Manuscript

Environmental Science and Pollution Research, January 2018, Volume 25, Issue 3, pp 2194–2210
DOI:10.1007/s11356-017-0521-1

Variations of spatial-temporal in surface ozone over Ushuaia and Antarctic region: An observation from *insitu* measurement and historical data

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The final published version (version of record) is available online at DOI:10.1007/s11356-017-0521-1. Please refer to any applicable publisher terms of use.

Abstract

In the troposphere, surface O_3 acts as Greenhouse gases (GHGs) which contribute to the global warming. Polar region and nearby land area such as Peninsula Antarctic and Ushuaia are an important areas to observe the surface O_3 variability. Here, we presented the spatial and temporal of surface O_3 from latest *insitu* observation during Malaysian Antarctic Scientific Expedition Cruise 2016 (MASEC'16) and multi-years historical data obtained online from World Meteorology Organization of World Data Center for Greenhouse Gases (WMO WDCGG). Furthermore, surface O_3 data from satellite data assimilation of Monitoring Atmospheric Composition and Climate (MACC) reanalysis from European Centre for Medium-Range Weather Forecasts (ECMWF) and NASA's Atmospheric Infrared Sounder (AIRS) satellite covering the period of the MASEC'16 cruise was constructed to document the data set and to give an indication of its quality compared to *in situ* observations. Finally, we used historical data Carbon Monoxide (CO) as a proxy of surface O_3 formation over Antarctic region. Our key findings is that the spatial distributions of surface O_3 mixing ratios from MASEC'16 and temporal were high over the Antarctic region including the Peninsula area compared to the Southern Ocean and Ushuaia which influenced by biogenic and anthropogenic O_3 precursors such as CO. MACC reanalysis showed surface O_3 levels are higher than observations from MASEC'16 by 40%, 47% and 43%.

Keywords*: *Surface O_3; Carbon Monoxide (CO); Seasonal cycles; Satellite and MACC reanalysis and HYSPLIT trajectories.

1.0 Introduction

Surface ozone (O_3) in the troposphere represents only a relatively small fraction of the total column O_3. Surface O_3 is now recognized for its important role in the chemical and radiative balance of the atmosphere (Oltmans et al., 1993). Increase of surface O_3 concentration over polar region can contributed to the surface ice warming lead to the sea level rise phenomena. The Antarctic region is an important study area with regard to understanding the distribution of surface O_3 and its precursors. Surface O_3 concentrations may vary from location to location. In polar regions water vapor content and UV radiation are much lower than other more temperate areas, leading to the longer lifetime of surface O_3 (~100 years) compared to other regions on Earth (Helmig et al., 2007a). Elevated surface O_3 over different continents has been observed on several occasions, for instance in Asian regions such as Malaysia (Latif et al., 2012 Awang et al., 2010; Ahamad et al., 2014) and China (Ge et la., 2012), European regions such as Mace Head, Ireland (Simmonds et al.,1997; Derwent et al., 2013), and the United States (Lin et al., 2000). Antarctic regions are of interest for surface O_3 research due to the low human population and therefore minimal anthropogenic influences on O_3. In this region O_3 levels are mostly controlled by natural processes and downwards transport from the stratosphere (Helmig et al., 2007a).

Ushuaia, Argentina is the nearest city to Antarctica, separated by a channel known as the Drake Passage (~1000 km wide) and may influence the surface O_3 mixing ratios over the Antarctic Peninsula. *In situ* measurements over Antarctica are difficult and expensive to obtain and so many scientists rely on freely available data from websites and satellite-based products for scientific

analysis. There remain many questions rises concerning the surface O_3 observations in terms of the relevant sources and sinks, temporal and spatial distributions, and physical and chemical processes. In this study, freely available temporal surface O_3 data from the World Meteorology Organization World Data Center for Green House Gases (WMO WDCGG) for Ushuaia and the Antarctic region (except Drake Passage) were relied on. Assimilations of satellite data on atmospheric composition, with a focus on O_3, have been carried out previously by Holm et al., 1999; Khattatov et al., 2000; Dethof and Holm, 2004; Geer et al., 2006; Arellano et al., 2007; Lahoz et al., 2007; Dragani, 2010, 2011, and global O_3 forecasts are now routinely produced by several meteorological centers (Inness et al., 2013). NASA's Atmospheric Infrared Sounder (AIRS) satellite-based products for atmospheric composition are freely available from NASA's website (http://giovanni.gsfc.nasa.gov/). The Monitoring Atmospheric Composition and Climate (MACC) global model assimilation system was developed by the European Centre for Medium-Range Weather Forecasts (ECMWF), a European international agency based in the UK. MACC is a research project with the aim of establishing core global and regional atmospheric environmental services for the European GMES (Global Monitoring for Environment and Security) initiative (Inness et al., 2013). The data from MACC were used in a previous study on the analysis of long term atmospheric composition data by Inness et al. (2013) to give indication of its quality compared to *in situ* observations. Their results showed the mean relative MACC reanalysis and ozonesonde tropospheric O_3 measurements were within ± 5 to 10% in the NH and over the Antarctic.

We present here measurements of surface O_3 mixing ratios in the marine boundary layer over Ushuaia, the southern part of the SO (the Drake Passage) and Coastal Antarctic Peninsula (CAP). The measurements were taken from an oceanographic research vessel during MASEC 2016 as part of the Sultan Mizan Antarctic Research Foundation Grant (YPASM) program and as part of the Malaysia Antarctic Research Program (MARP). The first objective of this study is to show a new cruise observation of surface O_3 over Ushuaia, the Drake Passage and CAP. Secondly, is to show multi years of temporal surface O_3 distribution over Ushuaia and Antarctica (Western, Eastern, Southern and Peninsula). This is followed by comparing the latest observations during MASEC'16 with spatio-temporal distributions across Ushuaia and Antarctica (Western, Eastern, Southern and Peninsula). This paper will also describe the NOAA AIRS satellite and MACC reanalysis of surface O_3 during the period of MASEC'16. The purpose of this is to validate data agreement between the NOAA satellite, MACC reanalysis and on-board O_3 measurements with sufficient density and continuity to deliver strongly consistent analyses between freely available satellite and global model products. Finally, this paper will discuss the multi-years temporal carbon monoxide (CO) and surface O_3 relationship over Ushuaia and the South Pole to investigate the influence of its precursor on the surface O_3 mixing ratio. In this study, 'long term' refers to the multi-year data and 'short term' refers to MASEC'16 data.

2.0 Measurement and sampling

MASEC'16 took place on the *RV Australis* between January 16th and February 8th 2016, from Ushuaia, Argentina to Darboux Island and back to Ushuaia (Graham Coast, the Antarctic Peninsula) as shown in Figure 2.1. On each cruise an EcoTech (Australia) model Serinus 10 O3 analyser

was used to measure the surface O3. The EcoTech was well maintained and had been calibrated prior to the expedition cruise. The calibration was based on a 7-point standard from low to high concentration, with a range of interest of 0.1 to 200 ppb (parts per billion by volume) and detection limits of 0 to 50 ppb. The O_3 analyzer later was calibrated again after the expedition to check for drifting of the calibration curve. The O_3 analyzer was installed at the back of the vessel and a 10 m long 1/4" ID Teflon sample line was used to draw air samples from an inlet at the bow of the vessel.

The cruise participants were from different scientific backgrounds, predominantly biology. The vessel sailed across sub-Antarctic and Antarctic regions with various conditions. *The RV Aus-tralis'* route started from the town of Ushuaia, Argentina (55°S, 68°W, population 42,000). The EcoTech was deployed from the 16th to the 18th January at Ushuaia and surface O_3 was measured for 24 hours. The EcoTech was then deployed for cruise measurements on the RV Aus-tralis from the 16th January and surface O_3 was measured from then to the end of the cruise on the 8th February. The vessel arrived at the South Korean King Sejong station on the 24th January and anchored for a day. The cruise then continued to the Antarctic Peninsula and ended at Graham Land (Darbeux Island) on the coast of the Antarctic Peninsula.

