

Isoprene hotspots at the Western Coast of Antarctic Peninsula during MASEC'16

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Abstract

Isoprene (C_5H_8) plays an important role in the formation of surface ozone (O_3) and the secondary organic aerosol (SOA) in the troposphere via its oxidation products from the photochemical reactions. Tropospheric O_3 and SOA can influenced radiation absorptions which can lead to the surface temperature increased. This study aims to determine hourly distribution of tropospheric isoprene over the Antarctic Peninsula during the Malaysian Antarctic Scientific Expedition Cruise 2016 (MASEC'16). *In situ* measurement of isoprene was taken over a 24-h period using a self-built, portable gas chromatography photoionization detector (PID), known as iDirac, on board the *RV Australis*. Biological parameters such as chlorophyll a (chl-a), particulate organic carbon (POC) and particulate inorganic carbon (PIC) detected by the Atmospheric Infrared Sounder (AIRS) aboard NASA's Aqua satellite during the cruise's period were compared to the measured isoprene. Hotspots of isoprene were measured, with isoprene being the highest over the region of King Sejong Research

Station on Barton Peninsula (King George Island), Deception Island (South Shetland Islands) and Booth Island (Argentine Islands region, with mixing ratios of ~5.0, ~0.9 and ~5.2 ppb, respectively. The AIRS satellite data showed that chl-a and POC concentrations over those isoprene hotspots were high and strongly correlated ($r^2 = 0.71$, $p < 0.01$) with values ~2-28 mgm^{-3} and 200-900 mgm^{-3} , respectively. The NAME model analysis showed that the hotspots coincided with times when the air has recently passed over coastlines. When low isoprene was observed, the air had not passed over coastlines in the past few days. Backward trajectory analysis showed that air masses from other marine regions may have lifted the isoprene emitted by marine macro- and micro-algae and terrestrial vegetation in the hotspot areas. In situ measurement of atmospheric gases is difficult and expensive to conduct especially on small vessel. However, we believe our findings can be used for isoprene hotspot estimation over the Western Coast of of Antarctic Peninsula. We suggest that more *in situ* measurement and biological samplings need to be conducted in the future in order to understand the photochemical process of isoprene emission over Western Coast of of the Antarctic Peninsula.

Keywords; *Isoprene, NAME model, Antarctic Peninsula, marine algae.*

1.0 Introduction

Isoprene or 2 - methyl - 1,3 - butadiene (C_5H_8) is the most common biogenic volatile organic compound (BVOCs), making up 500–750 Tg of the annual global carbon emissions (Guenther et al., 2006). It is believed that productive areas such as the ocean, coastal upwelling regions, and wetlands can emit isoprene (Bonsang et al., 1992; Broadgate et al., 2004; Holst et al., 2008) at rates that can considerably influence atmospheric chemistry in remote marine and coastal regions (Liakakou et al., 2007). Isoprene plays an important role in

the production of Secondary Organic Aerosol (SOA) in the marine boundary layer (Hu et al., 2013; Tuet et al., 2017). SOA particles may change the climate in areas where they are produced as they absorb and scatter solar radiation and served as cloud condensation nuclei (CCN) (Stubenrauch et al., 2013; Wylie et al., 2005). Biogenic VOCs (BVOCs) are identified as the dominant global SOA precursors in the atmosphere, compared to anthropogenic VOCs (Piccot et al., 1992; Guenther et al., 1995). SOA particles formed by the oxidation of isoprene emitted by phytoplankton could significantly affect the chemical composition and number of marine CCN (Meskhidze and Nenes, 2006).

Marine organisms such as heterotrophic bacteria, marine phytoplankton, and seaweeds can all emit isoprene. In order to simplify the characterization of marine isoprene production, individual species have been grouped as follows: chlorophytes, coccolithophores, haptophytes, cyanobacteria, nitrogen fixers, diatoms, dinoflagellates, picoeukaryotes, and unclassified species. Isoprene production rates among several phytoplankton functional types vary significantly. Even among different species of diatoms isoprene production can range from 0 to 410 cell⁻¹ day⁻¹ in one species of diatom or 67 μmol (g chl)⁻¹ day⁻¹ for a second diatom species, two of the highest production rates reported for any species. Isoprene production by bacteria was also recently observed in estuary sediments at levels of 0.15 to 0.71 pmoles cm⁻² hr⁻¹.

Global research on isoprene emission over have evolved rapidly via research campaigns (Hackenberg, et al., 2017), with published reports on regions all over the world such as Finland (Kourtchev et al., 2005), Hungary (Ion et al., 2005), the United States (Lewandowski et al., 2008), China (Hu et al., 2008) and the Arctic (Fu et al., 2009). Nevertheless, all of these studies were conducted over continental areas. Observations of isoprene over marine areas in the Southern Hemisphere such as the Antarctic are still limited.

A few studies on marine BVOCs such as halocarbons have reported that chlorophyll-a (chl-a), a marker of biological productivity, can be used as a bio indicator for hot spots of isoprene emission in tropical seawater (Yokouchi et al., 1997; Quack et al., 2004; Carpenter et al., 2009; Mohd Nadzir et al., 2014) and in Antarctic ice (Sturges et al., 1993; Lartunus et al., 1998). These studies showed that high levels of chl-a will increase the mixing ratios of brominated halocarbon compounds, which are released by seaweeds, phytoplankton and algae. Moore et al., 1998 demonstrated in laboratory experiments that several marine halocarbons are released by marine diatoms. Exton et al., 2013 reported a number of studies on isoprene production by laboratory cultures of marine microalgae, thus showing the capability of many species to release isoprene (see Table 1 in Exton et al., 2013). High productivity of chl-a has been observed along Graham Coast, in the west coast of the Antarctic Peninsula (CAP). For example, Marrari et al., 2007 reported a high content of chl-a over the western CAP (55–75°S, 50–80°W). While, high primary production by diatoms and phytoplankton, fuelled primarily by deep-sourced macronutrients, was responsible for the high nutrients observed over CAP (Henley et al., 2016).

Globally, different methods to measure and estimate isoprene levels have been used, such as in-situ measurement (Bonsang et al., 1992; Sinha et al., 2007), remote sensing (Palmer and Shaw, 2005; Arnold et al., 2009) and modelling (Arnold et al., 2009). Recently, Numerical Atmospheric-dispersion Modelling Environment (NAME) is used to model a wide range of atmospheric dispersion events (Ashfold et al., 2014, 2015; Webster et al., 2003; Morrison and Webster, 2005; Jones et al., 2007).

The main target of this study is to report the distribution of isoprene mixing ratio and the possible hotspots of isoprene via continuous atmospheric in-situ measurement over the

Western Coast of Antarctic Peninsula (WCAP) during the Malaysia Antarctic Scientific Expedition Cruise (MASEC'16).

2.0 Methodology

2.1 Instrumentation

Field measurements of isoprene currently rely on the deployment of large, expensive instruments, on the collection of air samples in flasks, or on using adsorbent tubes for off-line analysis. In this study, a new portable GC-photoionization detector (PID), known as iDirac, was used. iDirac was developed at the University of Cambridge as a low-cost, lightweight instrument with sensitivity to isoprene at ambient levels, with a detection limit of 20 ppt and a sampling time of around 5 min. iDirac was constructed after the success of μ Dirac (see Gostlow et al., 2008; Robinson et al., 2014) and was used to measure tropical forest isoprene during the Biodiversity And Land-use Impacts (BALI) campaign on tropical ecosystem function, which was held in 2015 in Borneo, Malaysia (Bolas et al., in prep.). A diagram of the iDirac system is shown in Figure 2.1. Nitrogen gas was used as a carrier gas, and the unit required 10 W of power consumption and was controlled using an Arduino and Raspberry Pi interface with wireless connection built in. The unit can be used without a laptop in the field, with two sample inlets and one calibration port for calibrating gas injection onto the PID. The target detection limit is 100 ppt over a 5min sampling period.

