



Local Emissions and Regional Wildfires Influence Refractory Black Carbon Observations Near Palmer Station, Antarctica

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Antarctica is often regarded as the most pristine continent on Earth. However, local human activity can be significant point sources of production of contaminants, as well as light absorbing aerosols, such as black carbon (BC). In May 2015, over the Austral fall season (at the beginning of the accumulation season), surface snow was sampled at eight sites along a 1.7 km transect extending from Palmer Station, Antarctica. Two additional sites were sampled on Biscoe Point 14 km from the station. Snow samples were analyzed for refractory black carbon (rBC) with a Single Particle Soot Photometer (SP2). rBC concentrations increased with proximity to the Palmer Station 1.2–16.5 $\mu\text{g-rBC/L-H}_2\text{O}$ ($4.7 \pm 4.9 \mu\text{g-rBC/L-H}_2\text{O}$) and were higher than other studies of rBC in snow, such as in the McMurdo Dry Valleys, Antarctica (MDV) and the Clean Air Sector of the South Pole Station (CAS-SP), except on the more remote Biscoe Island, 0.4–1.2 $\mu\text{g-rBC/L-H}_2\text{O}$, which had similar background concentrations to the MDV and CAS-SP, 0.3–1.2 ($0.6 \pm 0.3 \mu\text{g-rBC/L-H}_2\text{O}$) and (0.14–0.80 $\mu\text{g-rBC/L-H}_2\text{O}$), respectively. However, concentrations were lower than previous observations at South Pole Station downwind of the generator and long the runway (6.6–7000 $\mu\text{g-rBC/L-H}_2\text{O}$). Palmer Station is located on the southwestern coast of Anvers Island which lies off the western coast of the Antarctic Peninsula at 64° 46'S, 64° 03'W. Comparison with the Navy Aerosol Analysis Prediction System (NAAPS) model show that wildfire smoke may have reached this region of the Antarctic continent during the time period of the deposition of this seasonal snow, suggesting the increase in rBC may be a combination of local combustion of fossil fuels and regional wildfires. Although significant increases in rBC concentrations are found within a km of Palmer Station, like the South Pole Station, rBC is limited to a few kms from the station. Additionally, these measurements of rBC, which may be the only BC measurements in snow on the Antarctic Peninsula, show that background levels are similar to other locations on the continent.

Keywords: black carbon, snow, Antarctica, local impact, wildfires and biomass burning, fossil fuel emissions

INTRODUCTION

Palmer Station is the smallest of the three permanent scientific research stations operated by the United States Antarctic Program (USAP). It is located on the southwestern coast of Anvers Island which lies off the western coast of the Antarctic Peninsula at 64° 46'S, 64° 03'W (Figure 1). The current station, which was commissioned on 20 March 1968 supports U.S. scientific research in the Antarctic Peninsula Region. It replaced “Old Palmer Station” which was established in 1965 on Amsler Island adjacent to the British Antarctic Survey’s Base N, which was built in 1955 and abandoned in 1958. Palmer Station currently comprises two major and three smaller buildings, a boat dock and pier. Its maximum capacity is 44 individuals in the summer and approximately 20 people in winter. The R/V Laurence M. Gould regularly services the station. It is located within and supports research for the Palmer Long Term Ecological Research (LTER) site, which was established in the Fall of 1990.

Black carbon (BC) is a light-absorbing aerosol generated from the incomplete combustion of biomass burning and fossil fuels (Goldberg, 1985). BC influences atmospheric radiation and air quality (Bond et al., 2013) and the deposition of BC on snow/ice reduces the surface albedo (Warren and Wiscombe, 1980) and can lead to earlier and more rapid snow/ice melt (Xu et al., 2009). Previous studies have confirmed the presence of BC in snow and ice on the Antarctic continent (Warren and Wiscombe, 1980; Bisiaux et al., 2011, 2012; Bauer et al., 2013; Khan et al., 2016, 2017, 2018; Casey et al., 2017).

