

# CH<sub>4</sub> Monitoring and Background Concentration at Zhongshan Station, Antarctica

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#### Abstract

Background CH<sub>4</sub> concentration and seasonal variations measured at Zhongshan Station (69°22'2"S, 76°21'49"E, 18.5 m) in Antarctica from 2008 through 2013 are presented and discussed. From 2008-2013 CH<sub>4</sub> was measured in weekly flask samples and started on line measurement by Picarro CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>O analyzer from March, 2010-2013. These CH<sub>4</sub> measurements show the expected growth period of CH<sub>4</sub> concentration during February (Antarctic spring) with a peak in September (fall). Irrespective of wind direction, CH<sub>4</sub> concentrations distribute evenly after the removal of polluted air from station operations, accounting for 1% of the data. The mean daily cycle of CH<sub>4</sub> concentration is similar to those at other stations in Antarctica showing that CH<sub>4</sub> observed in Antarctica is fully mixed in the atmosphere as it is transported from the northern through the southern hemisphere. The annual CH<sub>4</sub> increase in recent years at Zhongshan station is 4.8 ppb·yr<sup>-1</sup>.

# **Keywords**

Antarctica, Zhongshan Station, CH<sub>4</sub>, Background CH<sub>4</sub>, Characteristics

# **1. Introduction**

The Intergovernmental Panel on Climate Change (IPCC) [1] states that the CH4 content of the atmosphere ranks

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as the second most important greenhouse gas following CO<sub>2</sub>. The residence time of CH<sub>4</sub> in the atmosphere is about 12 years with a strong infrared adsorption band at 7.66  $\mu$ m that allows it to effectively adsorb long-wave radiation from the earth [2] [3]. The contribution of a single CH<sub>4</sub> molecule to the greenhouse effect is approximately 25 times greater than that of a molecule of CO<sub>2</sub>, and its contribution to total global radiative forcing is 18.1% [4]-[6].

Approximately 40% of the CH<sub>4</sub> discharged into air comes from natural sources such as wetlands whereas 60% is from anthropogenic influenced sources such as ruminants, paddies, fossil fuel production, landfills and biomass burning. The CH<sub>4</sub> reaction with the hydroxyl radical (OH) is its major sink [7] [8]. Given the probable increasing discharges from manmade sources, the current CH<sub>4</sub> content in the global atmosphere (global average of ~1837 ppb in August 2015) is ~265% of the pre-industrial level of ~700 ppb [9] [10]. The growth rate of CH<sub>4</sub> reduced to ~0 from 1999-2006 from 13 ppb·yr<sup>-1</sup> in the early 1980s. CH<sub>4</sub> concentrations then began growing again in 2007. The seasonal CH<sub>4</sub> content of the atmosphere is cyclical with CH<sub>4</sub> concentrations higher in winter in the northern hemisphere with seasonal changes in the southern hemisphere lagging by 8 - 9 months. During the years 1986-1994, the average minimum and maximum CH<sub>4</sub> levels were recorded at the end of June and at the beginning of February, respectively at the NOAA Barrow, Alaska Baseline Observatory (71.32 N; 156.61 W) [11]. At the Xinglong Station in China, the minimum and maximum levels occurred during May-September and October-December respectively [12].

In the southern hemisphere, the minimum and maximum values were observed in early March and late September at Syowa Station [13] and the South Pole [14]-[16]. The Antarctic region is exposed to the least influence of human activities; hence this region is regarded as being the background of the global atmosphere [17] [18]. With the support of China's Action Plan in the Fourth International Polar Year (2008/2009), the Antarctic Zhongshan Station atmospheric background monitoring station was established. Both continuous *in situ* and weekly flask sample measurements of  $CH_4$  are part of the research program at Zhongshan station as well as continuous meteorology measurements.

In the current research, we analyzed  $CH_4$  data from 2008 to 2013 at Zhongshan for concentrations, seasonality and trends in relation to meteorology. The Zhongshan data were compared with other Antarctic stations and these inter comparisons form an important segment of this report.