During the measurement, the iDirac was deployed onboard the RV Australis. Air was sampled through a 1/4" OD PFA tube located on the upper deck, with the inlet ~ 10 m above the ocean surface and adjusted at each sampling time to face the prevailing wind. Each air sample was pre-concentrated using an adsorbent trap (10 mg of Carboxen-1016 60/80 mesh).

The trap was then flash heated and the gaseous constituents were separated in a dual column system, the pre-column was a 2m long, 1-mm inside-diameter (ID) packed column (Thames Restek 5%RT-1200 1.75%Bentone-34 SILPT-W 100/120) and the main column was a 2m long, 1 mm ID packed column (Thames Restek OPN-RESL-C 80/100). The main column exhausts onto the PID membrane. As the instrument was designed to run unattended, the Arduino controlled software ran chromatograms according to a pre-determined sequence of samples bracketed by calibration chromatograms, each calibration chromatograms also bracketed with a blank. The instrument is configured with a Raspberry Pi interface remotely. The sequence included frequent calibrations using frequent randomised volume injections of a known concentration calibration cylinder for conversion of signal to mixing ratio and also for correction of instrument sensitivity drift and precision determination.

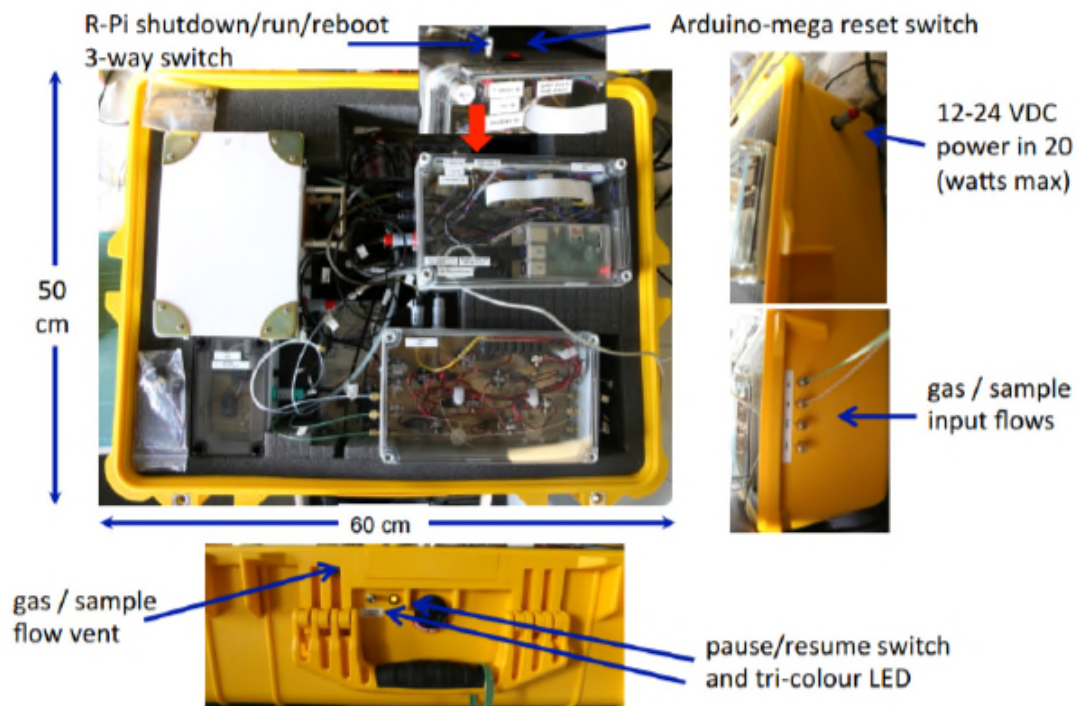


Figure 2.1 Diagram of the iDirac PID system. The inlet can be fed with either ambient air or an air sample from a flask. (Bolas et al., in prep).

2.2 Calibration of iDirac

Samples were calibrated by running frequent chromatograms from EnTech (USA)'s 1800 psi sample sulfinert cylinder, which was decanted from a high quality isoprene standard at a concentration of 10 ppb (British Oxygen Company, United Kingdom). The sequence also ran calibrations at a range of different volumes so that instrument response curves were generated for isoprene to allow for non-linearity. The response curves were fit using a straight line. Chromatograms and system data were stored on a host computer for later analysis using the in-house software to determine peak heights for the target compounds, which were then converted into mixing ratios by comparison with the calibration standards.

2.3 Field deployment

MASEC'16 was undertaken on the *RV Australis* between 16 January and 8 February 2016, from Ushuaia, Argentina to the Drake Passage in the Southern Ocean (SO), to the Graham Coast on the Antarctic Peninsula (Darboux Island, 65° 23.824'S, 64° 12.868'W), and back to Ushuaia (Figure 2.2). iDirac was deployed onboard the vessel and measurements of isoprene were taken over a 24-h period. The vessel sailed across the sub-Antarctic and Antarctic

regions through various weather and sea conditions.

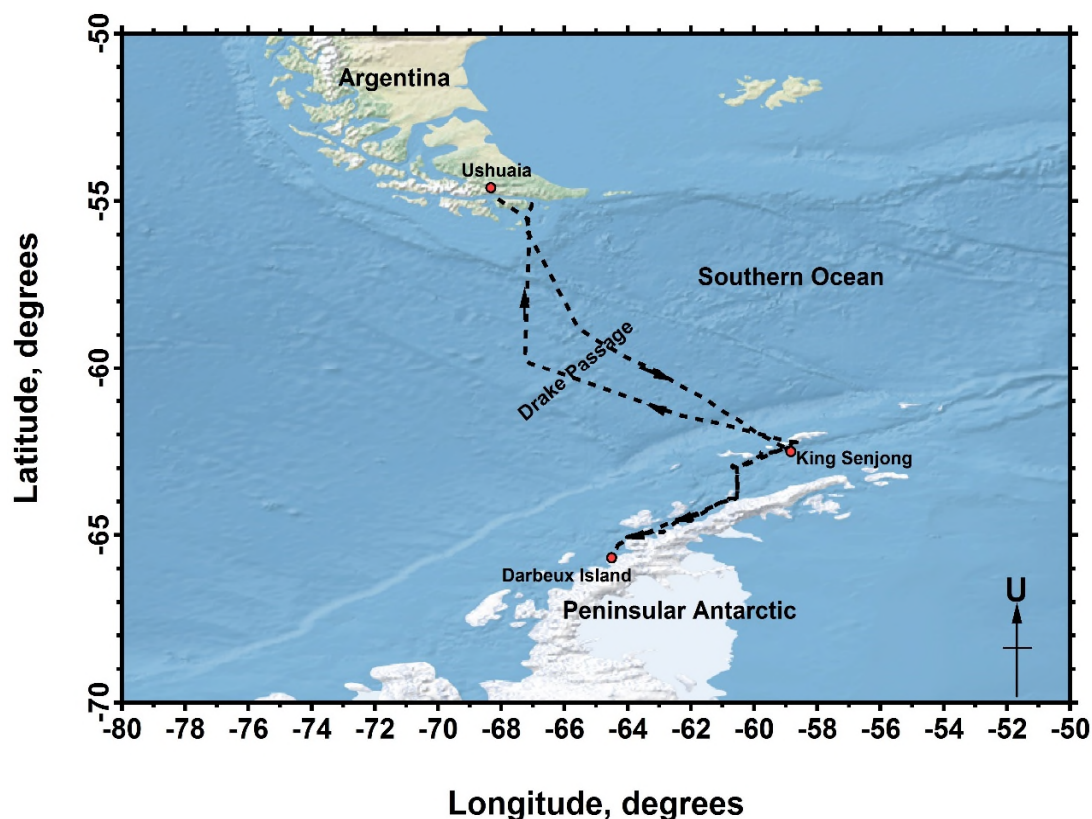


Figure 2.2 Cruise route of the *RV Australis* during MASEC'16.