The primary sources of BC to the southern hemisphere has been identified as biomass burning in Australia, South America, and Africa (Crutzen and Andreae, 1990). Variations in seasonal and decadal long-range BC transport to Antarctica have been observed to be due to changes in climate and the resulting influence on biomass burning in the Southern Hemisphere. Ice cores from Law Dome and the West Antarctic Ice Sheet (WAIS) showed significant annual to decadal variability (Bisiaux et al., 2012) where rBC transport to Antarctica was affected by ENSO climate patterns due to changes in biomass burning as a result of arid conditions.

Despite the perception that the Antarctic environment is pristine, it is subjected to diverse anthropogenic impacts on local to regional scales and these impacts are of concern (e.g., Tin et al., 2009). Over the past 25 years, the chemical signature of BC in the surface waters of McMurdo Dry Valley (MDV) lakes has shifted toward modern anthropogenic sources of BC (Khan et al., 2016), whereas a BC chemical signature of ancient biomass burning has been preserved in the lake bottom waters. The recent shift may be due to local combustion of fossil fuels from combustion toilets, diesel generators, all-terrain vehicles, and helicopters, which contribute 3.4×10^5 g aerosol elemental carbon annually in the MDV (Lyons et al., 2000). Additionally, previous studies on the Antarctic continent have found the South Pole Station creates enough local pollution to reduce the surface albedo of snow downwind of the station (Warren and Wiscombe, 1980; Warren and Clarke, 1990) and along the runway, leading to refractory black carbon (rBC) concentrations of (6.6–7000 $\mu\text{g-rBC/L-H}_2\text{O}$) (Casey et al., 2017). rBC is defined

