Author's response to the editor and reviewers

Dear TC editor and referees,

Please find below the point-by-point response to the reviews including a list of all relevant changes and a marked-up manuscript version. Please note the responses to the referees presented here are the same responses as submitted on February 27th - we added them in this .pdf file for your convenience.

We hope all raised questions have been responded, and are looking forward the re-review.

We thank you for your time reviewing our manuscript.

Luciano Marquetto (first author)

Response to Anonymous Referee #1 comment

Received and published: 19 December 2019

Dear Anonymous Referee,
We thank you for your time, expertise, and helpful suggestions.

We apologize for the inconvenience that Marquetto et al. (2019) was not available during the review process. Marquetto et al. (2019) was accepted for publication in October 2019 and will be available online in April 2020 in "Advances in Atmospheric Sciences" as Marquetto et al. (2020). We have added the accepted manuscript as supplementary material for your review. Considering our system setup and calibrations carried out for the SP2, we believe the rBC concentrations found in this work are solid results, as described with more details along the text.

We made several improvements to the manuscript based on the reviewer's suggestions. First, we opted to remove the 2008 trace element records from the dating section. Although the 2015 and 2008 cores presented an overlap of 7 years (2002-2008), there is a 20% distortion between them in order to match both. This raised an issue about using a core 850 m away, with topographical differences, to date the rBC core. We decided this brings more uncertainty to our work than using the 2015 trace element record to constrain the dating down to 2002, and then base the rest of the dating on the relations of rBC, Na, Sr and S observed for the 2015-2002 period.

We also removed the sodium record from the spectral analysis and comparison of rBC and Na transport, as the 2015-2002 Na record is too short to show cycles in the spectrum.

On the other hand, we added atmospheric transport simulations using the HYSPLIT model to identify BC source areas. Results corroborated our initial conclusions of Australia and New Zealand as the most probable sources of BC to the TT07 drilling site, and indicated limited influence of South American air masses. More information is presented at the end of this document, after responses to reviewer's suggestions.

We also added a comparison of the Antarctic rBC records with snow accumulation, elevation and distance from open sea. In East Antarctica, rBC concentrations have a negative correlation with snow accumulation and positive correlation with elevation and distance to the sea, whereas in West Antarctica rBC concentrations present a positive correlation with snow accumulation and a negative correlation with elevation and distance to the sea. These opposite trends may indicate differences in rBC transport to East and West Antarctica. While for East Antarctica upper tropospheric transport and dry deposition may be the main controllers of rBC concentrations (Bisiaux et al., 2012b)*, for*

West Antarctica rBC concentrations may be modulated by intrusion of air masses from the marine boundary layer, contrary to what was previously suggested (Bisiaux et al., 2012a)*. Low elevations in West Antarctica facilitates the intrusion of moisture-rich cyclones and the transport of aerosols inland* (Neff and Bertler, 2015; Nicolas and Bromwich, 2011)*, while the positive relationship between West Antarctica rBC concentrations and snow accumulation may indicate rBC to be primarily deposited through wet deposition, being scavenged along the coastal regions were snow accumulation is higher. More information is presented at the end of this document, after responses to reviewer's suggestions.*

The rBC record we present in this work is from an unique area – the Pine Island/Institute Glacier Divide, where air masses from the Weddel and Bellingshausen Seas converge (Parish and Bromwich, 2007), and is the highest altitude rBC core collected in West Antarctica. Considering all these improvements and new findings, we believe our manuscript is suitable for The Cryosphere.

Please find our responses in italic, while we kept your original comments in normal text.

Original referee comment:

This manuscript by Marquetto et al presents a 47 yr black carbon record from a 20- m firn core recovered from the Pine Island Glacier in West Antarctica. The authors measured rBC using the SP2 method, and dated the core primarily using the seasonal cycle of rBC. Potential southern hemisphere rBC source regions to this site were explored by correlating the seasonal cycle of rBC to Australian and South American fire spot data and GFED biomass burning emissions estimates as well as by comparing the power spectrum of rBC to large-scale atmospheric patterns (ENSO, AAO, and ASL) and fire spot data.
While Antarctic rBC records are important for understanding changes in southern hemisphere biomass burning as well as radiative forcing, and undoubtedly an immense amount of work went into developing this highly-resolved dataset, the interpretation and discussion are not thorough or novel enough to add significantly to the understanding of rBC deposition in West Antarctica. The discussion focused on three analyses: SNICAR snow albedo modeling, identifying continental emissions sources, and linking rBC to atmospheric circulation using spectral analysis. The SNICAR modeling showed that rBC deposition at this site has little to no effect on snow albedo, which is not unexpected given the extremely low rBC concentrations and (as noted by the authors) has already been shown for clean Antarctic snow (Casey et al., 2017). The identification of source regions by comparing seasonal cycles in observed rBC and GFED fire emissions is purely correlativeâ˘A˘ TI do not think is a strong enough approach, especially with my concerns about dating, to draw conclusions about source regions without a more robust approach that would consider atmospheric transport and magnitude of biomass

burning emissions. Finally, the spectral analysis was similar to that conducted by Bisiaux et al. (2012) for the WAIS Divide and Law Dome rBC records and does not provide any concrete new links between atmospheric circulation and Antarctic rBC. Furthermore, I have concerns about the factor of 2-3 lower rBC concentrations compared to other West Antarctic ice cores (see comments below).
Overall, since the conclusions do not add substantial new insight or understanding to rBC deposition and mainly confirm what is already known, I do not think this manuscript is suitable for the scope of The Cryosphere.
I have two major concerns about the methods: 1.) rBC measurements, and 2.) dating.

We respond to the two major concerns below.

1. rBC measurements: The rBC concentrations presented in this study are a factor of 2-3 lower than rBC concentrations in other West Antarctic cores, including the WAIS Divide ice core as well as other measurements from Pine Island Glacier (Pasteris et al., 2014). Note that rBC measurements from early 1900s to 2006 from Pine Island Glacier (as well as Thwaites Glacier and the divide between Pine Island and Thwaites Glaciers) were previously published in Pasteris et al. (2014) and are also 2-3x higher than the concentrations presented in this manuscript- it would be worth including this citation and even comparing to this published dataset to see how the magnitude and temporal variability of the records compare.

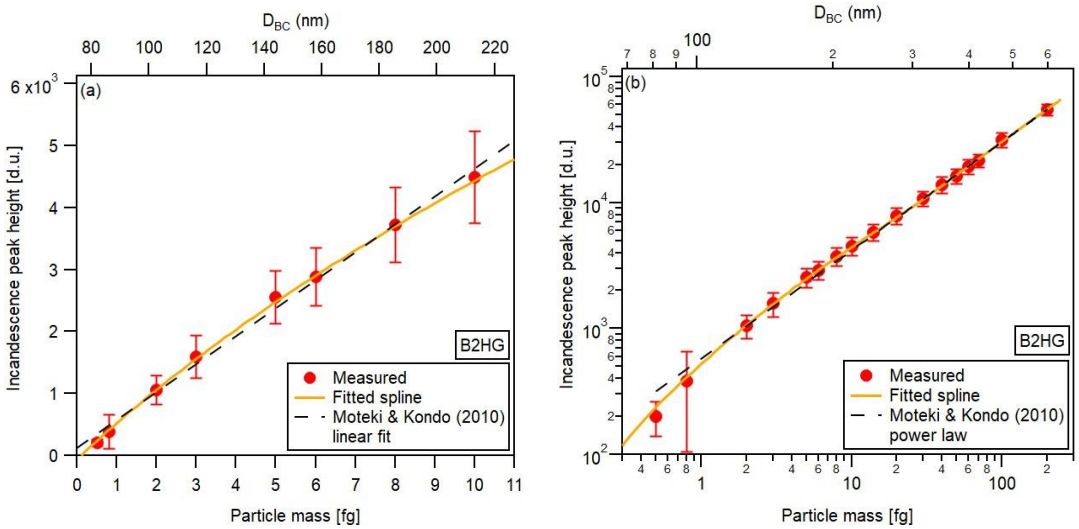
We included Pasteris et al. (2014) *as a citation along our manuscript and added their data as comparison in section 4.4. Thank you for pointing this out.*

The authors need to provide more information to determine if this offset is real or a result of the SP2 calibration/analytical system. Since the referenced Marquetto et al. (2019) manuscript does not appear to be published at the time of this review, please include details on the SP2 internal/external calibration in this manuscript.

We believe the lower rBC concentrations found by this work are not due to less-than-optimal SP2/analytical setting, and are, in fact, a reflection of the true rBC concentration in the samples. We were diligent in maintaining low background concentrations for this study, and detailed specifics on the methodology are provided in this response and in the revised manuscript.

We attached Marquetto et al. (2020) so you can check the internal and external calibration thoroughly. In short, internal calibration was carried out using a Centrifugal Particle Mass Analyzer (CPMA) to select 23 particle masses from 0.5 fg to 800 fg from an Aquadag solution. Each selected mass ran for 30 min to 6 h to provide statistically significant particle triggers to calibrate the SP2, and calibration curves were then generated for all SP2 channels. The data presented in the manuscript in review is from the duplicated extended range broadband detector (B2HG), as this channel gave the

best-fit calibration curve (spline) of all channels in the 0.5 – 200 fg range, but with an upper detection limit at ~ D_{BC} = 600 nm. The external calibration was carried out daily using five fresh Aquadag standards ranging from 0.01 to 1.0 µg L^{-1} and one environmental standard (diluted meltwater of a snow sample from Table Mountain, WY, USA) of known concentration (0.18 ± 0.04 µg L^{-1}).



Calibration curves for the (a) B2HG channel (0.5 < M < 10 fg – linear scale), (b) B2HG channel (0.5 < M < 200 fg – logarithmic scale) obtained from the internal calibration carried out using the SP2+CPMA.

Please note that Marquetto et al. (2020) present a comparison between two subsampling methods (solid state cutting and continuous melter system) – both resulted in statistically similar rBC concentrations.

How were the ice samples melted (room temperature?), and how soon before SP2 analysis were they melted (lines 96-97)? Wendl et al. (2014) show how rBC is lost after melting during sample storage in polypropylene vials over just a few days (with proportionally greater losses for low-concentration samples).

We added in section 3.3 the sentence: "Samples were melted at room temperature or in a tepid bath not exceeding 25°C, sonicated for 15 min, and then analyzed (in less than 1 h after melting)." This is also described in (Marquetto et al., 2020).

How often was 5% HNO3 used to clean the system (line 118), and how did you determine when the acid was flushed from the system? Wendl et al. (2014) also discuss how acidification can result in significant loss of rBC.

The results regarding acidification presented in Wendl et al. 2014 were conducted at Central Washington University, where we conducted this research, so we are well aware of these findings. Rather, we were very diligent to maintain the system at the MQ background level (at 0-0.5 particles cm^{-3}, translating to less than 0.01 µg L^{-1} rBC concentration). When MQ levels increased to 0.5 particles cm^{-3}, the HNO3 was used to clean the TruFlo liquid flow monitor and the nebulized. The HNO3 was only used on three days during the 43 working days, sometimes more than once a day. We ran the solution for 10 to 30 min from the peristaltic pump to the nebulizer outlet tubing (disconnected from the SP2). After using the acid we ran MQ water (MilliQ-Element, Millipore, 18.2 MΩ cm) for at least double the time we ran the acid. After connecting the SP2 back, we ran MQ water for at least 15 min. These are the procedures used in the Ice Core Laboratory (CWU), where the samples were analyzed.

What kind of tubing was used to transport the aerosol from the Marin 5 nebulizer to the SP2?

We used black conductive tubing from Simolex Rubber Corporation (Plymouth, USA) - http://simolex.com/product/conductive-silicone-extrusion-products-tubing/. This is the standard tubing that comes with the SP2.

2. The description of the dating, namely the role of the datasets from the Schwanck et al. (2017) study, is vague. Since much of the analysis, including the seasonal cycle correlations and spectral analysis, require precise dating, more explanation of the dating must be given. The annual picks in Fig. 1 are consistently on the austral summer (January) decrease of rBC concentration, but appear to be inconsistently placed across the S, Sr, and Na records.

We opted to use only the 2015 trace element record for dating and constrain the rest of the dating based on the rBC well defined seasonality for West Antarctica (Arienzo et al., 2017; Bisiaux et al., 2012a; Winstrup et al., 2017) *and for the Pine Island Glacier* (Pasteris et al., 2014).

To improve our dating for these first meters we reviewed sample resolution for the rBC and trace element cores, and added an additional parameter to dating: the maxima in the non-sea-salt sulfur to sodium (nssS/Na) ratio, a robust seasonal indicator that peaks around the new year (Arienzo et al., 2017). *This parameter helps in the identification of the annual layers more than the Na and S records alone. Non-sea-salt sulfur was calculated using Eq. 3 to 6 from* Schwanck et al. (2017) *and references therein.*

We consider this dating to have ±2 years uncertainty. The first uncertain year is located at 6.18 m (between 2003 and 2002, figure 2a), where S and nssS/Na peak but no full cycle is observed in the rBC record. We did not consider this to be a year, as rBC does not present a full cycle. The second uncertain year is located at 18.14 m (year 1973, figure 2b) where there is no clear rBC peak but snow accumulation would be

anomalously high if considered to be only a year instead of two. We consider this to be an annual pick and consequently two years, as there is no evidence of higher-than-normal snow accumulation in the region for this period (Kaspari et al., 2004).

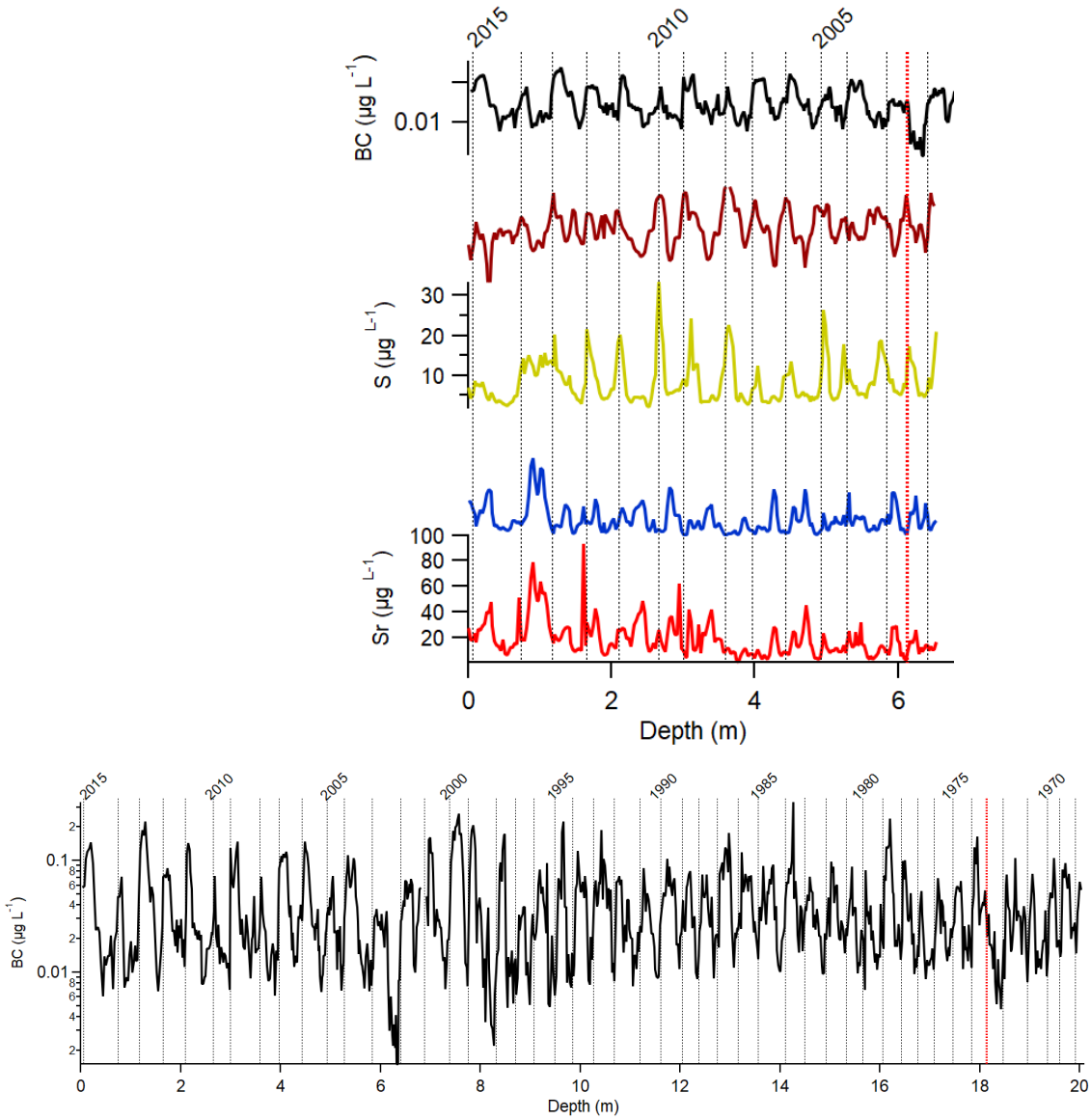


Figure 2. (a) Dating of the snow and firn core based on rBC and using S, Sr, Na and nssS/Na records from nearby core (see section 3.6) as support for the first 6.5 meters. Dashed lines indicate estimated New Year and red dotted line indicate uncertainty in dating, explained in the text. (b) Dating for the full core (y axis logarithmic). Red dotted line indicates uncertainty in dating, as explaned in the text.

Is the S, Sr, and Na data shown in Fig. 2 all from the Schwanck et al. core from _1 km away?

We opted to not use the 2008 record, which means the S, Sr and Na records in the next revision will be from the 2015 core collected a meter apart from the rBC record, down only to 6.5 m.

I would expect cores 1 km apart to have a depth offset, so I would not be confident in correlating the picks from TT07 to the Schwanck et al. core without a common dataset to both cores to linking the cores in depth. Without showing that the chemical species from the TT07 core and Schwanck core are not offset in depth, it is not advisable to guide the dating of the TT07 core with data from the Schwanck et al. core, and likewise not justified to apply annual picks based on rBC in TT07 core to the Schwanck core Na record (I can't tell if the Na spectral analysis was conducted on the TT07 age scale or the original Schwanck et al. age scale). How does the Schwanck et al. data compare to the 5.6 m of S, Sr, and Na data for the core taken immediately adjacent to the rBC core (mentioned on lines 154-155)? There should be a few years of overlapping data to compare and that would at least be a start to justify comparing the two cores in depth.

There is an overlap in the two cores, from 2008-2002, although a perfect match in peaks means a 20% distortion in the records (~0.2 water equivalent meters difference between the 2008 and 2015 cores). Due to this we decided not to use data from Schwanck et al. (2017) for dating anymore.

