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RESEARCH ARTICLE

Spatial-temporal variations in surface ozone over Ushuaia and the Antarctic region: observations from in situ measurements, satellite data, and global models

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Abstract The Antarctic continent is known to be an unpopulated region due to its extreme weather and climate conditions. However, the air quality over this continent can be affected by long-lived anthropogenic pollutants from the mainland. The Argentinian region of Ushuaia is often the main source area of accumulated hazardous gases over the Antarctic Peninsula. The main objective of this study is to report the first in situ observations yet known of surface ozone (O_3) over Ushuaia, the Drake Passage, and Coastal Antarctic Peninsula (CAP) on board the *RV Australis* during the Malaysian Antarctic Scientific Expedition Cruise 2016 (MASEC'16). Hourly O_3 data was measured contin-

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uously for 23 days using an EcoTech O_3 analyzer. To understand more about the distribution of surface O_3 over the Antarctic, we present the spatial and temporal of surface O_3 of long-term data (2009–2015) obtained online from the World Meteorology Organization of World Data Centre for greenhouse gases (WMO WDCGG). Furthermore, surface O_3 satellite data from the free online NOAA-Atmospheric Infrared Sounder (AIRS) database and online data assimilation from the European Centre for Medium-Range Weather Forecasts (ECMWF)-Monitoring Atmospheric Composition and Climate (MACC) were used. The data from both online products are compared to document the data sets and to give an indication of its quality towards in situ data. Finally, we used past carbon monoxide (CO) data as a proxy of surface O_3 formation over Ushuaia and the Antarctic region. Our key findings were that the surface O_3 mixing ratio during MASEC'16 increased from a minimum of 5 ppb to ~ 10–13 ppb approaching the Drake Passage and the Coastal Antarctic Peninsula (CAP) region. The anthropogenic and biogenic O_3 precursors from Ushuaia and the marine region influenced the mixing ratio of surface O_3 over the Drake Passage and CAP region. The past data from WDCGG showed that the annual O_3 cycle has a maximum during the winter of 30 to 35 ppb between June and August and a minimum during the summer (January to February) of 10 to 20 ppb. The surface O_3 mixing ratio during the summer was controlled by photochemical processes in the presence of sunlight, leading to the depletion process. During the winter, the photochemical production of surface O_3 was more dominant. The NOAA-AIRS and ECMWF-MACC analysis agreed well with the MASEC'16 data but twice were higher during the expedition period. Finally, the CO past data showed the surface O_3 mixing ratio was influenced by the CO mixing ratio over both the Ushuaia and Antarctic regions. Peak surface O_3 and CO hourly mixing ratios reached up to ~ 38 ppb (O_3) and ~ 500 ppb (CO) over Ushuaia. High CO over Ushuaia led to the depletion process of surface O_3 over the region. Monthly CO mixing ratio over Antarctic (South Pole) were low, leading to the production of surface O_3 over the Antarctic region.

Keywords Surface O_3 · Carbon monoxide (CO) · Seasonal cycles · Satellite and MACC reanalysis and HYSPLIT trajectories

Introduction

The climate change phenomena may affect atmospheric photochemistry conditions globally, including over the polar region. The change in temperature will change atmospheric pollution concentrations, especially in sensitive environment such as the polar regions. It should be noted that any changes in air pollution characteristics from polar regions will affect the climate globally. Polar regions such as the Antarctic are of interest for surface ozone (O_3) research for several reasons. First, anthropogenic sources and sinks are scarce because of low human population density and the absence of industrial activities (Neff et al. 2008; Wang et al. 2011). Secondly, in the Antarctic, surface O_3 is mostly determined by natural processes and upward and downward transport from the stratosphere (Neff et al. 2008). Therefore, O_3 data from these higher latitudes are of particular value for assessing background O_3 and are an indicator for hemispheric levels in the determination of global O_3 changes and trends (Neff et al. 2008).

The interest in surface O_3 chemistry, its sources, and sinks is driven by the importance of its role in atmospheric oxidation chemistry, its harmful effects on human and other living things, and its contribution to radiative forcing (Oltmans 1993). In contrast to CO_2 and CH_4, O_3 is much more difficult to quantify, especially in the polar regions. Firstly, O_3 is a reactive gas and it is not preserved in the ice surface, and therefore, no records are available that span times before the development of O_3 measurement capabilities in the Antarctic (Neff et al. 2008). Secondly, O_3 is involved in complex production and destruction chemistry, which causes O_3 concentrations to vary widely on geographical and temporal scales. In polar regions, water vapor content and UV radiation are much lower than other parts of the world, leading to longer lifetimes of surface O_3 (~ 100 days) (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 al. 2012); European regions such as Mace Head, Ireland (Simmonds et al. 1997; Derwent et al. 2003); and the USA (Li et al. 2000).

O_3 precursor emissions play an important role in the distributions of surface O_3 in the atmosphere. In the Antarctic, NO_x can be emitted from snow and it has shown that the production of surface O_3 can occur in Antarctica via the photolysis reaction from NO_x emissions (Neff et al. 2008). This

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denitrification resulting in NO_x emissions in summer was identified over Antarctica (Jones et al. 1999, 2000, 2001; Davis et al. 2001). Previous studies have shown surface O_3 and NO_x over polar regions exhibit diurnal cycles and are anti-correlated, and the cycle is determined by the UV radiation intensity (Kumar et al. 2006). Anthropogenic contributions to O_3 precursors such as NO_x or CO can be transported from the mainland (South America) and also biogenic sources, to the Antarctic continent. The anthropogenic O_3 precursors were believed to be localized and time variant (Kumar et al. 2006). Therefore, the dramatic surface O_3 loss during high UV radiation (summer) is of great interest. Previous in situ data of surface O_3 over the Antarctic has been reported by studies from several research stations such as Neumayer (Crawford et al. 2001, Frieß et al. 2004), Concordia (Legrand et al. 2009), Marambio (Taalas et al. 1993), and Syowa (Murayama et al. 1992). In general, these have been studied as individual events, or short-term time series of surface measurements.

In this study, we added more stations of in situ long-term observations of surface O_3 over Ushuaia (Argentina) and the Antarctic, including the Peninsula, namely Marambio (MM) (Argentina), Neumayer (NM) (Germany), Syowa (SY) (Japan), SPO (USA), and Halley Bay (HB) (UK). Data from the World Meteorology Organization World Data Centre for Green House Gases (WMO WDCGG) were relied on. In addition, satellite data of atmospheric air pollutants are becoming more widely used in the decision-making and environmental management activities of many part for research activities (Duncan et al. 2014).

Data assimilations used in global models from satellite data such as by the Monitoring Atmospheric Composition and Climate (MACC) project are also commonly used in atmospheric composition analysis (Inness et al. 2013, Inness et al. 2015). The MACC combined state-of-the-art atmospheric modeling with earth observation data to provide information services covering European air quality, global atmospheric composition, climate, and UV and solar energy (Innes 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 Northern Hemisphere (NH) and over the Antarctic.

Thus, the combination of real-time in situ observation, satellite data, and data assimilation in global models over such region like the Antarctic is a priority in this study. Therefore, assimilations of satellite data on atmospheric composition, with a focus on surface O_3, will be used for data comparison to assess its quality. Satellite data assimilation has been carried out previously (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 2011), and global O_3 forecasts are now routinely produced by several meteorological centers (Inness et al. 2013). NOAA (National Oceanic and Atmospheric Administration) Atmospheric Infrared Sounder (AIRS) satellite-based products for atmospheric composition are freely available from NASA's website (http://giovanni.gsfc.nasa.gov/). A barrier to using these types of data is the inherent difficulties associated with steps such as accessing, processing, and properly interpreting them. The importance of this study also lies in the fact that Antarctica is a remote continent where a study using even a small data set on any atmospheric trace gases has much scientific value. Although studies on surface O_3 over Antarctica were available in the literature, information of its distributions over the Drake Passage and the coast of the Antarctic Peninsula is still unknown.

We present here measurements of surface O_3 mixing ratios in the marine boundary layer over Ushuaia, the southern part of the Southern Ocean (SO) (the Drake Passage), and 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 was to show a new cruise observation of surface O_3 over Ushuaia, the Drake Passage, and CAP. Secondly, it was to show a long-term (5-year) data set of temporal surface O_3 distribution over Ushuaia and five research stations in Antarctica (Western, Eastern, Southern, and Peninsula), namely MM, NM, SY, SPO, and HB, from WDCGG data. These measurements are important because the geographic and climate conditions over Ushuaia and the Antarctic region are completely different. The differences between these two areas may influence the atmospheric conditions. The five-year long-term data set will be compared with Malaysian Antarctic Scientific Expedition Cruise 2016 (MASEC'16) data for spatial-temporal distributions of surface O_3 over the Antarctic region. In addition, satellite and global data assimilations will be compared with observations from MASEC'16. The purpose of this comparison 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-year 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. We also used the "mixing ratio" (concentration) term as the principal measurement of atmospheric composition.