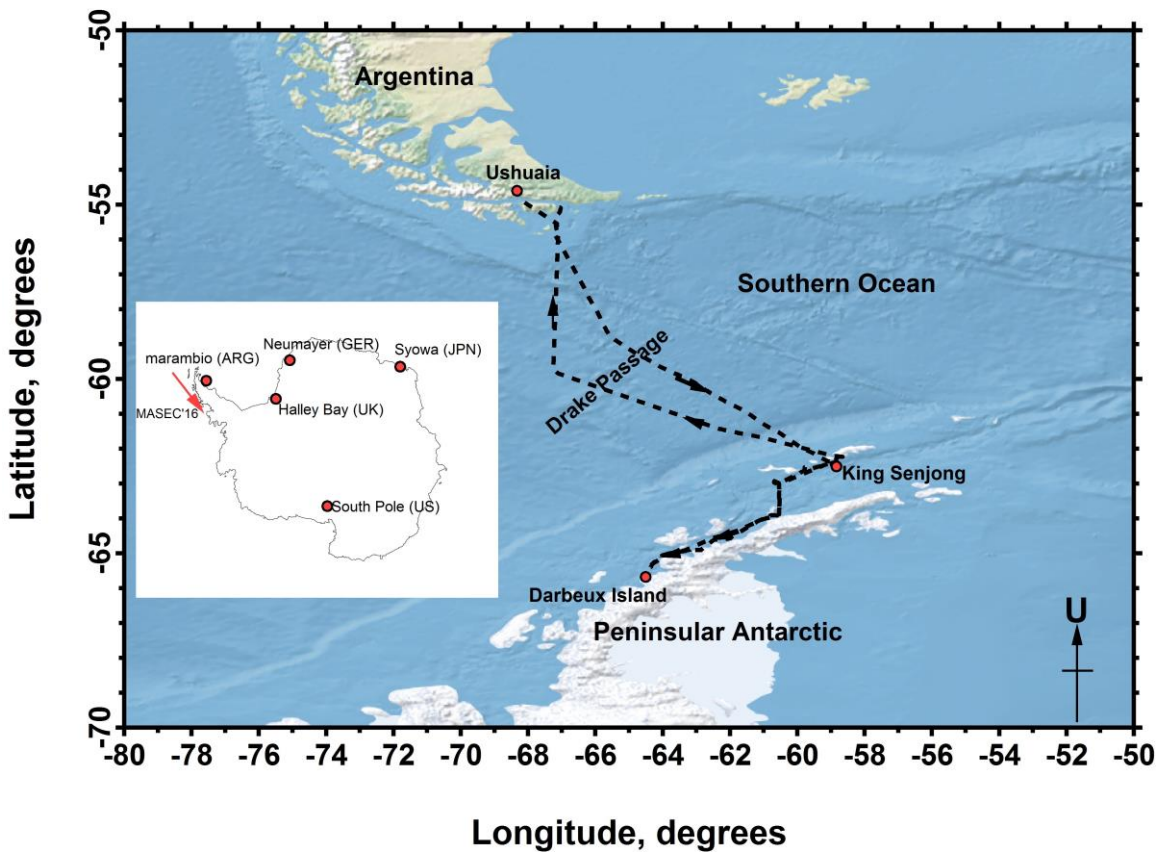

Figure 2.1 Cruise route during MASEC'16 and five selected stations which were used for multi-year data analysis in this study.

2.1 Data analysis

2.1.1 Spatial Surface O_3 data from MASEC'16 Temporal Surface O_3 Data

To illustrate long term updated measurements over Ushuaia and Antarctica, five years of data, from the 1st January 2009 to the 31st December 2015, were used from the WMO World Data Centre for Greenhouse Gases (http://ds.data.jma.go.jp/gmd/wdcgg/cgi-bin/wdcgg). However, the Ushuaia station data from WDCGG was available only until 2014. In this study, to investigate surface O_3 over Antarctica, six stations were selected for surface O_3 analysis. The other stations are Marambio (MM) (Argentina), NM (Germany), SY (Japan), SPO (USA) and Halley Bay (HB) (UK). All selected stations were chosen based on their location in Antarctica including the Peninsula. Later, for comparison purposes, long term WDCGG data will be compared with latest surface O_3 data from MASEC'16, focusing on the month of January each year (the cruise period). Furthermore, to see the history of mixing ratios over the measurement area during MASEC, cruise data will be compared with long term multi-years historical data from WDCGG.

2.1.2 Temporal Carbon Monoxide Data

To investigate the relationship between surface O_3 and its precursors, CO data was derived from WMO WDCGG. Long term hourly measurements of CO over Ushuaia from 1st January 2009 to 31st December 2013 were used. The CO data from the WDCGG database were limited over Antarctica. Thus, monthly CO mixing ratio data over the South Pole in the Antarctic region were used. CO mixing ratios are believed to be consistently low over Antarctica compared to Ushuaia. Thus, CO over the SPO are used to represent the whole region of Antarctica. The correlation plot between surface O_3 and CO will be constructed to investigate the distribution of surface O_3 mixing ratios over Ushuaia and Antarctica.

2.1.3 Satellite-Derived AIRS and MACC Reanalysis

The surface O_3 data recorded during MASEC'16 were validated using the corresponding monthly averages of the long term (multi-year) data, which is freely available online satellite and model data. The surface O_3 (at 1000 hPa) mixing ratios were derived from the NASA Atmospheric Infrared Sounder or AIRS. AIRS is the second platform of NASA's Earth Observing System satellite-which can be derived from "Giovanni" online database (http://giovanni.gsfc.nasa.gov/) and were used to determine apparent surface O_3 values in the $1\times1^\circ$ grid square nearest to each sampling point.

The MACC reanalysis of surface O_3 (1000 hPa) values in the $0.125^\circ\times0.125^\circ$ grid square nearest to each sampling point were taken from Centre for Medium-Range Weather Forecasts http://apps.ecmwf.int/datasets/data/. The data from the MACC reanalysis were retrieved for January and February 2016 in the area where the MASEC'16 occurred. For further investigation, MASEC'16 data for Ushuaia, the Drake Passage and the CAP region were compared with AIRS satellite and MACC reanalysis data which will be discussed in the next section.

2.2 Trajectory analysis

To investigate the potential sources contributing to O_3 production in the marine boundary layer of the SO, the air mass history of the atmosphere was studied using backward trajectory analysis. A 120 h backward trajectory was computed from 00:00 UTC located at 500 m above ground level at each station location for each of the days with high O_3 levels. The selected height level of the particles released ensured that the trajectories started in the atmospheric boundary layer. The back trajectories and horizontal dispersion were calculated using version 4.9 of the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) developed by the NOAA's Air Resource Laboratory (ARL) (Draxler and Rolph, 2003; Rolph 2003). A back trajectory does not provide any information pertaining to surface O_3 mixing ratio or air parcel dispersion in the atmosphere, i.e. width or depth, but can provide the path of an air mass backwards in time to estimate the potential sources.

3.0 Results and discussion

3.1 Meteorological Conditions during MASEC'16

Meteorological data such as atmospheric temperature, wind speed and wind direction were recorded on board during the sampling period. The ambient temperatures were in the range of 5 to 13°C, 3 to 8°C and -1 to 4°C for Ushuaia, the Southern Ocean (SO) and the coast of the Ant-arctic Peninsula, respectively. Relative humidity at Ushuaia was lower than the SO and CAP and in the range 50-75%. The SO has the highest humidity in the range 80-90% and CAP with values in the range 75-90%. The Antarctic continental region has lower humidity but the Peninsula region has a stronger influence of moisture from the ocean. The wind speed and directions were also recorded on board over Ushuaia, the SO and CAP. The selected raw data during sampling from on board reanalysis with ZyGrib 6.2.3 soft-ware is shown in Figure 3.1. Generally the wind direction was from the southwest for those three regions. Wind speeds were high at the beginning of the cruise (17th January 2016) over the SO with speeds of 30 to 38 ms^{-1}. When the vessel arrived at the CAP the wind speeds were in the range of 20 to 25 ms^{-1}. The humidity and wind speed may be able to influence the surface O_3 distributions of gases in the atmosphere.