2.4 Trajectory Analysis

In order to investigate the potential sources which may contribute to isoprene production in the marine boundary layer of the WCAP, the air mass history of the atmosphere was estimated using backward trajectory analysis. A five-day, 120-h backward trajectory was computed from 00:00, 06:00, 12:00, and 18:00 UTC at 500 m A.G.L from each station's location for each of the high isoprene days. The selected height level of the particles released ensured that the trajectories started in the atmospheric boundary layer (Eva and Lambin, 1998). The back trajectories and horizontal dispersion clustering were calculated using

version 4.9 of the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) developed by the National Oceanic and Atmospheric Administration (NOAA)'s Air Resource Laboratory (ARL) (Draxler and Rolph, 2003; Rolph 2003). A back trajectory does not provide any information about surface O₃ isoprene mixing ratio or air parcel dispersion in the atmosphere, i.e. width or thickness, but can project the path of an air mass backwards in time to estimate the potential sources.

2.5 Chl-a and POC derived from satellite

Daily chl-a and particulate organic carbon (POC) data at 4.63 km resolution were obtained from the European Space Agency's GlobColour project (<http://www.globcolour.info>), which provides a merged product from multiple sensors with improved coverage that has undergone extensive validation (Durand et al., 2007) and applied in the Southern Ocean (Taylor et al., 2013), Arctic Ocean (Cherkasheva et al., 2014), Pacific Ocean (Chow et al., 2017). At the time of the cruise, chl-a and POC data was a merged product from the Moderate Resolution Imaging Spectroradiometer (MODIS) onboard the Aqua satellite (MODIS-Aqua) and Visible Infrared Imaging Radiometer Suite (VIIRS) sensors.

3.0 Results

3.1 Meteorological Conditions during MASEC'16

Meteorological data such as atmospheric temperature, wind speed and wind direction were recorded on board during the whole period of sampling. The ambient temperatures were in the range of 5 to 13°C, 3 to 8°C and -1 to 4°C for Ushuaia, the Drake Passage and the WCAP, respectively. Relative humidity over Ushuaia was lower than the Drake Passage and maritime

Antarctic in the range of 50-75%. The Drake Passage had the highest humidity in the range of 80-90%, while WCAP recorded values in the range of 75-90%. According to Wilson et al., (1979), the continental (eastern) Antarctic has lower humidity, but the WCAP region (maritime Antarctic) receives more influence of moisture from the ocean.

Wind speed and direction were also recorded on board over Ushuaia, the SO and WCAP. Selected raw data during sampling from onboard reanalysis with the ZyGrib 6.2.3 software is shown in Figure 3.1. Mostly, the wind direction was coming from the southwest for those three regions. Wind speed was recorded high at the beginning of the cruise (17th January 2016) over the SO with 30 to 38ms⁻¹. When the vessel arrived at maritime Antarctica, wind speed was within the range of 20 to 25 ms⁻¹. Humidity and wind speed may influence the distribution of gases in the atmosphere.

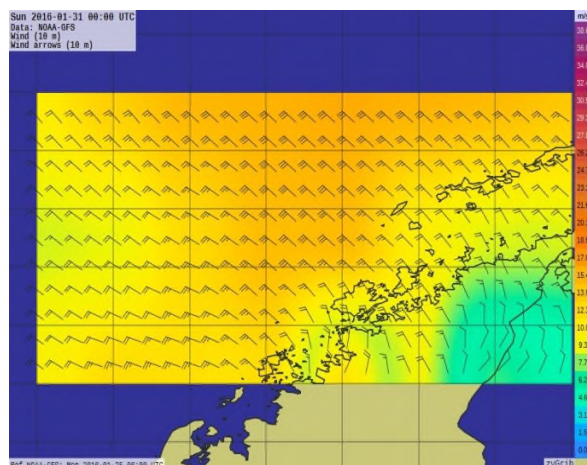
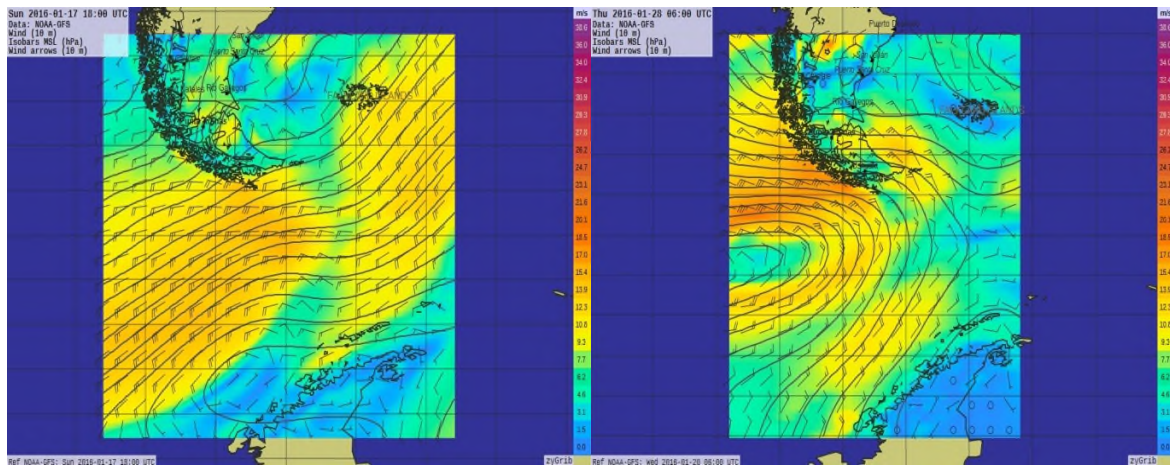


Figure 3.1 Wind speed (ms^{-1}) and direction during sampling in the beginning, middle and end of MASEC'16 in the studied Western Coast of Antarctic Peninsula

3.2 Isoprene mixing ratios during MASEC'16 and hot spot identification

In this section, we present data from continuous in-situ measurement of isoprene by iDirac over the Drake Passage and WCAP. Isoprene mixing ratios over Ushuaia, the Drake Passage and WCAP are shown in Figure 3.2. Overall data were difficult to analyse due to uncertainties of the measurements taken over the hotspot areas. The instrument was unstable on some occasions during the study period due to strong waves that rocked the vessel. For example, the mixing ratios of isoprene were almost zero (below detection limit) over the Drake Passage and increased up to ~ 5.2 ppb with high uncertainties (based on 50%) as the vessel approached the surroundings of King Sejong station (Barton Peninsula, King George Island, $62^{\circ} 13.000'S$, $58^{\circ} 47.000'W$). The vessel arrived at the King Sejong station on the 24th January and anchored for a day.

The data appeared reliable starting from 26 to 28 January, with ~ 0.2 to ~ 0.9 ppb (based on 2% uncertainties) over Deception Island ($62.940900^{\circ} S$, $60.555400^{\circ} W$). Isoprene mixing ratios rapidly increased up to ~ 5 ppb with high uncertainties as approaching Booth Island ($65^{\circ} 4.800S$, $64^{\circ} 0.000'W$). The observed increases of isoprene over CAP were believed to be linked to emissions from biological organisms such as macro and micro algae in seawater and ice. This is supported by the observed chl-a concentrations in the seawater, which are representative of biological productivity and will be explained in the next section.