Measurement and sampling

MASEC'16 took place on board the *RV Australis* between 16th January and 8th February 2016 from Ushuaia, Argentina, to Darboux Island and back to Ushuaia (Graham Coast, the Antarctic Peninsula) as shown in Fig. 1. On each cruise, an EcoTech (Australia) model Serinus 10 O_3 analyzer was used to measure the surface O_3. 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 accuracy or precision of the EcoTech is 0.5 ppb or 0.2%. 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 with the inlet adjusted at each sampling time to face the prevailing wind.

The cruise participants were from different scientific backgrounds, predominantly biology. The vessel sailed across the sub-Antarctic and Antarctic regions with various conditions. The *RV Australis* 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 h. The EcoTech was then deployed for cruise measurements on the *RV Australis* 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.

Data analysis

To illustrate multi-year updated measurements over Ushuaia and Antarctica, 5 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, five stations were selected for surface O_3 analysis. The stations were 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. The surface O_3 data recorded during MASEC'16 were validated using the corresponding monthly averages of the multi-year data. The AIRS satellite-derived surface O_3 (1000 hPa) concentrations were derived from the NASA "Giovanni" online database (http://giovanni.gsfc.nasa.gov/) and were used to determine apparent surface O_3 values in the 1 × 1° grid square nearest to each sampling point. The MACC reanalysis of surface O_3 (1000 hPa) values in the 0.125° × 0.125° grid square nearest to each sampling point was taken from http://apps.ecmwf.int/datasets/data/.

To investigate the relationship between surface O_3 and its precursors, CO data was derived from WMO WDCGG. Multi-year 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 is used to represent the whole region of Antarctica. The correlation plot between surface O_3 and CO will be constructed to investigate their correlation over Ushuaia and Antarctica.

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 (BT) analysis. The BTs were calculated using version 4.9 of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by the NOAA's Air Resource Laboratory (ARL) (Draxler and Rolph 2003; Rolph 2003) and were replotted using the IGOR Pro 6.0.3, a powerful graphical software (WaveMetrics, OR, USA) to visualize the pathways of the true image of Antarctica region. 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 the interest in this work. Trajectory start times of 00:00, 06:00, 12:00, and 18:00 (UTC) were chosen. As an input of the trajectory model, data was downloaded from the NOAA website (link: ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis). Marine boundary layer height was also computed using the HYSPLIT algorithm. The data of boundary layer height was annotated to the trajectories with a color-coded. The selected height level of the particles released ensured that the trajectories started in the atmospheric boundary layer (Eva and Lambin 1998). 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.

Results and discussion

Meteorological conditions during Malaysian Antarctic Scientific Expedition Cruise 2016

Meteorological data such as atmospheric temperature, wind speed, and wind direction were recorded on board during the

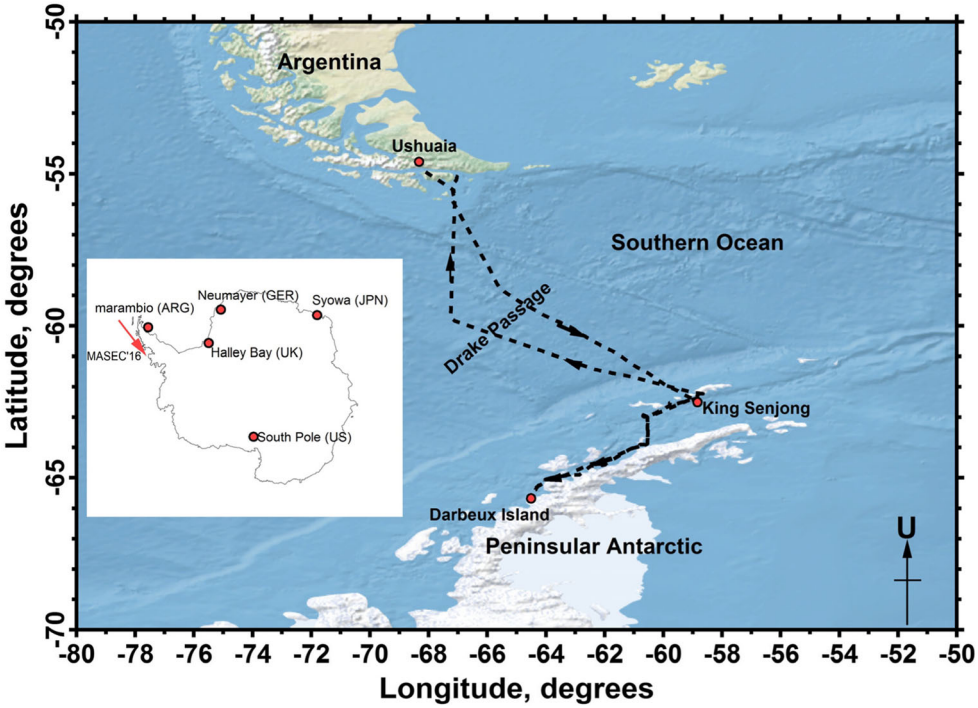

Fig. 1 Cruise route during MASEC'16 and five selected stations which were used for multi-year data analysis in this study

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 SO, and CAP, respectively. Relative humidity over Ushuaia was lower than the SO and CAP with the values of 50 to 75%. The SO had the highest humidity in the range of 80 to 90% and CAP had values in the range of 75 to 90%. According to Wilson et al. (1979), the Antarctic region has low humidity compared to the Peninsula region. The wind speed and directions were also recorded on board over Ushuaia, the SO, and CAP. The meteorological data such as wind speed and directions during the cruise period were retrieved with ZyGrib 6.2.3 software. 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 the values of 30 to 38 ms^{-1}. As 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.

Latest observation on spatial distributions of surface O_3 (Malaysian Antarctic Scientific Expedition Cruise 2016)

Ushuaia and the drake passage In this section, we report hourly surface O_3 during the expedition period. Since the period is short, the results only represent the duration of the expedition period and route, not the entire region. 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 Fig. 3. 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 keep 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 traveling 2000 km from Ushuaia into the SO. A previous study by Johnson et al. (1990) 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 2000, 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. BT 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.

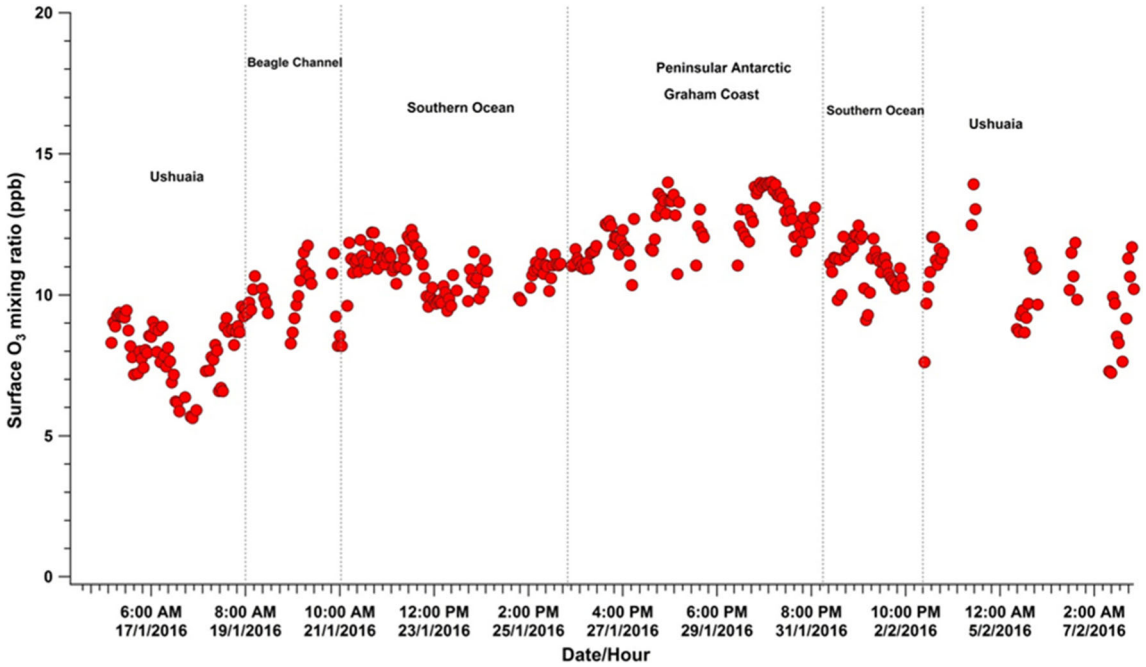

Fig. 2 Hourly surface O_3 mixing ratio data from the on board O_3 analyzer during MASEC'16

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 (Fig. 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 can 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. 1992). 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.