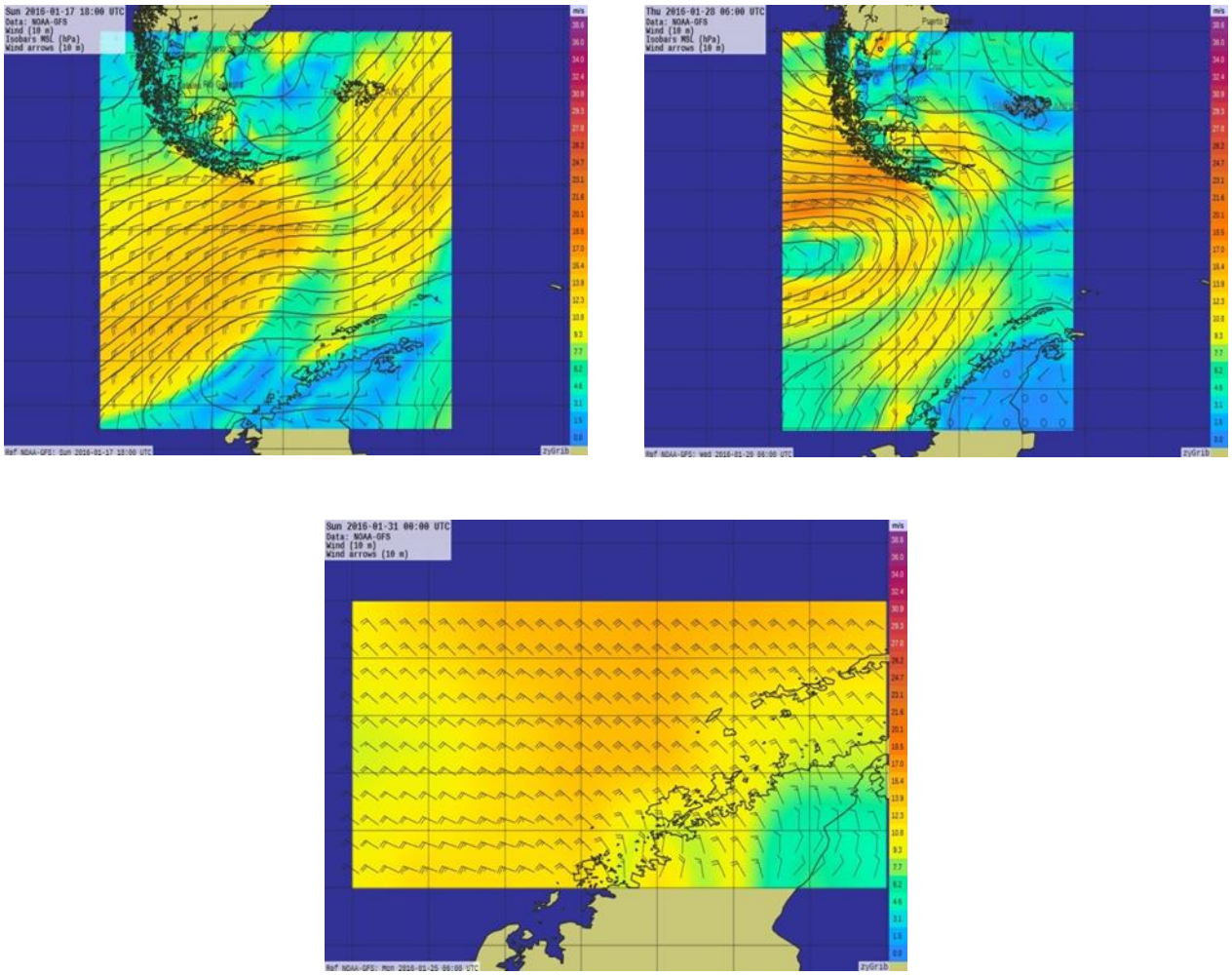

Figure 3.1 Wind speed (ms^{-1}) and wind directions during sampling period beginning, middle and end of MASEC'16.

3.2 Latest observation on Spatial distributions of Surface O_3 (MASEC'16)

Ushuaia and the Drake Passage: Hourly surface O_3 mixing ratios were measured from the 16th to the 19th January 2016 prior to departure. Surface O_3 mixing ratios over Ushuaia, the Drake Passage and CAP are shown in Figure 3.2. Surface O_3 measurements from Ushuaia were observed in the range of ~4 to ~13 ppb. These values were slightly lower than the previous measurements observed by Boylan et al. (2015) over Ushuaia in 2008 with values of 12 to 27 ppb (during January). This region is known for high winds and turbulent seas, which keeps the atmosphere well mixed and the day to day variations in O_3 to a minimum (Boylan et al., 2015). Over the Drake Passage, the surface O_3 mixing ratios decreased as the Beagle Channel was approached (~4.2 ppb) and increased over the open ocean (~12.3 ppb). Previous measurements over the SO by Boylan et al. (2015) observed that surface O_3 mixing ratio increased up to 25 ppb travelling 2000 km from Ushuaia into the SO. Previous study by Johnson et al. (1997) found that the surface O_3 mixing ratios were in the range

of 5 to 30 ppb and 10 to 30 ppb at lower latitudes over the Pacific Ocean and the Indian Ocean, respectively. In this study, changes in surface O_3 mixing ratios in the marine boundary layer (MBL) from the Beagle Channel to the open ocean are believed to be influenced by chemical processes (sea-spray) and air transport from land (Argentina). Sea-spray aerosol may produce O_3 precursors such as nitryl chloride ($ClNO_2$) (Johnson et al., 1990). In addition, OH and Cl radicals in the MBL can also increase surface O_3 formation with Cl (Monks et al., 2000; Monks, 2005; Conley et al., 2011). The observations over the Drake Passage in this study are likely to be influenced by the sea-spray process and anthropogenic activities from South America such as Southern Argentina. Backward trajectory analysis over Ushuaia and the Drake Passage will be discussed in the next section to estimate factors which may influence the mixing ratio of surface O_3.

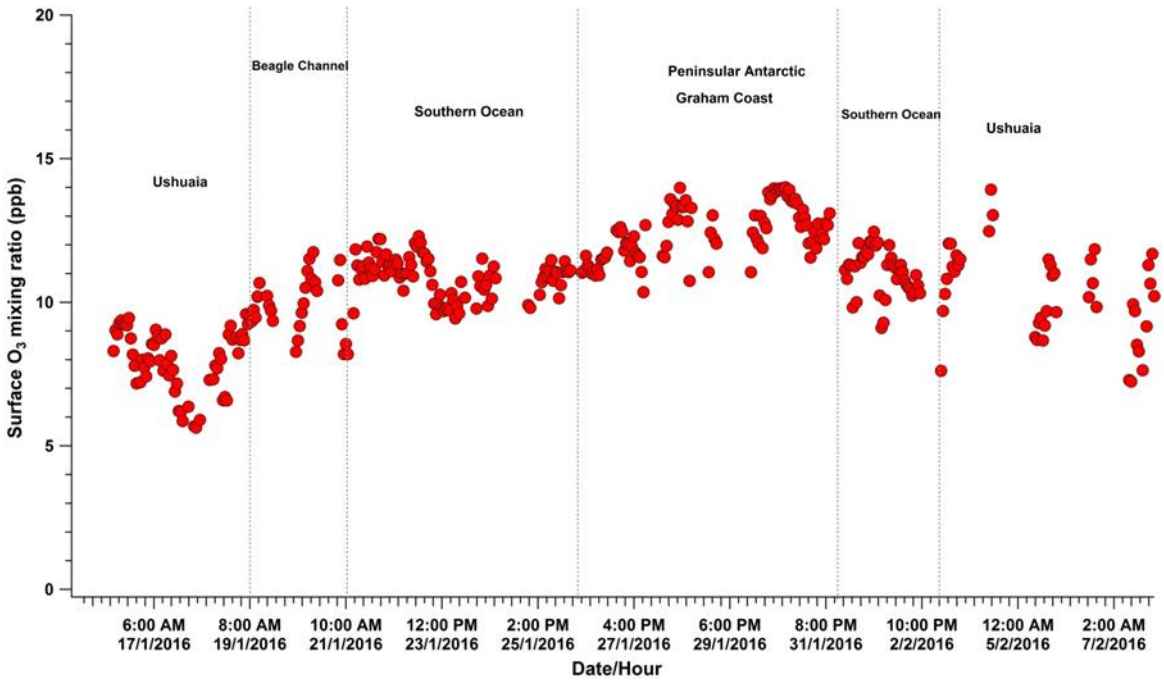

Figure 3.2 Hourly Surface O_3 mixing ratio data from the on-board O_3 analyser during MASEC'16.

Antarctic Peninsula: Long and short term levels of surface O_3 in the Antarctic Peninsula are still poorly understood. In this study, the spatial distributions of surface O_3 mixing ratios were measured over Ushuaia to CAP during MASEC'16. The mixing ratios were high over CAP compared to Ushuaia and the Drake Passage (Figure 3.2). The Graham Land coast recorded the highest surface O_3 mixing ratio compared to other locations along the cruise with a value of ~15 ppb. Coastal surface O_3 mixing ratios may contribute to the transport of O_3-rich air and subsequent photochemical loss in the MBL. The cumulative Biogenic Volatile Organic Compounds (BVOCs), including bromine-containing compounds, in the marine environment also be involved in surface O_3 formation with the presence of solar radiation (Chameides and Davis, 1980; Davis et al., 1996). It has been reported that algae in ice can release significant amounts of halocarbons into the atmosphere (Sturges et al., 1997). Thus, it is postulated that the high surface O_3 formation observed in this

study was due to photochemical processes in the MBL and stratospheric O_3 over the CAP sink.

3.3 Temporal distributions of surface O_3 over Ushuaia, SO and Antarctic (Historical data)

Ushuaia and the Southern Ocean: The five-year data analyses are shown in box-and-whisker plots in Figure 3.3. The surface O_3 mixing ratios consistently decreased during the summer (January) and increased during the winter each year. The yearly mixing ratios over Ushuaia were consistent throughout the years (from 2009 to 2013) with ranges of 11 to 19 ppb and 22 to 32 ppb during the summer and winter, respectively. The mixing ratios increase during the summer and decrease during the winter (Boylan et al., 2015). The monthly variability in surface O_3 ranges between 12 and 27 ppbv in the available data (see Figure 6 in Boylan et al., 2015). Surface O_3 mixing ratios over the SO measured from 29th February to 9th April 2008 during the Gas-EX cruise in the same study range from 10 to 27 ppbv. Nevertheless, the SO data from the Gas-EX cruise were from the northern side of the SO (east of Ushuaia ground-based measurements in Boylan et al., 2015). Currently, there is still a lack of observations of surface O_3 over the southern part of the SO (the Drake Passage) towards the Antarctic Peninsula.