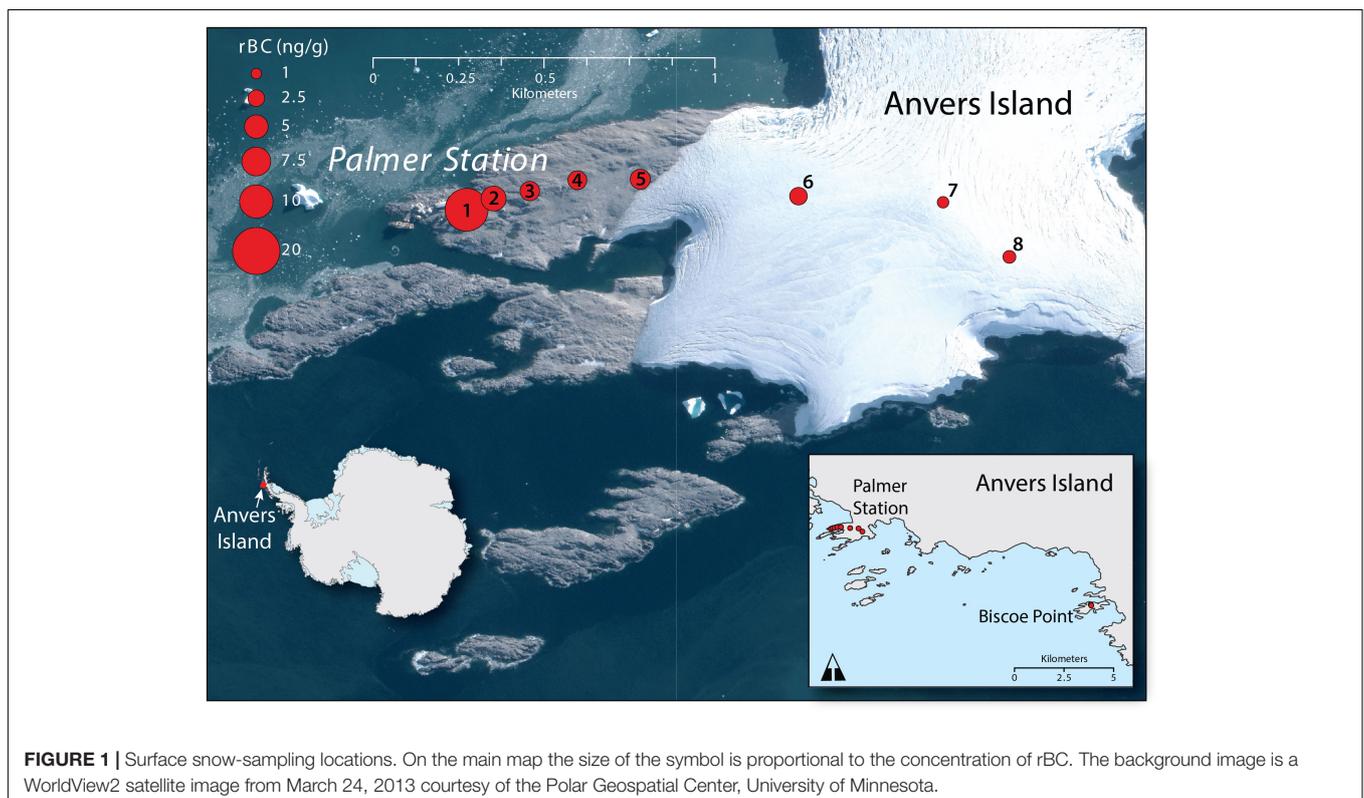
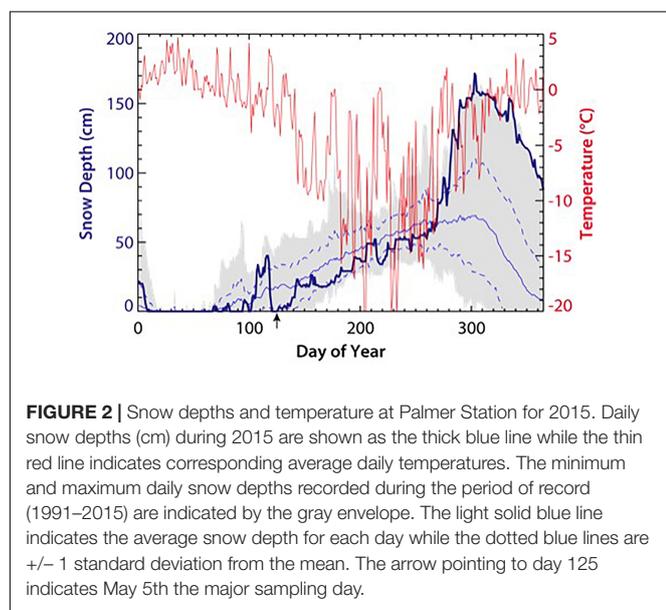


TABLE 1 | rBC concentrations in snow collected along a transect away from Palmer Station.

Site	Date of collection	Latitude	Longitude	Elevation (m)	Distance from station center (m)	rBC ($\mu\text{g-rBC/L-H}_2\text{O}$)
1	5-5-15	-64.774308	-64.051365	14	101	16.5
2	5-5-15	-64.774024	-64.049693	10	182	5.6
3	5-5-15	-64.773842	-64.047456	20	280	3.4
4	5-5-15	-64.773575	-64.044523	23	431	3.2
5	5-5-15	-64.773576	-64.040653	19	614	3.6
6	5-5-15	-64.774092	-64.030936	92	1072	2.8
7	5-5-15	-64.774315	-64.022048	121	1495	1.2
8	5-5-15	-64.775788	-64.018024	101	1695	1.5
9	5-1-15	-64.810521	-63.776677	10	13760	0.4
10	5-1-15	-64.810972	-63.776185	15	13800	1.2

rBC concentrations are the average of three sample duplicates.



as BC detected via laser-induced incandescence via Single Particle Soot Photometer (SP2) (Petzold et al., 2013).