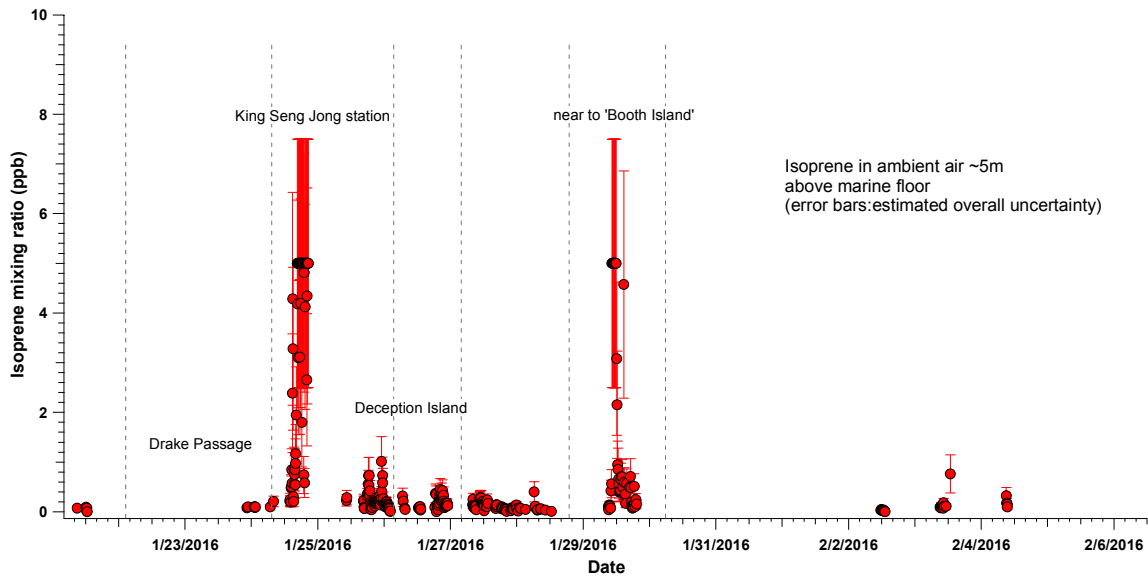


Figure 3.2 Isoprene mixing ratios measured by iDirac GC during MASEC'16 in the Western Coast of Antarctic Peninsula region

3.3 Satellite-derived biological parameters

Values of chl-a and POC were used to estimate biological activity during the sampling time. Maps of the sampling area showing values for these two parameters were downloaded from GlobColour's website, as shown in Figure 3.3. Biological activity appeared to be high in the WCAP region, as evident by chl-a and POC values ranging from ~ 2 to 28 mgm^{-3} and 200 to 900 mgm^{-3} , respectively. A study by Marrari et al., 2007 reported Sea-Viewing Wide Field-of-View Sensor (SeaWiFS)-derived chl-a concentrations over the CAP ranged from 0.01 to 20 mg m^{-3} during the period from 1997 to 2004. Arrigo and van Dijken, 2003 reported SeaWiFS-derived chl-a concentrations from a phytoplankton bloom near Marguerite Bay (southern CAP), while Garibotti et al., 2003 and Meyer et al., 2003 observed summer chl-a concentrations up to 17.86 mgm^{-3} in 1997 and 25 mgm^{-3} in 2000, respectively,

in Marguerite Bay. These findings show that the southern sector of the Antarctic Peninsula is home to large phytoplankton blooms (Marrari et al., 2007).

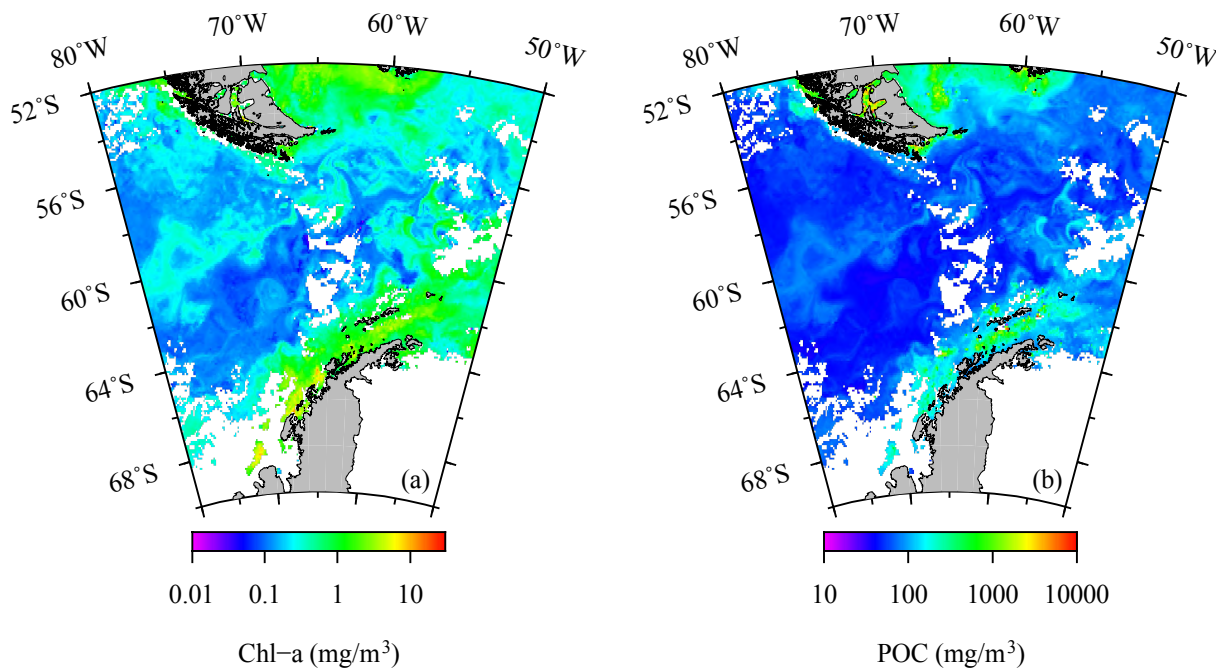


Figure 3.3 Composite images of daily a) chl-a and b) POC derived from the GlobColour project during the sampling period from 21 January to 2 February 2016

3.4 Biological influences on isoprene hot spots

High biological activity was observed by satellite over WCAP (Figure 3.3), which coincides with hot spots of isoprene emission over the WCAP during MASEC'16 (Figure 3.4a). The correlation (Spearman rank) between satellite-derived POC and isoprene was significantly strong ($p < 0.001$) with r^2 values at 0.67 (Figure 3.4b). No significant correlation was observed between chl-a and isoprene concentrations, due mainly to two high isoprene concentrations. This indicates that isoprene emissions during the cruise were not limited to phytoplankton and POC is a better indicator of biogenic source of isoprene from the ocean.

Ciccioli et al., (1996) reported isoprene mixing ratios over four selected sites over Terra Nova Bay (Continental Antarctica) (74°49'59.99" S 164°29'59.99" E) to be in the range of 0.28 to 0.41 ppb, believed to be emitted from lichen and mosses. These are the only organisms living in Antarctica capable of performing reduced photosynthetic activity (see Table 2 in Ciccioli et al., 1996).

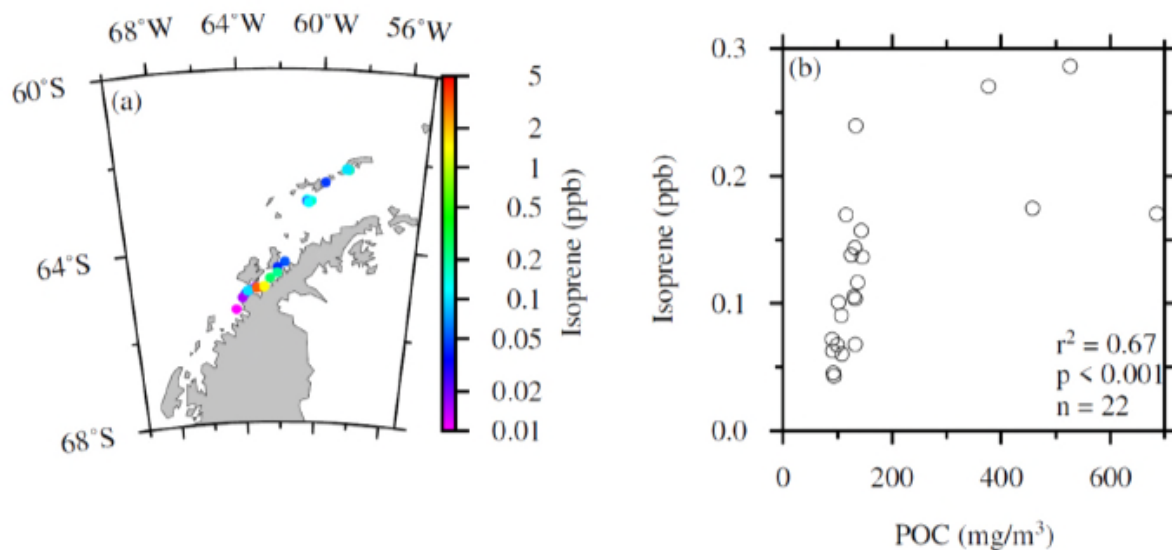


Figure 3.4 a) Aqua-MODIS satellite-derived chl-a overlaid with isoprene mixing ratios over the WCAP during MASEC'16 and b) Scatter plot showing significant correlation between POC and isoprene