Antarctic region: The characteristic of geographical, climate and chemical environment are important in determine the surface O_3 mixing ratio over Antarctic region. Three main sources of surface O_3 were believed can influenced such as i) horizontal transport to or from middle latitude, ii) vertical exchange with the O_3 rich stratosphere and ii) chemical destruction or production within the domain (Niki and Becker., 1993). In this study, six stations were chosen for comparison across the different regions in Antarctica to represent the northern (including the Peninsula), southern, central, eastern and western regions. Most data were recorded successfully, with the exception of some data from the MM station (Peninsula). The annual O_3 cycle in Figure 3.3 showed that high level surface O_3 occurred during the winter (June to August) and decreased during the summer (January to February) each year. This observation was consistent with the observation by Helmig et al. (2007). Table 1 shows the summary of the multi-year surface O_3 mixing ratios over the five stations in this study. According to Sturges et al., 1992, ice-coverage is fluctuates seasonally this mean algae or bacteria Br-produced in ice-water coverage are players in ocean-chemical interaction which will varied the surface O_3 in the boundary layer.

The unique character of the summertime surface O_3 behavior can be seen in the comparison of the seasonal variation at central (SPO) and coastal stations. The unique characteristic is referring to the depletion process due to halogen photochemical reaction in the present of sunlight during summer time. The seasonal pattern at HB, NM and SY is typical of other coastal locations in Antarctica observed by Oltmans and Komhyr (1976) and Helmig et al. (2007a). At those three locations (see Figure 3.3) spring (August-September-October) mixing ratios of surface O_3 values begin to decline towards a seasonal minimum in January each year. Furthermore, with reduced levels of O_3 in the stratosphere, enhanced amounts of ultraviolet radiation penetrate the troposphere lead to the O_3 photolysis in the near surface (Schnell et al., 1991). Furthermore, reduction of surface O_3 towards the summer was seen throughout the southern hemisphere by Oltmans and Levy II (1994), and is associated with strong photochemical loss processes during the summer in an environment where

low NO concentrations prevail and there are long daylight periods (Ayers et al., 1992). However, periodic events over SPO with the highest values of the year are seen during the entire winter, where the mixing ratios over SPO were still higher than other stations with values of 25 to 27 ppb (September to December).

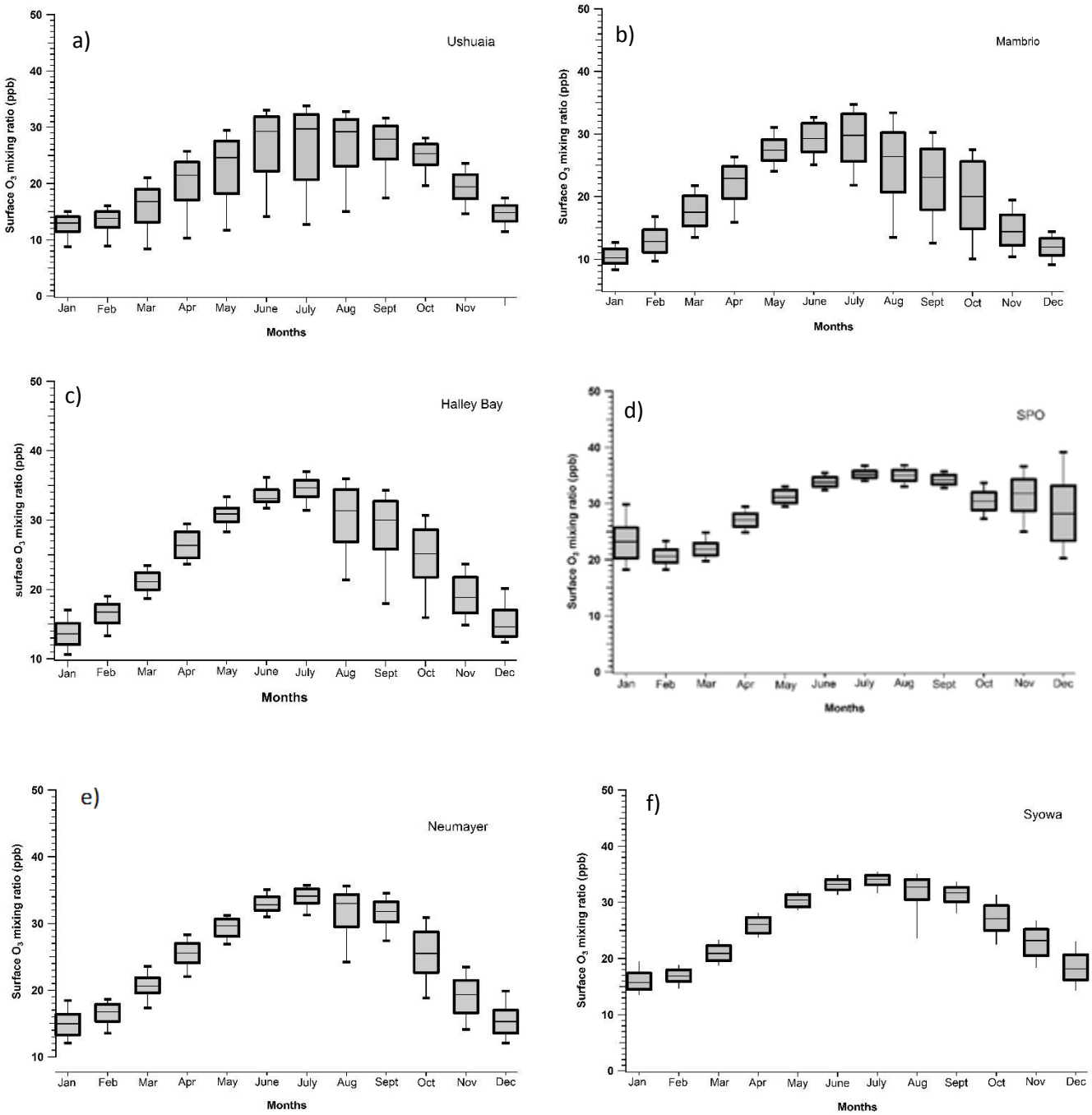

Figure 3.3 Box-and-whisker plots for the multi-year surface O_3 observations at a) Ushuaia b) Mambrio c) Halley Bay d) SPO e) Neumayer and f) Syowa. In each panel, the colored boxes show the data falling between the 25th and 75th percentiles, with the median value shown as a black

horizontal line inside each box. The vertical black lines above and below each box indicate the 95th and 5th percentiles respectively.

Previous observations showed that high events over SPO are characterized by calm winds, high solar radiation and sustained stable boundary layer conditions compared to other location in Antarctica (Davis et al., 2004; Helmig et al., 2007b; Neff et al., 2007). In addition, deposited nitrate results in fluxes of NO_x out of the snowpack into the atmosphere (Oncley et al., 2004). This causes NO mixing ratios in the surface layer to frequently reach ~500 pptv (Davis et al., 2001, 2004) and causes surface O_3 formation that is reflected in the SPO record (Crawford et al., 2001; Chen et al., 2004). During March to October each year all stations have similar surface O_3 levels but they differ from one another during the late spring and summer. In this study, MM is the only Peninsula coastal station which has data available from WMO WDCGG. Figure 3.3 shows the event of elevated surface O_3 with the values reaching from 50 (February 2012 and 2014) to 60 ppb (September 2014). During January over MM, the surface O_3 was the lowest with a value of ~16 ppb; this supported by the latest observation during MASEC over CAP with a value of ~15 ppb as mentioned earlier. The transport of polluted air from continental South America could be another source for increases in surface O_3 at MM station.

Table 1 Summary data of multi-year from five selected stations over the Antarctic region

Site/year	coordinate	2010	2011	2012	2013	2014	2015
Northern							
Neumayer	70°39′00″ S 8°15′00″ W	25.0* 26.4** 6.9***	24.5* 25.2** 7.3***	25.4* 26.7** 6.9***	25.4* 23.9** 6.8***	23.5* 23.9** 6.8***	
Halley Bay	75°36′16″ S 26°12′32″ W	24.8* 26.0** 6.9***	24.0* 24.7** 7.1***	23.7* 24.8** 6.1***	26.0* 27.0** 6.7***	23.3* 22.4** 8.4***	
Marambio (Peninsula)	64°14′40″ S 56°39′24″ W		14.7* 15.0** ±2.5***	18.9* 12.0** ±4.2***	18.9* 11.1** 1.6***	23.0* 11.1** 2.7***	21.9* 14.3** 3.9***

Central							
		29.6*	29.1*	29.1*	28.5*	29.4*	28.3*
South Pole	89°59′51″S	30.9**	30.3**	30.7**	28.5**	28.5**	27.6**
(SPO)	139°16′22″ E	4.6***	5.2***	5.5***	5.4***	5.3***	4.9***
Eastern							
		24.9*	25.7*	25.6*	26.1*	26.1*	24.4*
Syowa	69°00′15″S	26.2**	26.1**	26.9**	26.6**	26.5**	24.2**
	39°34′54″E	5.9***	7.4***	6.4***	6.6***	6.9***	7.1***

Note *Average
**Median
***Standard Deviation (±)

3.4 Comparison of long term and MASEC'16 (January-February data)

The overall seasonal cycles for the multi-year data in the previous section shows that the mixing ratio of surface O_3 during the summer was lower than in winter. This is explained the loss of stratospheric O_3 and the photochemical destruction in spring and summer (Legrand et al., 2016). Similar patterns, observed by Helmig et al. (2007) where O_3 declines during the spring-summer time, are caused by enhanced O_3 sinks compared to O_3 production and transport.