Environmental protection of Antarctica is internationally recognized and documented in the Antarctic Treaty (Watts, 1992). The Treaty and its annexes set forth national responsibilities to protect the environment. Individual treaty nations then enact national legislation, which regulates each country's nationals while in Antarctica. The Treaty's environmental protection practices were clarified and enhanced by the Protocol on Environmental Protection (often referred to as the Madrid Protocol), which entered into force in 1998 (Stokke and Vidas, 1998). The Protocol recognized that effective management of human impact on the continent required the monitoring of human activities. The snow samples in this study collected were collected as part of a program to design a long-term environmental monitoring program for Palmer Station similar to the program implemented for USAP's much larger McMurdo Station (Kennicutt et al., 2010; Klein et al., 2014). While the spatial extent of anthropogenic impacts around

Antarctic research stations varies by contaminant or type of impact, these impacts are generally limited to a few hundred meters or few kilometers from the station. This study provides an initial estimate of the spatial extent of Palmer Station's BC emissions on the local environment.

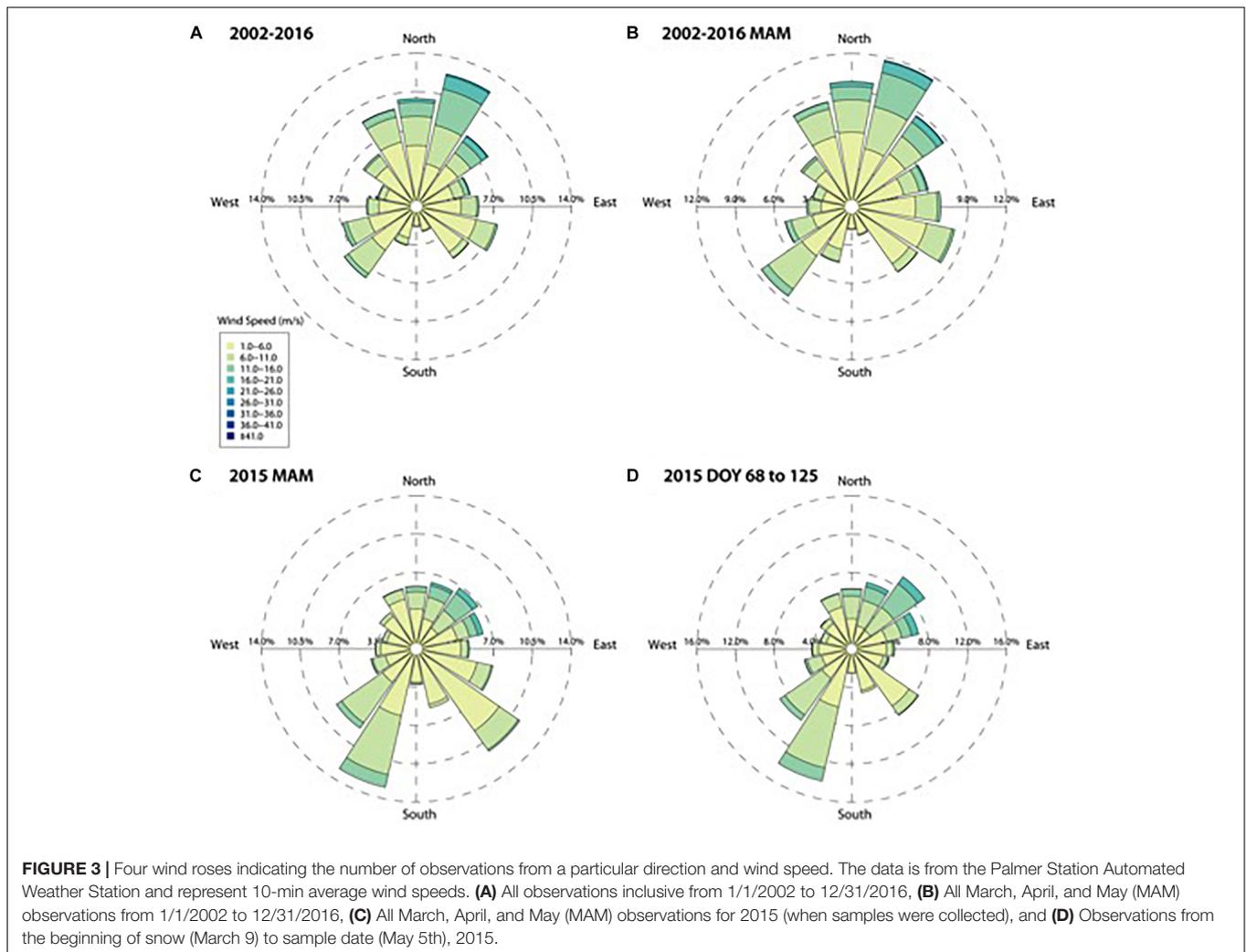
MATERIALS AND METHODS

Site Description

As with other USAP facilities, Palmer Station operates on petroleum and station activities produce hydrocarbon emissions. For Fiscal Years 2006–2010, fuel consumption at Palmer Station averaged 104,792 gallons annually. Of this, 80% was consumed by the station's power plant, 19% for heating and hot water and 1% for vehicles (RSA Engineering, 2011). Two 250 kW Caterpillar engine generators (circa 1998) supply power to Palmer Station and heat to the building in which they are located. Oil boilers provide hot water for the other buildings. Machinery and small boats, at the time of this study, primarily inflatable Zodiacs, are also operated on station. A small incinerator is operated sporadically to incinerate poultry waste and a small wood-burning stove operates in one of Palmer's two main buildings. Palmer Station has $\sim 20\%$ of the population of the South Pole at its maximum.