Isoprene is naturally synthesized and emitted by many, but not all, plant species (Scholefield et al., 2004; Vickers et al., 2009). It is synthesized through the methyl-erythritol 4-phosphate pathway (MEP pathway, also called the non-mevalonate pathway) in the chloroplasts of plants. One of the two end products of MEP pathway, dimethylallylpyrophosphate (DMAPP), is catalysed by the enzyme isoprene synthase to form isoprene (Sharkey et al., 2008). However, in the Antarctic, there are no trees or shrubs, and only two species of flowering plants can be found: *Deschampsia antarctica* E. Desv. (Antarctic hairgrass) and *Colobanthus quitensis* (Kunth) Bartl. (Antarctic pearlwort). The

vegetation is formed mainly by lower plants such as mosses and liverwort, along with lichens, fungi and algae, which are all adapted to survive in the extreme environment (Alpert et al., 2006; Lee et al., 2014).

From our field observations during the sampling period, there were many seaweeds floating in the coastal waters and stranded on the coastline (as shown in figure 3.5). According to the seaweed diversity checklist reported by Mystikou et al., 2016, a total of 41 macroalgal species (7 brown, 27 red, 6 green, 1 chrysophyte) have been recorded in southern Adelaide Island and northern Marguerite Bay on the Antarctic Peninsula. In addition, three classes of algae were reported to be distributed in the sub-Antarctic and Antarctic regions, which include seven species of brown algae (*Colpomenia peregrina* (Sauvageau) Hamel, *Dictyota dichotoma* Suhr, *Hincksia ovata* (Kjellman) P.C.Silva, *Hincksia sandriana* (Zanardini) P.C.Silva, *Myriotrichia claviformis* Harvey, *Punctaria latifolia* Greville, *Syringoderma australe* Levring), four red algae (*Erythrotrichia carnea* (Dillwyn) J.Agardh, *Paraglossum salicifolium* (Reinsch) Showe M.Lin, Fredericq & Hommersand, *Phycodryis antarctica* (Skottsberg) Skottsberg, *Plumariopsis eatonii* (Dickie) De Toni), one green alga (*Chaetomorpha aerea* (Dillwyn) Kützing), and one oomycete, *Anisolpidium ectocarpii* Karling (Mystikou et al., 2016). For further analysis, flask sampling over hotspot areas will be discussed in section 3.6.

In this study, terrestrial vegetation (moss communities), red seaweeds (*Rhodymenia* sp.) and brown algae (*Himantothallus grandifolius* (A.Gepp & E.S.Gepp) Zinova and *Desmarestia menziesii* J.Agardh) were found in high abundance at the sampling sites around the coastal areas of King George Island (where King Sejong Research Station is located), Deception Island and Booth Island, and may have influenced isoprene emissions over the hot spot areas (Figure 3.2). The flora observed over isoprene hotspot areas along Graham Coast in the CAP during MASEC'16 are listed in Table 1. In all other locations that showed low mixing ratios

(~0.2 to 0.4 ppb) during MASEC'16, we observed low abundance of algae and low ambient temperatures.

Temperature ranges detected during the summer season at the sampling sites in King Sejong Research Station (5 to 13°C), Deception Island (3 to 8°C) and Booth Island (-1 to 4°C), which also may have influenced the high isoprene mixing ratios observed. A report by Sharkey and Singaas (1995) indicated that isoprene emission by plants may be related to the surrounding temperature. Plant isoprene emission has been observed to greatly increase with temperature and peak at around 40°C (Sharkey et al., 2008). Isoprene synthesis may be one of the mechanisms that plants use to combat abiotic stressors as discussed in the thermotolerance hypothesis. Plants can synthesize isoprene to protect against moderate heat stress (~40°C). It may also protect plants against large fluctuations in leaf temperature. Isoprene is incorporated into and helps stabilize cell membranes in response to heat stress (Sharkey et al., 2008).

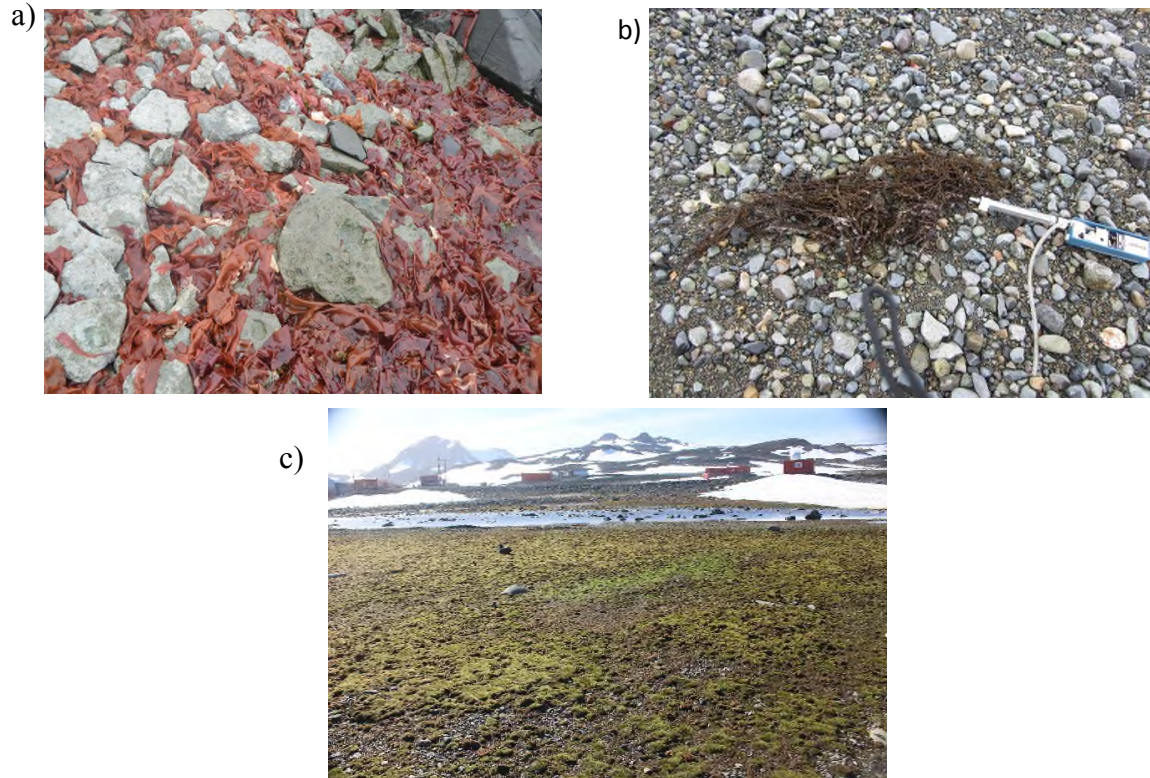


Figure 3.5 ‘Hotspots’ area of King Sejong Research Station which dominated by a) *Himantothallus grandifolius* and b) *Desmarestia menziesii* as well as the moss communities c).