In this section, data from January and February (summer) from the long term multi-year data set and the MASEC'16 data of surface O_3 over Antarctic are compared. Figure 3.4 shows that the mixing ratios for Ushuaia and the five stations in Antarctica were consistent during January and February each year, similar to earlier observations (see Helmig et al., 2007; Legrand et al., 2009). The SPO shows the highest mixing ratios over the Antarctic region, ranging from ~20 to 30 ppb. MM, HB, NM and SY recorded similar values for the mixing ratios of 6 to 16 ppb, 8 to 16 ppb, 8 to 20 ppb and 10 to 22 ppb, respectively. The January data for Ushuaia during January 2009 to 2013 showed that the surface O_3 ranged between ~10-15 ppb, which is slightly lower than previous measurements by Boylan et al. (2015). The surface O_3 is believed to be influenced by O_3 precursors the nearby city center of Ushuaia during the MASEC'16 cruise period. As previously mentioned, O_3 precursors such as CO and NO_x from polluted area may influence the formation of surface O_3 over Ushuaia.

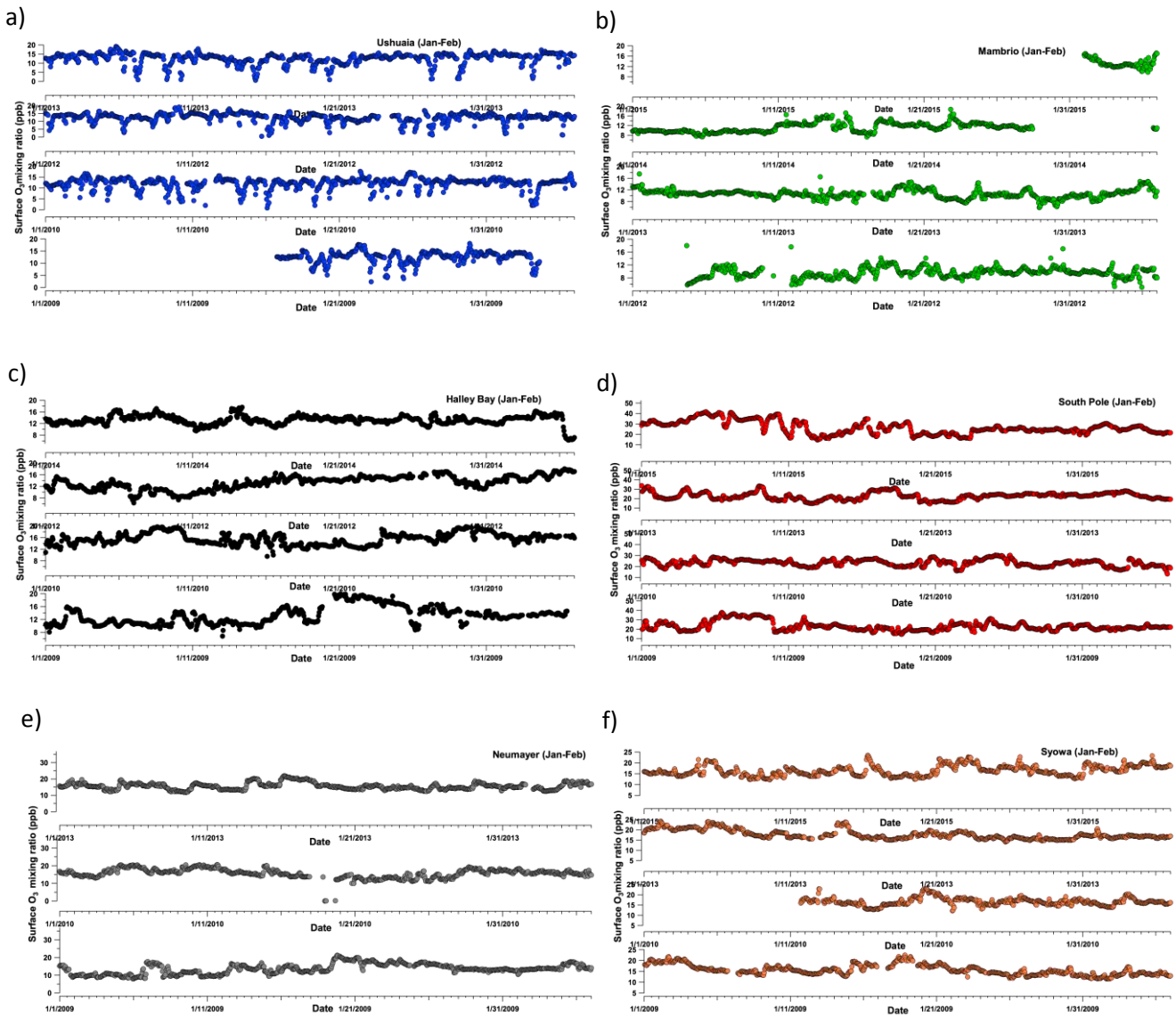

Figure 3.4 Long term measurements of hourly surface O_3 during January and February from WMO WDCGG over a) Ushuaia b) Mambrio c) Halley Bay d) SPO e) Neumayer and f) Syowa.

3.5 Satellite and MACC reanalysis

The data from NOAA AIRS satellite products and MACC reanalysis were retrieved for January and February 2016, when MASEC'16 occurred. The Satellite AIRS surface O_3 data at 1000 hPa during the period of MASEC'16 was extracted from the NASA Goddard "Giovanni" online database (http://oceancolor.gsfc. nasa.gov/SeaWiFS/). The daily averages for Ushuaia and the Antarctic Peninsula were compared with MASEC'16 and are shown in Figure 3.5. The average daily mixing ratios of surface O_3 patterns were similar but the values were slightly higher in the case of satellite data (1000 hPa) with values in the range ~14 to 23 ppb compared to the cruise data with daily average values of ~7 to 12 ppb. Nevertheless, both the datasets showed high mixing ratios

over the Antarctic Peninsula compared to Ushuaia. The average daily levels over Ushuaia and the Antarctic Peninsula between the AIRS satellite and the cruise data were significantly correlated with r^2=0.48 and p<0.01.

As shown in Figure 3.6, the hourly surface O_3 mixing ratios from the MACC reanalysis (1000 hPa) were slightly higher compared to the *in situ* MASEC'16 data, with daily values of ~9 to 22 ppb and 7 to 12 ppb for the MACC reanalysis and MASEC'16, respectively. The correlation between the MACC reanalysis and MASEC'16 was positive with r^2=0.46, p<0.01. The statistical values for the NOAA AIRS, the MACC reanalysis and MASEC'16 are summarized in Table 2. In Figure 3.6, the MACC reanalysis shows monthly mixing ratios of surface O_3 increased when approaching the Antarctic region.

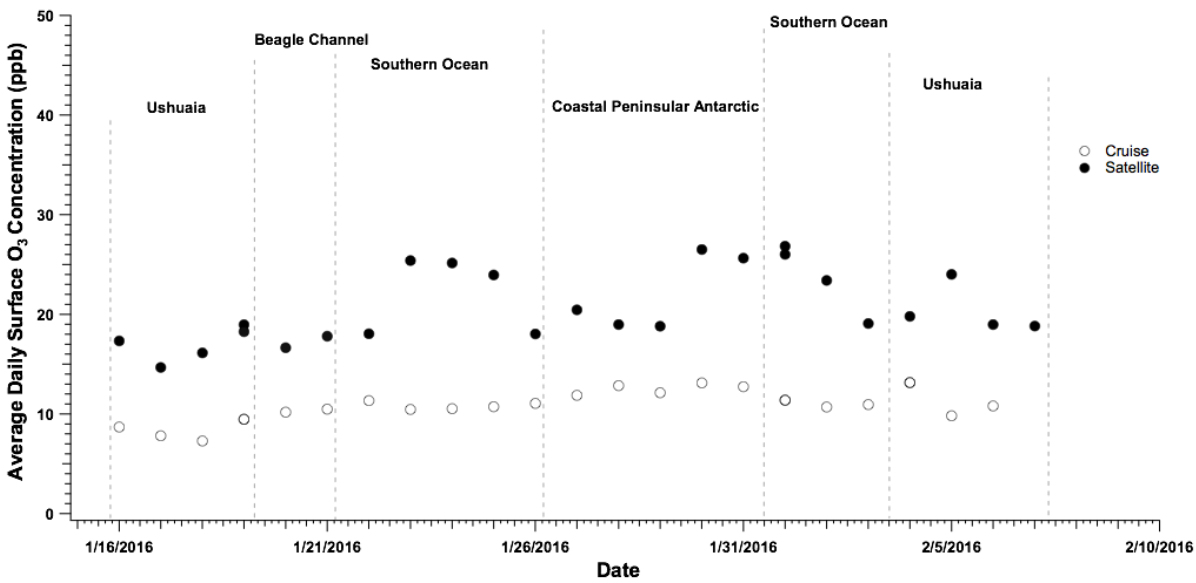

Figure 3.5 Average daily surface O_3 mixing ratio from the AIRS satellite and *in situ* MASEC'16 measurements