The Research/Vessel (R/V) Laurence M. Gould (LMG), operated by Lockheed Martin, supports Science and operations at Palmer Station. The LMG is a 230 foot long ice-classed ABS-A1 research and resupply vessel on a long-term charter from Offshore Service Vessels LLC. The LMG has two main engines (Caterpillar 3606) and three generators (Caterpillar 3508). USAP's larger vessel, the Nathaniel B. Palmer, services Palmer Station occasionally and approximately a dozen cruise vessels visit the station each year.

The LMG typically averages 8–9 visits to Palmer Station each year (RSA Engineering, 2011). During the period of snow accumulation in this study, the LMG made three cruises to Palmer Station LMG 15-02 (2/13-3/16), 15-03 (3/20-4/4), and 15-04 (4/7-5/11). Based on analysis of the LMGs navigational data (Aronson, 2015; O'Brien et al., 2015) and cruise history (United States Antarctic Program [USAP], 2018), the LMG spent



approximately 13 days docked at Palmer Station from the first day of snow accumulation March 9th through sample collection on May 5th.

Snow Measurements

On 5 May 2015, during a period without recent snowfalls, surface snow samples were collected for rBC analysis at eight sites along a 1.7 km transect extending eastward from Palmer Station. These sites were augmented by samples collected from two more remote sites located approximately 14 km from Palmer Station on Biscoe Point (now an island) situated within the Biscoe Point Antarctic Specially Protected Area (ASP) No. 139 on 1 May 2015. Entry to an ASP requires special permitting to sample these pristine sites (Figure 1).

At each site three replicate sample duplicates were collected. rBC concentrations reported in Table 1 are the average of the three sample duplicates. Snow was collected in 500 ml glass jars which were pre-cleaned to meet Environmental Protection Agency (EPA) Protocol A Level 1 standards for contaminants. Samples were obtained by placing the opening of the glass jar perpendicular to the horizontal surface of the snowpack and

pressing the jar through the snowpack until the snow completely filled the jar. Care was taken so the surface was only sampled once per replicate.

