Journal of Hazardous Materials 317 (2016) 362–372

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Total gaseous mercury along a transect from coastal to central Antarctic: Spatial and diurnal variations

Jiancheng Wang [a], Lulu Zhang [a], Zhouqing Xie [a,b,*]

[a] Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China
[b] Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

HIGHLIGHTS

- TGM varied considerably in the Antarctic boundary layer.
- Spatial distribution of TGM is related to topography.
- TGM showed clear diurnal variations at Dome A.
- The diurnal variations of TGM are likely caused by a combination of processes.

ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 20 May 2016
Accepted 22 May 2016
Available online 2 June 2016

Keywords:
Total gaseous mercury (TGM)
Antarctic
Spatial distribution
Diurnal cycling

ABSTRACT

Total gaseous mercury (TGM) in the atmospheric boundary layer was investigated along a transect from coastal (Zhongshan Station; 69°22′25″S, 76°22′14″E) to central (Kunlun Station; 80°25′2″S, 77°6′47″E) Antarctic from December 16, 2012 to February 6, 2013. TGM varied considerably from 0.32 to 2.34 ng m^{-3} with a mean value of 0.91 ng m^{-3}. Spatially, relatively high values occurred near the coastal region and on the central plateau with altitude higher than 3000 m above sea level. This distribution pattern cannot be accounted for simply by the influence of mercury emission from the ocean. Changes in TGM were also found to be related to the topography. TGM was higher in the inland flat region (290–800 km from the coast) than in the inland transition zones with steep slopes (800–1000 km from the coast). Temporally, diurnal cycling of TGM was clearly observed at Kunlun Station, with the lowest value occurring typically at midnight, and the peak value at midday. This diurnal pattern was attributed to the reemission of gaseous elemental mercury (GEM) from the snow pack, the oxidization of GEM and convective mixing.

1. Introduction

Mercury (Hg) is noxious and becomes potentially bioavailable by transformation to more toxic compounds [1]. Due to its ubiquitous presence and neurotoxicity, mercury attracts considerable interest with respect to a global health concern. Although atmospheric mercury constitutes a minor component of mercury compared with that in soil or water, its long residence time and thus long-range transport are important pathways by which mercury is distributed globally, even in remote polar regions [2]. Atmospheric mercury is often operationally distinguished into three main species, i.e. gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particle-bound mercury (PBM). The sum of GEM and RGM is often referred to as total gaseous mercury (TGM). GEM is typically the dominant form of mercury in ambient air, and the distribution of GEM is often characterized by a relatively constant concentration range over broad regions [3,4]. RGM and PBM are easily scavenged by dry and wet deposition, with a half-life ranging from a few hours to a week [5]. GEM could be oxidized to RGM by atmospheric oxidants such as O_3 and reactive bromine species (e.g., Br and BrO) [6–8]. Atmospheric mercury has been extensively monitored at numerous sites in the Northern Hemisphere (NH) including the Arctic. However, monitoring in the Southern Hemisphere (SH) remains scarce, especially in the Antarctic [2]. As such, the role of the vast Antarctic plateau in the global mercury cycle remains not well understood.

Antarctica is a large continent that is mostly covered by ice and snow. Compared with the Arctic, Antarctica is considered to be even less affected by anthropogenic influences [2]. However, enhanced bioaccumulation of mercury deposition in the local terrestrial ecosystem indicated that anthropogenic mercury could

* Corresponding author at: Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China.
E-mail address: zqxie@ustc.edu.cn (Z. Xie).

http://dx.doi.org/10.1016/j.jhazmat.2016.05.068
0304-3894/

affect such remote areas [9]. Vandal et al. [10] reported mercury deposition spanning the past 34000 years from ice cores, which could serve as a paleo-productivity indicator of the past. Total mercury in surface snow has also been widely studied, and the results have been greatly variable. Some studies have reported extremely high mercury concentrations, such as 198 ng L^{-1} at the South Pole [11], 40–430 ng L^{-1} in coastal sea ice regions (near McMurdo) [12], and 4.2–194.4 ng L^{-1} (mean value of 47.0 ng L^{-1}) between Dumont d'Urville and Dome Concordia station [13]. On the contrary, other studies have reported much lower values, such as those the surface snow samples along a transect from Zhongshan Station to Dome A (ranging from 0.2 to 8.3 ng L^{-1}) [14], and from the coast to Dome Fuji <0.4 to 10.8 ng L^{-1}) [15]. Elevated concentrations of mercury in the surface snow were found in the inland regions of higher altitudes and farther away from the coast [14,15]. The deposition of mercury in snow and ice is possible due to the oxidation of gaseous mercury by oxidants that occur in such cold environment, such as sea-salt-derived halogens [2]. Direct atmospheric mercury measurements are therefore critically needed for understanding mercury exchange between air and snow, and interpreting the mercury data obtained from ice cores. Considering the vast extent of the Antarctic continent, and potentially large amounts of mercury stored on the Antarctic continent, these phenomena could be crucial at a regional scale, even in the worldwide budget.