Temporal distributions of surface O_3 over Ushuaia, Southern Ocean, and Antarctic (multi-year data)

Ushuaia and the Southern Ocean The multi-year data analyses are shown in box-and-whisker plots in Fig. 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 Fig. 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 characteristics of the geographical, climatic, and chemical environment are important in determining the surface O_3 mixing ratio over the Antarctic region. Three main sources of surface O_3 were believed to influence concentrations: (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 the review of surface O_3 over six stations in the Antarctic region by Neff et al. 2008, the period of the study was from 1973 to 2005. In our study, we reported recent analysis for five stations (2010 to 2014 and 2015) over each part of the Antarctic covering southern, central, eastern, and western regions (including the Peninsula).

Most data were recorded successfully, with the exception of some data from the MM station (Peninsula). The annual O_3 cycle in Fig. 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 Neff et al. (2008).

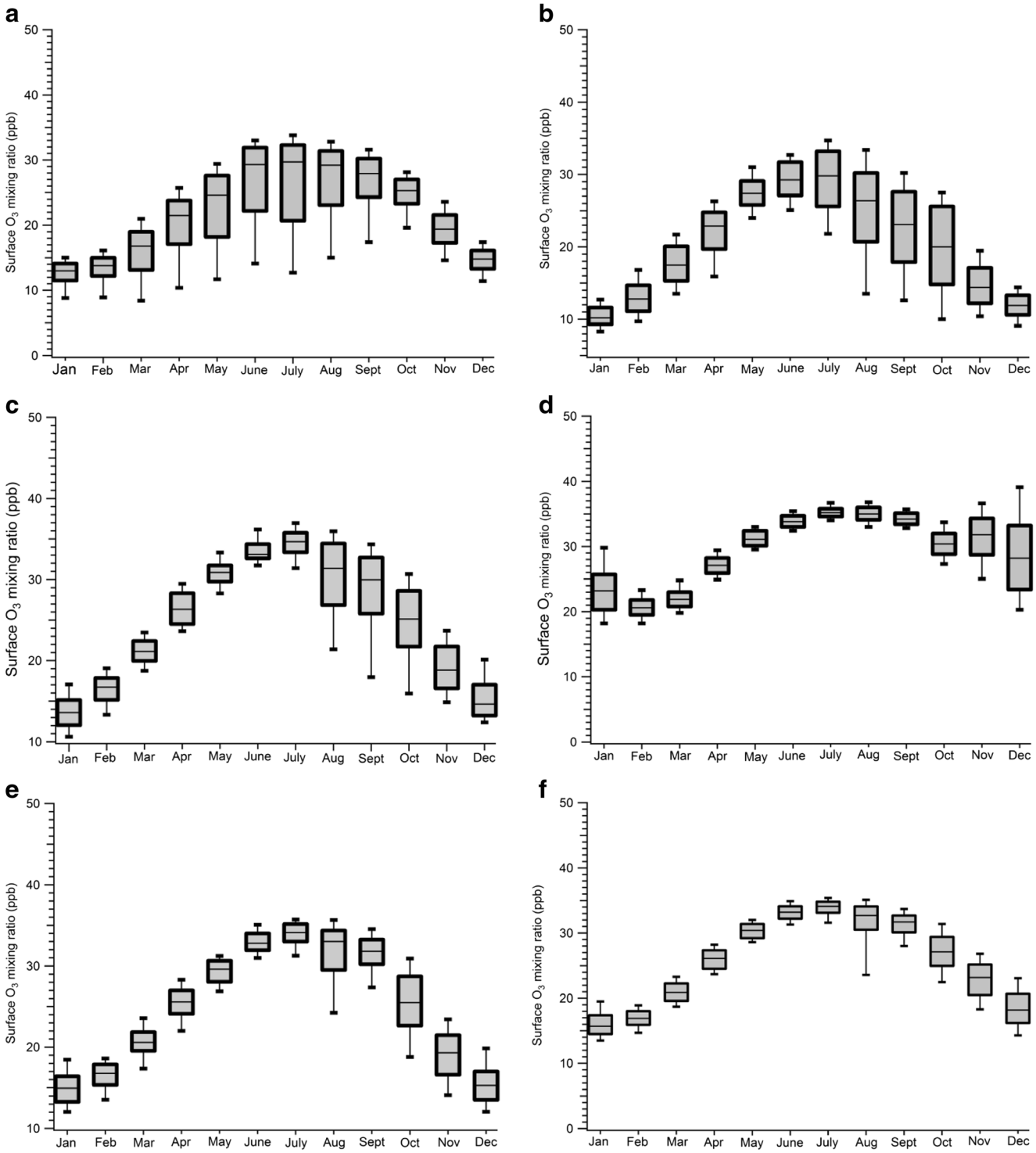

Fig. 3 Box-and-whisker plots for the multi-year surface O_3 observations at **a** Ushuaia, **b** Marambio **c** Halley Bay, **d** SPO, **e** Neumayer, and **f** Syowa. In each panel, the colored boxes show the data falling between the 25th and 75th percentiles, with the median value shown as a black horizontal line inside each box. The vertical black lines above and below each box indicate the 95th and 5th percentiles, respectively

Low CO and NO_x environments over the Antarctic where more O_3 destruction than O_3 production during the summer months result in a decline of ambient O_3 level (Neff et al. 2008). 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. (1997), ice-coverage fluctuates seasonally, meaning algae- or bacteria-produced bromine will also fluctuate, implying in ice-water coverage is a player in the ocean-

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

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

*Average

**Median

***Standard deviation

chemical interaction which will vary 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 reactions in the presence of sunlight during the summer. 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

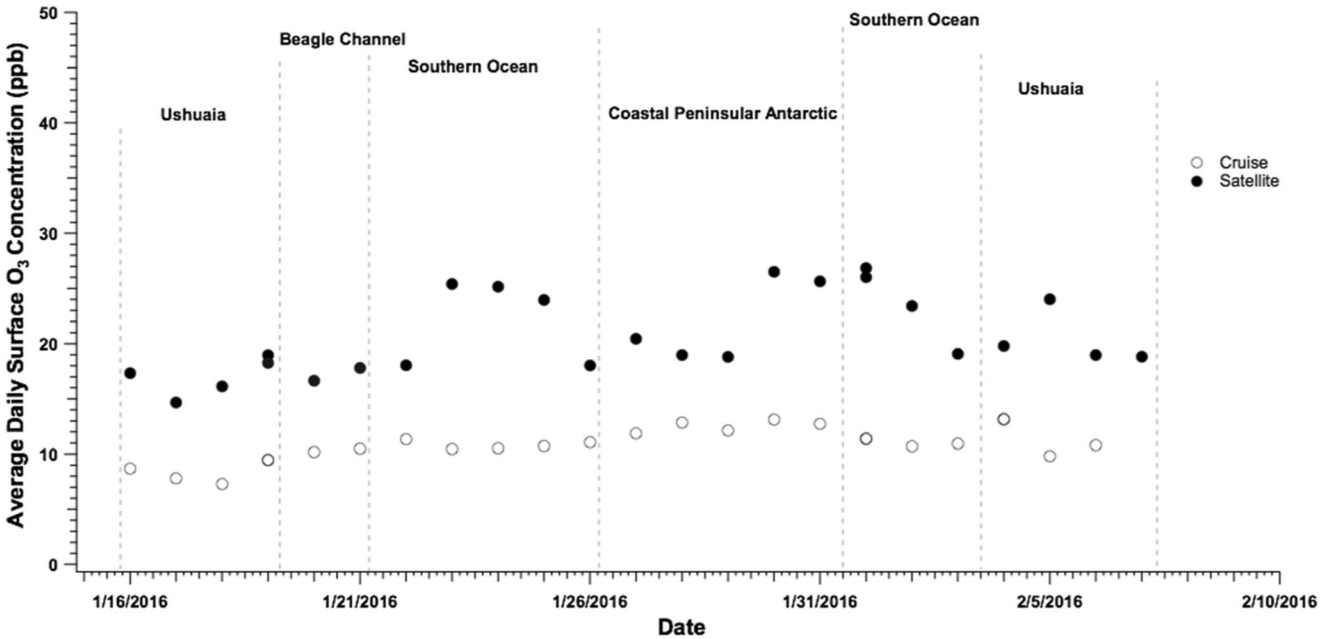

Fig. 4 Average daily surface O_3 mixing ratio from the AIRS satellite and in situ MASEC'16 measurements