Furthermore, there appears to be circular logic between the dating and seasonal comparison to GFED. If indeed the drop in rBC concentration at the end of the austral summer was used as the primary annual pick, and this pick was justified by GFED/fire spot seasonality as stated in lines 161-163, how can you then draw meaningful conclusions about the timing of rBC vs. GFED (in Fig. 6a) to identify source regions? The rBC and GFED are already inherently linked based on how you defined the dating of the core. Based on GFED seasonality in Fig. 6a, BC emissions drop in November for Asia/Africa/S. America, two months before the January drop for Australia/NZ. Even a month or two difference on where the rBC drop is assigned could have significant implications for the correlations used in section 4.6 (based on n=12 months) which are used to underpin the conclusion on lines 286-289. It would be much more appropriate to date the TT07 core using an independent chemical species, and then use the independent dating to examine the rBC seasonality.

We do not see the dating as circular logic due to the use of GFED4s/fire spots data. We changed the text in section 3.6 to clarify this point:

"We considered the new year to match the end of what we define as the austral dry season, as this is a reliable tie point in the record due to the abrupt drop in rBC concentrations. Previous studies have demonstrated that rBC deposition occurs in

winter/spring, mostly September to December. For example: Arienzo et al. (2017) observed rBC concentrations to peak in September in the WAIS Divide ice core; Winstrup et al., (2017) used annual variations in rBC as the most reliable annual tracer for the Roosevelt Island Climate Evolution (RICE) ice core, stating that rBC tends to peak earlier in the year than January 1st. Pasteris et al. (2014) also corroborates rBC to peak in October and drop after for the Pine Island and Thwaites Glaciers, with lowest values from February to June. Bisiaux et al. (2012a) state that sub-annual rBC concentrations are highly seasonal in the WAIS Divide ice core for the period spanning 1850-2000 - low austral wet season and high austral dry season concentrations - and presented annual picks in the drop in rBC concentrations, as in this work. This is also consistent with the BC emission estimates from GFED4s and the fire spot databases from Australia and South America."

As for dating the core using independent chemical species, we used the trace element data as a secondary parameter to dating due to the offset that could exist between it and the rBC record. Samples are not co registered, they were not analyzed from the same core and same vial, so their resolution will be different. Using the independent chemical species to date the rBC record in monthly resolution would lead to greater uncertainty than using the rBC dating, especially considering rBC seasonality is already well defined in West Antarctica (Arienzo et al. 2017; Bisiaux et al., 2012; Winstrup et al., 2017; Pasteris et al. 2014).

Other comments

Lines 14-15: Please specify what you mean by wet and dry season? I assume southern hemisphere wet/dry season, not at the ice core site (also on lines 145-146).

We mean austral dry and wet season. Added the word "austral" in all dry/wet season citations.

Lines 87 and 82: Is Marquetto et al. (2019) published and available?

Marquetto et al. (2019) was accepted for publication in October 2019 and will be available online in April 2020 in "Advances in Atmospheric Sciences" as Marquetto et al. (2020). We have added the accepted manuscript as supplementary material for your review.

Lines 83 and 90: Same heading title for sections 3.2 and 3.3.

Corrected. Section 3.3 should be entitled: "Laboratory and vial cleaning".

Line 116: Did you average the rBC data for the full 5 minutes that it was run? Can you quantify the stability of the measurement with a standard deviation over the time period averaged?

The total rBC mass during the period of measurement, along with liquid and air flows, is used to calculate the rBC concentration for each sample using the Paul Scherrer Institute SP2 toolkit 4.200f. During sample analysis we monitored the samples to ensure that the incandescent particle concentration was stable. Liquid and air flows are also stable during analysis, as described in lines 108-115, leading to a robust measurement. We don't see the utility in in applying a standard deviation to the time period averaged, as the liquid concentration is based on the entire sampled period. The total mass of the measured particles is what is used in the calculation. For Antarctic samples, particularly the low concentration wet season (austral summer/fall), the concentrations are very low (0.015 ug/L). At these low concentrations particles are crossing the SP2 laser at a regular, but intermittent rate (i.e., the SP2 incandescent concentration can be stable, maintaining incandescent particle concentrations at 0-2 particles/cc during the analysis period).

We observed, though, that stability of the measurements depends more on sample rBC concentration than analysis time. Marquetto et al. (2020) presents this reproducibility test. We analyzed samples more than once and for different times (5, 20 and 40 minutes), and our coefficient of variation (mean of all measurements of the sample × standard deviation) did not vary with different measurement times, but was much higher for concentrations lower than 0.03 µg L^{-1} (25.7 ± 16.9%) than for higher concentrations (for concentrations between 0.03 and 0.07 µg L^{-1}, it was 10.4 ± 6.6%, and for concentrations higher than 0.07 µg L^{-1} it was 7.3 ± 4.4%.

Lines 135-143: The Brazilian hotspot data is defined here, but never mentioned in the results and discussion section. Can it be omitted? Or did it result in a null finding?

It resulted in a null finding. Line 318 briefly talks about that: "All other spectra showed only well-marked annual periodicities and intra annual periodicities of 2 and 3 cycles per year (0.5 and 0.3-year bands, not shown)."

We changed the sentence to: "All other spectra (including Programa Queimadas satellite data) showed only well-marked annual periodicities and intra annual periodicities of 2 and 3 cycles per year (0.5 and 0.3-year bands, not shown)."

Line 140: How do the timeseries of the fire hotspot data compare to the rBC data? You only compare the power spectrums in this study. Do years with more hotspots correspond to years with more rBC deposition?

This comparison can be seen in the figure below (Fig. S3 in Marquetto et al. (2020)). Years with more hotspots do not necessarily correspond to years with more rBC deposition. This is the reason why we compared the power spectrums, to identify increases and decreases in common for the datasets without looking only at the absolute values. rBC concentrations in Antarctica are not only a result of BC emissions, but also of atmospheric transport, deposition during transport and physical processes in the drilling site (Bisiaux et al. 2012), so we do not expect hotspots intensity to necessarily match years with more rBC deposition.

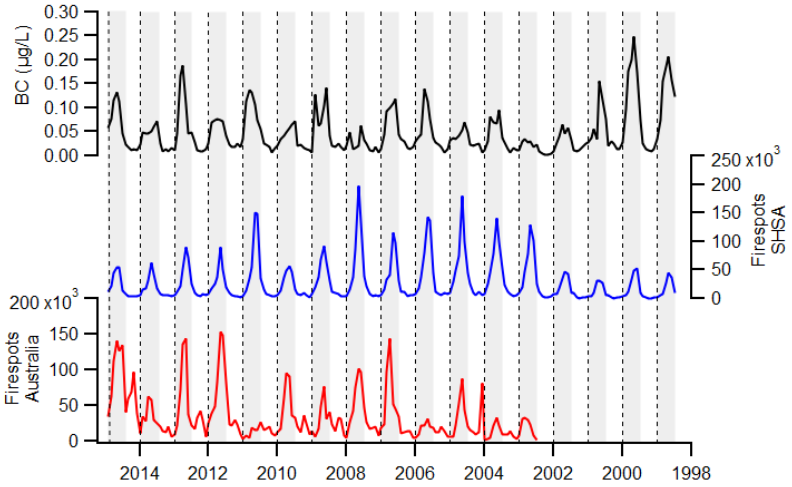


Fig. S3 from Marquetto et al. (2020). TT07 rBC record (rescaled to monthly resolution) compared to Southern Hemisphere South America (SHSA) and Australian/New Zealand firespot records.

Lines 147-148: Please define Na, Sr, and S before using abbreviations

Added definition in the abstract and in the manuscript (lines 14-15).

Lines 167-173: Please plot the average of the two density profiles in Fig. 3 that the quadratic equation was fit to.

Plotted. Density was averaged using curve fitting (polynomial terms = 3). Figure and caption are as follows:

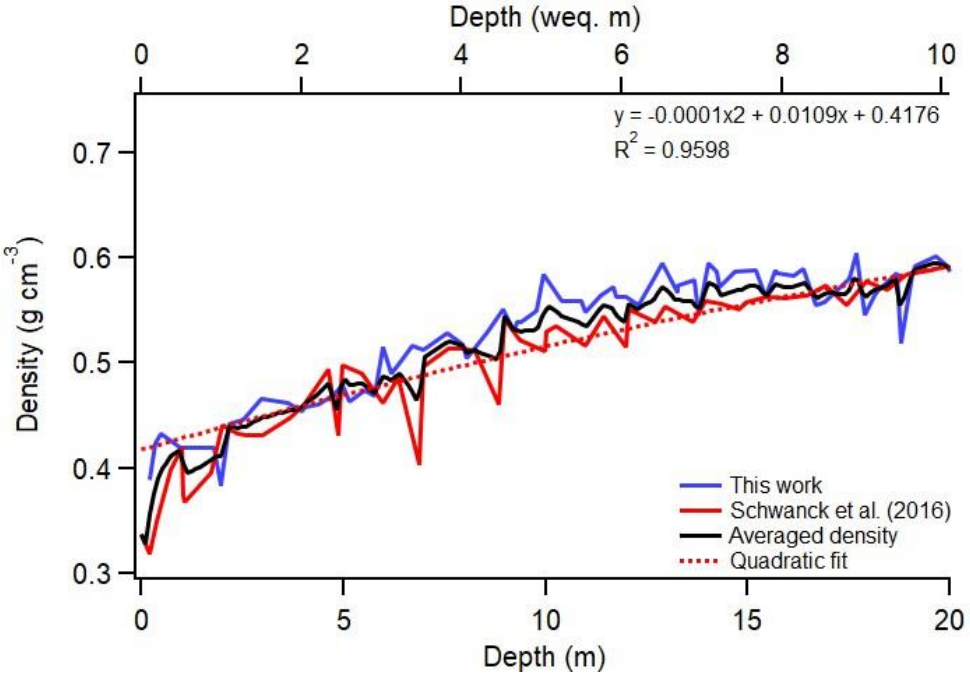


Figure 3. TT07 density profile (blue). Depth is presented in meters and water equivalent (weq) meters. The quadratic fit was calculated from the average density profile (black) from this work and from Schwanck et al. (2016).

Line 180: Please explicitly state which months went into the summer/fall and winter/spring averages.

Added to the text: summer/fall (wet season – January to June); winter/spring (dry season – July to December). We also corrected this specific line, where wet and dry season were attributed to the wrong annual seasons:

"We present our data as summer/fall (~~dry~~ wet season – January to June) concentrations and winter/spring (~~wet~~ dry season – July to December) concentrations."

Line 193 and 296: Is the Na record you use for spectral analysis from the TT07 core, or is it from Schwanck et al.? If it is from Schwanck et al., have you changed the dating?

We removed the sodium record from the spectral analysis and comparison of rBC and Na transport, as the 2015-2002 Na record is too short to show cycles in the spectrum.

Lines 211-212: Per comments above, please clarify what dating is used for which chemical species.

We removed the sodium record from the spectral analysis and comparison of rBC and Na transport, as the 2015-2002 Na record is too short to show cycles in the spectrum.

Lines 244-246: Please include comparison to rBC data from Pasteris et al. (2014) from Pine Island Glacier.

We included Pasteris et al. (2014) as a citation along our manuscript and added their data as comparison in section 4.4. Thank you for pointing this out.

Line 338: Abstract says record extends from 1968-2015.

Corrected the date to 1968-2015.

Figure 1: Please check location of B40 ice core site.

Corrected B40 site and added locations from Pasteris et al. (2014) – THW, DIV and PIG (see below)

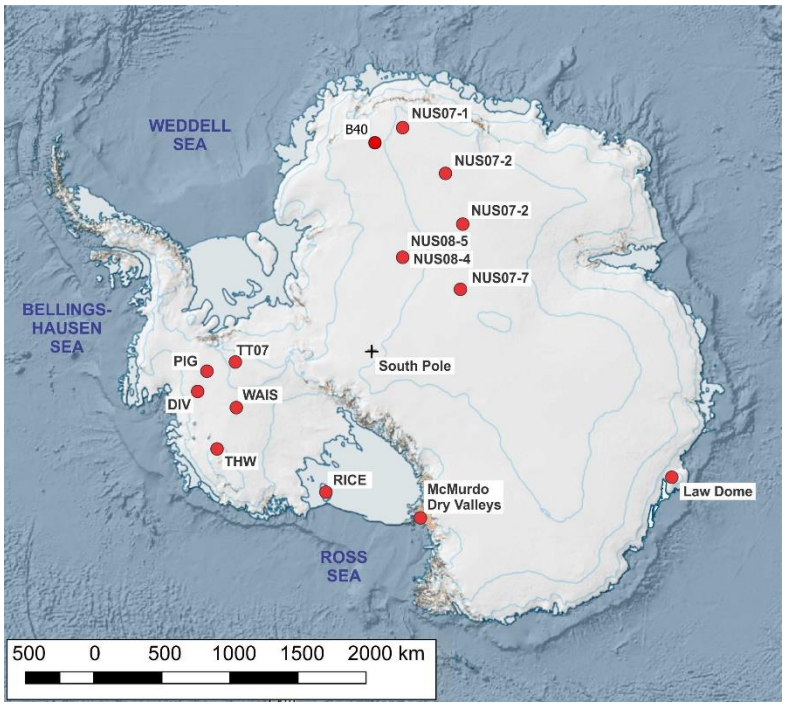


Figure 2: Please define which records are from the TT07 core and which are from Schwank et al.

As commented above, we decided not to present the 2008 core from Schwanck et al. (2017) for the dating.

Figures 4, 5: It would be helpful to include the standard deviation (or standard error) of the measurements that went into the annual averages and wet/dry season plots as an error bar.

We added the geometric standard deviation (GSD) of annual and wet/dry rBC concentrations, as in the image and caption below. We did not include standard deviations in Figure 5 as the GSD for rBC annual average is already presented in Figure 4. We opted to present GSD in shaded area instead of error bars for readability, especially in the top graph.

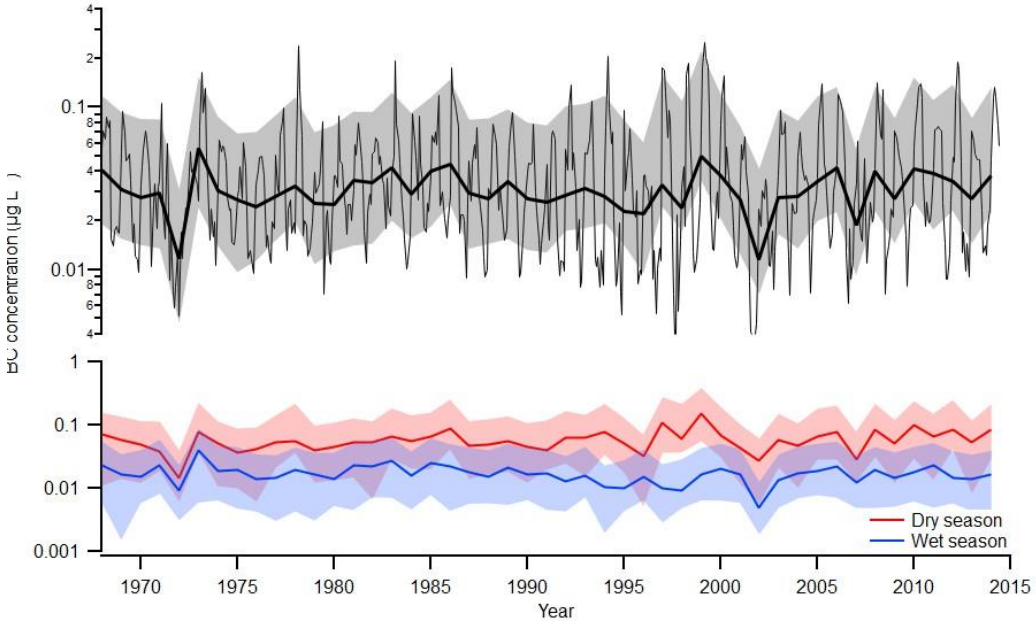


Figure 4. (top) rBC concentrations for the entire core. Black thick line represents annual averages, while black thin line represents monthly values. (bottom) Dry season and wet season average concentrations per year. Note the y axis scale is logarithmic. Shaded areas in both top and bottom represent one geometric standard deviation of the monthly values.

Figures 6, 8: Again, it would be helpful to have an estimate of uncertainty on the seasonal cycles.

Added the geometric standard deviation to Figure 6 (for rBC), as below. We decided not to present the Na and rBC seasonality comparison anymore, as there is no point relating Na and rBC now that we are not talking about cycle differences in the spectral analysis.

Note that the geometric standard deviation is broad for rBC, which was expected considering concentrations are very low and seasonal peaks vary with time (e.g. the rBC dry season peak in 1999 is much higher than the 2002 dry season peak).

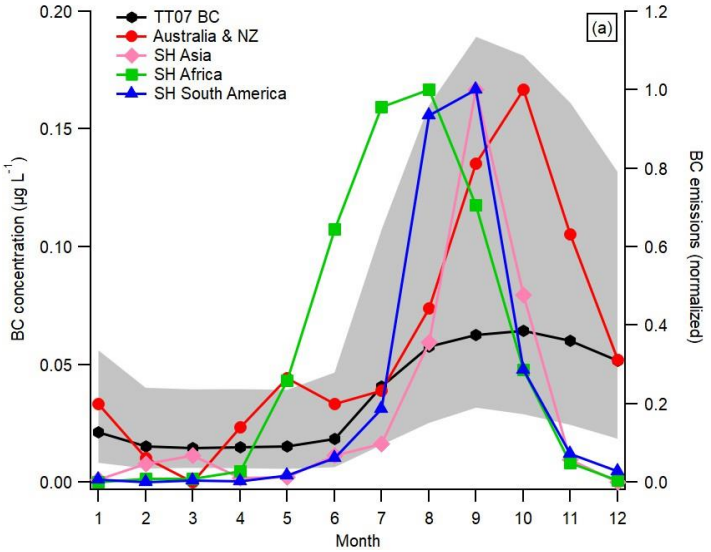


Figure 6(a). TT07 rBC (monthly averages, 1968-2014) and BC emissions estimated from GFED4s for the four SH regions (normalized, 1997-2014). Shaded area indicates rBC geometric standard deviation.

Figure 7: Did you use rBC flux or concentration for the spectral analysis?

We used rBC concentration. Added this information to the figure caption.

Figure 8: Could the broad Na peak over 4 months be a result of mixing/matching Na data and depth picks between the TT07 and Schwanck et al. cores?

As mentioned above, we are not comparing Na and rBC cycles anymore.

Table 4: Please include Pasteris et al. (2014) rBC data.

We included Pasteris et al. (2014) as a citation along our manuscript and added their data as comparison in section 4.4. Thank you for pointing this out.

Additional information regarding HYSPLIT model:

We added atmospheric transport simulations from using the HYSPLIT model to identify BC source areas. We added two additional sections, one in methodology and another in results. They are as follows:

3. Methodology

3.10 Particle trajectory simulations

In order to simulate rBC particle trajectories from source areas to the TT07 drilling site, we used the Hybrid Single-Particle Lagrangian Integrated Trajectory v4 model (HYSPLIT - Draxler and Rolph, 2003; Stein et al., 2015), from NOAA. Hysplit is a complete system for computing simple or complex transport and deposition simulations (Stein et al., 2015) that has been used in Antarctica by several authors (Dixon et al., 2011; Markle et al., 2012; Marquetto et al., 2015; Schwanck et al., 2016a, 2017; Sinclair et al., 2010).