After collection, snow samples were kept frozen at Palmer Station, during their transport to Punta Arenas, Chile and onward to Texas A&M University until they were shipped to the Institute of Arctic and Alpine Research (INSTAAR) in Boulder, CO and then transferred to the Earth System Research Laboratory at the National Oceanic and Atmospheric Administration for rBC analysis. Snow samples were then melted for the first time immediately before analysis. The thirty surface snow samples were analyzed for rBC mass mixing ratios (MMR). Briefly, snow samples were melted, then immediately aerosolized with a carefully calibrated nebulizer and sampled with an SP2 following the approach of Schwarz et al. (2012). The SP2 has excellent sensitivity and selectivity for rBC with minimal interference from non-BC materials and was calibrated with fullerene soot (Alfa Aesar, Woodbridge, MA, United States, Lot F12S011). Here, a CETAC Marin-5 nebulizer interfaced with the SP2, following the same protocol as Katich et al. (2017). The size-dependent nebulization efficiency was characterized

with concentration standards of polystyrene latex spheres (PSLs) in the size range 220–3000 nm diameter, confirming low sensitivity to particle size over this range, consistent with recent results with concentric pneumatic nebulizers (Lim et al., 2014; Wendl et al., 2014; Mori et al., 2016; Katich et al., 2017). Size distributions were measured for samples with higher concentrations, and these indicated no appreciable contribution to rBC mass above 0.7 μm . Hence no size dependent corrections were applied for nebulizer size dependence. Background rBC contamination levels were bounded by measuring blank samples. Deionized water was used to flush the nebulization system between snow samples to reduce line contamination. Further, measurements of rBC concentrations in blank water samples were interspersed amongst snow samples to bound background contamination levels in the system. This averaged 0.43 $\mu\text{g/L}$ over 15 blank water measurements, indicating a low enough background to avoid significant interference with the rBC MMR measurements. The blanks provide an upper bound on possible contaminants associated with the estimated 60% uncertainty for rBC MMR in the snow, which conservatively accounts for uncertainties dominated by calibration issues (Schwarz et al., 2012).

Local Meteorological Observations

Information on local meteorological conditions during the period of early snow accumulation in 2015 was obtained from two sources. Local Daily Summaries provided daily weather observations including snow depth and accumulation measurements recorded by Palmer Station personnel and were obtained from the Antarctic Meteorological Research Center (AMRC) at the University of Wisconsin (Antarctic Meteorological Research Center [AMRC], 2018) 2-min observations from the Palmer Automated Weather System (PALMOS) available from the Palmer Station Antarctica LTER (Long Term Ecological Research Network-Network Data Portal [LTER-NDP], 2017) were used to investigate wind speed and directions during the period of snow accumulation. Analysis of the weather observations was accomplished using the Anaconda Scientific Python Distribution. The wind roses are produced using IDL software (Fanning, 2019). All mapping was accomplished using ArcMap or ArcGIS Pro.

Aerosol Transport Modeling

Smoke aerosol optical depth (AOD) and concentrations from biomass burning comes from the Navy Aerosol Analysis and Prediction System (NAAPS) reanalysis (Lynch et al., 2016), which was developed and validated at the Naval Research Laboratory. The NAAPS model was used to explore regional and long-range biomass burning smoke transport events during the study period. It is a global $1^\circ \times 1^\circ$ decade-long 6-hourly aerosol reanalysis product. It utilizes a modified version of the NAAPS as its core and assimilates quality controlled retrievals of AOD from Moderate Resolution Imaging Spectroradiometer (MODIS) on Aqua and Terra, as well as the Multi-angle Imaging Spectroradiometer (MISR) on Terra (Zhang and Reid, 2006; Hyer et al., 2011; Shi et al., 2014). NAAPS characterizes anthropogenic and biogenic fine aerosol (including primary and

secondary organic aerosols and sulfate), biomass burning smoke, dust, and marine sea salt aerosols. Biomass burning smoke is derived from near-real time thermal anomaly satellite based data used to construct smoke source functions (Reid et al., 2009), with orbital corrections on MODIS-based regional tunings and emissions. The fine and coarse mode reanalysis AOD at 550 nm is shown to be in agreement with the ground-based global scale sun photometer network Aerosol Robotic Network AOD (Holben et al., 1998).