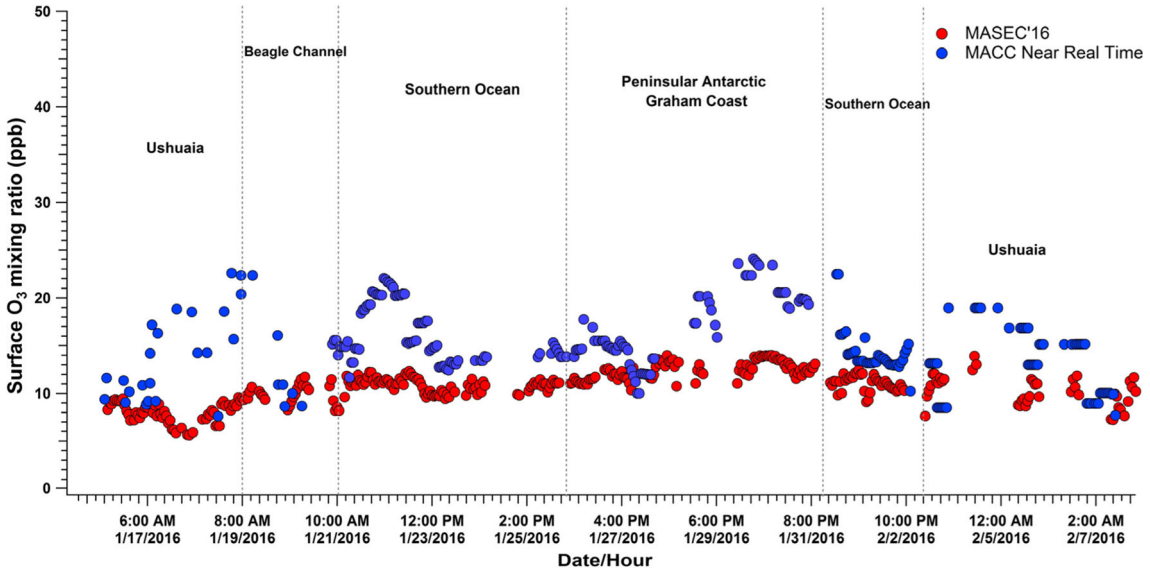

Fig. 5 Hourly surface O_3 mixing ratios from the MACC reanalysis and in situ MASEC'16 measurements

locations (see Fig. 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 UV radiation penetrate the troposphere leading to O_3 photolysis in the near-surface atmosphere (Schnell et al. 1991). Furthermore, a 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).

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 locations in Antarctica (Davis et al. 2004; Helmig et al. 2007b; Neff et al. 2017). In addition, deposited nitrate results in fluxes of NO_x out of the snowpack into the atmosphere (Oncley et al. 2004). This caused NO mixing ratios in the surface layer to frequently reach ~ 500 pptv (Davis et al. 2001, 2004) and 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 had similar surface O_3 levels but they differed from one another during the late spring and summer. In this study, MM was the only Peninsula coastal station which had data available from WMO WDCGG. Figure 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 was supported by the latest observation during MASEC over CAP with a value of ~ 15 ppb as mentioned earlier. The transport of

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***

*Average

**Median

***Standard deviation

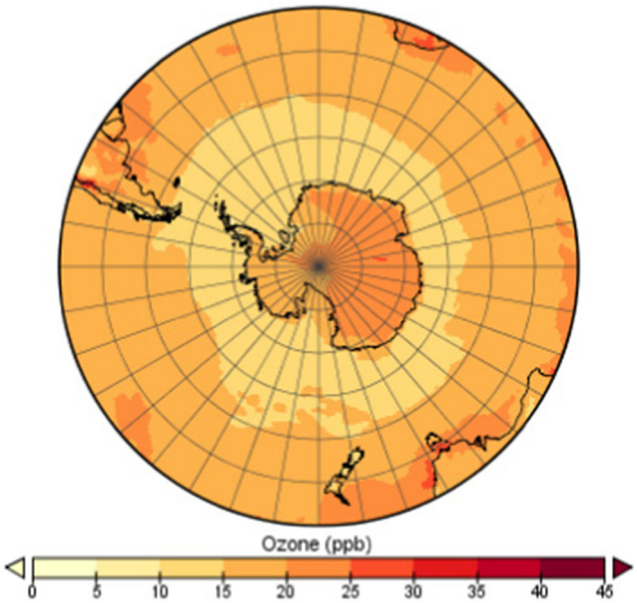

Fig. 6 MACC reanalysis of surface O_3 monthly mixing ratio during MASEC'16

polluted air from continental South America could be another source for increases in surface O_3 at MM station.

Satellite and Monitoring Atmospheric Composition and Climate reanalysis in comparison with Malaysian Antarctic Scientific Expedition Cruise 2016 data

The data from NOAA-AIRS satellite products and MACC reanalysis were retrieved for Jan/Feb 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 data and are shown in Fig. 4. 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 for the in situ data. According to Duncan et al. (2014), the development of a surface O_3 satellite product is fraught with many obstacles, so that such a product is not currently feasible. First, the portion of the tropospheric O_3 is about ten times less than the amount in the stratospheric O_3, making it very difficult for satellite instruments to discriminate between the stratospheric and tropospheric surface O_3 amounts (Duncan et al. 2014). Nevertheless, the tropospheric O_3 data sometimes correlates well with surface data, including in urban areas (Kar et al. 2010).

In this study, the findings are not necessarily surprising even if satellite observations were slightly higher than in situ. Similar findings by Mohd Nadzir et al. 2014, on satellite-based products where they observed the satellite-derived chlorophyll-a, were overestimated compared to the in situ observations over the marine region. In this study, the observed surface O_3 concentrations might originate over a wide geographic area and were not necessarily driven solely by localized emissions. In this context, satellite-derived surface O_3, also providing information from a wider area, may potentially be more relevant than in situ measurements. Nevertheless, both the data sets showed high concentrations over the

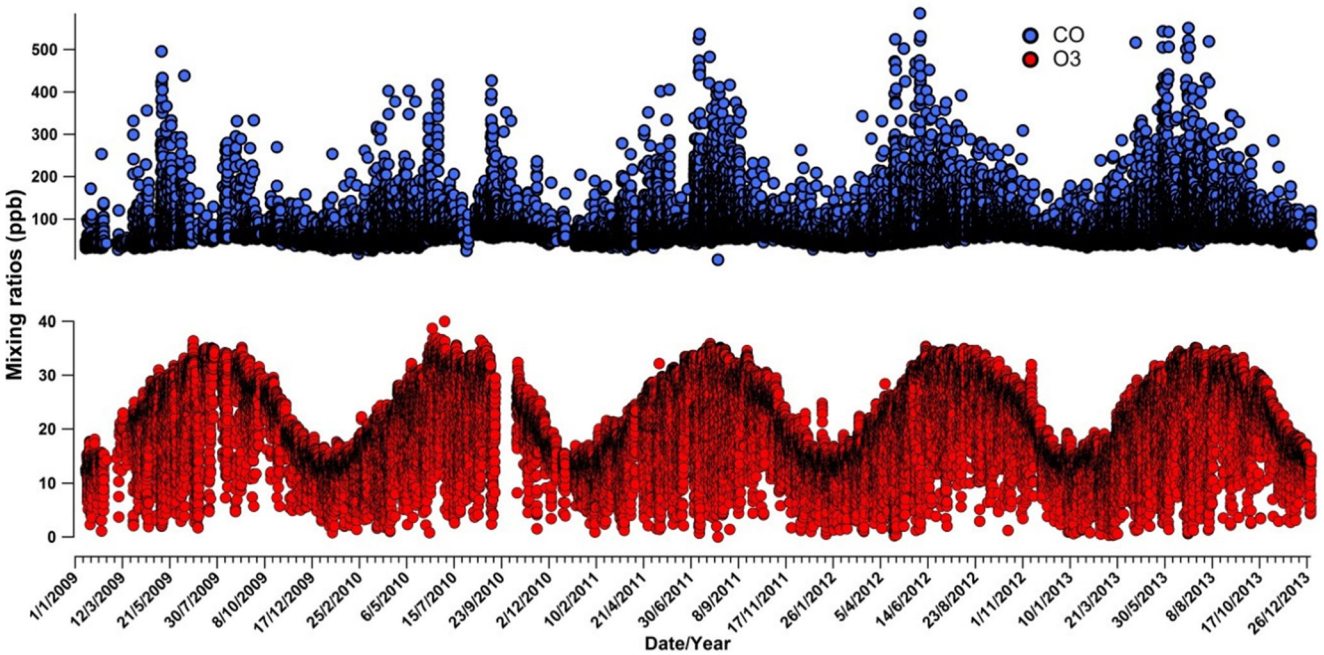

Fig. 7 Hourly surface O_3 and CO mixing ratios over Ushuaia from 1st January to 31st December 2013