We used global reanalysis data from the National Centers for Environmental Prediction (NCEP) and the National Center for Atmospheric Research (NCAR) – the NCEP/NCAR data set – and ran 10-day (240 h) back-trajectories, every 5 days, from 1968 to 2015, at an initial height of 1000 m. We consider 10 days to be an appropriate simulation time as this is the estimated maximum lifetime of BC in the troposphere (IPCC et al., 2013). An initial height of 1000 m was used in order to minimize disturbance from the underlying terrain, but still maintaining a link with the surface wind field (Sinclair et al., 2010). To identify main airflow patterns at the TT07 drilling site, the individual trajectories were separated into dry and wet seasons (depending on day and month of each run) and simulations from each season were grouped into five clusters using the HYSPLIT model's cluster analysis algorithm.

4. Results

4.8 Particle trajectory simulations using HYSPLIT

We simulated particle transport during the austral wet and dry seasons as another mean of addressing rBC source areas. We ran the HYSPLIT back-trajectory model every five days from 1968 to 2015, for 10 days each (estimated maximum BC lifetime in the troposphere) and clustered the results in five groups for the wet and dry seasons (Fig. 9).

The majority of simulated air parcels arriving at the drilling site presented a slow-moving trajectory (speed is proportional to trajectory length), reflecting a local/regional influence more than long-range transport from other continents (clusters 3 and 4 in Figure 9). This local/regional influence is observed both in the wet and dry seasons, although during the former the contribution of air masses from the Antarctic Peninsula and across (Weddell Sea) are higher than during the latter. A fast-moving, year-round, continental group is also present (cluster 5), and may partly represent katabatic winds flowing from the continent's higher altitudes (East Antarctica) towards lower-altitude West Antarctica. The strongest contribution of long-range air parcels is from the South Pacific (clusters 1 and 2). These air masses are also fast-moving and present slight

seasonal variations, shifting pole wards during the wet season, when they represent 34% of all air parcels, and away from Antarctica during the dry season, when they respond for 22% of all air parcels modelled.

Results from clusters 1 and 2, along with individual trajectories of each cluster (Fig. 10) support our conclusion that Australia and New Zealand are the most probable sources of rBC to the drilling site, considering tropospheric transport. The most visible influence of air parcels from these two countries to the drilling site can be seen in the individual trajectories of cluster 1 (Fig. 10) for both dry and wet season, while for cluster 2 and 4 there are trajectory variations from one season to another. The poleward shift of cluster 1 trajectories in the wet season (Fig. 9) may be a reason why the Australian emissions earlier in the year (May) are not visible in the TT07 rBC record. South American influence to the TT07 drilling site, on the other hand, is restricted to the higher latitude countries (Chile, Argentina), as shown in the individual trajectories of clusters 2, 3 and 5 (Fig. 10). This suggests that South American fires are not significant contributors to the rBC concentrations observed at the TT07 site when considering only tropospheric transport.

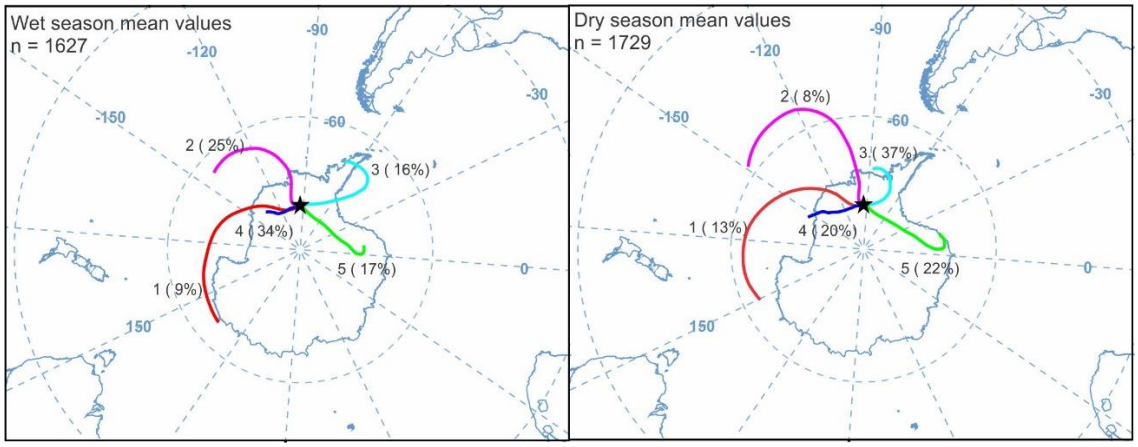


Figure 9. HYSPLIT clusters of 10-day back-trajectories ran every 5 days from 1968 to 2015 arriving at the TT07 drilling site. Results are separated by wet and dry season, and grouped in five clusters (percentage of trajectories for each cluster is shown in parenthesis). Number of trajectories (n) used for the cluster algorithm is shown at the top, on the left side.

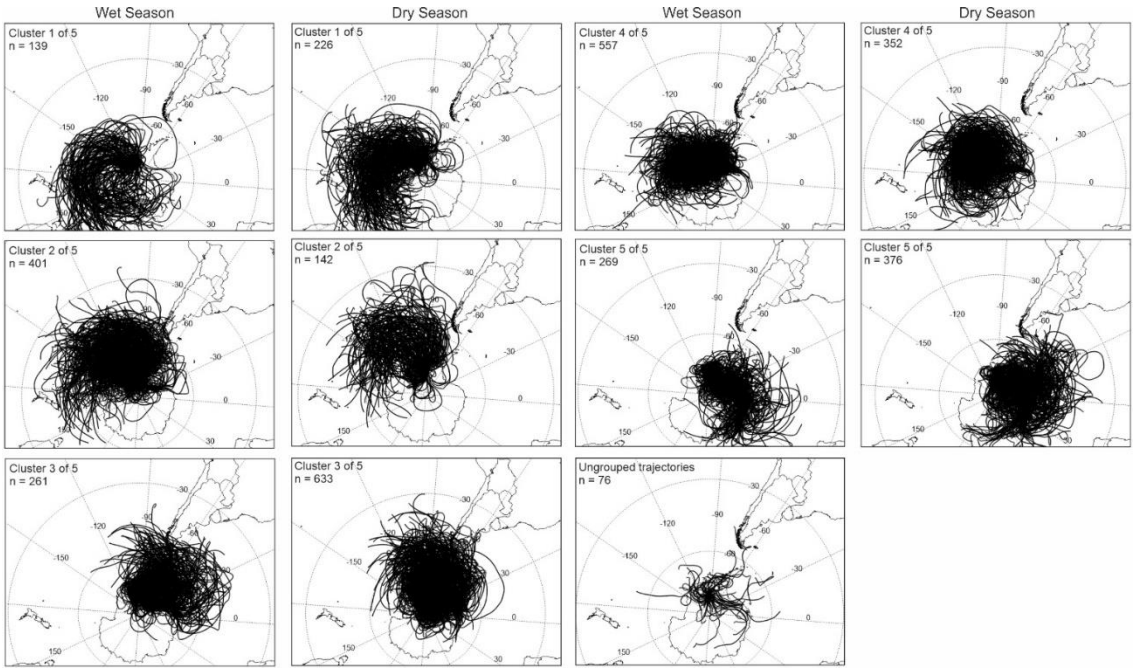


Figure 10. Individual trajectories used for the cluster analysis in figure 8. Number of trajectories (n) used for each cluster is shown at the top, on the left side. Clusters 1, 2 and 4 show air masses arriving from Australia and New Zealand to the TT07 drilling site, while clusters 2, 3 and 4 show the (limited) contribution of South American air parcels to the site. Similar clusters from wet and dry season are side by side for comparison. Wet season presented 76 ungrouped trajectories, while dry season presented none.

Additional information in section 4.4 of the manuscript:

Figure 6 shows a comparison of the above mentioned rBC records with snow accumulation, elevation and distance from open sea. Distance from the sea influences rBC fluxes in West Antarctica (Arienzo et al., 2017), and was calculated considering the median sea ice extent from 1981 to 2010 for September (Matsuoka et al., 2018), when rBC emissions start to rise in South America/Australia/New Zealand and rBC concentrations begin to rise in West Antarctica (Arienzo et al., 2017; Bisiaux et al., 2012b; Pasteris et al., 2014). We measured the distance from the rBC records to the closest open sea source (Amundsen sea for West Antarctic records, Lazarev to Cosmonauts sea for NUS0X-X and Mawson sea for Law Dome). We acknowledge this is a simplistic approximation and that the preferred air mass pathways from the sea to the points are not as straightforward, but for the scope of this work we consider this approximation sufficient.

No patterns are clear for both East and West Antarctica, whereas when considering the data from East and West Antarctica separately, opposite trends are observed. In East Antarctica, rBC concentrations have a negative correlation with snow accumulation and positive correlation with elevation and distance to the sea, whereas in West Antarctica rBC concentrations present a positive correlation with snow accumulation and a negative correlation with elevation and distance to the sea.

We observed that for East Antarctica, rBC x snow accumulation and rBC x elevation presented statistically significant correlations ($r^2 = 0.78$, $p < 0.01$ for the former and $r^2 = 0.79$, $p < 0.01$ for the latter). On the other hand, distance from the sea does not seem to correlate with rBC ($r^2 = 0.52$, $p = 0.06$).

For West Antarctica, relationships are the opposite: positive correlation between rBC concentrations and snow accumulation ($r^2 = 0.69$, $p = 0.08$) and negative correlations between rBC concentrations and elevation/distance from the sea ($r^2 = 0.30$, $p < 0.33$ for the former and $r^2 = 0.79$, $p < 0.05$ for the latter). McMurdo and South Pole points are not considered in this calculation as they likely reflect local contamination instead of long-range transport (Casey et al., 2017; Khan et al., 2018). Bisiaux et al. (2012b) have also observed negative (positive) relationships between rBC concentrations and snow accumulation (elevation) for East Antarctica, although their comparison also included the WAIS Divide point to the dataset.

These opposite trends may indicate differences in rBC transport to East and West Antarctica. While for East Antarctica upper tropospheric transport and dry deposition may be the main controllers of rBC concentrations (Bisiaux et al., 2012b), for West Antarctica rBC concentrations may be modulated by intrusion of air masses from the marine boundary layer. Low elevations in West Antarctica facilitates the intrusion of moisture-rich cyclones and the transport of aerosols inland (Neff and Bertler, 2015; Nicolas and Bromwich, 2011), while the positive relationship between West Antarctica rBC concentrations and snow accumulation may indicate rBC to be primarily deposited through wet deposition, being scavenged along the coastal regions were snow accumulation is higher.

Response to Anonymous Referee #2 comment

Received and published: 1 January 2020

Dear Anonymous Referee,

We thank you for your time, expertise, and helpful suggestions.

We apologize for the inconvenience that Marquetto et al. (2019) was not available during the review process. Marquetto et al. (2019) was accepted for publication in October 2019 and will be available online in April 2020 in "Advances in Atmospheric Sciences" as Marquetto et al. (2020). We have added the accepted manuscript as supplementary material for your review. Considering our system setup and calibrations carried out for the SP2, we believe the rBC concentrations found in this work are solid results, as described with more details along the text.

We made several improvements to the manuscript based on the reviewer's suggestions. First, we opted to remove the 2008 trace element records from the dating section. Although the 2015 and 2008 cores presented an overlap of 7 years (2002-2008), there is a 20% distortion between them in order to match both. This raised an issue about using a core 850 m away, with topographical differences, to date the rBC core. We decided this brings more uncertainty to our work than using the 2015 trace element record to constrain the dating down to 2002, and then base the rest of the dating on the relations of rBC, Na, Sr and S observed for the 2015-2002 period.

We also removed the sodium record from the spectral analysis and comparison of rBC and Na transport, as the 2015-2002 Na record is too short to show cycles in the spectrum.

On the other hand, we added atmospheric transport simulations using the HYSPLIT model to identify BC source areas. Results corroborated our initial conclusions of Australia and New Zealand as the most probable sources of BC to the TT07 drilling site, and indicated limited influence of South American air masses. More information is presented at the end of this document, after responses to reviewer's suggestions.

We also added a comparison of the Antarctic rBC records with snow accumulation, elevation and distance from open sea. In East Antarctica, rBC concentrations have a negative correlation with snow accumulation and positive correlation with elevation and distance to the sea, whereas in West Antarctica rBC concentrations present a positive

correlation with snow accumulation and a negative correlation with elevation and distance to the sea.

These opposite trends may indicate differences in rBC transport to East and West Antarctica. While for East Antarctica upper tropospheric transport and dry deposition may be the main controllers of rBC concentrations (Bisiaux et al., 2012b), for West Antarctica rBC concentrations may be modulated by intrusion of air masses from the marine boundary layer, contrary to what was previously suggested (Bisiaux et al., 2012a). Low elevations in West Antarctica facilitates the intrusion of moisture-rich cyclones and the transport of aerosols inland (Neff and Bertler, 2015; Nicolas and Bromwich, 2011), while the positive relationship between West Antarctica rBC concentrations and snow accumulation may indicate rBC to be primarily deposited through wet deposition, being scavenged along the coastal regions were snow accumulation is higher.

The rBC record we present in this work is from an unique area – the Pine Island/Institute Glacier Divide, where air masses from the Weddel and Bellingshausen Seas converge (Parish and Bromwich, 2007), and is the highest altitude rBC core collected in West Antarctica. Considering all these improvements and new findings, we believe our manuscript is suitable for The Cryosphere.

Please find our responses in italic, while we kept your original comments in normal text.

Original referee comment:

The paper provides a 47-year ice core record of refractory black carbon (rBC) from West Antarctica, specifically Pine Island Glacier. rBC was analyzed by a Single Particle Soot Photometer. The core was dated to 1968, primarily using seasonality of rBC. BC impacts on snow albedo were modeled using the Snow, Ice, Aerosol, Radiation (SNICAR) model. BC emissions were explored with fire spot inventories and spectral analysis was conducted by the REDFIT method.
With respect to the TC guidelines: 1. The paper provides additional field observations of rBC in snow and ice in a data-sparse region of the cryosphere. Making field observations like this available to the community is important for refining our understanding of impurities in the cryosphere and their impact on surface albedo of the Antarctic ice sheet. 2. While the paper provides an additional valuable dataset, it is unclear to me whether the record interpretation is particularly novel. 3. The main finding appears to be that BC transport to the site is not related to marine air masses, which has previously been shown in other ice core records in Antarctica (i.e. Bisiaux et al., 2012). 4. The analytical details appear to be outline in Marquetto et al., 2019, however, I am having trouble locating the manuscript. 5. Thus, I have some remaining analytical questions outlined below. 6. Having access to Marquetto et al., 2019 would assist with reproducibility. 7. The authors provide credit to related work, but I think they should further identify/emphasize the novelty of their contribution. 8. The title clearly reflects the content of

the paper. 9. The abstract provides a concise and complete summary of the existing manuscript. 10. The paper could have benefited from more thorough proofreading before submission; there are some typos. 11. Please refer to 10. 12. Black carbon and refractory black carbon are abbreviated at times and then spelled out at others (i.e. Lines 36, 67, 338). 13. Current figures and tables seem to appropriately support the text. 14. The number of references seems appropriate. 15. The Marquetto et al., 2019 paper would have been useful supplementary information.

Responses
4: Marquetto et al. (2019) was accepted for publication in October 2019 and will be available online in April 2020 in "Advances in Atmospheric Sciences" as Marquetto et al. (2020). The accepted manuscript has been added as supplementary material.
5: Along with providing the Marquetto et al. (2020) file, we added additional analytical information in the manuscript based on your suggestions, as is detailed below.
6: Marquetto et al. (2020) is available as supplementary information.
7: We improved our manuscript, as already mentioned above. Additional information is given at the end of this document, after responses to the reviewer.
12: We are now consistent with using abbreviated versions.
15: Marquetto et al. (2020) is available as supplementary information.

Specific Suggestions:

Line 29: Typo: 'while there they change'

Changed the sentence to: "BC particles stay in the atmosphere for just one week to 10 days (Bond et al., 2013; Ni et al., 2014), but ~~while there~~ during that time they change the direct radiative forcing..."

Line 45 – 48: Sentence could be restructured for clarity.

Changed the sentence to: "More ice core records are needed to understand the spatial variability of BC transport and deposition to Antarctica, as well as to improve general circulation models (Bisiaux et al., 2012b). In this work we add another high-temporal-resolution rBC record from a West Antarctic snow and firn core to the existing literature, in order to contribute to the understanding of BC temporal and spatial variability in Antarctica.

Line 58 – 61: This section could be expanded, including more specific references.

Added more information in this section, see below in red color:

The core (TT07) was drilled in the 2014-2015 austral summer on the Pine Island Glacier (West Antarctica) at 79°55'34.6"S, 94°21'13.3"W (elevation 2122 m above sea level – a.s.l.), near the Mount Johns Nunatak (located 70 km NE of the drilling site) (Fig. 1) and close to the Institute/Pine Island ice divide. The drilling site was chosen due to its relatively high accumulation rate, that ensures a well preserved seasonal stratigraphic record (Schwanck et al., 2016; Thoen et al., 2018), as well as the region being influenced by air masses from the Weddel, Amundsen and Belingshausen seas (Parish and Bromwich, 2007; Thoen et al., 2018).
The West Antarctic Ice Sheet (WAIS) presents lower elevation and lower coastal slopes than the East Antarctic Ice Sheet (EAIS), which facilitates the intrusion of moisture-rich cyclones to the interior of the continent and the transport of aerosols inland (Neff and Bertler, 2015; Nicolas and Bromwich, 2011). *Katabatic winds at the drill site are not as strong as they are in most of West Antarctica, due to the higher site elevation compared to the surrounding region* (Parish and Bromwich, 2007). *Seasonal differences in atmospheric transport have been reported for the TT07 drilling site, with particle trajectories during the austral summer being slow moving and more locally influenced, while during the winter, air trajectories are influenced by oceanic air masses due to strong westerlies. The majority of air masses arrive from the Amundsen Sea and, secondarily, from across the Antarctic Peninsula and Weddell Sea* (Schwanck et al., 2017). *These are also the preferred pathway for dust particles* (Neff and Bertler, 2015).

Line 77: I cannot find Marquetto et al., 2019 online. Thus, a lot of important analytical details seem to be missing from this manuscript. For example, how long before analysis were the samples melted?

Marquetto et al. (2020) has been added as a supplement. We added melt time information in the first paragraph of section 3.3: "Samples were melted at room temperature or in a tepid bath not exceeding 25°C, sonicated for 15 min, and then analyzed with one hour of melting."

Lines 83 and 90: Duplicate sub-section titles.

Corrected. Section 3.3 should be entitled: "Laboratory and vial cleaning".

Line 87: Why were polypropylene vials used instead of glass vials? Was particle loss explored with leaching on the vials? Additionally, how long did the samples sit in the vials before analysis?

Polypropylene vials are widely used for rBC analysis in the SP2. Previous work has tested polypropylene vs glass, and found that polypropylene vials are as suitable to glass

unless the sample is left in the liquid state for an extended period of time (Wendl et al., 2014)*, which was not the case in this study. Samples were melted shortly after analysis.*

Line 146: I don't think Sr is mentioned in Legand and Mayewski, 1997.