RESULTS AND DISCUSSION

rBC Concentrations

rBC concentrations in surface snow decrease with increasing distance from Palmer Station (Figure 1 and Table 1). Elevated rBC concentrations were found near the station, 16.5–1.5 $\mu\text{g-rBC/L-H}_2\text{O}$, especially as compared to the low concentrations found on Biscoe Island, 0.4 and 1.2 $\mu\text{g-rBC/L-H}_2\text{O}$. This suggests that the station's influence on rBC extends at least 1 km from

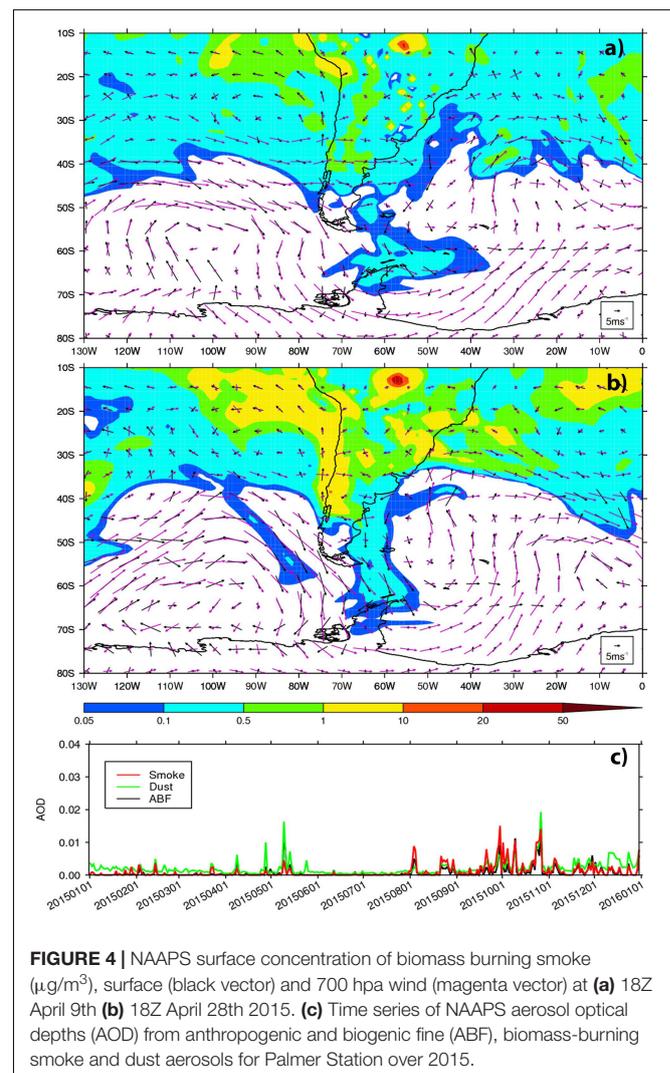


FIGURE 4 | NAAPS surface concentration of biomass burning smoke ($\mu\text{g}/\text{m}^3$), surface (black vector) and 700 hpa wind (magenta vector) at (a) 18Z April 9th (b) 18Z April 28th 2015. (c) Time series of NAAPS aerosol optical depths (AOD) from anthropogenic and biogenic fine (ABF), biomass-burning smoke and dust aerosols for Palmer Station over 2015.

the station. rBC concentrations in this study near Palmer station were higher than other studies of rBC in snow on the Antarctic continent, such as in the MDV, 0.3–1.2 $\mu\text{g-rBC/L-H}_2\text{O}$, except on the more remote Biscoe Island, 0.4 and 1.2 $\mu\text{g-rBC/L-H}_2\text{O}$, which like the MDV, has restrictions to entry, and had similar background concentrations indicative of long-range atmospheric transport. However, concentrations in this study were less than previous findings downwind of the generator and along the runway at the South Pole Station (6.6–7000 $\mu\text{g-rBC/L-H}_2\text{O}$) (Casey et al., 2017). It should be noted that Palmer Station has $\sim 20\%$ of the population of the South Pole at its maximum. Additionally, samples from the clean air sector at the South Pole (0.14–0.80 $\mu\text{g-rBC/L-H}_2\text{O}$) (Casey et al., 2017) contained similar background concentrations of rBC as found in this study and in the MDV. Although, significant increases in rBC concentrations are found within a km of Palmer Station, like the South Pole Station, rBC is limited to a few kms from station.