Table 1 Flora observed over isoprene hot spot regions during MASEC’16

Taxa	Location	Remarks
<i>Himantothallus grandifolius</i>	King George Island, Deception Island and Booth Island	Antarctic phytobenthos were found stranded on the coastline and floating in seawater
<i>Desmarestia menziesii</i>	King George Island and Booth Island	Key-canopy forming species were found stranded on the coastline
<i>Rhodomenia</i> sp.	King George Island	Red algae were found stranded on the coastline
<i>Moss communities</i>	King George Island, Deception Island and Booth Island	Mosses were dominant all over the coast Mosses were found growing on the cliffs and rocks

3.5 NAME analysis

The NAME dispersion model was used to model the air mass histories from the ship measurement locations. The model was run backwards in time for 48 h (GMT), for 3 h periods along the cruise. The average latitude and longitude during those 3 h was used, and the particles were released from random heights between 0-100m above ground level. From these backwards runs, footprint maps were generated. These show the time-integrated number of particles that pass through the model planetary boundary layer in the 48 h prior to the observation. Note that the areas where the particle densities are highest are where the air has been in the hours immediately prior to the measurement. This is where the measured isoprene could have been directly picked up from emission sources, as isoprene has a typical lifetime of 3 h (Atkinson, 2000). The lower density areas give an indication of the location of the air prior to this, where other emissions may have been encountered.

Figure 3.6 shows the footprint of isoprene from the NAME reanalysis from 24th January 2015 when the mixing ratios of isoprene were relatively high isoprene over King Sejong station. The wind direction were blew from north east (NE). This suggests a strong isoprene source from the NE. This could be along the coastlines of the small islands contains various types of macro and micro algae seen under the footprint. This can be link to the rich chl-a over the hot spot emissions area as describe in previous section. When the mixing ratio was low, the footprints no longer cover the same coastlines, but are mostly over the ocean as shown in figure 3.7.

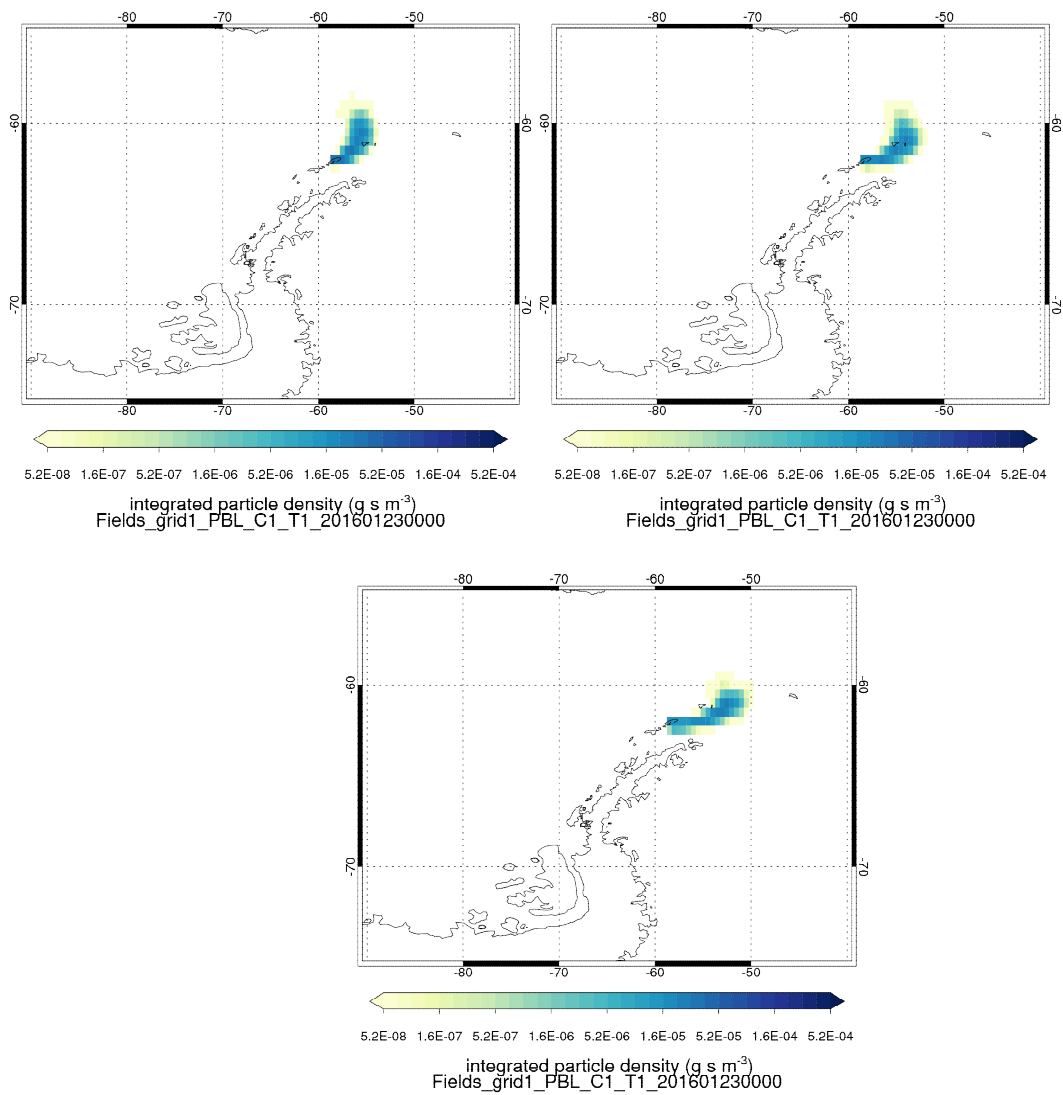


Figure 3.6 Footprints from 24/01/2016 1200 to 1500 (top left) and 1500 to 1800 (top right) and 1800 to 2100 (bottom left) at King Sejong station.

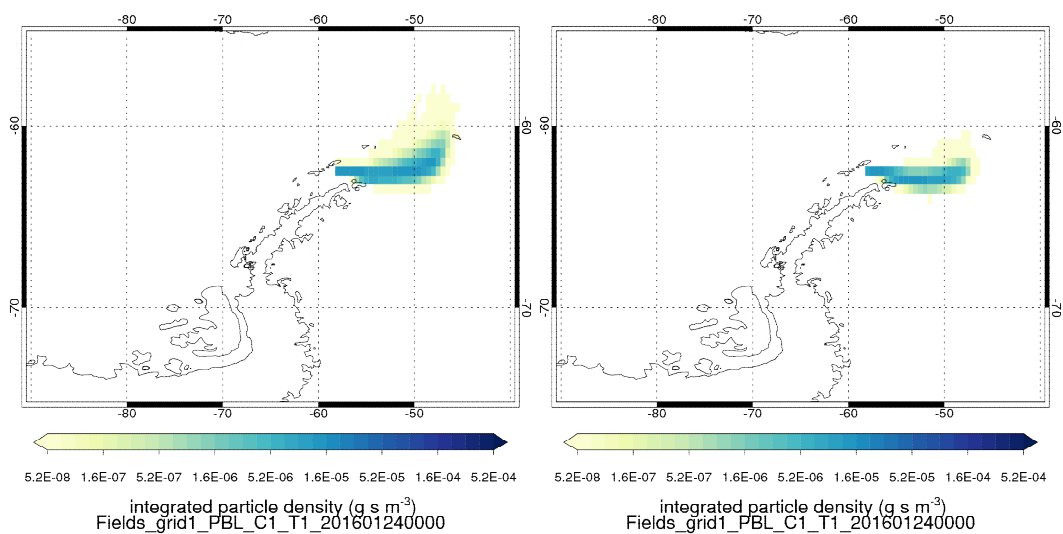


Figure 3.7 Footprints from 25/01/2016 0900 to 1200 (left) and 1500 to 1800 (right) at King Sejong.

In figure 3.8, at Deception Island, there are medium levels (~1 ppb) of isoprene here, and the footprints now lie slightly more over the coastline, although it is a different coastline to before. We believed, there are less strong emitters from these coastlines due to the type of emitter, or because of the weather conditions.