Corrected and added bibliography for Sr, as Legrand and Mayewski (1997) cite only Na. The full sentence is now: "Na and Sr also peak in the dry season (during winter) due to intense atmospheric circulation and transport (Legrand and Mayewski, 1997; Schwanck et al., 2017). Increased marine biogenic activity reflects an increase in S in late austral summer (Schwanck et al., 2017; Sigl et al., 2016) .

Line 197: Suggest 'fit' as opposed to 'fitted'.

Suggestion accepted, thank you.

Line 199: Suggest using the same past tense, 'chose' as opposed to 'choose'.

Suggestion accepted, thank you.

Section 4.1 Dating: Given that the main findings of the paper rely on dating based on seasonality of the rBC record, I think this section could be expanded. For example, the authors could add more discussion as to why the authors think the addition of the rBC record to the layer counting would lead to a dating difference of one year or more, with respect to the core collected nearby that was analyzed for trace elements.

We opted to use only the 2015 trace element record for dating and constrain the rest of the dating based on the rBC well defined seasonality for West Antarctica (Arienzo et al. 2017; Bisiaux et al., 2012; Winstrup et al., 2017) and for the Pine Island Glacier (Pasteris et al. 2014).

To improve our dating for these first meters we reviewed sample resolution for the rBC and trace element cores, and added an additional parameter to dating: the maxima in the non-sea-salt sulfur to sodium (nssS/Na) ratio, a robust seasonal indicator that peaks around the new year (Arienzo et al. 2017). This parameter helps in the identification of the annual layers more than the Na and S records alone. Non-sea-salt sulfur was calculated using Eq. 3 to 6 from Schwanck et al. (2017) and references therein.

We consider this dating to have ±2 years uncertainty. The first uncertain year is located at 6.18 m (between 2003 and 2002, figure 2a), where S and nssS/Na peak but no full cycle is observed in the rBC record. We did not consider this to be a year, as rBC does not present a full cycle. The second uncertain year is located at 18.14 m (year 1973,

figure 2b) where there is no clear rBC peak but snow accumulation would be anomalously high if considered to be only a year instead of two. We consider this to be an annual pick and consequently two years, as there is no evidence of higher-than-normal snow accumulation in the region for this period (Kaspari et al., 2004).

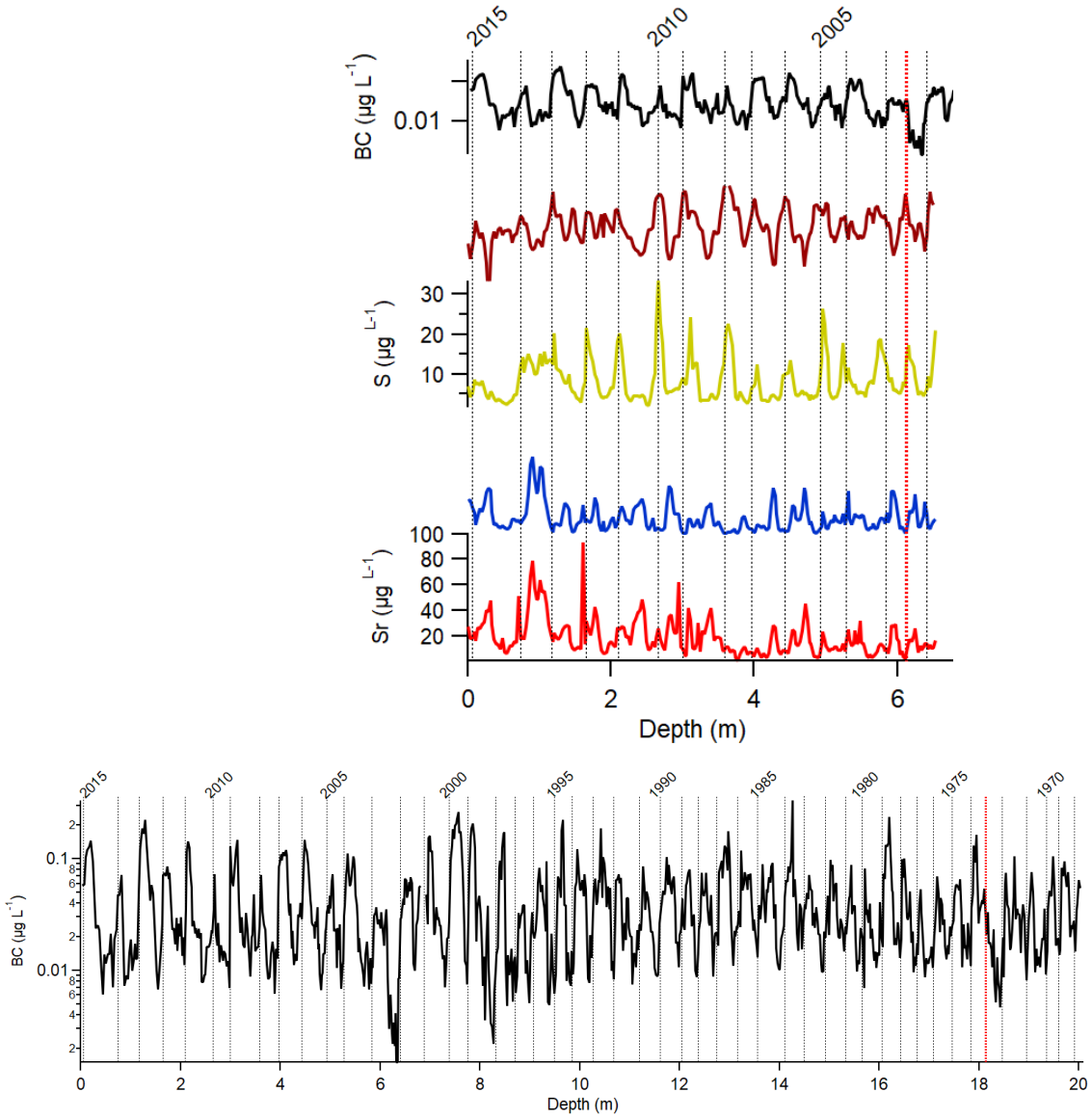


Figure 2. (a) Dating of the snow and firn core based on rBC and using S, Sr, Na and nssS/Na records from nearby core (see section 3.6) as support for the first 6.5 meters. Dashed lines indicate estimated New Year and red dotted line indicate uncertainty in dating, explained in the text. (b) Dating for the full core (y axis logarithmic). Red dotted line indicates uncertainty in dating, as explaned in the text.

Line 338: The starting date here (1969 – 2015) does not match the abstract or Table 4 (1968 – 2015).

Corrected the date to 1968-2015.

Figure 4 Legend: Suggest (bottom) instead of (base).

Suggestion accepted, thank you.

Additional information regarding HYSPLIT model:

We added atmospheric transport simulations from using the HYSPLIT model to identify BC source areas. We added two additional sections, one in methodology and another in results. They are as follows:

3. Methodology

3.10 Particle trajectory simulations

In order to simulate rBC particle trajectories from source areas to the TT07 drilling site, we used the Hybrid Single-Particle Lagrangian Integrated Trajectory v4 model (HYSPLIT - Draxler and Rolph, 2003; Stein et al., 2015), from NOAA. Hysplit is a complete system for computing simple or complex transport and deposition simulations (Stein et al., 2015) that has been used in Antarctica by several authors (Dixon et al., 2011; Markle et al., 2012; Marquetto et al., 2015; Schwanck et al., 2016a, 2017; Sinclair et al., 2010).

We used global reanalysis data from the National Centers for Environmental Prediction (NCEP) and the National Center for Atmospheric Research (NCAR) – the NCEP/NCAR data set – and ran 10-day (240 h) back-trajectories, every 5 days, from 1968 to 2015, at an initial height of 1000 m. We consider 10 days to be an appropriate simulation time as this is the estimated maximum lifetime of BC in the troposphere (IPCC et al., 2013). An initial height of 1000 m was used in order to minimize disturbance from the underlying terrain, but still maintaining a link with the surface wind field (Sinclair et al., 2010). To identify main airflow patterns at the TT07 drilling site, the individual trajectories were separated into dry and wet seasons (depending on day and month of each run) and

simulations from each season were grouped into five clusters using the HYSPLIT model's cluster analysis algorithm.

4. Results

4.8 Particle trajectory simulations using HYSPLIT

We simulated particle transport during the austral wet and dry seasons as another mean of addressing rBC source areas. We ran the HYSPLIT back-trajectory model every five days from 1968 to 2015, for 10 days each (estimated maximum BC lifetime in the troposphere) and clustered the results in five groups for the wet and dry seasons (Fig. 9).

The majority of simulated air parcels arriving at the drilling site presented a slow-moving trajectory (speed is proportional to trajectory length), reflecting a local/regional influence more than long-range transport from other continents (clusters 3 and 4 in Figure 9). This local/regional influence is observed both in the wet and dry seasons, although during the former the contribution of air masses from the Antarctic Peninsula and across (Weddell Sea) are higher than during the latter. A fast-moving, year-round, continental group is also present (cluster 5), and may partly represent katabatic winds flowing from the continent's higher altitudes (East Antarctica) towards lower-altitude West Antarctica. The strongest contribution of long-range air parcels is from the South Pacific (clusters 1 and 2). These air masses are also fast-moving and present slight seasonal variations, shifting pole wards during the wet season, when they represent 34% of all air parcels, and away from Antarctica during the dry season, when they respond for 22% of all air parcels modelled.

Results from clusters 1 and 2, along with individual trajectories of each cluster (Fig. 10) support our conclusion that Australia and New Zealand are the most probable sources of rBC to the drilling site, considering tropospheric transport. The most visible influence of air parcels from these two countries to the drilling site can be seen in the individual trajectories of cluster 1 (Fig. 10) for both dry and wet season, while for cluster 2 and 4 there are trajectory variations from one season to another. The poleward shift of cluster 1 trajectories in the wet season (Fig. 9) may be a reason why the Australian emissions earlier in the year (May) are not visible in the TT07 rBC record. South American influence to the TT07 drilling site, on the other hand, is restricted to the higher latitude countries (Chile, Argentina), as shown in the individual trajectories of clusters 2, 3 and 5 (Fig. 10). This suggests that South American fires are not significant contributors to the rBC concentrations observed at the TT07 site when considering only tropospheric transport.

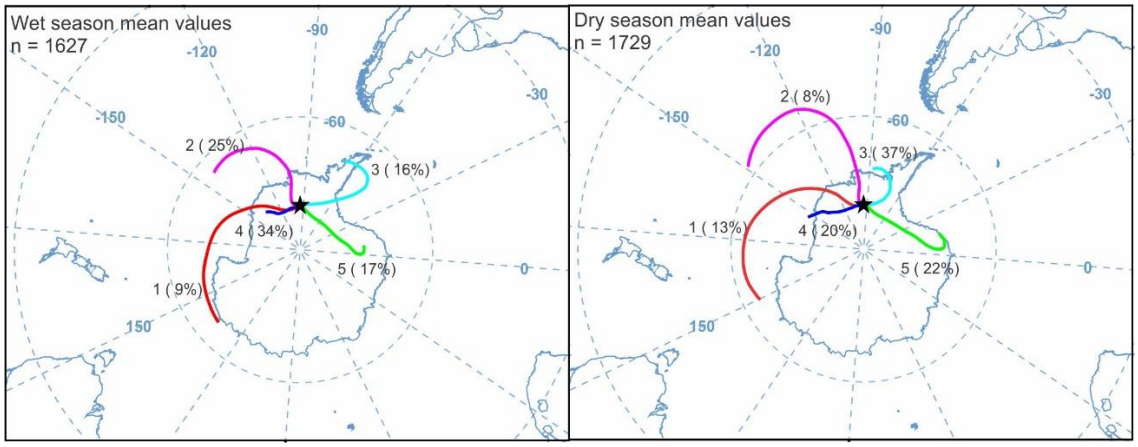
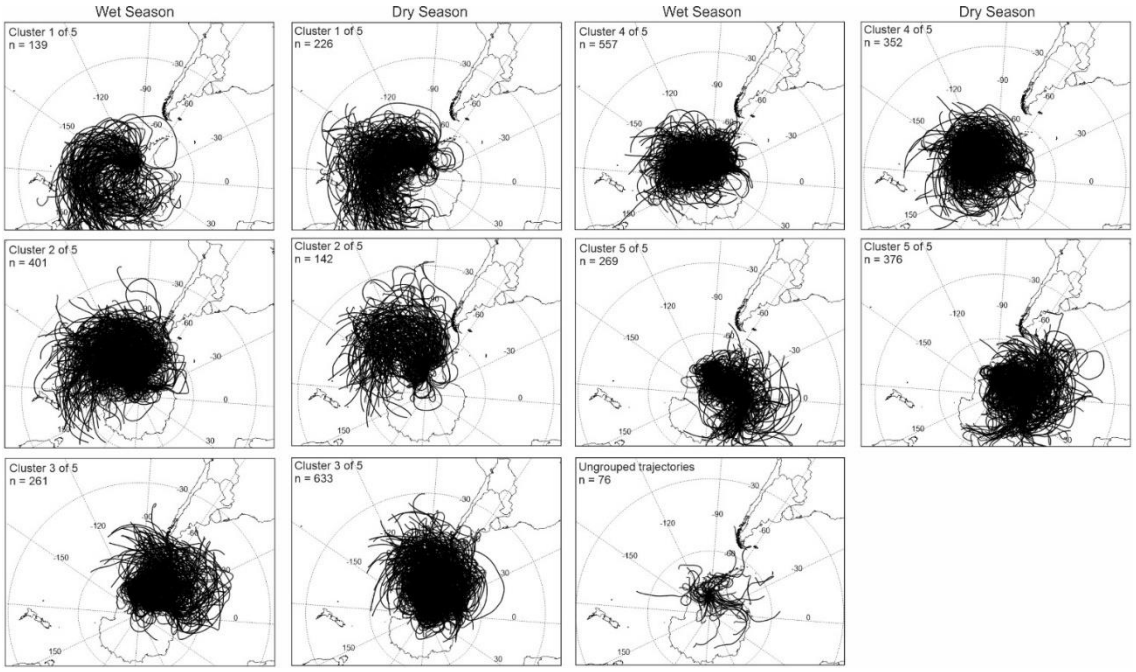


Figure 9. HYSPLIT clusters of 10-day back-trajectories ran every 5 days from 1968 to 2015 arriving at the TT07 drilling site. Results are separated by wet and dry season, and grouped in five clusters (percentage of trajectories for each cluster is shown in parenthesis). Number of trajectories (n) used for the cluster algorithm is shown at the top, on the left side.



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Additional information in section 4.4 of the manuscript:

Figure 6 shows a comparison of the above mentioned rBC records with snow accumulation, elevation and distance from open sea. Distance from the sea influences rBC fluxes in West Antarctica (Arienzo et al., 2017), and was calculated considering the median sea ice extent from 1981 to 2010 for September (Matsuoka et al., 2018), when rBC emissions start to rise in South America/Australia/New Zealand and rBC concentrations begin to rise in West Antarctica (Arienzo et al., 2017; Bisiaux et al., 2012b; Pasteris et al., 2014). We measured the distance from the rBC records to the closest open sea source (Amundsen sea for West Antarctic records, Lazarev to Cosmonauts sea for NUS0X-X and Mawson sea for Law Dome). We acknowledge this is a simplistic approximation and that the preferred air mass pathways from the sea to the points are not as straightforward, but for the scope of this work we consider this approximation sufficient.

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These opposite trends may indicate differences in rBC transport to East and West Antarctica. While for East Antarctica upper tropospheric transport and dry deposition may be the main controllers of rBC concentrations (Bisiaux et al., 2012b), for West Antarctica rBC concentrations may be modulated by intrusion of air masses from the

marine boundary layer. Low elevations in West Antarctica facilitates the intrusion of moisture-rich cyclones and the transport of aerosols inland (Neff and Bertler, 2015; Nicolas and Bromwich, 2011), while the positive relationship between West Antarctica rBC concentrations and snow accumulation may indicate rBC to be primarily deposited through wet deposition, being scavenged along the coastal regions were snow accumulation is higher.

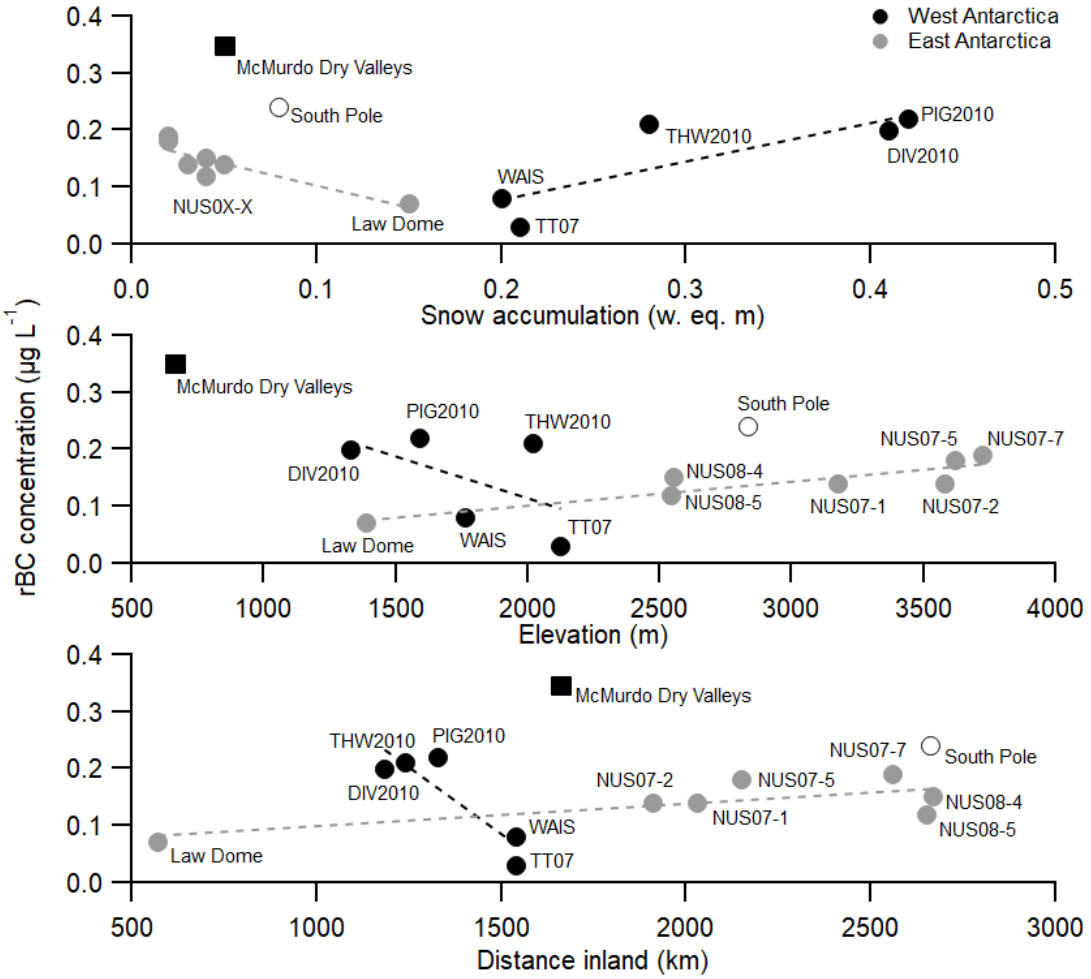

Figure 6. rBC records from Antarctica. rBC concentrations plotted against snow accumulation, elevation and distance from the sea. Solid lines indicate statistically significant correlations ($p < 0.05$), while dashed lines indicate not significant correlations ($p > 0.05$).