#### 2. Observation Point and Monitoring Instruments

#### 2.1. Site Location

Located along the coast of East Antarctica, Zhongshan Station (Figure 1) is China's second year-round Antarctic research station. Factors such as power generation, traffic, and human activities in the region were considered when placing gas, aerosol and meteorological observation sites around the station site. The main facility for the  $CH_4$  monitoring systems is located in a small sampling building on a flat, bare rock in the west side of the so called Tian'e Range at the northwest end of the station (69°22'2'S, 76°21'49''E, at an elevation of 18.5 m). These observation facilities are 400 m upwind of the power generation building and garbage incinerator.

#### 2.2. Instrumentation

Since March, 2010, CH<sub>4</sub> is measured on line with a G1301 high-precision CO<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub>O analyzer from Picarro (USA). The sample air intake is fashioned from 10 mm Syflex 1300 pipe with a flow of 6 L·min<sup>-1</sup>. Sample air is passed through a 7  $\mu$ m membrane filter prior to entering a KNF air sample transfer pump with a delivery pressure of 103.4 kPa (15 psi). Most of the moisture in the sample air is removed with a cold trap operated at 0°C. A small secondary pressure release valve at the back of cold trap is used to smooth the sample flow by reducing the influence of a possible "dead volume" in the trap. The resulting flow is set to 200 m1·mol<sup>-1</sup> feeding into a selector valve used to route either sample air or standard gas. A high-precision flow controller at the front of the analyzer ensures a steady flow during analysis [19] [20]. The frequency and accuracy of analyzing the sample gas was 10 s and ±1 ppb, respectively, satisfying the requirement of WMO-GAW criteria for these measurements. Two parallel glass flasks air samples are collected each week in clean air outside the observatory for later analysis of CH<sub>4</sub> and CO<sub>2</sub> in the atmospheric composition laboratory of the China Meteorological Administration, Beijing. From 2008 to 2013 weekly flask samples were collected. Further information on methods and analytical instrument are presented in References [21] [22].

## 3. Data Treatment

Data gathered under abnormal conditions such as instrument failure, maintenance of facilities and power failure as well as data during zero-gas measurement periods are deleted from the data record. Original data are then adjusted according to daily zero-gas measurement values. The standard deviations of the daily zero-gas measurements were concentrated within the range of 0 - 0.5 ppb as shown in Figure 2.

All data were processed as averages after the abnormal values from the original data were removed using a variance test  $|x_i - \overline{x}| > 3\sigma$ , where  $x_i$  is the observational data,  $\overline{x}$  is the average value and  $\sigma$  is the standard deviation. The integrity rate of online CH<sub>4</sub> observational data was 95.9%.

## 4. Winds Influencing on CH<sub>4</sub> Concentration

Above data processing cannot completely exclude the impact of emissions from the station area. Wind is an important factor influencing observational data [22] [23]. Winds measured at 10 m over Zhongshan Station were



Figure 1. Locations of monitoring stations in Antarctica relative to Zhongshan Station.



Figure 2. Standard deviations of daily zero-gas measurements at Zhongshan Station from 2010 to 2013.

binned into 16 intervals of 22.5° each. The average seasonal  $CH_4$  concentration was binned with the average wind speed then subjected to further statistical analyses. East wind (45° - 135°) prevails all year round with a frequency of 83.1%, indicating that airflow reaching the station comes mainly from the Antarctic ice sheet and western oceans. Wind frequency (WF), average wind speed (WS), and average  $CH_4$  content in 16 directions during the four seasons from 2010 to 2013 are presented in **Figure 3**. From **Figure 3** it may be observed that there is a large annual cycle in  $CH_4$  with largest concentrations in the Antarctic winter-spring and lowest in summer-autumn. Westerly winds in all seasons exhibit the highest average  $CH_4$  content with the highest annual concentrations in summer-autumn.

Power generation for the station is northwest (downwind) of the  $CH_4$  sampling location because of the prevailing easterly winds. Note that the highest frequency of winds from that sector was only 2.4% thus minimizing



**Figure 3.** Wind frequency (WF) and average wind speed (WS) in 16 directions and average  $CH_4$  content during spring (September-November), summer (December-February), autumn (March-May), and winter (June-August) at Zhongshan Station from 2010 to 2013.

the potential for contamination from the power plant and incinerator.