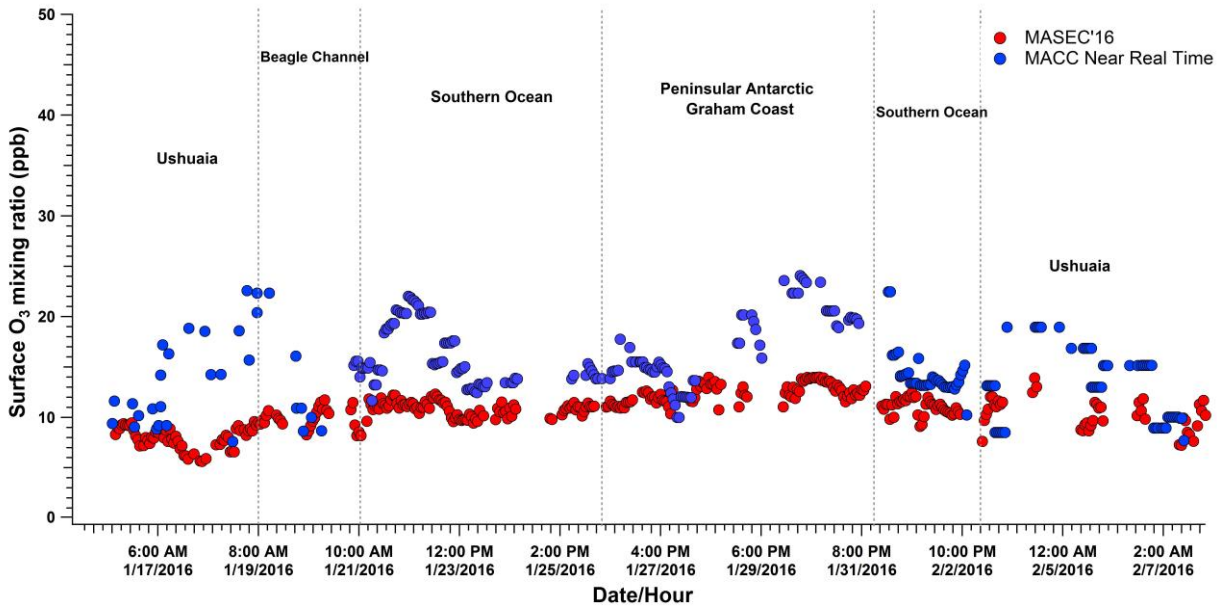

Figure 3.6 Hourly surface O_3 mixing ratios from the MACC reanalysis and *in situ* MASEC'16 measurements

Table 2 Statistical data of surface O_3 from MACC reanalysis and MASEC'16

	This study (Hourly)	MACC reanalysis (Hourly)	AIRS Satellite (Daily)
The Antarctic Peninsula	10.31*	20.17*	19.59*
	10.58**	20.25**	19.64**
	±1.81***	±1.10***	±0.64***
The Drake Passage	8.67*	22.60*	14.28*
	9.50**	17.91**	14.81**
	±2.96***	±1.82***	±1.02***
Ushuaia	6.85*	19.04*	13.54*
	7.45**	16.59**	14.12**
	±2.18***	±2.07***	±0.84***

Note *Average
**Median
***Standard Deviation (±)

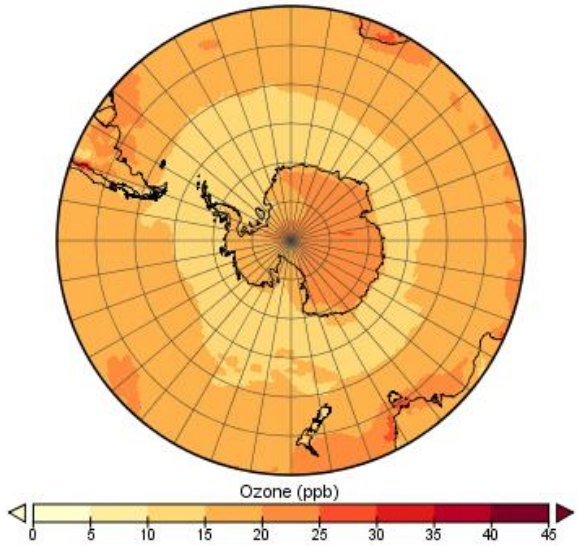

Figure 3.7 MACC reanalysis of surface O_3 monthly mixing ratio during MASEC'16.

3.6 Carbon monoxide influenced over surface O_3

3.6.1 Long term Monthly mixing ratio of CO

Ushuaia: It has been well recognized that the photochemical oxidation of CO, CH_4 and other hydrocarbons in the atmosphere will produce O_3, provided NO_x and VOCs concentrations are above a critical limit, while these same photochemical oxidation reactions will destroy O_3 if the NO_x mixing ratio is below this critical limit. To investigate the influence of CO on surface O_3 concentration, we have plotted a 4 year (1st January 2009 to 31st December 2013) time series of hourly CO and surface O_3 from WMO WDCGG over Ushuaia. This period of observation is used to identify the pattern of surface O_3 and its precursors such as CO. There is a lack of NO_x data available online, including WDCGG. Thus, in this study, CO (as an indicator of NO_x) data was used to investigate the influence on O_3 formation. CO is emitted from incomplete combustion and has an atmospheric lifetime of a few months in the atmosphere.

The diurnal cycle of surface O_3 and CO were consistent as shown in Figure 3.8. CO and surface O_3 mixing ratios increased from March to July and decreased from September to February each year. The peak of surface O_3 and CO mixing ratios reached up to ~38 ppb (O_3) and ~500 ppb (CO) when approaching the end of March every year. The mixing ratios of surface O_3 decreased from July to December every year. The high CO mixing ratios in the summer every year influenced the surface O_3 depletion in the presence of NO_x in the atmosphere. This depletion process occurred due to the titration of NO_x reducing O_3 to O_2. The NO_x mixing ratio was high over Ushuaia due to the high CO emitted from Ushuaia city. This may be the reason why surface O_3 mixing ratios were low during January every year. Nevertheless, the CO and surface O_3 showed both mixing ratios increased during winter. This may be influenced by meteorological factors such as seasonal wind speed and directions. A negative correlation between surface O_3 and CO is observed during January

every year with r^2 values of ~-0.78, $p<0.01$ and ~-0.81, $p<0.01$for January 2009 and January 2013 (Figure 3.9). Negative correlations may result from surface O_3 chemical loss and surface deposition (Cardenas et al., 1998; Parrish et al., 1998; Harris et al., 2000).

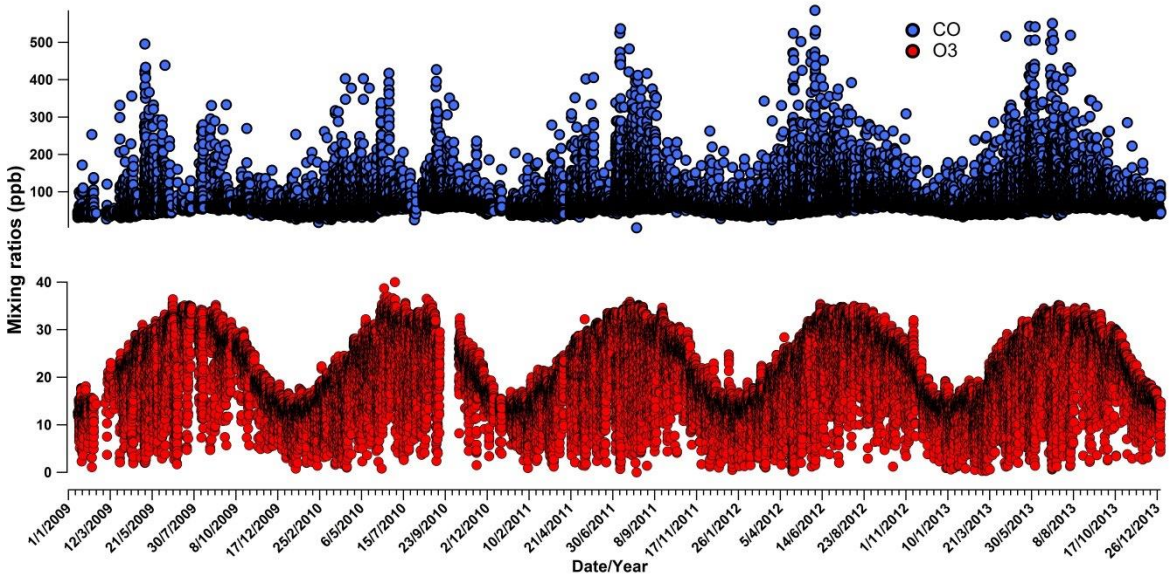

Figure 3.8 Hourly surface O_3 and CO mixing ratios over Ushuaia from 1st January to 31st December 2013

