless AMDEs are registrated in winter seasons (Fig. 2, E-F) (Pankratov et al., 2013).

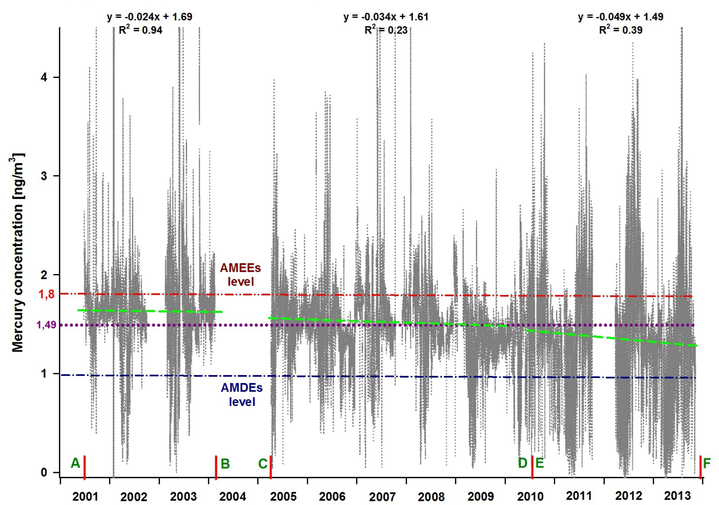

Fig 2. Long-term series of atmospheric mercury measurement at the Amderma station from 2001-2013; a linear approximation the annual trend in averages of mercury (green dashed line).

Daily dynamic of atmospheric mercury duringthe polar spring and winter

Since mid-January the duration of the day starts to increase but solar energy is not enough to activate the photochemical reactions, as the predominant type of solar radiation is diffuse rather than direct one (Fig. 3 a, purple line). However, mercury depletion events were reported at the time and the maximum number of events were registered in January 2011 (18 events, the maximum duration was 46 hours). In the spring, since the second half of March (Fig. 3, b), the angle of declination of the sun increases and the incoming total solar energy is sufficient to activate the photochemical reactions. However, during two moths (March–May) there was no linear relationship between the decline of the sun above the horizon (red solid line) and the number of mercury depletion events (Fig. 3, b).

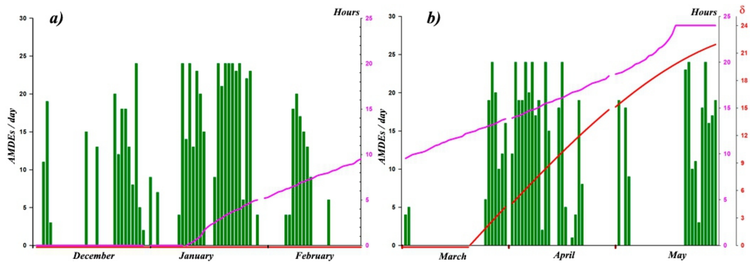

Fig. 3. Number of decreased values of mercury concentration in the atmosphere during the day (bar chart). The purple line is duration of the day (hours), the red line is declination of the sun above the horizon (δ) for the period December-January 2010–2011 (a) and March-May 2011 (b).

For the winter (December-January) period, the maximum number (in total, 495) of lowered values of mercury concentration and AMDEs (32 events) were recorded in 2010–2011. Such situation was previously observed only in winter of 2006–2007 (13 events). As there is no direct sunlight in mentioned period, the removal of mercury from the atmosphere may be caused by combination of physical and chemical processes that are not related to photochemistry. Starting mid-January, although duration of the day increases, but solar energy is not enough to activate photochemical reactions and predominant type of solar radiation is diffuse rather than direct one. However, AMDEs were still reported at that time (18 events were registered in January 2011).