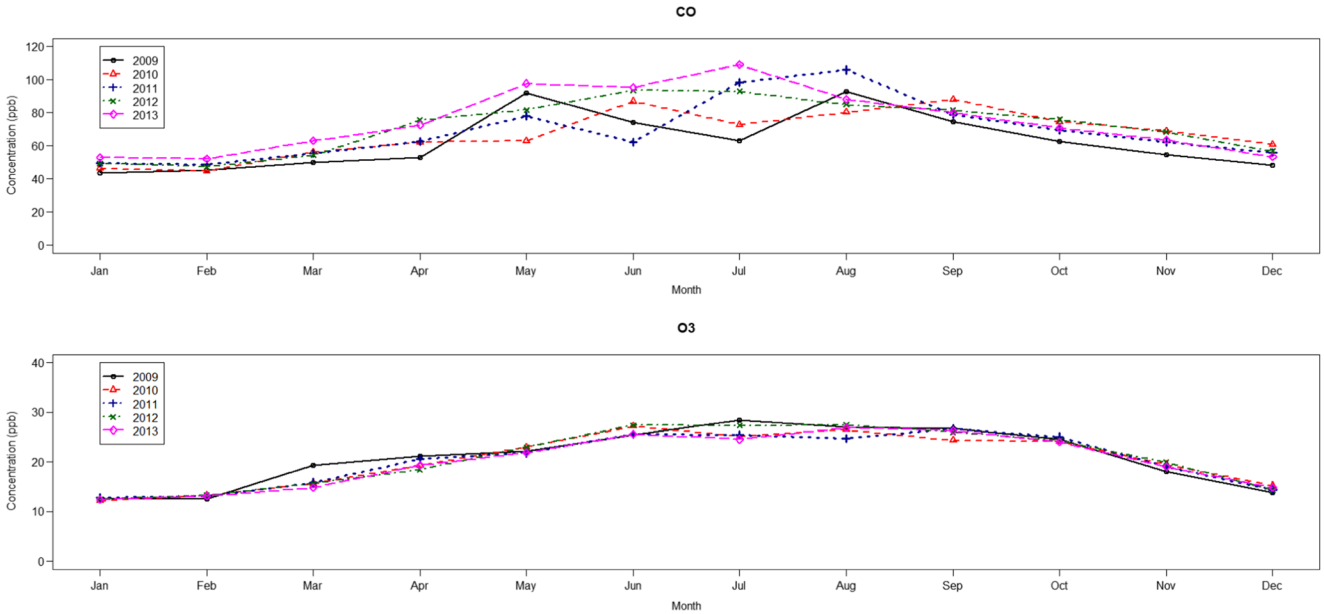

Fig. 8 Inter-annual seasonal variations of CO (upper panel) and O_3 (lower panel) over Ushuaia from 2009 to 2013

Antarctic Peninsula compared to Ushuaia. The average daily levels over Ushuaia and the Antarctic Peninsula between the AIRS satellite and the cruise data were correlated with $r^2 = 0.48$ and $p < 0.01$. There are difficulties in comparing satellite data to in situ measurements, but we believe that this type of comparison still provides valuable information from a data-sparse region.

As shown in Fig. 5, the hourly surface O_3 mixing ratios from the MACC reanalysis (1000 hPa) were slightly higher (almost 2× 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. This type of observation was also reported by Inness et al. (2014) on tropospheric O_3 over Antarctica. They reported the reanalysis biases between MACC and ozonesondes are within ± 5–10% in the NH and over the Antarctic. The explanation details of the reanalysis biases were well explained in Inness et al. (2013). The MACC model's background column value is calculated as a simple vertical integral between the top and the bottom pressure given by the partial or total column, at the time and location of the observation (Innes et al. 2013). The observation error and background error covariance matrices in the model determine the uncertainties in the assimilated data (Innes et al. 2013). In this study, 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 Fig. 6, the MACC reanalysis shows monthly mixing ratios of surface O_3 increased when approaching the Antarctic region.

Table 3 Statistical data for CO and surface O_3 data over Ushuaia from 2009 to 2013

	CO		O_3	
Months	Average	SD (±)	Average	SD (±)
Jan	48.82	15.80	12.62	2.70
Feb	48.05	18.24	13.14	3.23
Mar	56.85	31.12	15.94	4.68
Apr	65.64	47.22	19.46	6.07
May	82.03	61.52	22.36	6.78
Jun	83.39	60.70	25.59	7.79
Jul	94.19	63.09	25.96	8.26
Aug	91.87	53.02	25.84	7.36
Sep	81.39	40.90	25.93	5.96
Oct	71.14	21.04	24.38	4.01
Nov	63.87	16.94	19.12	3.71
Dec	54.63	14.41	14.37	2.71

Carbon monoxide influence over surface O_3

Multi-year 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 volatile organic carbon (VOC) 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

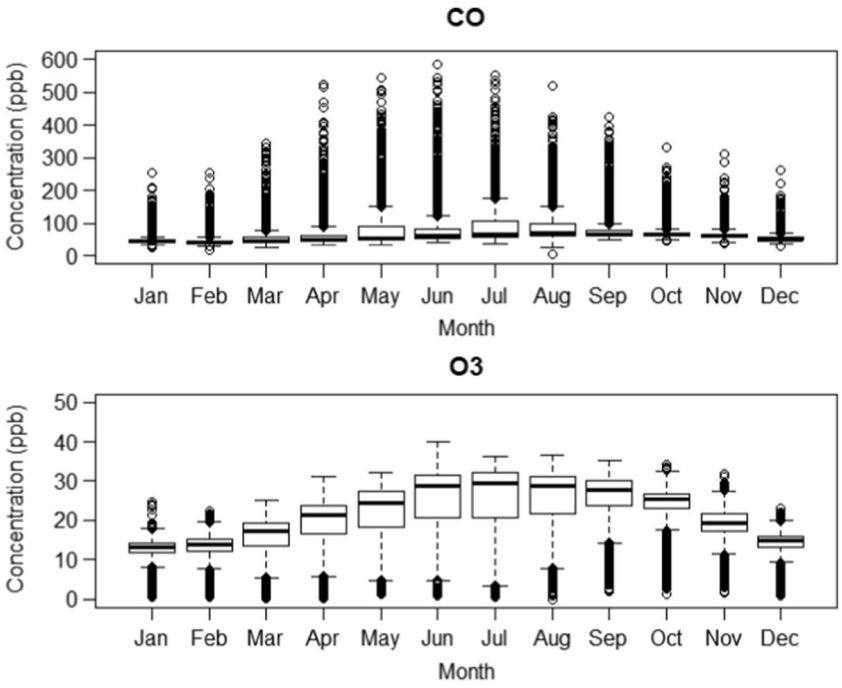

Fig. 9 Seasonal monthly average variations of CO (upper panel) and surface O_3 (lower panel) over Ushuaia from 2009 to 2013

the pattern of surface O_3 and its precursors such as CO. There is a lack of NO_x data available online, including from WDCGG. Thus, in this study, CO (as an indicator of NO_x) data was used to investigate the influence on O_3 formation.

The diurnal cycle of surface O_3 and CO was consistent as shown in Fig. 7 and 8.Table 3 shows the average monthly and standard deviation for CO and surface O_3 data from 2009 to 2013. 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 as shown in Fig. 8. The high CO mixing ratios in the summer (January) 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. Figure 9 shows seasonal monthly average variations of surface CO and O_3 over Ushuaia from 2009 to 2013. 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 (Fig. 10).

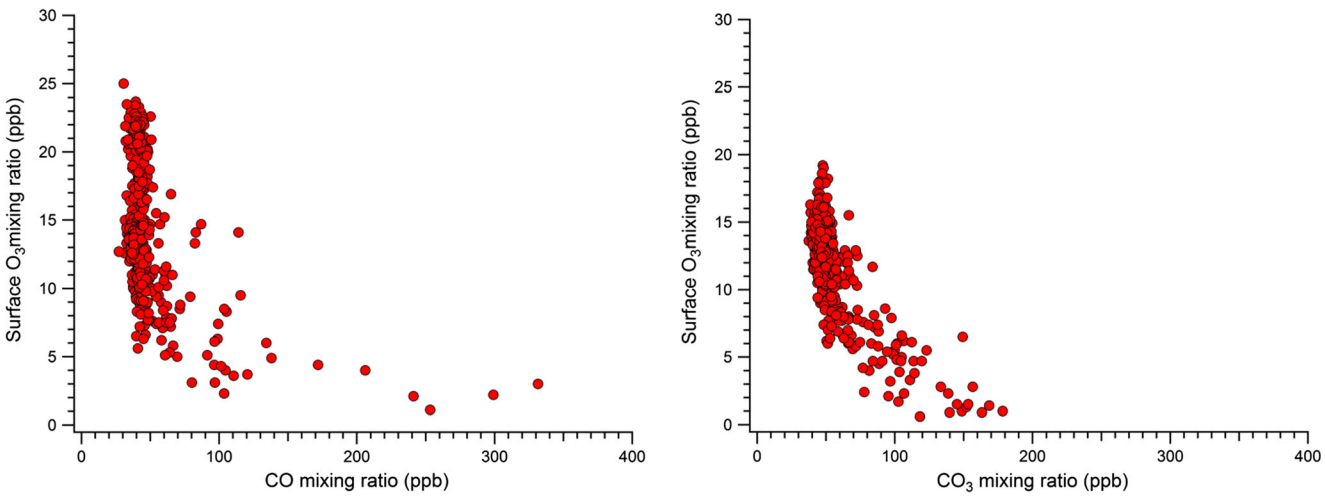

Fig. 10 Correlation of hourly surface O_3 and CO mixing ratios over Ushuaia January 2009 (right) and January 2013 (left)