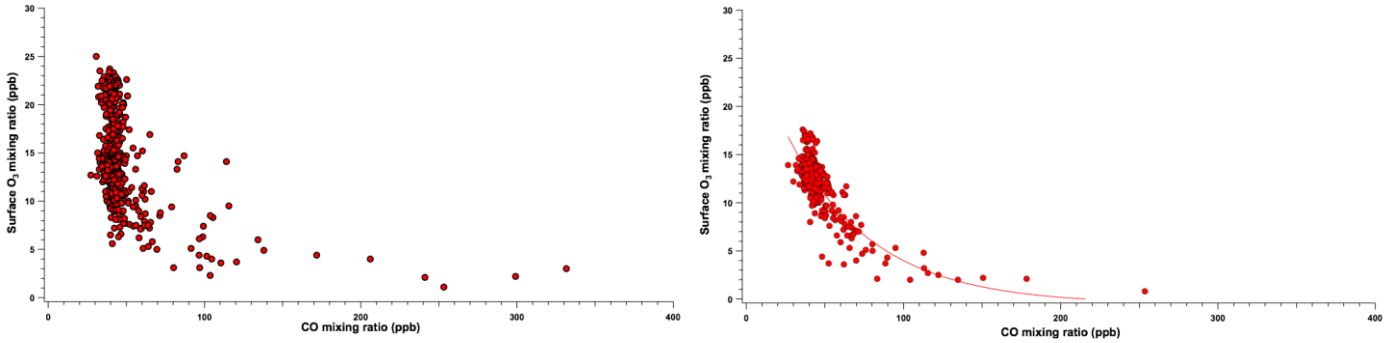

Figure 3.9 Correlation of hourly surface O_3 and CO mixing ratios over Ushuaia January 2009 (right) and January 2013 (left)

Antarctic: In the Antarctic region transport activity, for tourism (cruise ships) and scientific activities (research ships) is rapidly increasing. Thus, there is the additional risk of CO pollution from exhaust fumes into the Antarctic atmosphere. In contrast to Ushuaia hourly data, only the monthly average data of CO mixing ratio over SPO were available from WMO WDCGG. The monthly CO mixing ratios over SPO were consistently low during the whole period of 2009 to 2015. This is due to the absence of human activities over the Antarctic compared to Ushuaia. According to Yurganov

et al., 2009. The CO has a pronounced seasonal cycle in the Arctic and in mid-latitudes of the northern hemisphere. OH variations appear to be the most obvious cause of this cycle (Yurganov et al., 2009).

The surface O_3 mixing ratios increased as CO increased over SPO as shown in Figure 4.0. The CO mixing ratio was much lower than polluted areas, with minimum and maximum values of 38 and 53 ppb, respectively. Due to the lower CO mixing ratio, the NO_x mixing ratio is expected to be low over the boundary layer of the Antarctic. Thus, the surface O_3 formation is more pronounced compared to Ushuaia during the summer. As discussed earlier, surface O_3 formation over SPO is likely to be influenced by the sink of stratospheric O_3 into the troposphere and the accumulation of NO_x in the ice surface (Davis et al., 2001, 2004). Positive correlations observed between surface O_3 and CO over SPO and r^2 for each year were in the region of ~0.78, $p < 0.01$ (Figure 4.1). Figure 4.2 for the MACC reanalysis shows the monthly mixing ratio of surface CO was high over Ushuaia compared to the Antarctic region during MASEC'16. Positive surface air correlations observed is believed to be linked to the topographic of the center of the Antarctic region.

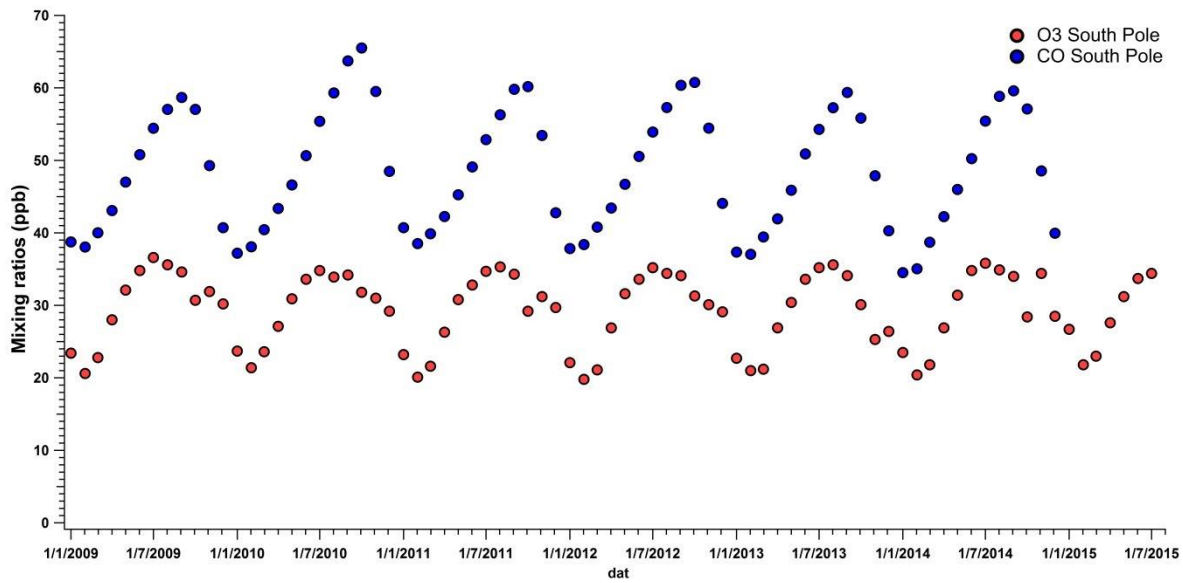

Figure 4.0 Monthly surface O_3 and CO mixing ratios over Ushuaia from 1st January to 1st January 2015.

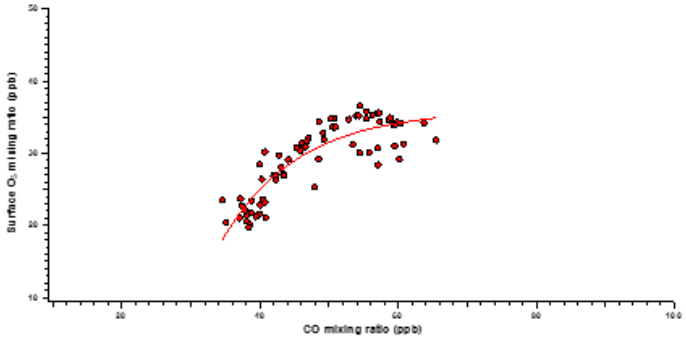

Figure 4.1 Correlation of monthly average 2009 to 2015 surface O_3 and CO over SPO.

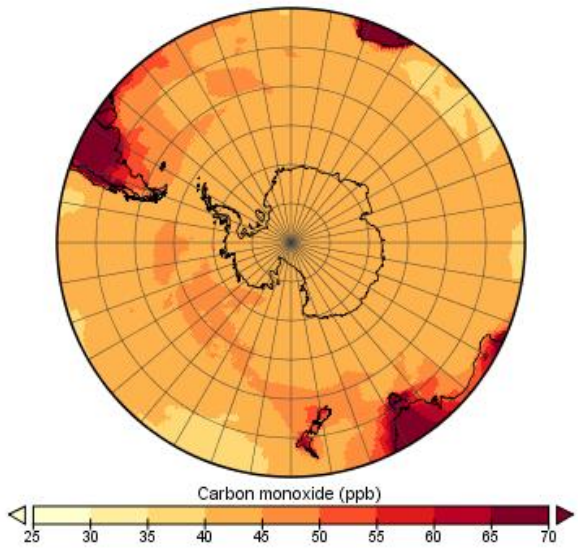

Figure 4.2 MACC reanalysis of surface CO monthly mixing ratio during MASEC'16.

3.7 Backward trajectory analysis

The travel pathways of the backward trajectories (BT) at Ushuaia, SO and CAP were plotted (Figure 4.3). The BTs were calculated using HYSPLIT 4.9, and were re-plotted using the IGOR Pro 6.0.1, a powerful graphical software (WaveMetrics, OR, USA). A release height of about 500 m for 120 h back trajectories with 6 h intervals was chosen to identify the origin of the air masses at the receptor point of interest in this study. Trajectory start time was chosen as 00:00 (UTC). Using the HYSPLIT 4.9 version of the model, the BTs were estimated for each day and compiled into IGOR Pro to visualize the pathways in the Antarctic region. As an input of the trajectory model, the dataset was downloaded from the NOAA website (link: ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis).