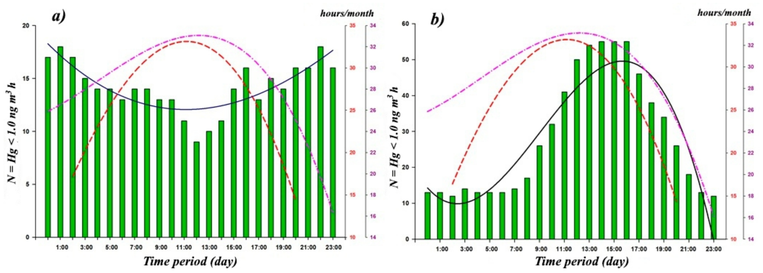

Fig. 4. Daily dynamics of the AMDEs number (mercury concentration < 1.0 ng m^{-3} h) in the spring of 2005 (a) and 2011 (b). Solid line is a polynomial trend line. Dashed red line and dash dotted purple line are polynomial trend lines of solar activity in March and May, respectively.

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Parallel measurement of AMDEs frequence using GEM analyzers Tekran 2537A and Lumex RA-915AM

In 2015 at the polar station Amderma the mercury analyzer Lumex RA-915AM was installed to measure background concentrations of GEM in parallel with Tekran 2527A. A mercury analyzer with a more simplified configuration, installation and maintenance as compared to Tekran 2527A but with the similar reliability and precision is a great necessity for the Russian Arctic. Lumex RA-915AM is a candidate considering the good correlation between parallel measurements of Tekran 2527A and Lumex RA-915AM of low GEM concentrations (R2 = 0.95) at mid-latitudes. During the winter and spring 2015-2016 Tekran 2527A registered the expected number of AMDEs (about 30% of measurements), while Lumex RA-915A registered as AMDEs only 5% of

It can be assumed that the different number of registered AMDEs in the parallel measurement of GEM Tekran 2527A and Lumex RA-915AM analyzers is due to the following reasons:

Blocking sorption sites of pure gold sorbent used in the Tekran 2527A analyzer by high concentrations of halogens (bromides and sulfates) associated with increased content of marine aerosol, which are usually accompanied by AMDEs. As a result, the efficiency of GEM trapping by the gold sorbent can be reduced.

Sorption competition of GEM with products of catalytic conversion of organic substances on the surface of a gold sorbent (as known, a gold sorbent can serve as a catalyst for various chemical processes).

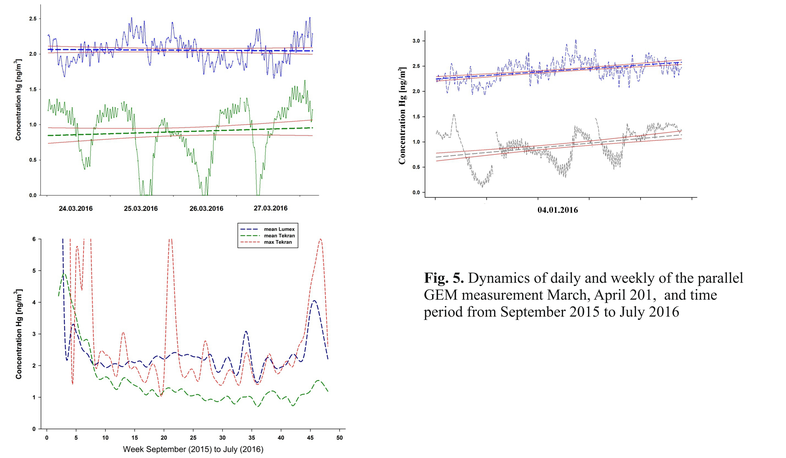

Fig. 5. Dynamics of daily and weekly of the parallel GEM measurement March, April 201, and time period from September 2015 to July 2016

Conclusions

1. **The results raise the issue of the problem of registration of AMDEs in the Arctic.**
2. **For the first time, as a result of parallel measurements of GEM by the Tekran 2527A and Lumex RA-915AM analyzers, the difference in the number of registered cases of AMDEs was revealed.**
3. **Lumex RA-915AM uses a direct GEM registration system in the ambient air, while Tekran 2527A uses an additional sorption concentrating phase.**
4. **The observed effect requires confirmation and further parallel measurements of GEM in other polar regions using mercury analyzers of various recording systems.**

Acknowledgements

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