The CH<sub>4</sub> content in west winds during autumn is slightly elevated which may be real, but also be an artifact of the small sample size of 0.6% of the total wind observations. Apart from these few autumn data, the CH<sub>4</sub> concentrations over a single season do not significantly change with wind direction suggesting that wind direction at Zhongshan Station exerts little influence on CH<sub>4</sub> concentrations.

To analyze the effects of wind speed on CH<sub>4</sub> measured at the station, the wind speed data from 2010 to 2013 were divided in seven groups:  $\leq 0.5 \text{ m}\cdot\text{s}^{-1}$ ,  $0.5 - 3 \text{ m}\cdot\text{s}^{-1}$ ,  $3 - 6 \text{ m}\cdot\text{s}^{-1}$ ,  $6 - 10 \text{ m}\cdot\text{s}^{-1}$ ,  $10 - 15 \text{ m}\cdot\text{s}^{-1}$ ,  $15 - 20 \text{ m}\cdot\text{s}^{-1}$ , and  $>20 \text{ m}\cdot\text{s}^{-1}$  and plotted along with corresponding CH<sub>4</sub> concentrations as shown in Figure 4. Numerically, up to 94.7% of the wind speeds at Zhongshan Station fall in the range of  $0.5 - 3 \text{ m}\cdot\text{s}^{-1}$ . The wind frequency in the group of  $>20 \text{ m}\cdot\text{s}^{-1}$  is 1%. The wind in the group of  $\leq 0.5 \text{ m}\cdot\text{s}^{-1}$ , which can be seen as calm, demonstrates a frequency of 0.3% and is associated with occasional fluctuations in CH<sub>4</sub> concentrations indicating a possible local influence on the measurements, or the small sample size has biased the data slightly. In other wind speed bands, CH<sub>4</sub> content in each season does not change with changes in wind speed implying an even distribution of upwind CH<sub>4</sub> concentrations. This also suggests that the influence of local pollution on CH<sub>4</sub> concentrations at the Zhongshan Station is minimal.

To know the reliability of the *in situ*  $CH_4$  measurements, Figure 5 shows the relationship between air samples analyzed  $CH_4$  content and on line observed data from 2010-2013. There was excellent agreement with a correlation coefficient of 0.975. Based on these observations, it is felt that it is reasonable to use flask measurements



Figure 4. Wind frequencies in four seasons and corresponding CH<sub>4</sub> content at Zhongshan Station.



Figure 5. Correlation between *in situ* observational  $CH_4$  concentrations and corresponding flask sampling and analysis conducted in Beijing at a later date.

from the years 2008 and 2013 prior to the initiation of *in situ* measurements to extend the  $CH_4$  record back in time.

#### 5. Variation Characteristics of CH<sub>4</sub> Concentration

The average  $CH_4$  concentration per hour of the day and the standard deviation for the years (2010-2013) is presented in **Figure 6** for January (summer), April (autumn), July (winter), and October (spring). The daily standard deviation shows peak values within the range  $0.3 \sim 0.6$  ppb with over 90% of data are between 0.3 and 1.5 ppb. The standard deviation shows that at the same moment in different seasons, the standard deviation is highest in spring and the lowest in summer. The average daily variation is 0.9, 0.5, 0.4, and 0.8 ppb for summer, autumn, winter, and spring, respectively. This indicates the absence of strong local sources and sinks around Zhongshan Station which in turn suggests that the  $CH_4$  concentrations observed at Zhongshan are probably representative of the  $CH_4$  background of a larger region of Antarctica.

The hourly average continuous *in situ* CH<sub>4</sub> data record for Zhongshan for 2010-2013 is presented in Figure 7 where it may be observed that the lowest CH<sub>4</sub> concentrations were measured in February (summer) and the largest in late September-early October (spring). A steady annual increase in CH<sub>4</sub> concentrations is evident in the four year record. Occasionally, there are large, three to five day regime changes in CH<sub>4</sub> concentrations at Zhongshan Station related to maritime air mass intrusions exemplified by a decrease in air pressure, increase in air temperature and an increase in vapor pressure. One such event is presented in Figure 8 for August 3rd through 5th, 2011 during the season when CH<sub>4</sub> concentrations were reaching their annual peak. Over this 3 day



**Figure 6.** Average hourly CH<sub>4</sub> content and daily variations of maximum and minimum at Zhongshan Station in January, April, July, and October.