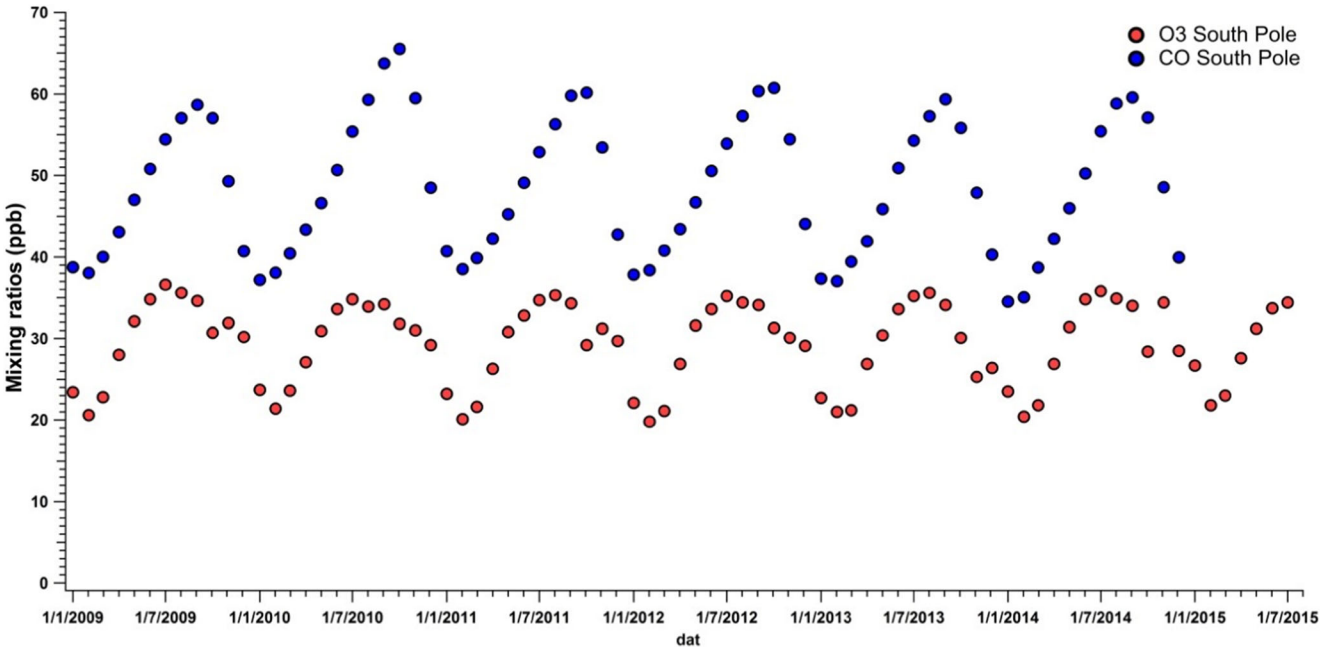

Fig. 11 Monthly surface O_3 and CO mixing ratios over SPO from 1st January to 1st January 2015

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 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.

The surface O_3 mixing ratios increased as CO increased over SPO as shown in Fig. 11. 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, $p < 0.01$ (Fig. 12). Figure 13 for the MACC reanalysis shows the monthly mixing ratio of surface

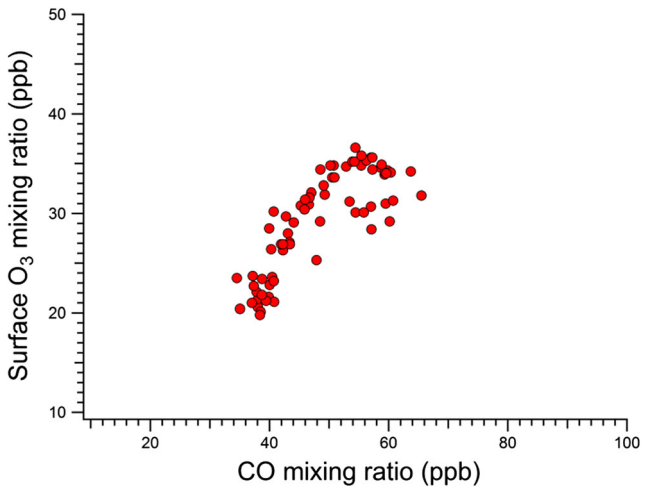

Fig. 12 Correlation of monthly 2009 to 2015 surface O_3 and CO over SPO

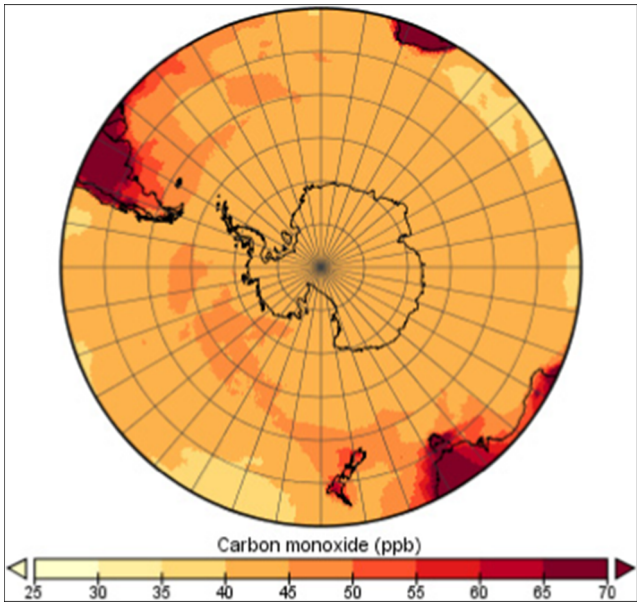

Fig. 13 MACC reanalysis of surface CO monthly mixing ratio during MASEC'16

CO was high over Ushuaia compared to the Antarctic region during MASEC'16.

Backward trajectory analysis

The travel pathways of the BTs at Ushuaia, SO, and CAP were plotted (Fig. 14). 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 data set 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 the 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 northwest (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 traveled from the west to the south before they arrived at the CAP region during 25th to 26th