The period of the BTs was the 16th to 19th January 2016, the 22nd to 24th January 2016, the

25th to 26th January 2016 and the 28th to 31st January 2016 for Ushuaia, SO and two anchored stations along CAP, respectively. On the trajectories, the mixing height of the MBL (m) was also estimated using the in-built HYSPLIT model. The BTs at Ushuaia originated from the north-west (NW) direction and around the monitoring station the mixing height was about 300 - 400 m from the 16th to 19th January 2016. Over the SO, the BTs were transported from the NW and the mainland of the Antarctic Peninsula. The mixing height of MBL was about 600 m. However, the BTs travelled from the west to the south before they arrived at the CAP region during 25th to 26th January 2016. The BTs originating from the west during the 28th to 31st January 2016 were with the lowest height of MBL as compared to the MBL of other durations and places in the Antarctic region. The results of the trajectories can be interpreted with the elevation of surface level O_3 as well as the change to the height of MBL. During the cruise in the CAP, the mixing ratios of surface O_3 were higher compared to other locations. During the shift of surface O_3, the air mass originated from the SO as well as the mainland around Ushuaia, an area that experienced high concentrations of O_3 precursors such as NO_x and CO. The noted shift of air mass in this region may in part influence the anthropogenic impact on the formation of surface O_3 that might move with air masses around the Antarctic Peninsula. As referred to in the previous section, NOx titration reduces O_3 in the Ushuaia region. The mixing ratios of NO_x and CO were high at Ushuaia city due to anthropogenic activities. Even though the mixing height was relatively lower in this region, the heterogeneous reactions involved in the titration process decreases the O_3 mixing ratio. Another determinant of surface O_3 elevation is ambient pressure gradient. The pressure level was relatively lower in the Peninsula region which altered the mixing ratio of surface O_3 consistently. In contrast, the higher-pressure levels at Ushuaia were observed which indicates the reason of the low mixing ratio of surface O_3. The potential temperature (θ) also shown on the BTs (not included in the list of Figures) and the Figures showed an elevation of potential temperature compared to the Ushuaia region. Therefore, the potential temperature is another potential determinant in describing the variation of surface O_3 in the Antarctica region. The elevated surface O_3 in the Antarctic Peninsula is consistent with the lower MBL in this region.

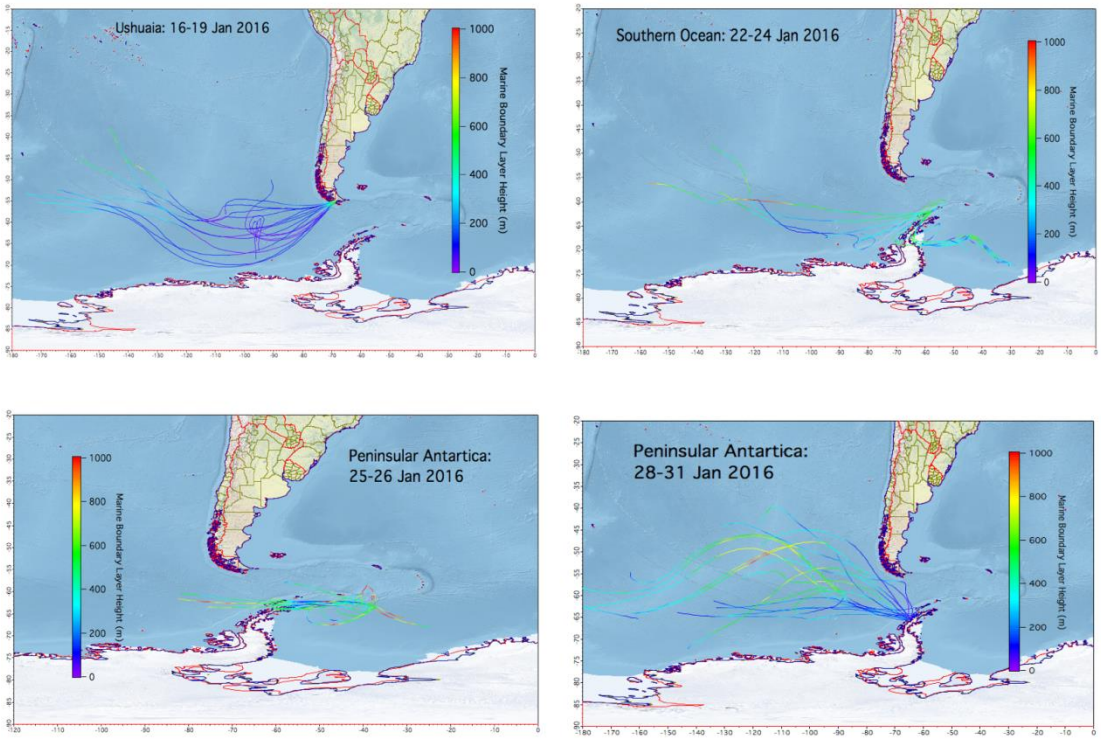

Figure 4.3 Backward trajectories transport of air masses in the MBL during MASEC'16

4.0 Conclusion

Surface O_3 levels are believed to be a result of a combination of a complex conditions and processes dependent on the location and to the proximity to the coast, the stratospheric O_3 sink, O_3 precursor distribution and human influences. Short term measurement during MASEC'16 and historical long term measurements of surface O_3 over Ushuaia and Antarctic were achieved. A new set of measurements of surface O_3 over Ushuaia, the Drake Passage and CAP was successfully conducted throughout the cruise campaign. The results from the MASEC'16 cruise mixing ratios were high, in the order of CAP>The Drake Passage>Ushuaia along the route of the cruise. The long term surface O_3 data showed strong seasonal cycles over Ushuaia and the Antarctic. Long term observations of surface O_3 over Ushuaia using WMO WDCGG showed levels decreased during the summer (January) and increased during the winter each year. The long term surface O_3 mixing ratios over five stations in Antarctica were consistent each year. Surface O_3 over SPO was the highest recorded among the stations, where transport of O_3 from stratosphere was a stronger influence over this region. Photochemical reactions and the transport of O_3-rich air from marine areas, ice and land, as well as the stratospheric O_3 sink, are all believed to influence O_3 levels over the CAP region. The January and February levels from the WDCGG multi-years analysis of surface O_3 over Ushuaia were between ~10 to 15 ppb, which is similar to the observations made during MASEC'16. The depletion of O_3 was dominant during these months (summer) due to the titration of NO_x (photochemical reaction) over polluted areas like Ushuaia compared to the Antarctic region. This is supported by high mixing ratios of CO over Ushuaia, in the range ~38 to ~500 ppb. The surface O_3 levels were consistent throughout January and February each year for most of stations in Antarctica. The formation processes of surface O_3 over the SPO were dominant with the highest

mixing ratios observed, ranging between ~20 to 30 ppb. This can be explained by the low CO (with the assumption of less NO_x) ranges of 38 to 53 ppb over the Antarctic atmosphere. The surface O_3 mixing ratio measured over CAP was the highest, approaching ~15 ppb. The satellite and MACC reanalysis data showed a consistent pattern of the surface O_3 mixing ratios with the *insitu* observations during MASEC'16. Both satellite AIRS and MACC were slightly higher ~40 to 50% than *insitu* MASEC'16. The back trajectories showed potential anthropogenic and biogenic impacts on the formation of surface O_3 over the study areas. In the near future, more long term *in situ* measurements are needed over the Drake Passage and the Antarctic Peninsula since these regions are close to anthropogenic influences and lack of accessible data.

Acknowledgements

We would like to thank Sultan Mizan Antarctic Research Foundation Grant (YPASM) program registered as ZF-2015-001 as part of the Malaysia Antarctic Research Programme (MARP) under Malaysian Ministry of Science, Technology and Innovation (MOSTI) and Universiti Kebangsaan Malaysia (UKM) GUP-2014-041 for giving opportunities and financial support for the Centre Tropical System & Climate Change (IKLIM) UKM to participate in this scientific cruise. Secondly, we like to thank MASEC'16 scientists on board *R/V Australis's* and their crews and Envirotech Sdn. Bhd who helped a lot on the exploration activities and Dr. Rose Norman (UK) for her assistance in proofreading this article. This study relies on archived surface O_3 data sets that were retrieved from the WMO World Data Centre for Greenhouse Gases (http://gaw.kishou.go.jp/wdcgg.html). We would like also to thank all international research stations who provided all data to the website.

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Nadzir, M.S.M., Ashfold, M.J., Khan, M.F. et al. Spatial-temporal variations in surface ozone over Ushuaia and the Antarctic region: observations from in situ measurements, satellite data, and global models. Environmental Science and Pollution Research, January 2018, Volume 25, Issue 3, pp. 2194-2210

https://doi.org/10.1007/s11356-017-0521-1

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