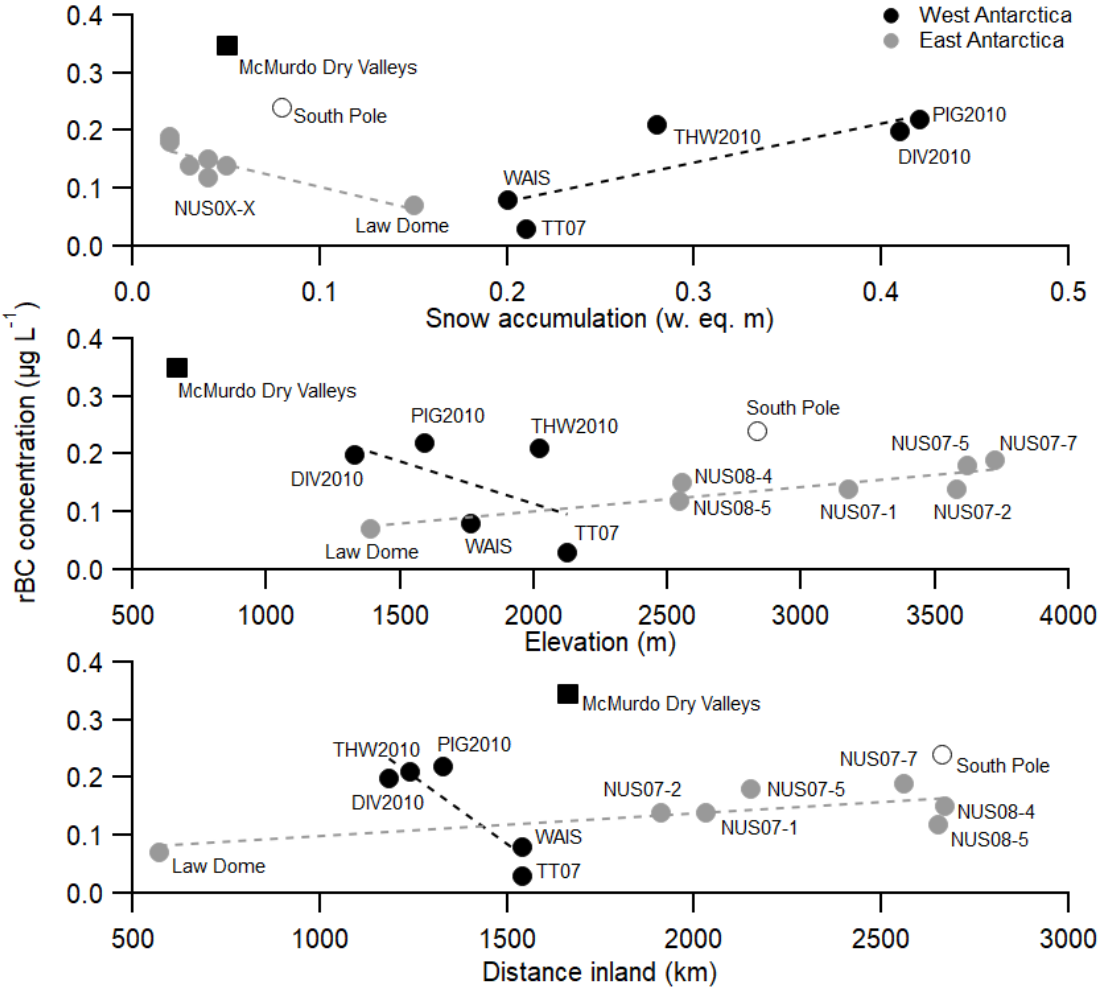

Figure 6. rBC records from Antarctica. rBC concentrations plotted against snow accumulation, elevation and distance from the sea. Solid lines indicate statistically significant correlations ($p < 0.05$), while dashed lines indicate not significant correlations ($p > 0.05$).

Refractory Black carbon (rBC) variability in a 47-year West Antarctic Snow and Firn core

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Abstract. Black carbon (BC) is an important climate-forcing agent that affects snow albedo. In this work, we present a record of refractory black carbon (rBC) variability, measured from a 20-meter deep snow and firn core drilled in West Antarctica (79°55'34.6"S, 94°21'13.3"W, 2122 m above sea level) during the 2014-2015 austral summer. This is the highest elevation rBC record from West Antarctica. The core was analyzed using a Single Particle Soot Photometer (SP2) coupled to a CETAC Marin-5 nebulizer. Results show a well-defined seasonality with geometric mean concentrations of 0.015 µg L^{-1} for the wet season (austral summer/fall) and 0.057 µg L^{-1} for the dry season (austral winter/spring). The core was dated to 47 years (1968-2015) using rBC seasonality as the main parameter, along with Sodium (Na), Sulfur (S) and Strontium (Sr) variations. The annual rBC concentration geometric mean was 0.03 µg L^{-1}, the lowest of all rBC cores in Antarctica referenced in this work, while the annual rBC flux was 6.25 µg m^{-2} a^{-1}, the lowest flux in West Antarctica rBC records. No long-term trend was observed~~.~~. Snow albedo reductions at the site due to BC were simulated using SNICAR-online and found to be insignificant ~~very low~~ (-0.48%) compared to clean snow ~~(-0.48%)~~. Fire spots inventory and BC emission estimates from the Southern Hemisphere suggest Australia and Southern Hemisphere South America as the most probable emission sources of BC to the drilling site, whereas Hysplit model particle transport simulations from 1968 to 2015 support Australia and New Zealand as rBC sources, with limited contributions from South America. Spectral analysis (REDFIT method) of the BC record showed cycles related to the Antarctic Oscillation (AAO) and ~~but not~~ to El Niño Southern Oscillation (ENSO), but cycles in common with the Amundsen Sea Low (ASL) were not detected.~~, and comparison with the co-registered Na record suggests that BC transport to the site is not related to the intrusion of marine air masses.~~ Correlation of rBC records in Antarctica with snow accumulation, elevation and distance to the sea suggests rBC transport to East Antarctica is different from transport to West Antarctica.

1 Introduction

Black carbon (BC) is a carbonaceous aerosol formed during incomplete combustion of biomass and fossil fuels, characterized by strong absorption of visible light and resistance to chemical transformation (Petzold et al., 2013), and plays an important role in the climatic system by being able to alter the planetary albedo (McConnell et al., 2007; Ni et al., 2014). ~~Black carbon~~BC-containing aerosols are the species most commonly identified as being short-lived climate forcers, along with methane and ozone (AMAP, 2015). BC particles stay in the atmosphere for just one week to ten days (Bond et al., 2013; Ni et al., 2014), but during that time ~~while there~~ they change the direct radiative forcing at the top of the atmosphere by absorbing and scattering sunlight, with high spatial and temporal variability on regional scales (Bond et al., 2013). In some parts of the globe, the impact of BC on the climate can be even higher than greenhouse gasses (Bice et al., 2009). Globally BC is estimated to be second only to CO_2 in its contribution to climate forcing, with +1.1 W m^{-2} for the industrial era (1750-2005) (Bond et al., 2013; Ramanathan and Carmichael, 2008)

Increases in BC concentrations in the cryosphere since the industrial revolution have been observed, with most studies focusing on the Arctic, the Himalayas, and European glaciers as these ice caps are close to large urban centers and consequently are influenced by these. Antarctica is a pristine environment far from the rest of the world, but ~~black carbon~~BC can still be found in its atmosphere, snow and ice, as shown by early studies (Chýlek et al., 1987, 1992; Warren and Clarke, 1990). Although there are local emissions of BC due to scientific and touristic activities (Casey et al., 2017; Stohl and Sodemann, 2010), Antarctic ice also records Southern Hemisphere (SH) emissions and long-range transport of BC from low and mid-latitudes (Bisiaux et al., 2012a, 2012b; Pasteris et al., 2014), with BC concentrations in Antarctica being linked to biomass burning from South America, Africa and Australia (Arienzo et al., 2017; Koch et al., 2007; Stohl and Sodemann, 2010). Even tropical latitude emissions have a measurable influence on the continent (Fiebig et al., 2009).

Although there are several records of SH paleo-biomass burning, there are only a few publications on BC variability in ice cores from Antarctica. Some of those are focused on centennial-millennial timescales (Arienzo et al., 2017; Chýlek et al., 1992), and others on annual to decadal scales (Bisiaux et al., 2012a, 2012b; Pasteris et al., 2014). ~~As m~~More ice core records are needed to understand the spatial variability of BC transport and deposition to Antarctica, as well as to improve general circulation models (Bisiaux et al., 2012b)~~, this work aims to add another high temporal resolution rBC record from a West Antarctic snow and firn core to the existing literature~~. In this work we present a new West Antarctic high-temporal-resolution rBC snow/firn core record. This record is the highest West Antarctic rBC record produced to date, and contributes to the understanding of BC temporal and spatial variability in Antarctica.

2 Site Description and Field Campaign

The core (TT07) was drilled in the 2014-2015 austral summer on the Pine Island Glacier (West Antarctica) at 79°55'34.6"S, 94°21'13.3"W (elevation 2122 m above sea level – a.s.l.), near the Mount Johns Nunatak (located 70 km NE of the drilling site) (Fig. 1) and close to the Institute/Pine Island ice divide. The drilling site was chosen due to its relatively high

accumulation rate, which ensures seasonally preserved stratigraphic resolution (Schwanck et al., 2016; Thoen et al., 2018), and due to the region's interesting pattern of atmospheric circulation, originating from the confluence of air masses from the Weddell, Amundsen and Bellingshausen seas (Parish and Bromwich, 2007; Thoen et al., 2018).

The West Antarctic Ice Sheet (WAIS) is lower elevation and has lower coastal slopes than the East Antarctic Ice Sheet (EAIS), which facilitates the intrusion of moisture-rich cyclones to the interior of the continent and the transport of aerosols inland (Neff and Bertler, 2015; Nicolas and Bromwich, 2011). Katabatic winds are not as strong in the drilling site region as they are in most of West Antarctica, due to the higher site elevation compared to the surroundings (Parish and Bromwich, 2007). Seasonal differences in atmospheric transport have been reported for the TT07 drilling site, with particle trajectories during the austral summer being slow moving and more locally influenced, while during the winter, air trajectories are influenced by oceanic air masses due to strong westerlies. The majority of air masses arrive from the Amundsen Sea and, secondarily, from across the Antarctic Peninsula and Weddell Sea (Schwanck et al., 2017). These are also the preferred pathway for dust particles (Neff and Bertler, 2015).

We used a Mark III auger (Kovacs Enterprises, Inc.) coupled with an electrical drive powered by a generator (kept downwind at a minimum of 30 meters away) to retrieve the core. The Mark III auger recovers cylinders of 7.25cm diameter and up to one meter long. All sections of the core were weighed in the field, packed in polyethylene bags and then stored in high-density styrofoam boxes. These boxes were sent by air to Punta Arenas (Chile), then to a deposit in Bangor (ME, US) for storing and finally to the Central Washington University Ice Core Laboratory (Ellensburg, WA), where it was kept at -18°C in a clean cold room until sub-sampling and analysis.

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3 Methods

3.1 rBC analytical method

We used an extended range Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA) at the Department of Geological Sciences, Central Washington University (CWU - WA, USA) to analyze our samples. The particle size range detected by the SP2 at CWU is 80-2000 nm mass-equivalent diameter for the incandescent signal, assuming a void-free ~~black carbon~~BC density of 1.8 g cm^{-3} (Moteki and Kondo, 2010).

The SP2 measures the number and size of rBC particles using laser-induced incandescence, and was used in a variety of studies for BC in snow and ice (Bisiaux et al., 2012a, 2012b; Casey et al., 2017; Kaspari et al., 2014, 2015, 2011; McConnell et al., 2007; Osmont et al., 2018a, 2018b). In this work we use the recommended terminology by Petzold et al. (2013) and present results from the SP2 as refractory black carbon (rBC).

As the SP2 was initially designed to analyze rBC from the atmosphere (dry aerosol), a necessary step to run liquid samples is their nebulization before being coupled to the sample inlet of the SP2. For this, we used a CETAC Marin 5, described in detail by Mori et al. (2016). The authors found a good nebulizing efficiency of 50.0 ± 4.4% and no size dependency in the diameter range of 200-2000 nm. Katich et al. (2017) managed to get nebulization efficiencies near 100% with their equipment set up. We calculated the CWU Marin-5 nebulization efficiency to be 68.3 ± 5.9% (1σ) based on the external calibration carried out every working day using Aquadag standards (Marquetto et al., 2020). We found a decrease in nebulization efficiency during the laboratory work period (-0.31% per working day or -13.3% over the 43 working days), but we assume the nebulization efficiency to remain stable between the measurement of the standard and the samples measured for the day, as Katich et al. (2017). We attribute this decrease to the Marin-5 but do not see any apparent cause. Liquid pump flow rates were kept constant at 0.14 ± 0.02 mL min^{-1} during analysis.

For details of the CWU SP2 internal and external calibration, refer to Marquetto et al. (2020).

3.2 Laboratory and vial cleaning

Regular, intensive cleaning was carried out inside the cold room for all surfaces/parts/equipment in contact with the core using ethanol and laboratory-grade paper tissues. Tyvek suits (DuPont, Wilmington, DE, USA) and sterile plastic gloves were used at all times in the cold room during the core processing.

Vials used to store the samples (50 mL polypropylene vials) were soaked in Milli-Q water for 24 hours and rinsed three times. This process was repeated two more times, in a total of three days soaked in Milli-Q water and nine rinses. The vials were left to dry, covered from direct contact, in the laboratory.

3.3 ~~Laboratory and vial cleaning~~Sample preparation

The sample preparation process consists of removing the outer layers of the core, as these are prone to contamination during drilling, handling and transport of the core (Tao et al., 2001). In the cold room, we partitioned the 21 sections of the core longitudinally, using a bandsaw with a meat grade, stainless steel bandsaw blade. For every cutting session, a Milli-Q (MQ) ice stick, previously prepared, was cut at the beginning, to guarantee a clean blade for the snow and firn core. After cutting the core in the bandsaw, we hand scraped the resulting snow and firn sticks with a ceramic knife in a laminar flow hood (still in the cold room) and cut them in 2 – 2.5 cm samples with the same knife (resulting in ~40 samples per section). We stored the samples in the pre-cleaned 50 mL polypropylene vials and kept them frozen until analysis. Samples were melted at room temperature or in a tepid bath not exceeding 25°C, sonicated for 15 min, and then analyzed (in less than 1 h after melting). The resulting rBC concentrations using this subsampling method were compared to subsampling using a continuous melter system for the first 8 meters of the core, and results for both methods were statistically the same (Marquetto et al., 2020).

From all steps of the sample preparation, the band saw cutting in the cold room proved to be the most prone to contaminate samples. An intensive decontamination process was carried out during a month, before we could start working with the core itself. In order to reach acceptable background levels for this step (around 0.02 µg L^{-1}), we replaced and modified some

components of the band saw. We replaced the rubber tires for urethane ones; the carbon blade for a meat grade, stainless steel blade; the original plastic blade guides for ceramic ones; manufactured an acrylic blade guard, as the original plastic guard was chipping. Before using the new blade, we burned it using a blowtorch and map/pro gas (propylene with <0.5% propane) to remove any residues/oils present, then cleaned it with ethanol. For detachable parts, a detergent was used, followed by ethanol and MQ water. For parts inside the cold room, ethanol was used. We also prepared ice sticks of MQ water to cut in the band saw and help clean the blade.

3.4 Whole-system setup

The setup for the system in use at CWU is as it follows: The melted sample is dispensed to the Marin-5 nebulizer by a Reglo Digital peristaltic pump (ISMATEC, Wertheim, Germany) at 0.14 ± 0.02 mL min^{-1} and monitored by a TruFlo Sample Monitor (Glass Expansion, Port Melbourne, Australia). The Marin-5 nebulizer receives standard laboratory air at 1,000 sccm (1.000 L min^{-1}), regulated by an Alicat Flow Controller (Alicat Scientific, Tucson, AZ, USA) connected to a Drierite Gas Purifier, which removes any moisture or particulates from the air. The nebulizer heating and cooling temperatures are set to 110°C and 5°C, respectively, following (Mori et al., 2016). We used Tygon LFL tubing ID 1.02mm (Saint-Gobain Performance Plastics, France) for sample to nebulizer connection. The SP2 flow is maintained at 120 volumetric cm^3 min^{-1} (vccm). YAG laser power for this project stayed constant above 5.0 V.

Samples were analyzed for 5 minutes each. Procedural blanks (MQ water) were run at the beginning and end of every working day, and also every 15-20 samples. Background levels were kept at 0-0.5 particles cm^{-3} (translating to less than 0.01 µg L^{-1} rBC concentration), and a 5% HNO3 solution was used for cleaning the tubing and nebulizer when needed. For the SP2 to go back to background levels, only MQ water was used. Peristaltic pump tubing replacement was necessary only once during the process. The limit of detection (LOD) of the method was estimated to be 1.61x10-3 µg L^{-1} based on procedural blanks measured to characterize the instrument detection limit (mean + 3σ, n=30).

Data processing was performed with the SP2 Toolkit 4.200 developed by the Laboratory of Atmospheric Chemistry at Paul Scherer Institute (PSI), and was used on the scientific data analysis software IGOR Pro version 6.3.

3.5 Fire spots and BC emission database

To help define the dating of the core and to investigate potential emission source regions, we compared our results with two different datasets: BC emission estimates from the Global Fire Emission Database version 4s (GFED4s - Van Der Werf et al., 2017) for the SH (SH South America, SH Africa, Australia and Equatorial Asia) and the Australian and Brazilian satellite programs, that count the fire spots (number of active fires) in Oceania and South America, respectively.

The GFED4s (https://www.globalfiredata.org/data.html) is based on the Carnegie-Ames-Stanford Approach biogeochemical model (Giglio et al., 2013), and has several improvements compared with the earlier version, including burned area and emissions from small fires as these could be substantial at a global scale (Randerson et al., 2012). BC emission estimates are given in 10^9 g and separated by region of the globe with a spatial resolution of 0.25 degree latitude by a 0.25 degree

longitude. For the Southern Hemisphere, four regions are identified: Southern Hemisphere Africa (SHAF), Southern Hemisphere South America (SHSA), Australia and New Zealand (AUS) and Equatorial Asia (EQAS).