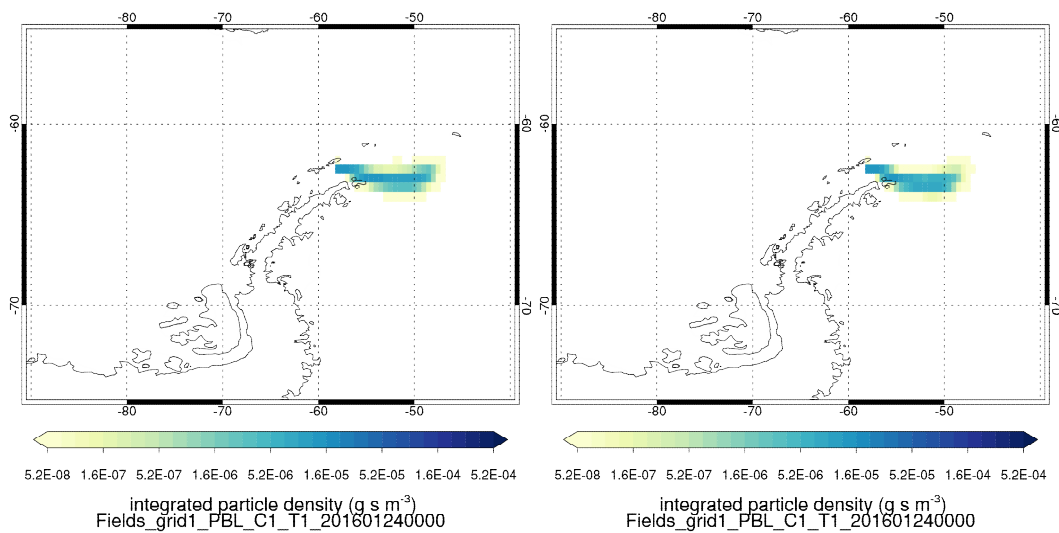


Figure 3.8 Footprints from 26/01/2016 0000 to 0300 (left) 0300 to 0600 (right) at Deception Island.

In figure 3.9, following footprints the air was coming from North West (NW) over Booth Island, perhaps the strong isoprene emitters are again from the islands at the top of the footprint (at around 60W and 62S). The highest isoprene is observed when the footprint has higher densities over this island. Booth Island has sparse cryptogam vegetation. In addition, the satellite chl-a also shown that the Graham Coast has high mixing ratio of chl-a near Booth Island. This concluded that, the mosses may produce significant level of isoprene mixing ratios. When low mixing ratio of isoprene observed over Booth Island, the

air mass was coming mainly from ocean as shown in figure 4.0. It is clearly showed that, the air mass may bring the isoprene gases from the island nearby rather than the ocean.

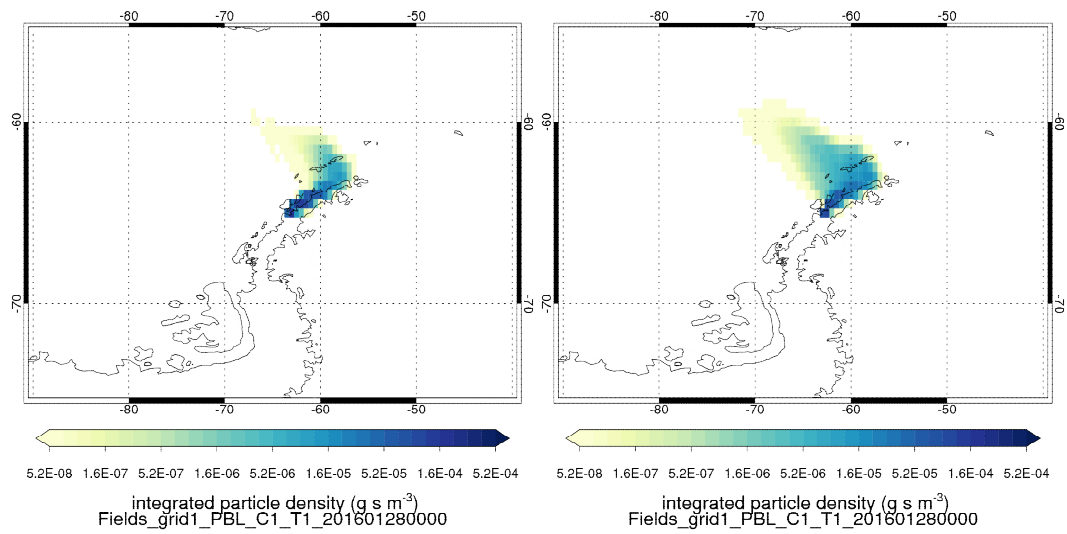


Figure 3.9 Footprint from 29/01/2016 0900 to 1200 (left) and 1200 to 1500 (right) over Booth Island.

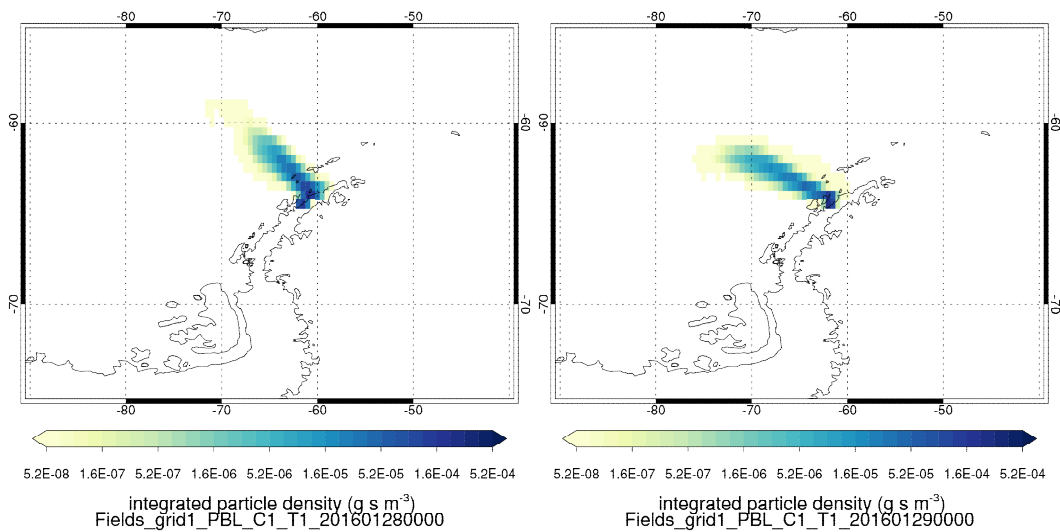


Figure 4.0 Footprint from 29/01/2016 2100 to 0000 (left) and 30/01/2016 0600 to 0900 (right) over Booth Island.

3.6 Backward trajectory analysis

In this section, we describe the influence of air mass backward trajectories to investigate probable sources of isoprene. The backward trajectories (BTs) of air masses at the King

Sejong, Deception Island and Booth Island research stations were plotted (Figure 4.1). The cluster of BTs were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT version 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 trajectory with 6 h intervals was chosen to identify the origin of the air masses at the receiving points of interest in this study. Trajectory start time was set at 00:00, 03:00, 06:00, 09:00, 12:00, 15:00, 18:00, and 21:00 UTC, along with three additional start times at 01:00, 04:00 and 07:00 to create a sufficient number of trajectories for the clustering process. Using the model in HYSPLIT version 4.9, BTs were estimated for each day and compiled into IGOR Pro to visualize the pathways over the true image of the Antarctic region. As an input of the trajectory model, a dataset was downloaded from the NOAA website (link: <ftp://arlftp.arlhq.noaa.gov/pub/archives/reanalysis>).