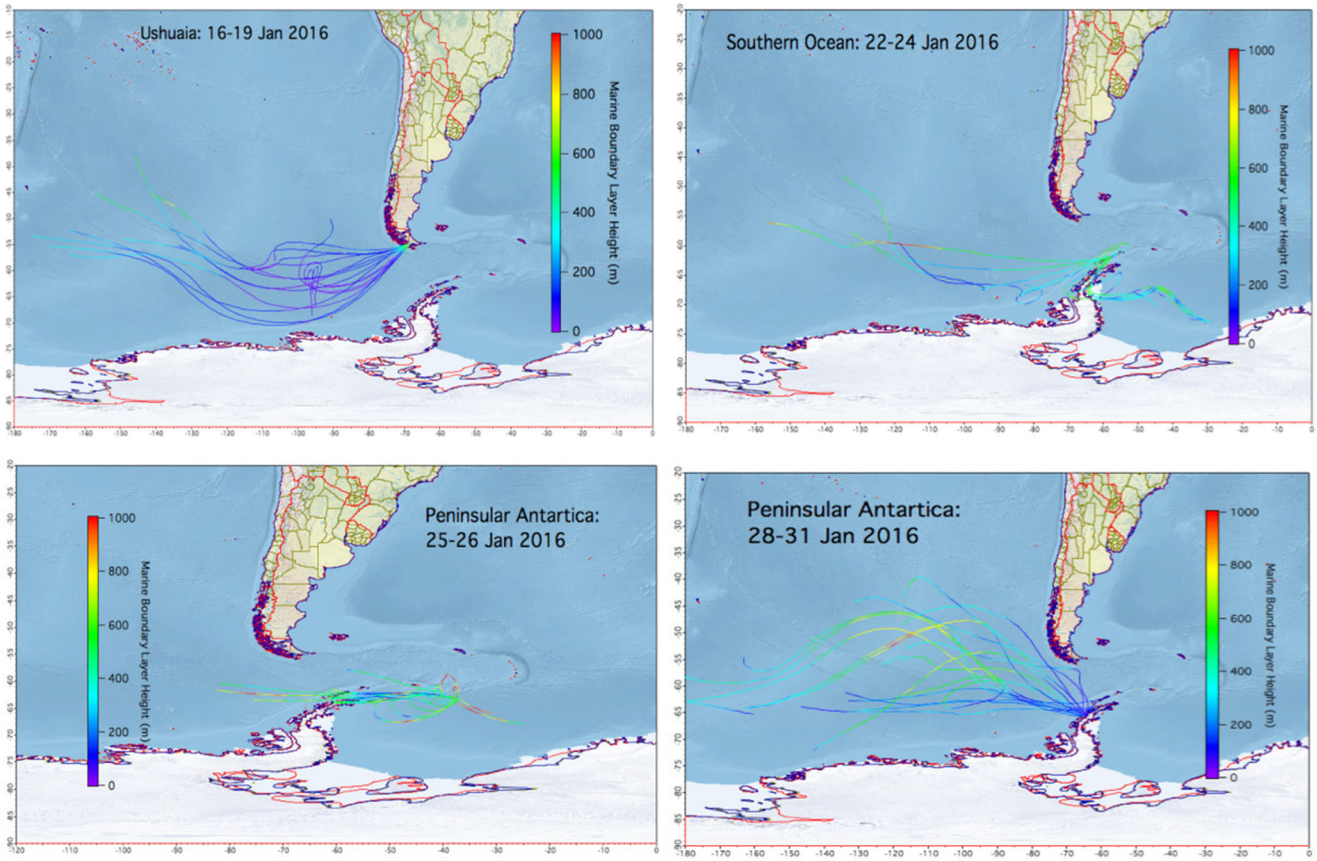

Fig. 14 Backward trajectories transport of air masses in the MBL during MASEC'16

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, NO_x 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 decrease 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, higher pressure levels at Ushuaia were observed which indicate 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.

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 the proximity to the coast, the stratospheric O_3 sink, O_3 precursor distribution, and human influences. Short-term (MASEC'16) and multi-year (WDCGG) 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 achieved throughout the cruise campaign. The results from the MASEC'16 cruise mixing ratios were high, in the order of CAP > the Drake Passage > CAP along the route of the cruise. The multi-year surface O_3 data showed strong seasonal cycles over Ushuaia and the Antarctic. Multi-year 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 multi-year 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 the 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 Antarctic region. The January/February levels from the WDCGG multi-year 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) with 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 and was similar to observations during MASEC'16. Both the satellite and MACC mixing ratio patterns are generally in very good agreement with observations over Ushuaia, the Drake Passage, and CAP but the values were slightly higher, ~ 40 to 50%, than 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.

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References

Ahamad F, Latif MT, Tang R, Juneng L, Dominick D, Juahir H (2014) Variation of surface ozone exceedance around Klang Valley, Malaysia. Atmos Res 71:251–259

Arellano AF Jr, Raeder K, Anderson JL, Hess PG, Emmons LK, Edwards DP, Pfister GG, Campos TL, Sachse GW (2007) Evaluating model performance of an ensemble-based chemical data assimilation system during INTEX-B field mission. Atmos Chem Phys 7:5695–5710. https://doi.org/10.5194/acp-7- 5695-2007

Awang NR, Ramli NA, Shukri YA, Elbayoumi M (2010) High nighttime ground-level ozone concentrations in Kemaman: NO and NO2 concentrations attributions. Aerosol Air Qual Res 15:1357–1366. https://doi.org/10.4209/aaqr.2015.01.0031

Ayers GP, Penkett SA, Gillet RW, Bandy B, Galbally IE, Meyer CP, Elsworth CM, Bentley ST, Forgan BW (1992) Evidence for photochemical control of ozone concentrations in unpolluted air. Nature 360:446–449

Boylan, P., Helmig, D., Oltmans, S. (2015) Ozone in the Atlantic Ocean marine boundary layer. https://doi.org/10.12952/journal.elementa.000045

Chameides WL, Davis DD (1980) Iodine: Its possible role in tropospheric photochemistry. J Geophys Res 85:7383–7393

Chen G, Davis D, Crawford J, Hutterli LM, Huey LG, Slusher D, Mauldin L, Eisele F, Tanner D, 561 Dibb J, Buhr M, McConnell J, Lefer B, Shetter R, Blake D, Song CH, Lombardi K, 562 Arnoldy J (2004) A reassessment of HOx South Pole chemistry based on observations 563 recorded during ISCAT 2000. Atmos Environ 38: 54515461

Crawford JH, Davis DD, Chen G, Buhr M, Oltmans S, Weller R, Mauldin L, Eisele F, Shetter R, Lefer B, Arimoto R, Hogan A (2001) Evidence for photochemical production of ozone at the South Pole surface. Geophys Res Lett 28:3641–3644

Conley SA, Faloona IC, Lenschow DH, Campos T, Heizer C (2011) A complete dynamical ozone budget measured in the tropical marine boundary layer during PASE. J Atmos Chem 68(1):55–70. https://doi.org/10.1007/s10874-011-9195-0

Davis DD, Nowak LB, Chen G, Buhr M, Arimoto R, Hogan A, Eisele F, Mauldin L, Tanner D, Shetter R, Lefer B, McMurry P (2001) Unexpected high levels of NO observed at South Pole. Geophys Res Lett 28:3625–3628

Davis D, Crawford J, Liu S, McKeen S, Bandy A, Thornton D, Rowland F, Blake D (1996) Potential impact of iodine on tropospheric levels of ozone and other critical oxidants. J Geophys Res 101:2135–2147

Davis DD, Eisele F, Chen G, Crawford J, Huey G, Tanner D, Slusher D, Mauldin L, Oncley S, Lenschow D, Semmer S, Shetter R, Lefer B, Arimoto R, Hogan A, Grube P, Lazzara M, Bandy A, Thornton D, Berresheim H, Bingemer H, Hutterli M, McConnell J, Bales R, Dibb J, Buhr M, Parko J, McMurry P, Swanson A, Meinardi S, Blake D (2004) An overview of ISCAT 2000. Atmos Environ 38:53635373. https://doi.org/10.1016/j.atmosenv.2004.05.037

Dethof A, Holm EV (2004) Ozone assimilation in the ERA-40 re-analysis project. Q. J. Roy. Meteor. Soc. 130:2851–2872

Dragani R (2011) On the quality of the ERA-Interim ozone reanalyses: comparisons with satellite data. Q J Roy Meteor Soc 137:1312–1326. https://doi.org/10.1002/qj.82110.1002/qj.821

Draxler R and Rolph G (2003) HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model access via NOAA ARL ready website (http://www.arl.noaa.gov/ready/hysplit4.html), NOAA Air Resources Laboratory, Silver Spring, MD

Derwent RG, Jenkin ME, Saunders SM, Pilling MJ, Simmonds PG, Passant NR, Dollard GJ, Dumitrean P, Kent A (2003) A photochemical ozone formation in north west Europe and its control. Atmos Environ 37:1983–1991

Duncan BN, Prados AI, Lamsal LN, Liu Y, Streets DG, Gupta P, Hilsenrath E, Kahn RA, Nielsen JE, Beyersdorf AJ, Burton SP, Fiore AM, Fishman J, Henze DK, Hostetler CA, Krotkov NA, Lee P, Lin M, Pawson S, Pfister G, Pickering KE, Pierce RB, Yoshida Y, Ziemba D (2014) Satellite data of atmospheric pollution for U.S. air quality applications: examples of applications, summary of data end-user resources, answers to FAQs, and common mistakes to avoid. Atmos Environ. https://doi.org/10.1016/j.atmosenv.2014.05.061

Frieß U, Hollwedel J, Konig-Langlo G, Wagner T, Platt U (2004) Dynamics and chemistry of troposphieric bromine explosion events in the Antarctic coastal region. J Geophys Res 109:D06305. https://doi.org/10.1029/2003JD004133

Ge BZ, Xu XB, Lin WL, Li J, Wang ZF (2012) Impact of the regional transport of urban Beijing pollutants on downwind areas in summer: ozone production efficiency analysis. Tellus B 64:17348. https://doi.org/10.3402/tellusb.v64i0.17348

Geer AJ, Peubey C, Bannister RN, Brugge R, Jackson DR, Lahoz WA, Migliorini S, O'Neill A, Swinbank R (2006) Assimilation of stratospheric ozone from MIPAS into a global general-circulation model: the September 2002 vortex split. Q J Roy Meteor Soc 132:231–257. https://doi.org/10.1256/qj.04.181

Helmig D, Oltmans SJ, Carlson D, Lamarque JF, Jones A, Labuschagne C, Anlauf K, Hayden K (2007a) A review of surface ozone in the polar regions. Atmos Environ 41:5138–5161. https://doi.org/10.1016/j.atmosenv.2006.09.053