The Sentinel Hotspots (https://www.ga.gov.au/scientific-topics/earth-obs/case-studies/mapping-bushfires) and the Programa Queimadas (http://www.inpe.br/queimadas/) are fire monitoring programs run by the government of Australia (Geoscience Australia) and Brazil (Instituto Nacional de Pesquisas Espaciais - INPE), respectively. Both programs use Moderate Resolution Imaging Spectroradiometer (MODIS), Advanced Very High-Resolution Radiometer (AVHRR) and Visible Infrared Radiometer Suite (VIIRS) sensors to detect areas of elevated infrared radiation. The Sentinel Hotspots holds data from 2002 to present, while the Programa Queimadas has a record of fire spots since 1998. The parameter "fire spot" used in both Australian and Brazilian fire monitoring programs do not translate directly to the dimension and intensity of the biomass burning events, but it holds a correlation with burned area (Andela et al., 2017) and thus can be used to help date the core and investigate potential emission sources.

3.6 Core dating

Antarctic ice core rBC records from other sites show a well-defined seasonality, with peak concentrations in austral winter-spring (dry season) due to increased biomass burning activity in the SH during this time of the year (Bisiaux et al., 2012b; Pasteris et al., 2014; Sand et al., 2017; Winstrup et al., 2017). Sodium (Na) and strontium (Sr) also peak in the austral dry season (during winter) due to intense atmospheric circulation and transport (Legrand and Mayewski, 1997; Schwanck et al., 2017). Increased marine biogenic activity reflects an increase in sulfur (S) in late austral summer (Schwanck et al., 2017; Sigl et al., 2016). Also, the maxima in the non-sea-salt sulfur to sodium (nssS/Na) ratio is a robust seasonal indicator and peaks around the new year (Arienzo et al. 2017). This parameter helps in the identification of the annual layers more than the Na and S records alone. Non-sea-salt sulfur was calculated using Eq. 3 to 6 from Schwanck et al. (2017) and references therein.

The core was dated by multi-parameter manual layer counting primarily driven by rBC seasonal variability, as this is a reliable parameter for dating in Antarctica (Sigl et al., 2016; Winstrup et al., 2017), and a well defined seasonality has already been observed for Pine Island glacier (Pasteris et al., 2014). We used S, Sr, ~~and~~ Na and nssS/Na records from a core drilled 1 meter away as additional parameters to the main counting~~, as these records show the more pronounced seasonal variability at the site (Schwanck et al., 2017)~~. The trace element records goes down only to ~ 6.5 m, so below 6.5 m the ice core is dated using the rBC record.

~~Down to around 5.60 meters deep, we used the S, Sr and Na records from a core retrieved a meter apart from the rBC core during the same expedition (January 2015). Deeper than that we used the S, Sr and Na records from Schwanck et al. (2017), from a core drilled in the same area (less than 1 km apart) in 2008 (spanning 1883-2008), as the core collected in 2015 was not analyzed for trace elements to the full depth. Both sets of trace element samples were subsampled and analyzed at the Climate Change Institute (CCI), University of Maine (USA), so some displacement from this record to the rBC one may~~

~~occur.~~ The trace elements were analyzed by the CCI Thermo Scientific ELEMENT 2 ICP- SFMS coupled to an ESI model SC-4 autosampler; working conditions and measurement parameters are described in Schwanck et al. (2016, 2017).

We considered the new year to match the end of what we define as the austral dry season, as this is a reliable tie point in the record due to the abrupt drop in rBC concentrations. Previous studies have demonstrated that rBC deposition occurs in winter/spring, mostly September to December. For example: Arienzo et al. (2017) observed rBC concentrations to peak in September in the WAIS Divide ice core; Winstrup et al., (2017) used annual variations in rBC as the most reliable annual tracer for the Roosevelt Island Climate Evolution (RICE) ice core, stating that rBC tends to peak earlier in the year than January 1st. Pasteris et al. (2014) also corroborates rBC to peak in October and drop after for the Pine Island and Thwaites Glaciers, with lowest values from February to June. Bisiaux et al. (2012b) state that sub-annual rBC concentrations are highly seasonal in the WAIS Divide ice core for the period spanning 1850-2000 - low austral wet season and high austral dry season concentrations - and presented annual picks in the drop in rBC concentrations, as in this work. This is also consistent with ~~based on~~ the BC emission estimates from GFED4s and the fire spot databases from Australia and South America. ~~This is also in agreement with Winstrup et al. (2017) as the authors state that BC tends to peak a little earlier than New Year in their records (Roosevelt Island Ice Core – RICE) and to Arienzo et al. (2017) as the WAIS Divide ice core presents rBC peaks in September. Also, the Pinatubo and Cerro Hudson eruptions (1991) identified in the record by Schwanck et al. (2016) and Thoen et al. (2018) were used as an absolute time horizon.~~

3.7 Snow accumulation, rBC concentrations and fluxes

To account for imperfections in the core geometry (and consequently imprecise density measurements), we averaged the core's density profile with the density profile from Schwanck et al. (2016) for a 45 m deep core drilled in the same region of West Antarctica, 850 m away from TT07. We then fitted a quadratic trend line in the average curve and used this trend line instead of the field measurements to calculate the annual snow accumulation, water equivalent (weq) and rBC fluxes. rBC fluxes were calculated by multiplying annual rBC means by annual snow accumulation.

We consider that the frequency distributions of the core rBC concentrations are lognormal, and so we present geometric means and geometric standard deviations as these are more appropriate than arithmetic calculations (Bisiaux et al., 2012a; Limpert et al., 2001). The geometric standard deviation is the multiplicative standard deviation (σ*), so the 68.3% interval of confidence is calculated as $_{\sigma}min_{conc}$ = geometric mean • geometric standard deviation, and $_{\sigma}max_{conc}$ = geometric mean/geometric standard deviation (Limpert et al., 2001). Also, correlation analysis was carried out using Mann-Kendall's test; we choose it as opposed to Spearman's test as confidence intervals are more reliable in the former (Kendall and Gibbons, 1990; Newson, 2002).

We present our data as austral summer/fall (~~dry~~ wet season: January to June) concentrations and austral winter/spring (~~wet~~ dry season: July to December) concentrations. Wet/dry season concentrations and annual concentration geometric means and standard deviations were calculated in the raw rBC measurements using the dating carried out to separate years and rBC

concentration variations to pinpoint the changes from dry season to wet season and vice-versa. Monthly mean concentrations were calculated by applying a linear interpolation in the raw measurements, resampling the dataset to 12 values per year.

3.8 rBC impact on snow albedo

To investigate BC impact on snow albedo we used the Snow, Ice, and Aerosol Radiation (SNICAR) online model (Flanner et al., 2007). We ran the model using the parameters presented in Table 1 with varying rBC concentrations: We used the wet and dry season geomeans, to analyze variations for both seasons, and the highest seasonal geomean found in the core, which occurred in the dry season. As our aim in this paper is BC, we simulated albedo changes considering only the particulate and disregarding any dust/volcanic ash influence. Snow grain size used was based on Gay et al. (2002).

3.9 Spectral analysis

In order to investigate periodic oscillations (cycles) in the TT07 core and BC atmospheric transport to the drilling site, we conducted a spectral analysis in the rBC ~~and Na~~ record~~s~~ using the REDFIT procedure described in detail in Schulz and Mudelsee (2002) in the 'Past – Paleontological Statistics' software version 3.25. The spectral analysis is motivated by the observation that the most predictable (regular) behavior of a time series is to be periodic (Ghil et al., 2002). The REDFIT method is a more advanced version of the simple Lomb periodogram, and can be used for evenly and unevenly sampled data. The model is fit~~ted~~ to an AR(1) red noise model, the bandwidth is the spectral resolution given as the width between the -6dB points and confidence levels of 90, 95 and 99% are presented (based on chi2) (Hammer, 2019).

We ch~~o~~ose this approach instead of estimation techniques for evenly spaced data (such as the Multitaper method) because interpolation in the time domain inevitably cause bias and alters the estimated spectrum of a time series (Schulz and Mudelsee, 2002). This way, we used the rBC ~~and Na~~ raw measurements (not resampled, only dated by year and separated by dry/wet season).

We compared the rBC ~~and Na spectra~~ spectrum with the El Niño–Southern Oscillation (ENSO), the Antarctic Oscillation (AAO) and the Amundsen Sea Low (ASL) spectra to observe possible influence of these in the rBC variability. While ENSO and AAO are well-known climate drivers, recent studies have shown the ASL has a profound effect on the West Antarctic climate (Hosking et al., 2013, 2016; Turner et al., 2013). We also compared the core records with the GFED4s BC emission estimates and the Satellite fire spots database to look for similarities between the datasets which could suggest BC emission sources to the drilling site. Table 2 shows the dataset used for the spectral analysis.

3.10 Particle trajectory simulations

In order to simulate rBC particle trajectories from source areas to the TT07 drilling site, we used the Hybrid Single-Particle Lagrangian Integrated Trajectory v4 model (HYSPLIT - Draxler and Rolph, 2003; Stein et al., 2015), from NOAA. Hysplit is a complete system for computing simple or complex transport and deposition simulations (Stein et al., 2015) that has been

used in Antarctica by several authors (Dixon et al., 2011; Markle et al., 2012; Marquetto et al., 2015; Schwanck et al., 2016a, 2017; Sinclair et al., 2010).

We used global reanalysis data from the National Centers for Environmental Prediction (NCEP) and the National Center for Atmospheric Research (NCAR) – the NCEP/NCAR data set – and ran 10-day (240 h) back-trajectories, every 5 days, from 1968 to 2015, at an initial height of 1000 m. We consider 10 days to be an appropriate simulation time as this is the estimated maximum lifetime of BC in the troposphere (IPCC et al., 2013). An initial height of 1000 m was used in order to minimize disturbance from the underlying terrain, but still maintaining a link with the surface wind field (Sinclair et al., 2010). To identify main airflow patterns at the TT07 drilling site, the individual trajectories were separated into dry and wet seasons (depending on day and month of each run) and simulations from each season were grouped into five clusters using the HYSPLIT model's cluster analysis algorithm.

4 Results and discussion

4.1 Dating

The core was dated to 47 years (1968-2015), and details are presented in Fig. 2. ~~Comparing to Schwanck et al. (2017), our dating differs by one year more considering the record in common for both cores We attribute this difference to the addition of the rBC record to the layer counting and to the use of different cores for rBC and trace elements (see section 3.6).~~ We consider this dating to have ±2 years uncertainty. The first uncertain year is located at 6.18 m (between 2003 and 2002, figure 2a), where S and nssS/Na peak but no full cycle is observed in the rBC record. We did not consider this to be a year, as rBC does not present a full cycle. The second uncertain year is located at 18.14 m (year 1973, figure 2b) where there is no clear rBC peak but snow accumulation would be anomalously high if considered to be only a year instead of two. We consider this to be an annual pick and consequently two years, as there is no evidence of higher-than-normal snow accumulation in the region for this period (Kaspari et al., 2004).

4.2 Core density and annual snow accumulation

The core density (measured in the field) ranged from 0.38 to 0.60 g cm^{-3}. Using the corrected density curve obtained from our field measurements and from Schwanck et al. (2016), we calculated that the 20.16 m length core represents 10.37 m weq m (Fig. 3).

Average annual snow accumulation is 0.21 ± 0.04 weq m per year, and varies little throughout the record, with an exception of a peak in accumulation of 0.31 weq m in 1971. The average accumulation is similar to what Banta et al. (2008) found for the WAIS Divide ice core for the last centuries (0.20 ± 0.03 weq m $year^{-1}$, elevation 1759 m a.s.l.) and to the higher altitude cores (>1700 m a.s.l.) from Kaspari et al. (2004) (0.18 to 0.23 weq m $year^{-1}$); although the latter work also presents lower altitude cores (1200 to 1600 m a.s.l.) closer to the drilling site with accumulation rates between 0.32 and 0.42 weq m $year^{-1}$.

4.3 rBC concentrations and fluxes

In agreement with others studies (Bisiaux et al., 2012a; Pasteris et al., 2014; Sand et al., 2017; Winstrup et al., 2017) we found a well-marked seasonal rBC cycle along the core, with the same pattern of low summer/fall and high winter/spring concentrations (Fig. 4). As we collected our samples in January and the drilling was carried out from the snow surface, our core starts approximately in the 2015 New Year. The core's annual rBC geometric mean concentration was 0.030 µg L^{-1} with a minimum of 0.001 µg L^{-1} and a maximum of 0.080 µg L^{-1}. Winter/spring (dry season) concentration geometric mean was 0.057 µg L^{-1}, while summer/fall (wet season) concentration geometric mean was 0.001 µg L^{-1}. Wet season average concentrations remained constant over time, while dry season average concentrations showed more variation with peak values in 1999 but no apparent trend. The main results from TT07 rBC analysis is summarized in Table 3.

We calculated annual rBC fluxes to account for potential biases in annual rBC concentrations due to changes in snow accumulation rates. Concentrations and fluxes follow a similar pattern along the core, as can be observed in Fig. 5. This means that rBC concentration variability likely reflects variations in BC emissions, transport and deposition at the site instead of reflecting changes in snow accumulation.

4.4 Comparison with other rBC records in Antarctica

BC has been studied in Antarctic snow since the late 1980s and early 1990s (Chýlek et al., 1987, 1992; Warren and Clarke, 1990). These initial studies used filter-based methods, which could under- or overestimate BC concentrations due to some analytical artefacts (Soto-García et al., 2011; Torres et al., 2014; Wang et al., 2012). Studies using the SP2 started appearing more than two decades later, aiming at recent snow rBC concentrations (Casey et al., 2017; Khan et al., 2019), near-surface air (Khan et al., 2018), recent-past ice cores (couple centuries - Bisiaux et al. (2012b, 2012a); Pasteris et al., (2014)) and the past millennia (Arienzo et al., 2017). From these, a few rBC records overlap temporally with the TT07 core presented in this work (Table 4). rBC concentrations are low at all sites (< 0.5 µg L^{-1}), thus small differences in concentration from one core to another could result in a 2-3 fold difference in rBC concentrations.

Pasteris et al. (2014) present rBC records from three high accumulation West Antarctic ice cores: Pine Island Glacier, Thwaites Glacier, and from the divide between the two sites (220, 750 and 370 km apart from TT07 core, respectively). The cores presented annual rBC concentrations of 0.22 µg L^{-1} (Pine Island), 0.21 µg L^{-1} (Thwaites) and 0.20 µg L^{-1} (Divide). The lower altitude cores (DIV2010 – 1329 m a.s.l. and PIG2010 – 1593 m a.s.l.) presented almost 1.5 times more snow accumulation than the higher altitude core (THW2010 – 2020 m a.s.l.), and almost 2 times more than TT07. The mean annual rBC concentrations from Pasteris et al. (2014) are almost six times higher than the rBC annual values observed in TT07. Higher rBC concentrations in Pasteris et al. (2014) could be a result of higher accumulation rates, considering that BC is primarily deposited through wet deposition (Flanner et al., 2007). This is discussed later on in this section.

The WAIS Divide rBC record from Bisiaux et al. (2012a) is located 350 km away from TT07, ~~the closest from TT07 (350 km apart), with~~ has similar accumulation rates to TT07, and ~~. The WAIS Divide~~ rBC annual concentration~~, though, is~~ 2.7

times higher than annual values from TT07 (0.08 µg L^{-1} at WAIS and 0.03 µg L^{-1} at TT07). The authors observed a steep increase in rBC concentrations in the WAIS core from 1970 to 2001 (~0.06 µg L^{-1} to ~0.11 µg L^{-1}) and related this to an increase in fossil fuel consumption and deforestation in the SH. This increasing trend was not observed in the TT07 core, that showed fairly stable annual concentrations and fluxes through time. Although the WAIS Divide core is located almost at the same distance from TT07 as DIV2010, and farther than PIG2010, its snow accumulation rates and rBC annual concentrations are more similar to TT07 than the cores from Pasteris et al. (2014).

The South Pole samples (1120 km from TT07) from Casey et al. (2017) were collected in early austral summer, possibly still reflecting the SH dry season. They present even higher rBC concentrations than Pasteris et al. (2014), although the samples were collected close to the Amundsen-Scott scientific station and even the "clean air sector" can present local influence, particularly in comparison to the TT07 remote site.

Khan et al. (2018) found rBC concentrations in the same order of magnitude as Casey et al. (2017), although the Dry Valleys collection site from Khan et al. (2018) was far from local interference of scientific station activities. The cores from Bisiaux et al. (2012b) (East Antarctica) present the highest elevations from the cited bibliography, and show similar rBC fluxes comparing to TT07, although these fluxes are a result of high rBC concentrations with low accumulation rates in East Antarctica, while the TT07 fluxes are the opposite – high accumulation rates (similar to the WAIS Divide core) with low rBC concentrations.

Figure 6 shows a comparison of the above mentioned rBC records with snow accumulation, elevation and distance from open sea. Distance from the sea influences rBC fluxes in West Antarctica (Arienzo et al., 2017), and was calculated considering the median sea ice extent from 1981 to 2010 for September (Matsuoka et al., 2018), when rBC emissions start to rise in South America/Australia/New Zealand and rBC concentrations begin to rise in West Antarctica (Arienzo et al., 2017; Bisiaux et al., 2012b; Pasteris et al., 2014). We measured the distance from the rBC records to the closest open sea source (Amundsen sea for West Antarctic records, Lazarev to Cosmonauts sea for NUS0X-X and Mawson sea for Law Dome). We acknowledge this is a simplistic approximation and that the preferred air mass pathways from the sea to the points are not as straightforward, but for the scope of this work we consider this approximation sufficient.

No patterns are clear for both East and West Antarctica, whereas when considering the data from East and West Antarctica separately, opposite trends are observed. In East Antarctica, rBC concentrations have a negative correlation with snow accumulation and positive correlation with elevation and distance to the sea, whereas in West Antarctica rBC concentrations present a positive correlation with snow accumulation and a negative correlation with elevation and distance to the sea.

We observed that for East Antarctica, rBC vs. snow accumulation and rBC vs. elevation presented statistically significant correlations ($r^2 = 0.78$, $p < 0.01$ for the former and $r^2 = 0.79$, $p < 0.01$ for the latter). On the other hand, distance from the sea is not signtificantly correlated with rBC ($r^2 = 0.52$, $p = 0.06$).

For West Antarctica, relationships are the opposite: positive correlation between rBC concentrations and snow accumulation ($r^2 = 0.69$, $p = 0.08$) and negative correlations between rBC concentrations and elevation/distance from the sea ($r^2 = 0.30$, $p < 0.33$ for the former and $r^2 = 0.79$, $p < 0.05$ for the latter). McMurdo and South Pole points are not considered in this

calculation as they likely reflect local contamination instead of long-range transport (Casey et al., 2017; Khan et al., 2018). Bisiaux et al. (2012b) have also observed negative (positive) relationships between rBC concentrations and snow accumulation (elevation) for East Antarctica, although their comparison also included the WAIS Divide point to the dataset. These opposite trends may indicate differences in rBC transport to East and West Antarctica. While for East Antarctica upper tropospheric transport and dry deposition may be the main controllers of rBC concentrations (Bisiaux et al., 2012b), for West Antarctica rBC concentrations may be modulated by intrusion of air masses from the marine boundary layer. Low elevations in West Antarctica facilitates the intrusion of moisture-rich cyclones and the transport of aerosols inland (Neff and Bertler, 2015; Nicolas and Bromwich, 2011), while the positive relationship between West Antarctica rBC concentrations and snow accumulation may indicate rBC to be primarily deposited through wet deposition, being scavenged along the coastal regions were snow accumulation is higher.