The period of the BTs was chosen as 23-25 January 2016, 25-27 January and 28-30 January 2016 for study points on King Sejong Station, Deception Island and Booth Island, respectively. At King Sejong Station, BTs were transported from the Southern Pacific Ocean (25%) and the Weddel Sea in the Atlantic Ocean (75%). Similarly, the cluster of BTs at Deception Island travelled from the Pacific Ocean (28%) and the South Atlantic Ocean (72%) during 25-27 January 2016. However, the cluster of BTs originated from the southern Pacific Ocean (50%) during the 28-30 January 2016. The predominant origins of the BTs represent the potential source region of the surface level isoprene at the King Sejong, Deception Island and the Booth Island stations. During the cruise along the WCAP, mixing ratios of isoprene were higher at King Sejong Station and Deception Island due to the emission sources in the hot spot areas over the South Atlantic Ocean. The responses of BTs were consistent with the chl-a and POC shown in Figure 3.4.

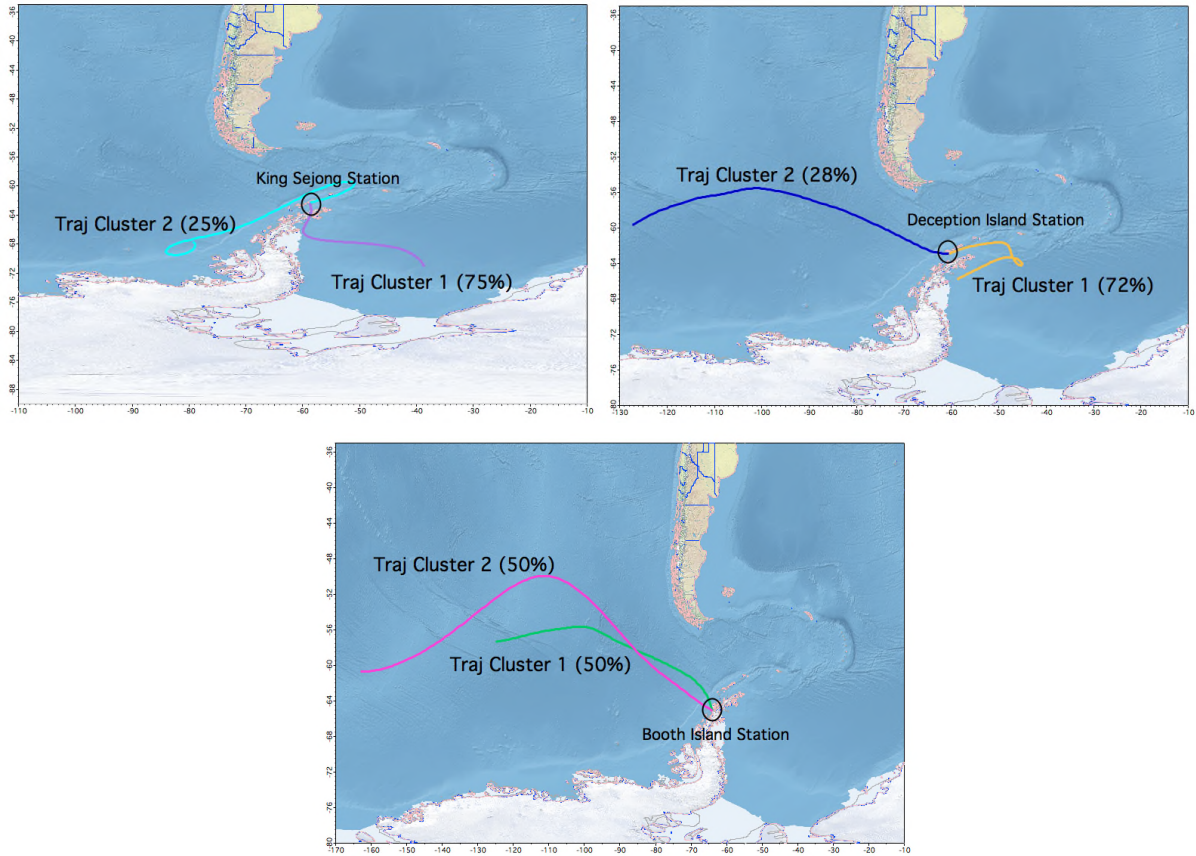


Figure 4.1 Backward trajectories of air mass transport in the marine boundary layer of maritime Antarctic during MASEC'16.

3.7 Previous data on isoprene from macro algae

Table 2 shows the seawater concentrations of isoprene from previous study which proven the macro algae can produce significantly isoprene into the air-sea interaction. Our study shows that mainly the Antarctic brown algae *Himantothallus grandifolius* and mosses were spotted at the coastal and floated (only macro algae) over the surface seawater. This could be attributed to the high biomass of the algal population at King George Island based on the measurement by iDirac. Nevertheless, we suggest that more studies need to be

conducted on Antarctic macro and micro algae to fully understand the mechanism and production of isoprene.

Broadgate et al. (2004) also reported that seawater concentration of isoprene was higher during the daytime compared to night-time. This observation was also made by Meskhidze et al. (2015) who measured isoprene emitted by phytoplankton. These findings from previous studies suggest that isoprene emission is influenced by light intensity and temperature. Hanson et al. (1999) reported *Sphagnum capillifolium* (Ehrh.) Hedw. moss collected from Wisconsin, USA emitted isoprene in the range of 1800000 ± 0.1 to 1000000 ± 0.8 pmol mol⁻¹ with increase in temperature. The authors also summarised isoprene emission from various types of mosses can emit high levels of isoprene (see Table 2 in Hanson et al., 1999). Nevertheless, we did not conduct air sampling above the moss communities at King George Island (see Figure 3.5), although we believe the mosses and probably vascular plants communities may have influenced the mixing ratios of isoprene over the WCAP. To the best of our knowledge, there is still a lack of observations made on terrestrial vegetation types.

From the observations made in this study, we can suggest that macroalgae and other marine organisms, terrestrial plants in the hot spot areas can either emit isoprene directly, or produce organic precursors that are rapidly converted to isoprene during the time of sampling at the WCAP.

Table 2 Mean and standard deviation (in parentheses) values of the measured isoprene mixing ratios from the literature (n.m.: not mentioned).

Species	Area & time	Mean (Standard deviation)	study	Instrument
<i>Ulva intestinalis</i> L.	Rock pool	865 pmol L ⁻¹	Broadgate et al., 2004	GC-FID
Mix of red, brown and green (<i>Ulva intestinalis</i>)	Rock pool	153 pmol L ⁻¹	Broadgate et al., 2004	GC-FID

4.0 Conclusion

The iDirac was successfully used for isoprene measurement purposes during MASEC'16. Nevertheless, due to weather conditions during certain periods, reliable *in situ* measurements were not obtained. However, overall the data can be used to estimate hotspots of C₅H₈ emission over the Western coast of Antarctic Peninsula. During MASEC'16, isoprene mixing ratios (with high uncertainties) increased from ~0.6 to 1 ppb over Deception Island, and from ~3 to 5 ppb over King George and Booth Island. Biological productivity was believed to influence mixing ratios. Satellite data showed that levels of chl-a and particulate carbon (both organic and inorganic) were high in the isoprene hotspot areas. This is supported by the direct observations in the area surrounding (rich of diatom algae blooming in the sea) the Ukrainian Vernadsky Station during the study period. Air mass history analysis using the NAME model showed that air in the isoprene hotspots had passed over coast lines in the day leading up to the measurement. When isoprene levels were low, air has not passed over coast lines in at least the past 2

days. Laboratory analysis of the air sampled by the flask canister showed that the brown alga *Himantothallus grandifolius* may have contributed to the high isoprene mixing ratios over King George Island. Furthermore, other biogenic sources such as other algae species, terrestrial plants, and bacteria may also contribute to isoprene emissions over the studied region. In future, we recommend that more *in situ* observations be made over the Western Coast of the Antarctic Peninsula and the rest of the Antarctic region to investigate in more detail the mechanisms of isoprene production. Also, biological samples need to be taken out for further analysis. The NAME model used in this study also showed that good validation and comparison with the *in situ* measurements.

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