Studies of gaseous mercury were first conducted in the Antarctic troposphere by De Mora et al. [16] in 1985. The results indicated very low values (0.23 ng m^{-3}) of gaseous mercury along the Antarctic coast. However, very high RGM and PBM (0.1–1 ng m^{-3}, accounting for approximately 50% of TGM) were reported in the ambient air in summer at the South Pole [11]. Dommergue et al. [13] presented unexpectedly high concentrations (0.2–2.3 ng m^{-3}, mean of 0.85 ng m^{-3}) and dynamic recycling of GEM at Concordia Station. Both Brooks et al. [11] and Dommergue et al. [13] suggested that mercury has a reemission/oxidation cycle that occurs in summer, but the mechanism remains unknown.

In this paper, we report the TGM concentrations in the atmospheric boundary layer along a transect from Zhongshan Station (69°22′25″S, 76°22′14″E), located on coastal Antarctic, to Kunlun Station (80°25′2″S, 77°6′46″E) in central Antarctic, from December 16, 2012, to February 6, 2013. The objective is to investigate the spatial and temporal distributions of atmospheric mercury from the coastal zone to the inland plateau, and to further understand the geochemical cycle of mercury over the Antarctic plateau.

2. Experimental methods

2.1. Location

Zhongshan Station (69°22′25″S, 76°22′14″E) is situated on the coast of Prydz Bay in eastern Antarctic. In summer, most of this region is ice free. Kunlun Station (80°25′2″S, 77°6′47″E) is located near (7 km) Dome A (80°22′51″S, 77°27′23″E), the highest elevation point on the Antarctic ice sheet (altitude 4090 m), approximately midway between the head of Lambert Glacier and the South Pole. Temperatures at Dome A fall below −80 °C throughout most of the winter period. This site is one of the driest locations on Earth and receives 1–3 cm of snow per year; however, there is an ice sheet at least 2400 m thick below this region. During the 29th Chinese Antarctic Research Expedition (CHINARE) in 2012–2013, the inland research expedition set out from Zhongshan Station on December 16, 2012, to Kunlun Station, and returned to Zhongshan Station on February 10, 2013. More information pertaining to this expedition can be found in other reports [14,17,18].

As shown in Fig. 1, many campsites were built during the outward- and inward-bound routes: ZS is Zhongshan Station (on the coast), KL is Kunlun Station (1270 km from the coast), A-P (∼1130 km distance) are outward-bound campsites from Zhongshan Station to Kunlun Station (Fig. 1a) from December 16, 2012, to January 3, 2013, and R-S (∼630 km distance) are the inward-bound campsites from Kunlun Station back to Zhongshan Station (Fig. 1b) from January 24 to February 6, 2013. Monitoring of TGM lasted for about 15 days continuously at Kunlun Station, but the monitoring duration was much shorter at other campsites. TGM concentrations of campsites E, G, H, I, L and W were absent due to the absence of electricity and harsh meteorological conditions. During the last sampling period, the carrier air (argon) for the instrument ran out and consequently, monitoring was terminated.

2.2. Experimental methods

During the expedition, we used an automatic vapor analyzer (Tekran 2537X, Tekran Inc., Toronto, Canada) for continuous monitoring of TGM values. Known for its stable performance, capable of continuous long-term and unattended operation, this analyzers have been extensively used by monitoring networks worldwide, including in the polar region [2,19], e.g., the coastal [12,20] and inland [11,13] Antarctic. The sampling inlet is located in the upwind direction, as far as possible (∼50 m, restricted by the power circuit) away from the campsites, and approximately 5 m above the snow surface. The sampling line was wrapped with a heated layer to maintain its temperature at 50 °C. During the 5-min sampling period, the air flowed at a rate of 1.5 L min^{-1} through a 0.45-μm PTFE filter (to prevent aerosols from entering) in front of the inlet before entering the analyzer, and an additional PTFE filter was housed at the end of the sampling line. The Tekran 2537X performed automated recalibrations every 24 h using an internal permeation source. As presented in Ebinghaus et al. [21] and Temme et al. [22], the measurements collected by the Tekran instrument represent TGM, as both GEM and RGM compounds are collected on the gold collectors and transformed to elemental mercury during amalgamation and thermal desorption. According to Steffen et al. [23], a large fraction of the gaseous mercury may be missed due to the obstruction of the two filters; the mercury that is unaccounted for consists of unknown fractions of PBM and/or RGM, which would be quickly scavenged by the snow surface. Therefore, the measured concentrations can be assumed to represent GEM only [13,24]. The TGM detection limit in our operation mode is lower than 0.1 ng m^{-3}. In this paper, the values of the TGM concentrations are reported in ng m^{-3} with 273.16 K and 1013 mbar as standard temperature and pressure, respectively. Similar methods have been used and described in our previous publications [25,26].

Meteorological data were downloaded from NOAA National Environmental Satellite, Date, and Information Service (NESDIS) [27], (http://gis.ncdc.noaa.gov/map/viewer/#app=cdo&cfg=isdsummaries&theme=isdsummaries),

including temperature (T), wind speed (SPD), and wind direction (DIR) on an hourly basis for the lower troposphere at Kunlun Station. The HYSPLIT transport and dispersion model [28] from NOAA-ARL (Air Resources Laboratory) (http://www.arl.noaa.gov/ready/hysplit4.html) was used to identify the potential source from selected points.

3. Results and discussion

3.1. General observations

TGM concentration time series in the boundary layer along the transect from Zhongshan station to Kunlun station and from Kunlun station back to Zhongshan station is shown in Fig. 2. The TGM concentrations ranged from 0.32 ng m^{-3} to 2.34 ng m^{-3}. The