4.5 BC impact on snow albedo

To investigate BC impact on snow albedo we used SNICAR-online to simulate three scenarios with the same parameters but varying rBC concentrations: We ran the model using the wet and dry season geomeans and the highest seasonal geomean (0.015, 0.057 and 0.105 µg L^{-1}, respectively). Results show that snow albedo reduction in the TT07 site due to BC is very low to non-existent (Table 5). This was already expected considering (observed) albedo reported by Casey et al. (2017): Although significant albedo reductions have been reported in more contaminated zones near the South Pole Station, the authors found a minor to negligible reduction to albedo for the "clean sector" snow.

We note that this albedo reduction occurs only in the austral summer, as the site is located almost at 80°S.

4.6 Emission sources and influence of transport on the record

Variability in ice core records reflects variability in BC emissions, atmospheric transport and deposition (Bisiaux et al., 2012a). As BC stays in the atmosphere for a short period of time (7 to 10 days; IPCC et al., (2013)), increases in BC emissions would rapidly reflect increases in BC concentrations in snow, and thus comparing the seasonality of the two records may help to elucidate source regions. To this end, we compared BC monthly emissions in the SH (from the GFED4s model) with ~~the~~ monthly rBC values from the TT07 ~~rBC~~ record (Fig. 7a). The BC seasonality at TT07, with increasing concentrations in July, a peak in October and minimum values in April-May, is the same as reported for the nearby Pine Island Glacier (Pasteris et al., 2014; Figure 1) indicating that comparing the TT07 seasonality to regional emissions is valid.

Some models indicate that the carbonaceous load in the Antarctic troposphere mainly originates from South American emissions (Koch et al., 2007); others recognize both South America and Australia as the main sources (Stohl and Sodemann, 2010). Although Southern Africa has the largest BC emissions in the SH, it is not considered to be a significant contributor to the aerosol load in Antarctica (Li et al., 2008; Neff and Bertler, 2015; Stohl and Sodemann, 2010). Both Australia (Bisiaux et al., 2012a) and South America (Arienzo et al., 2017) have been suggested as sources of BC to West Antarctica.

Figure ~~6a~~ 7a shows the rBC monthly average values for TT07 (1968-2014) and monthly-averaged BC emissions from GFED4s (1997 – 2015) for the four SH emission regions (regions defined in GFED4s, see website). rBC in the TT07 starts increasing considerably in July, peaks in October and shows high but decreasing concentrations until December.

African emissions ~~are shifted left,~~ increase~~ing~~ and decrease~~ing~~ earlier in the year compared with other SH emission sources and with the TT07 BC record (Kendall's tau = 0.30, p = 0.17, n = 12). Equatorial Asia BC emissions increases in August and peaks in September, not reflecting the initial rBC increase in TT07 record (Kendall's tau = 0.33, p = 0.13, n = 12). The increasing trend matches South American emissions, as they start rising in the same period, although peaking in September and dropping significantly after (Kendall's tau = 0.66, p < 0.01, n = 12). At last, Australia and New Zealand emit much less BC than the other three regions (Fig. ~~6~~7b) but atmospheric circulation favors aerosol transport from there to West Antarctica (Li et al., 2008; Neff and Bertler, 2015). Australian and New Zealand emissions start increasing in August and peak in October, falling later than the other regions (December) (Kendall's tau = 0.85, p < 0.01, n = 12). The correlation coefficients then indicate Australia/New Zealand as the most probable source region for BC at the site for the period studied, followed by SH South America. SH Africa and Equatorial Asia present much weaker correlations, which likely indicates these two regions do not contribute substantially to the rBC flux to the TT07 site. This is consistent with previous research (Arienzo et al., 2017; Bisiaux et al., 2012a).

There is a small increase in Australian emissions earlier in the year (May) that is not observed in the TT07 rBC monthly averages. This difference could be associated with the seasonal difference in particulate transport to Antarctica in winter/summer (Hara et al., 2008; Schwanck et al., 2017; Stohl and Sodemann, 2010).

4.7 Spectral analysis

We investigated further the possible emission sources and transport influences to the site using the REDFIT spectral analysis. We compared the rBC record with ENSO, AAO and ASL indexes~~, and to the TT07 Na record~~ (Fig. 8~~7~~)~~, as the latter is a sea-salt proxy modulated by atmospheric transport (Legrand and Mayewski, 1997; Sneed et al., 2011)~~. This investigation would give information about the effect of local to regional changes in atmospheric circulation on the BC records (Bisiaux et al., 2012a).

The TT07 rBC spectrum showed significant cycles in the 6-year band (AR1 Confidence Interval > 90%) and in the 2-year band (AR1 CI ~90%). Intra annual cycles in the 0.6 and 0.5 frequencies were also observed at a 95% confidence interval. Comparing the TT07 rBC record spectrum with the GFED4s and fire spots spectra, we identified similar periodicities only in the Sentinel Hotspots (Australia) record (Fig. 8~~7~~), more specifically in the 2 year band (AR1 CI ~90%), and in the 0.6 year band (AR1 CI >90%). All other spectra (including Programa Queimadas satellite data) showed only well-marked annual periodicities and intra annual periodicities of 2 and 3 cycles per year (0.5 and 0.3-year bands, not shown). We consider some of these intra annual cycles questionable, as the high-frequency end of the spectrum is often overestimated and can present

aliases, 'folded signals' of another frequency process (Mudelsee, 2010; Schulz and Mudelsee, 2002), in this case aliases of the annual cycle at the 0.5 and 0.3 year bands. Due to this, we do not consider 0.5 and 0.3-year cycles to be representative.

~~Sea salt transport to Antarctica (including Na) is modulated by sea level pressure (Kaspari et al., 2005; Sneed et al., 2011) and thus ASL, ENSO and ASL should influence its variability. AAO and ENSO periodicities were identified in the Na spectra (1.2 and 0.6- year band for AAO and only 0.8 year band for ENSO).~~ rBC and AAO ~~also~~ present similar cycles (2.1 and 0.6-year bands), as well as rBC and ENSO (2-year band). ~~rBC and Na spectrum show two periodicities in common, in the 1 year and 0.6 year band, but longer cycles are different. Also, differences in rBC/Na seasonality indicate the 1 year cycle does not match in the records: Na in the site typically peaks during austral winter (Schwanck et al., 2017), while rBC peaks in October, a 2 month difference between them (Fig. 8). The absence of longer than annual cycles in common and the difference in seasonality thus suggests rBC particles are not transported to the drilling site the same way as Na, by the intrusion of marine air masses.~~

Using the multitaper method, Bisiaux et al. (2012a) observed the rBC periodicities for the WAIS Divide ice core and Law Dome (both dated to 1850-2001). Although WAIS is closer to the TT07 drilling site (~350 km), the TT07 core presented similarities with the Law Dome spectrum (in the 6 and 2-year bands, not shown). It is not clear to us what the relation between the two sites could be, as the TT07 site location, annual accumulation and site elevation are more related to the WAIS ice core than to Law Dome (Table 4). Arienzo et al. (2017) used the multitaper method to analyze the WAIS Divide rBC flux for the period spanning 14k-6k years BP, and found a 6.6 year cycle (AR1 CI = 95%) and a 2.3 year cycle (AR1 CI > 95%), similar to the rBC cycles found in this work; although time scales and methodology used were different. Both Arienzo et al. (2017) and Bisiaux et al. (2012a) attribute the 2.3-year cycle to an indirect effect of the Quasi-Biennial Oscillation (QBO). Although the QBO circulation spans the equator to ~30°, QBO-generated variability can affect Antarctica (Strahan et al., 2015), in which case an upper troposphere/stratospheric component may be important to BC transport to the continent.

In summary, the spectral analysis suggests Australia and New Zealand as the most probable sources of rBC to the drilling site~~. rBC does not seem to be transported there the same way as Na, through intrusion of marine air masses~~. Also, rBC seems to be related to the AAO (0.6 and 2-year cycle), ~~but not~~ to ENSO (2-year cycle) but not to ~~and~~ ASL, and similarities between rBC cycles in the TT07 site and the WAIS Divide site have been observed.

4.8 Particle trajectory simulations using HYSPLIT

We simulated particle transport during the austral wet and dry seasons as another mean of addressing rBC source areas. We ran the HYSPLIT back-trajectory model every five days from 1968 to 2015, for 10 days each (estimated maximum BC lifetime in the troposphere) and clustered the results in five groups for the wet and dry seasons (Fig. 9).

The majority of simulated air parcels arriving at the drilling site presented a slow-moving trajectory (speed is proportional to trajectory length), reflecting a local/regional influence more than long-range transport from other continents (clusters 3 and 4

in Figure 9). This local/regional influence is observed both in the wet and dry seasons, although during the former the contribution of air masses from the Antarctic Peninsula and across (Weddell Sea) are higher than during the latter. A fast-moving, year-round, continental group is also present (cluster 5), and may partly represent katabatic winds flowing from the continent's higher altitudes (East Antarctica) towards lower-altitude West Antarctica. The strongest contribution of long-range air parcels is from the South Pacific (clusters 1 and 2). These air masses are also fast-moving and present slight seasonal variations, shifting pole wards during the wet season, when they represent 34% of all air parcels, and away from Antarctica during the dry season, when they respond for 22% of all air parcels modelled.

Results from clusters 1 and 2, along with individual trajectories of each cluster (Fig. 10) support our conclusion that Australia and New Zealand are the most probable sources of rBC to the drilling site, considering tropospheric transport. The most visible influence of air parcels from these two countries to the drilling site can be seen in the individual trajectories of cluster 1 (Fig. 10) for both dry and wet season, while for cluster 2 and 4 there are trajectory variations from one season to another. The poleward shift of cluster 1 trajectories in the wet season (Fig. 9) may be a reason why the Australian emissions earlier in the year (May) are not visible in the TT07 rBC record. South American influence to the TT07 drilling site, on the other hand, is restricted to the higher latitude countries (Chile, Argentina), as shown in the individual trajectories of clusters 2, 3 and 5 (Fig. 10). This suggests that South American fires are not significant contributors to the rBC concentrations observed at the TT07 site when considering only tropospheric transport.

5 Conclusions

BC in Antarctica has been studied only in the recent decades, but long-range anthropogenic influences have already been observed (Bisiaux et al., 2012a; Stohl and Sodemann, 2010). Models predict a continued increase in BC emissions from source areas (Bond et al., 2013) and a continued increase in BC flux to the Antarctic region, mostly to the Antarctic Peninsula and West Antarctica (Arienzo et al., 2017). Understanding the spatial variability of BC is then essential to predict BC's future impact on the continent.

We analyzed a 20-meter long snow/firn core from West Antarctica spanning ~~1969~~1968-2015 for ~~refractory black carbon~~rBC. Results show a well-defined seasonal variability in the record, with low (high) concentrations during the Southern Hemisphere wet (dry) season but no long-term trend along the 47 years of the core. Snow accumulation remained stable during this period. rBC annual concentrations were found to be the lowest in samples from the recent decades compared to other studies, while rBC annual fluxes compare with the low values found by Bisiaux et al. (2012b) for high elevation East Antarctica ice cores. Correlations between rBC and snow accumulation, elevation and distance to the sea for East and West Antarctica records indicate rBC transport and deposition might be different for each. SNICAR modeling indicated BC does not affect snow albedo significantly at the site, with a reduction of 0.48% and 0.41% for the highest rBC concentrations found in the core and for dry season geomean concentrations relative to clean snow, respectively. Negligible impact in albedo was observed for wet season geomean concentrations. BC emission estimates, ~~and~~ satellite data of fire spots and

HYSPLIT particle transport simulations suggest Australia and New Zealand as the main contributors to the rBC present in the TT07. Based on GFED4s emission estimates, SH South America may be a secondary contributor, although this is not supported by spectral analysis results or air mass trajectories. ~~, and SH South America as possible emission sources to the TT07 site.~~ Spectral analysis of the rBC shows ~~and Na record indicate mostly different periodicities (6.2, 2.2 and 1 year cycles for rBC and 1.2, 1 and 0.8 year cycles for Na), with exception of a 0.6 year cycle in common in both spectra. Also, seasonality of rBC and Na is different, with the former peaking in October (spring) while the latter peaks in August (winter). This suggests BC is not transported to the drilling site by the same mechanisms as sea-salt (marine air masses). While we observed~~ influence of AAO and ENSO periodicities; ~~in the rBC spectrum, ENSO and~~ ASL influences were not detected. ~~Also, the spectral analysis showed similarities between the TT07 rBC record and the WAIS Divide rBC record, but not for the same time span. For the present time (1968-2015), the rBC spectrum showed periodicities closer to the Law Dome site from Bisiaux et al. (2012a), although no relation between the two sites is evident.~~ This core is the highest elevation rBC core collected in West Antarctica and its low BC concentrations compared to previous studies indicates spatial variability in the transport and deposition of BC in West Antarctica.

Data availability: TT07 data is available upon request; auxiliary data can be downloaded from respective sources cited along this work.

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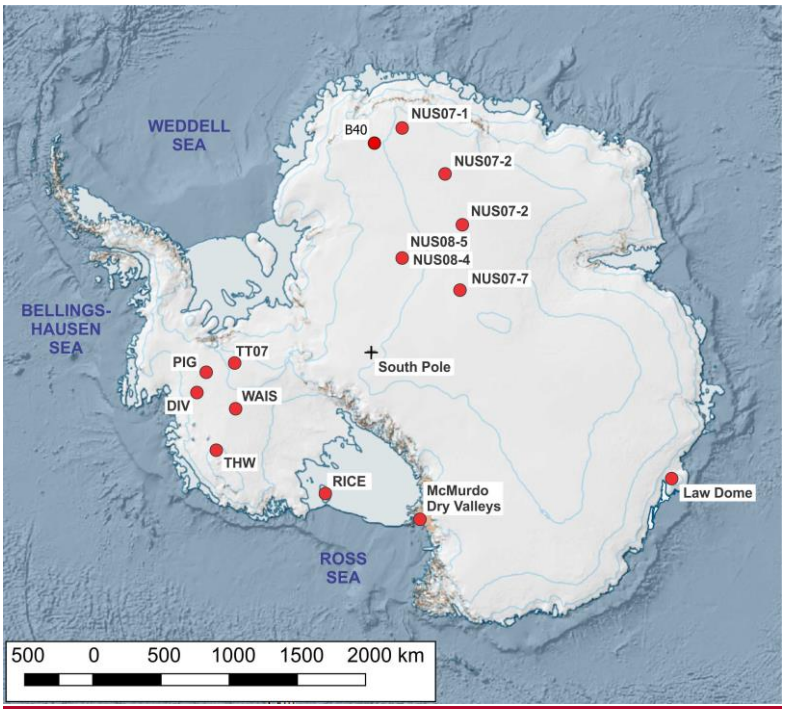
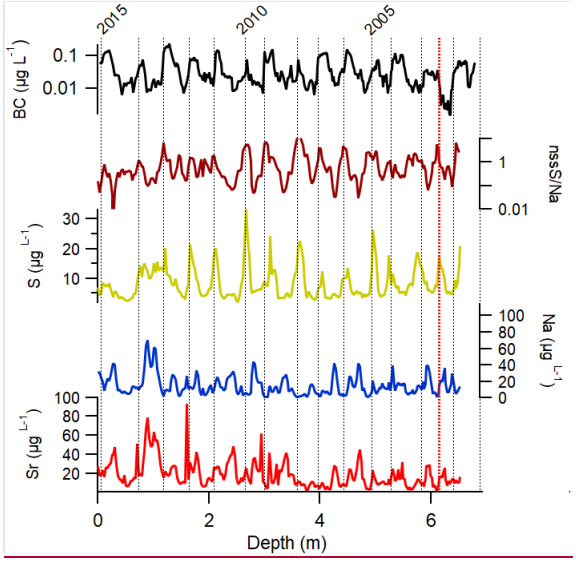


Figure 1. Drilling location for the snow and firn core analyzed in this work (TT07) and other points of interest mentioned in the text. Basemap from the Quantarctica Project (Matsuoka et al., 2018).



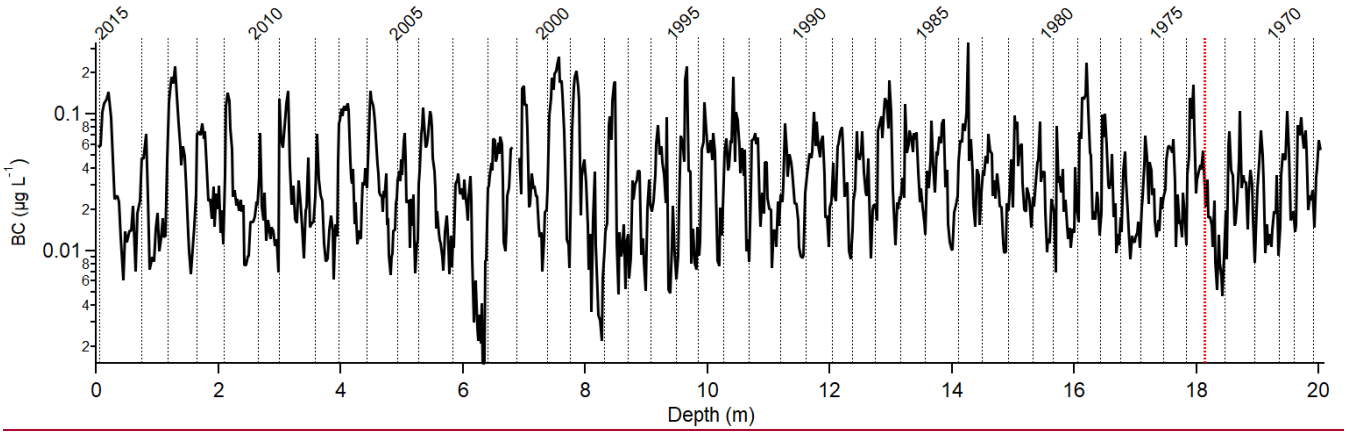


Figure 2. (a) Dating of the snow and firn core based on rBC and using S, Sr, Na and nssS/Na records from nearby core (see section 3.6) as support for the first 6.5 meters. Dashed lines indicate estimated New Year and red dotted line indicate uncertainty in dating, explained in the text. (b) Dating for the full core (y axis logarithmic). Red dotted line indicates uncertainty in dating, as explaned in the text.