Helmig D, Ganzeveld L, Butler T, Oltmans SJ (2007b) The role of ozone atmosphere-snow gas exchange on polar, boundary-layer tropospheric ozone—a review and sensitivity analysis. Atmos Chem Phys 7:15–30

Holm EV, Untch A, Simmons A, Saunders R, Bouttier F, and Andersson E (1999) Multivariate ozone assimilation in four-dimensional data assimilation, in: Proceedings of the Soda Workshop on Chemical Data Assimilation, 9–10 December 1998, KNMI, De Bilt, The Netherlands, 89–94

Inness A, Baier F, Benedetti A, Bouarar I, Chabrillat S, Clark H, Clerbaux C, Coheur P, Engelen RJ, Errera Q, Flemming J, George M, Granier C, Hadji-Lazaro J, Huijnen V, Hurtmans D, Jones L, Kaiser JW, Kapsomenakis J, Lefever K, Leitão J, Razinger M, Richter A, Schultz MG, Simmons AJ, Suttie M, Stein O, Thépaut J-N, Thouret V, Vrekoussis M, Zerefos C, the MACC team (2013) The MACC reanalysis: an 8 yr data set of atmospheric composition. Atmos Chem Phys 13:4073–4109. https://doi.org/10.5194/acp-2513-4073-2013

Inness A, Blechschmidt A-M, Bouarar I, Chabrillat S, Crepulja M, Engelen RJ, Eskes H, Flemming J, Gaudel A, Hendrick F, Huijnen V, Jones L, Kapsomenakis J, Katragkou E, Keppens A, Langerock B, de Mazière M, Melas D, Parrington M, Peuch VH, Razinger M, Richter A, Schultz MG, Suttie M, Thouret V, Vrekoussis M, Wagner A, Zerefos C (2015) Data assimilation of satellite retrieved ozone, carbon monoxide and nitrogen dioxide with ECMWF's composition-IFS. Atmos Chem Phys 15:5275–5303. https://doi.org/10.5194/acp-15-5275-2015

Johnson JE, Gammon RH, Larsen J, Bates TS, Oltmans SJ (1990) Ozone in the marine boundary layer over the Pacific and Indian Oceans: latitudinal gradients and diurnal cycles. J Geophys Res 95(D8): 11847–11856. https://doi.org/10.1029/JD095iD08p11847

Jones AE, Weller R, Minikin A, Wolff EW, Sturges WT, McIntyre HP, Leonard SR, Schrems O, Bauguitte S (1999) Oxidized nitrogen chemistry and speciation in the Antarctic troposphere. J Geophys Res 104:21,355–21,366

Jones AE, Weller R, Wolff EW, Jacobi HW (2000) Speciation and rate of photochemical NO and NO_2 production in Antarctic snow. Geophys Res Lett 27:345–348

Jones AE, Weller R, Anderson PS, Jacobi HW, Wolff EW, Schrems O, Miller H (2001) Measurements of NO_x emissions from the Antarctic snowpack. Geophys Res Lett 28:1499–1502

Kar J, Fishman J, Creilson JK, Richter A, Ziemke J, Chandra S (2010) Are there urban signatures in the tropospheric ozone column products derived from satellite measurements? Atmos Chem Phys 10: 5213e5222. https://doi.org/10.5194/acp-10-5213-2010

Khattatov BV, Lamarque J-F, Lyjak LV, Menard R, Levelt P, Tie X, Brasseur G, Gille JC (2000) Assimilation of satellite observations of long-lived chemical species in global chemistry transport models. J Geophys Res 105:29135–29144

Kumar A, Gupta VB, Jain SL, Ghude SD, Kulkarni PS (2006) Surface ozone variability between two different Antarctic sites. IJRSP 36: 59–64

Lahoz WA, Geer AJ, Bekki S, Bormann N, Ceccherini S, Elbern H, Errera Q, Eskes HJ, Fonteyn D, Jackson DR, Khattatov B, Marchand M, Massart S, Peuch V-H, Rharmili S, Ridolfi M, Segers A, Talagrand O, Thornton HE, Vik AF, von Clarmann T (2007) The assimilation of Envisat data (ASSET) project. Atmos Chem Phys 7:1773–1796. https://doi.org/10.5194/acp-7-1773-2007

Latif MT, Huey LS, Juneng L (2012) Variations of surface ozone concentration across the Klang Valley. Malaysia Atmos Environ 61:434–445

Legrand M, Preunkert S, Jourdain B, Gallée H, Goutail F, Weller R, Savarino J (2009) Year-round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia) sites in East Antarctica. J Geophys Res Atmos 114:D20306. https://doi.org/10.1029/2008JD011667

Lin C-YC, Jacob J, Munger JW, Fiore AM (2000) Increasing background ozone in surface air over the United States. Geophys Res Lett 27: 3465–3468

Mohd Nadzir MS, Phang SM, Abas MR, Abdul Rahman N, Abu Samah A, Sturges WT, Oram DE, Mills GP, Leedham EC, Pyle JA, Harris NRP, Robinson AD, Ashfold MJ, Mead MI, Latif MT, Khan MF, Amiruddin AM, Banan N, Hanafiah MM (2014) Bromocarbons in the tropical coastal and open ocean atmosphere during the 2009 Prime Expedition Scientific Cruise (PESC-09). Atmos Chem Phys 14:8137–8148. https://doi.org/10.5194/acp-14-8137-2014

Monks PS (2000) A review of the observations and origins of the spring ozone maximum. Atmos Environ 34:3545–3561. https://doi.org/10.1016/S1352-2310(00)00129-1

Monks PS (2005) Gas-phase radical chemistry in the troposphere. Chem Soc Rev 34:376–395. https://doi.org/10.1039/b307982c

Murayama S, Nakazawa T, Tanaka M, Aoki S, Kawaguchi S (1992) Variations of tropospheric ozone concentration over Syowa station. Antarctica, Tellus 44B:262–272

Neff W, Helmig D, Garchev A, Davis D (2008) A study of boundary layer behavior associated with high NO concentrations at the South Pole using a minisodar, tethered balloon, and sonic anemometer. Atmos Environ. https://doi.org/10.1016/j.atmosenv.2007.01.033.%2007

Niki H, Becker KH (1993) The tropospheric chemistry of ozone in the polar region, NATO ASI Series I. Global environmental change, Vol 7, Springer Verlag, 425 pp.

Oltmans SJ, Komhyr WD (1976) Surface ozone in Antarctica. J Geophys Res 81:5359–5364

Oltmans SJ (1993) Climatology of Arctic and Antarctic tropospheric ozone, in The tropospheric chemistry of ozone in the polar regions, eds Niki and Becker, NATO ASI Series I. Global Environmental Change, Vol 7, Springer Verlag, 425 pp.

Oltmans SJ, Levy H II (1994) Surface ozone measurements from a global network. Atmos Environ 28:9–24

Oncley SP, Buhr M, Lenschow DH, Davis D, Semmer SR (2004) Observations of summertime NO fluxes and boundary-layer height at the South Pole during ISCAT 2000 using scalar similarity. Atmos Environ 38:5389–5398

Rolph G (2003) Real-time Environmental Applications and Display System (READY) Website (http://www.arl.noaa.gov/ready/hysplit4.html), NOAA Air Resources Laboratory, Silver Spring, MD

Schnell RC, Liu SC, Oltmans SJ, Stone RS, Hofmann DJ, Dutton EG, Deshler T, Sturges WT, Harder JW, Sewell SD, Trainer M, Harris JM (1991) Decrease of summer tropospheric ozone concentrations in Antarctica. Nature 351:726–729

Simmonds PG, Seuring S, Nickless G, Derwent RG (1997) Segregation and interpretation of ozone and carbon monoxide measurements by air mass origin at the TOR station Mace Head, Ireland from 187 to 1995. J Atmos Chem 28:45–49

Sturges WT, Cota GF, Buckley PT (1992) Bromoform emission from Arctic ice algae. Nature 358:660–662

Sturges G, Cota F, Buckley PT (1997) Vertical profiles of bromoform in snow, sea ice, and seawater in the Canadian Arctic. J Geophys Res 102(C11):25073–25025,25083

Taalas P, Kyro E, Supperi A, Tafuri V, Ginzburg M (1993) Vertical distribution of tropospheric ozone in Antarctica and in the European Arctic. Tellus 45B:106–109

Wang Y, Zhang Y, Hao J Luo M (2011) Seasonal and spatial variability of surface ozone over China: contributions from background and domestic pollution. Atmos Chem Phys 11:3511–3525 https://doi.org/10.5194/acp-11-3511-2011

Yurganov L, McMillan WW, Grechko E, Dzhola A (2009) Analysis of global and regional CO burdens measured from space between 2000 and 2009 and validated by ground-based solar tracking spectrometers. Atmos Chem Phys Discuss 9:28475–24911 2009, http://www.atmos-chem-phys-discuss.net/9/28475/2009/