**Figure 7.** Time array of average daily CH<sub>4</sub> content at Zhongshan Station observed *in situ* from March 2010 to September 2013.



vapor pressure (e) and air pressure (p) from August 3rd to August 7th, 2011 at Zhongshan Station.

period, hourly average CH<sub>4</sub> concentrations decreased from 1771.3 ppb to 1762.8 ppb as air pressure decreased from 998 hPa to 965 hPa. Over the same period, air temperature rose by  $15^{\circ}$ C ( $-17.3^{\circ}$ C to  $-1.7^{\circ}$ C) while vapor pressure increased from 1 hPa to 5 hPa. Over the next two days as the air cooled and water vapor dropped, CH<sub>4</sub> concentrations recovered about 50% of their value of two days earlier and then stabilized at what was to be the new norm until another air mass change occurred. These step function air mass related shifts in CH<sub>4</sub> concentrations (decreases and increases) occur in all seasons as may be observed.

#### 6. Seasonal Variation and Trend of CH<sub>4</sub> Background Concentration

To evaluate the representativeness of *in situ* CH<sub>4</sub> measurements at Zhongshan Station, CH<sub>4</sub> data from Casey Station (66.28°S, 110.53°E) and Syowa Station (69°S, 39.6°E) obtained from the World Meteorological World Data Center for Greenhouse Gases (http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg/catalogue.cgi) were plotted together. Figure 9 displays the time series of average monthly CH<sub>4</sub> concentrations at Zhongshan, Casey, and Syowa. For Zhongshan, flask data from 2008 through 2009 are used and *in situ* data for 2010 through 2013. For Casey and Syowa, monthly flask data were used. The accuracy of flask data is discussed in References [24] [25]. From the data presented in Figure 9, it may be seen that there is close agreement between the CH<sub>4</sub> measurements at the three stations across the six year overlapping records. Over this period, it may be observed that monthly CH<sub>4</sub> concentrations ranged from a low of 1722 to a high of 1782 ppb with a fairly steady growth rate over a six year period.

Average monthly concentrations of  $CH_4$  at the three stations are shown in **Figure 10** where as mentioned before,  $CH_4$  content along the East Antarctic continent is lowest in February-March and reaches a peak in September-October. This annual cycle is related to the seasonal variations in  $CH_4$  sources and sinks: predominately transport from lower and middle latitudes in both the southern and northern hemispheres, and a possible small effect from Antarctic marine coastal biological processes [26] [27]. As such, the seasonal variation in  $CH_4$  is mainly caused by transport from the northern hemisphere in the general circulation of the global atmosphere.

Global annual contents and growth rates of CH<sub>4</sub> at six Antarctic stations (locations shown in **Figure 1**) from 2008 through 2013 are listed in **Table 1**. Little significant differences can be observed in the CH<sub>4</sub> concentrations measured at the six stations which are about 50 ppb lower than the global average. From 2008 through 2013, the average global CH<sub>4</sub> concentrations increased at a rate of ~5.2 ppb·yr<sup>-1</sup> whereas in Antarctica it increased between 4.5 - 5.2 ppb·yr<sup>-1</sup>. As such observations of background CH<sub>4</sub> concentrations in Antarctica faithfully reflect the changing background content of CH<sub>4</sub> globally.



**Figure 9.** Time series of monthly mean CH<sub>4</sub> concentrations at Zhongshan, Casey and Syowa Stations from 2008 to 2013.



Figure 10. Seasonal variations of monthly mean  $CH_4$  concentration at Zhongshan, Casey and Syowa Stations for monthly data from 2008 through 2013.