During 2015, Palmer Station recorded some of its highest snow depths over the period of record (Figure 2). The period preceding snow sampling on May 1st and 5th saw intermittent snow on the ground from March 9 to April 5 after which snow was continuously present at the station. It reached a depth of 40 cm in late April. However, April 28–30 saw air temperatures remaining above freezing and maximum air temperatures exceeding 4° causing snow to disappear at the Palmer snow stake on May 1st. Therefore, the snow sampled on May 1st and 5th represent the snow that remained in patches or on the glacier from the early period of well-above average snow accumulation.

The wind roses illustrated in Figure 3 show that surface winds during the snow accumulation period of the sampling differ from long-term averages for the entire year and the March to May (MAM) period. The period of snow accumulation captured by the sampling was characterized by a much higher occurrence of SSW surface winds than is typical.

NAAPS Model Results

According to the NAAPS analysis, a small amount of biomass burning smoke was transported southward from South America to Palmer Station on April 9, 2015 (Figure 4a) and on April, 28, 29, 2015 (Figure 4b). As evidenced by the NAAPS model plots, when there is southward wind blowing from South America, there is possible smoke transport to the Antarctic Peninsula (Figures 4a,b). Thus, it is possible that biomass burning smoke was deposited on the sampled snow layer. However, AOD time series of the study site for the whole year of 2015 (Figure 4c) show that the amount of smoke transported over the study period is smaller compared to the peak biomass season (September–October) transport. Palmer Station is located in the roaring circumpolar strong westerly wind belt; therefore sea salt is excluded in the time series plot, as it dominates the AOD signal.

SUMMARY AND CONCLUSION

These first observations of black carbon in seasonal snow on the Western Antarctic Peninsula show that rBC concentrations

are similar to other pristine regions of the continent, including the MDV and the South Pole. This study provides a preliminary quantification of the Palmer Station “emissions or black carbon footprint” (Brooks et al., 2018). rBC concentrations in surface snow decrease with increasing distance from the Palmer Station. Elevated rBC concentrations near the station appear to show the station’s local impact extends at least 1 km, as similarly found downwind of the South Pole station (Warren and Wiscombe, 1980; Casey et al., 2017). NAAPS model results show that smoke from regional wildfires occurring on the South American continent may have transported biomass burning derived rBC to the study site prior to sample collection. However, the AOD smoke signal over the Austral fall, when the samples were collected, is smaller than the peak southern hemisphere wildfire season in the Austral spring. Although the NAAPS AOD signal is smaller over the snow sample collection period than in the Austral spring, the background rBC concentrations found near Palmer Station and on Biscoe Island are likely a mix of locally produced BC and regional transport of smoke from wildfires.

In the future, this dataset can be improved by expansion both temporally and spatially, along Anvers Island, as well as the entire Antarctic Peninsula. Additionally, samples in this study were collected from snow remaining after an abnormally high early-season snowfall, followed by rapid and nearly total snow melt. Collection of samples over the entire snow season and immediately after snowfall would be an improvement, as well as over a larger spatial range. This is one of a small number of studies to look at the spatial footprint of airborne pollution around scientific installations on the continent. It demonstrates that for a station with a population of 44 the spatial footprint is somewhat limited and beyond 1 km the concentrations the pristine snow concentrations of the Western Antarctic Peninsula are similar to other pristine regions of the continent.

DATA AVAILABILITY

All measurement data generated are included in the manuscript, but further questions can be directed to alia.khan@wwu.edu.

AUTHOR CONTRIBUTIONS

AK and AGK conceived of the study. AGK conducted the sampling. AK and JK conducted the refractory black carbon analysis. PX conducted the NAAPS analysis. All authors contributed to the development, data analysis, and writing on the manuscript.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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