Table 1. Annual mean CH<sub>4</sub> concentrations and growth rates measured in Antarctica compared to the global average.

| Year      | Casey       | Palmer      | South Pole  | Halley      | Syowa       | Zhongshan   | Global      |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 2008      | 1740.3      | 1740.6      | 1742.7      | 1739.9      | 1740.2      | 1742.5      | 1798.0      |
| 2009      | 1743.4      | 1743.0      | 1744.0      | 1743.8      | 1744.0      | 1744.9      | 1803.0      |
| 2010      | 1749.2      | 1750.2      | 1750.5      | 1749.1      | 1748.6      | 1750.1      | 1808.0      |
| 2011      | 1757.6      | 1757.0      | 1758.6      | 1755.3      | 1756.3      | 1757.6      | 1813.0      |
| 2012      | 1762.0      | 1760.9      | 1762.7      | 1761.3      | 1761.7      | 1762.3      | 1819.0      |
| 2013      | 1766.3      | 1765.3      | 1766.2      | 1765.5      | 1764.8      | 1764.9      | 1824.0      |
| 2008-2009 | 3.1 (0.18%) | 2.4 (0.14%) | 1.2 (0.07%) | 4.0 (0.23%) | 3.8 (0.22%) | 2.3 (0.13%) | 5.0 (0.28%) |
| 2009-2010 | 5.8 (0.33%) | 7.2 (0.41%) | 6.6 (0.38%) | 5.3 (0.30%) | 4.7 (0.27%) | 5.3 (0.30%) | 5.0 (0.28%) |
| 2010-2011 | 8.4 (0.48%) | 6.8 (0.39%) | 8.0 (0.46%) | 6.2 (0.35%) | 7.7 (0.44%) | 7.5 (0.43%) | 5.0 (0.28%) |
| 2011-2012 | 4.4 (0.25%) | 3.9 (0.22%) | 4.2 (0.24%) | 6.0 (0.34%) | 5.4 (0.31%) | 4.7 (0.27%) | 6.0 (0.33%) |
| 2012-2013 | 4.3 (0.25%) | 4.4 (0.25%) | 3.5 (0.20%) | 4.2 (0.24%) | 3.0 (0.17%) | 2.6 (0.15%) | (0.27%)     |

#### 7. Discussion and Conclusions

One of the goals of this research was to determine if *in situ*  $CH_4$  measurements at Zhongshan Station were of high quality, consistent and stable over time and that error detection and data processing algorithms were adequate to produce an end product that would be accepted by the larger scientific community. Through regular measurements of calibration and zero gases, and the excellent agreement between *in situ*  $CH_4$  measurements and  $CH_4$  in air collected in flasks and analyzed in Beijing, we are confident that the *in situ* analyzer is producing acceptable data. By studying  $CH_4$  concentration in winds with different directions and speeds at Zhongshan Station, it was found that ~1% of the  $CH_4$  measurements were suspected of possibly being contaminated by station effluents. These data were removed from the record. Overall, the Zhongshan station data suggest that there are no strong natural local sources and sinks of  $CH_4$  in the proximity of the station.

Since there was excellent agreement between the *in situ* and flask measurements that overlapped from 2010 through 2013, we suggested that the flask measurements from 2008 to 2013, prior to the installation of the *in situ* analyzer, were also of high enough quality to be added to the Zhongshan record. Comparing this six year record with similar measurements from Casey and Syowa stations produced overlapping long term records that were essentially indistinguishable. These records follow the well-known annual cycle in  $CH_4$  concentrations in Antarctica with peaks in September-early October and troughs in February-March.

The *in situ*  $CH_4$  measurements at Zhongshan exhibit occasional, fairly rapid changes in concentration that generally signal a change to a new norm which may last for a few day to a few weeks. The study of one of these events showed that a decrease of ~10 ppb in  $CH_4$  in a day was associated with the arrival of a low pressure marine air mass that brought lower latitude air of lesser content  $CH_4$  to the station.

As noted earlier, average global CH<sub>4</sub> is growing at  $0.29\%.yr^{-1}$  and recent inter-annual CH<sub>4</sub> growth ranges from 5 ppb to 6 ppb. The CH<sub>4</sub> content in the Antarctic as reported in this study was found to be  $0.28\%.yr^{-1}$ , and the inter-annual growth ranged from 4.5 ppb to 5.2 ppb. Since the CH<sub>4</sub> data from Zhongshan Station are in excellent agreement with other stations on the East Antarctic coast, we suggest that the *in situ* measurements from Zhongshan may be well suited to study the finer details of the behavior of CH<sub>4</sub> in the Antarctic than weekly average measurements from flask samples.

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