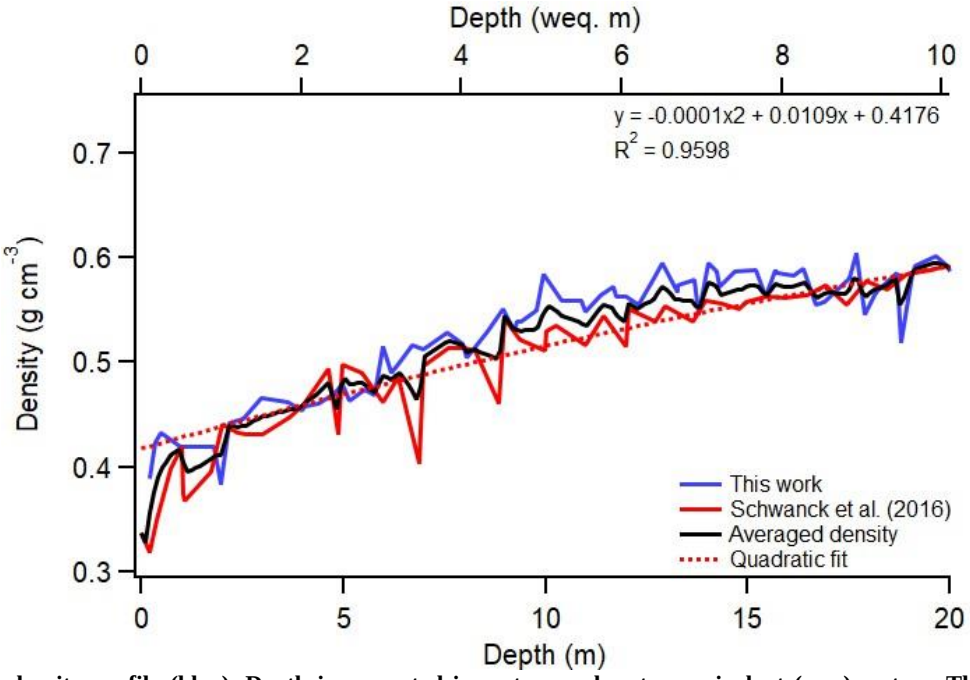


Figure 3. TT07 density profile (blue). Depth is presented in meters and water equivalent (weq) meters. The quadratic fit was calculated from the average density profile (black) from this work and from Schwanck et al. (2016).

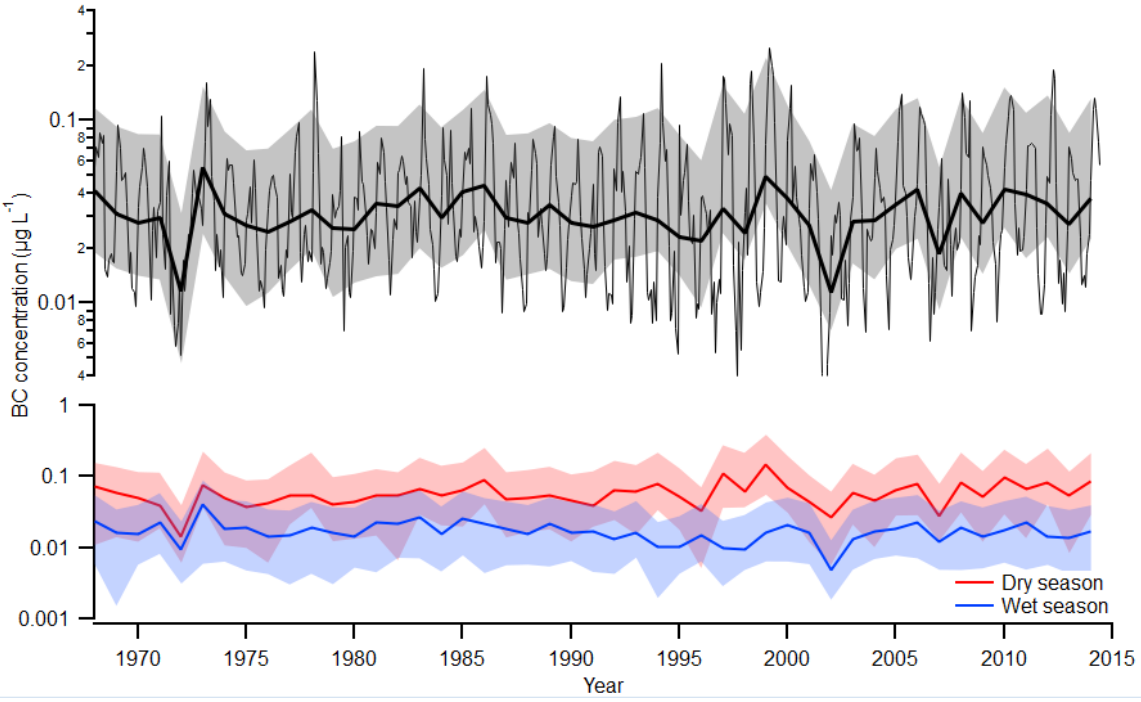


Figure 4. (top) rBC concentrations for the entire core. The black thick line represents annual averages, while the gray line represents monthly values. Note the y axis scale is logarithmic. (~~base~~bottom) Dry season and wet season average concentrations per year.

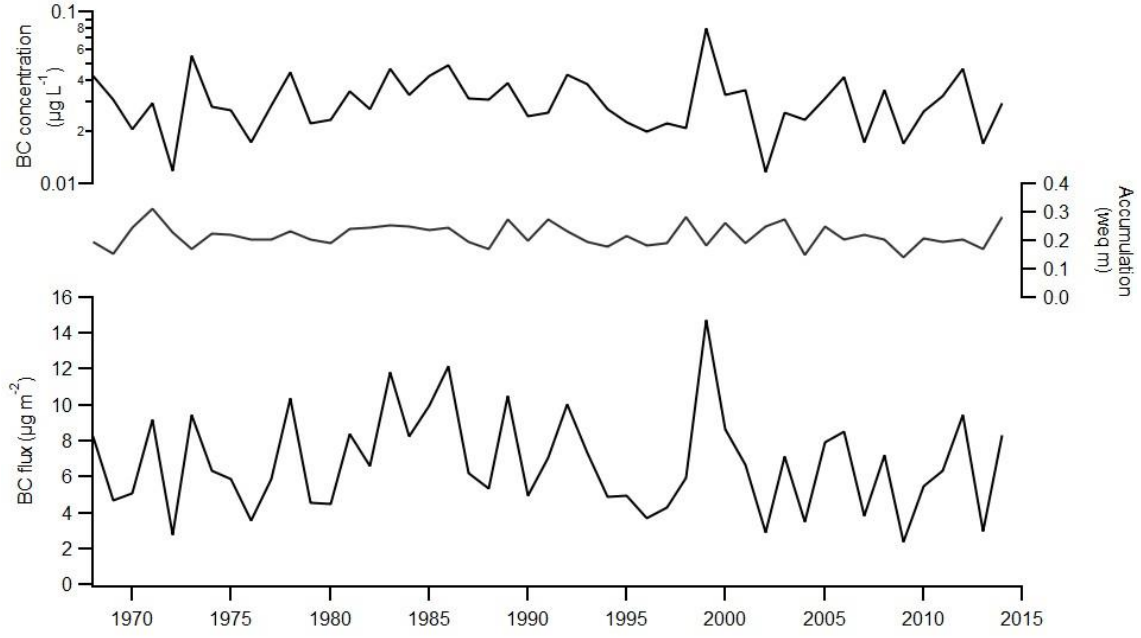


Figure 5. rBC concentrations (y axis logarithmic), accumulation and fluxes for TT07.

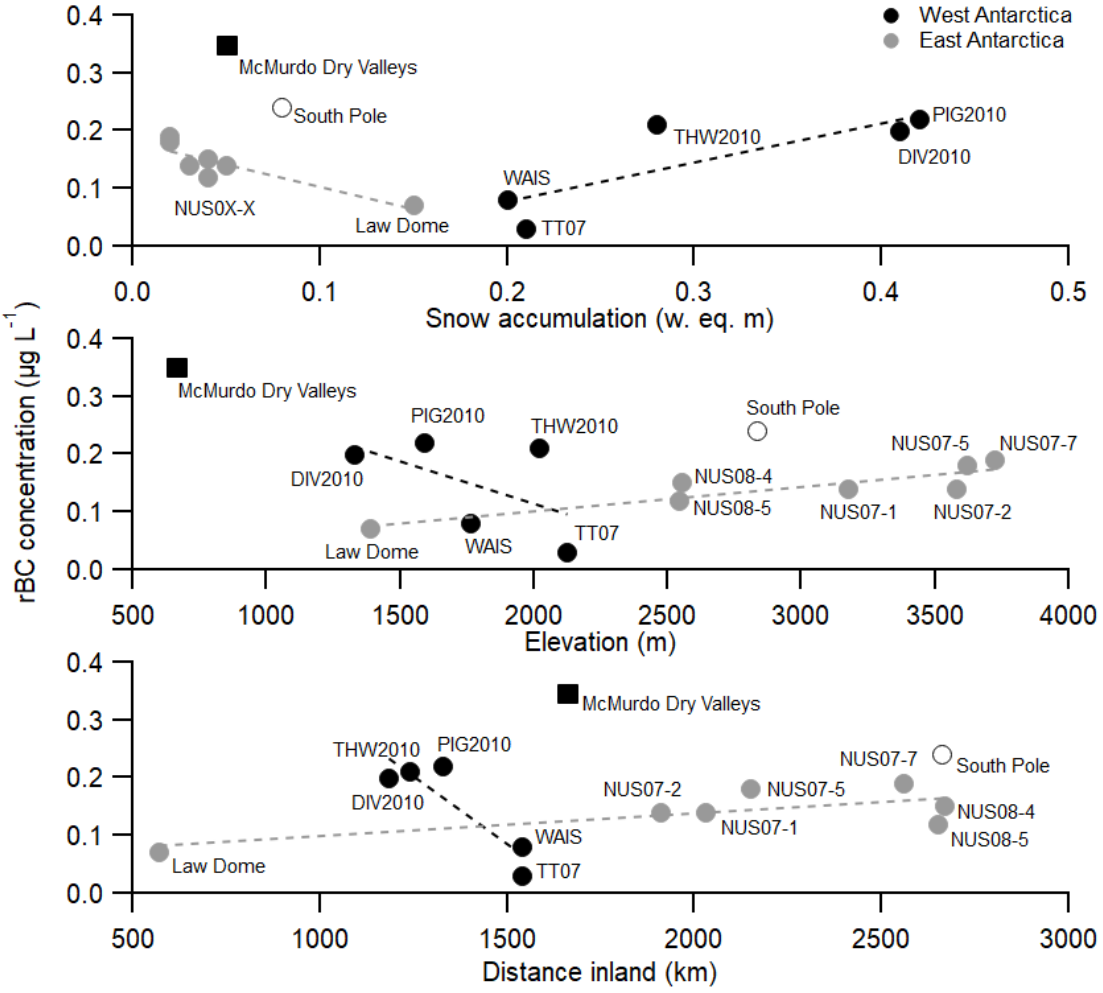


Figure 6. rBC records from Antarctica. rBC concentrations plotted against snow accumulation, elevation and distance from the sea. Solid lines indicate statistically significant correlations ($p < 0.05$), while dashed lines indicate not significant correlations ($p > 0.05$).

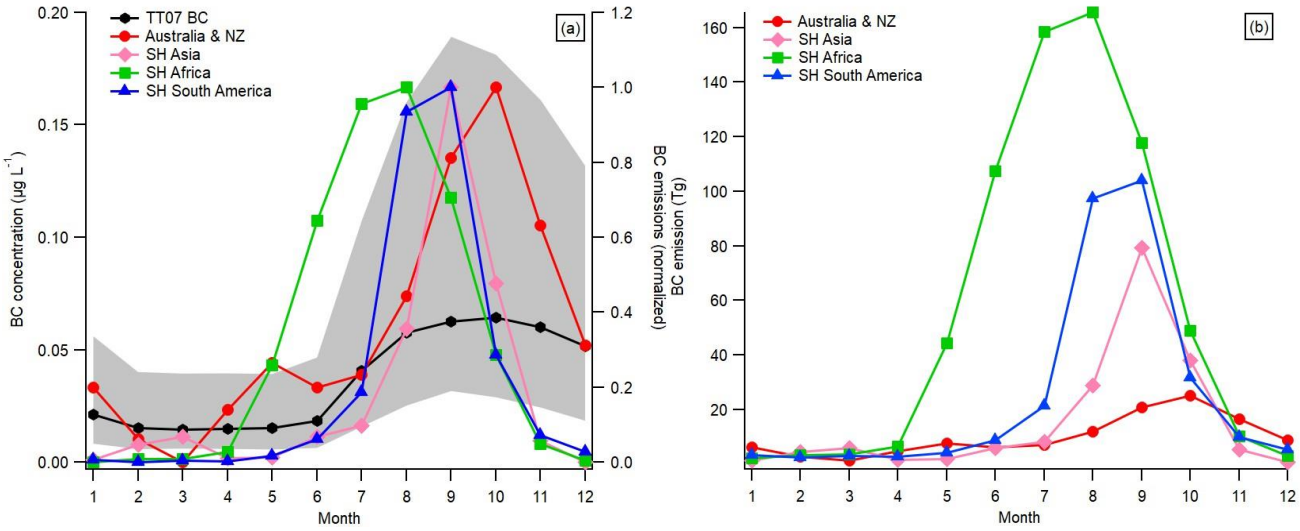
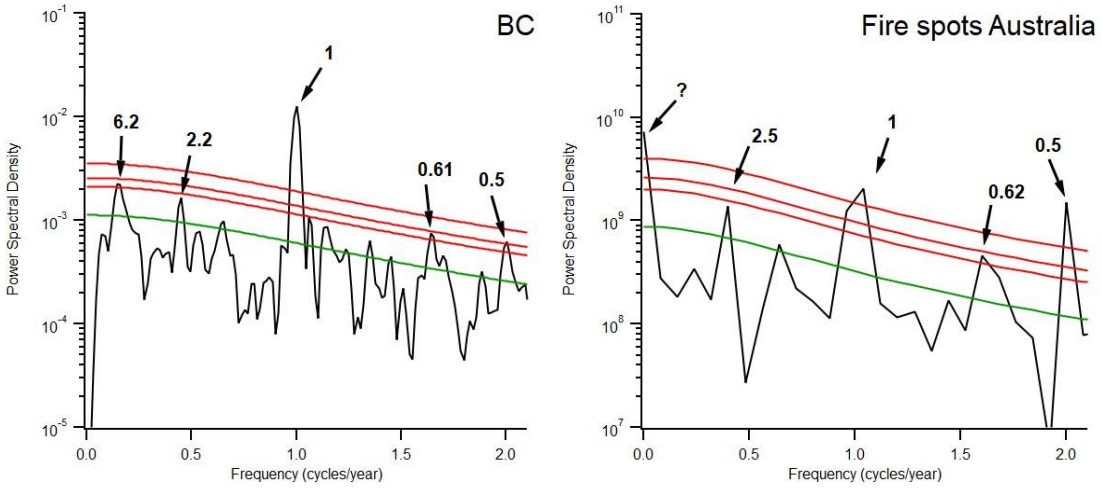


Figure ~~6~~7(a). TT07 rBC (monthly averages, 1968-2014) and BC emissions estimated from GFED4s for the four SH regions (normalized, 1997-2014). The shaded area represent 1 geometric standard deviation of monthly rBC values. (b) Absolute BC emissions estimated from GFED4s for the SH.



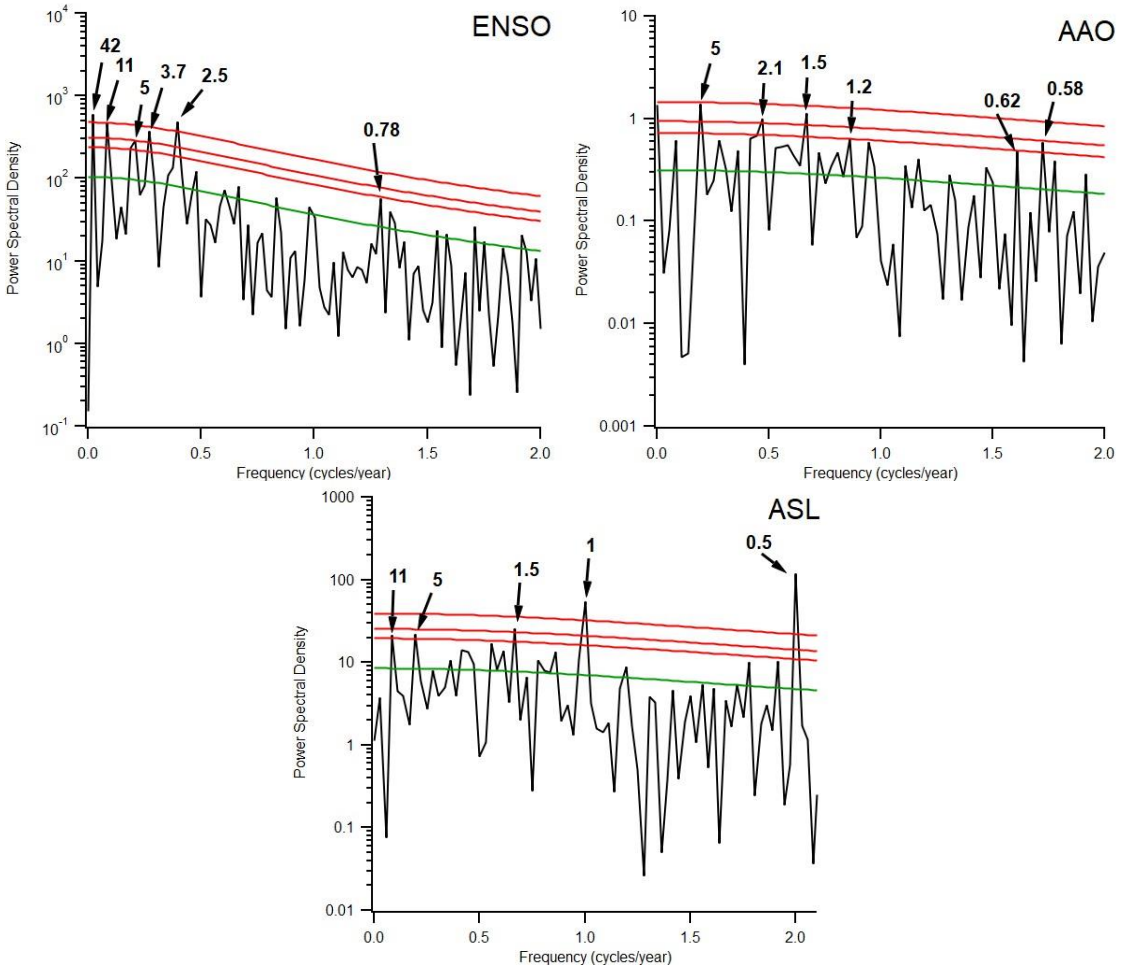


Figure ~~7~~8. Spectral analysis of the rBC concentrations ~~and Na records~~ and comparison with existing datasets (Sentinel Hotspots Australia, ASL, AAO and ENSO indexes). Numbers in bold indicate cycle frequency, in years. Red lines are confidence intervals 99% (top), 95% (middle) and 90% (bottom). Green line indicates AR1 red-noise background. The question mark in the Australian fire spots spectrum indicates a longer, unidentified cycle.

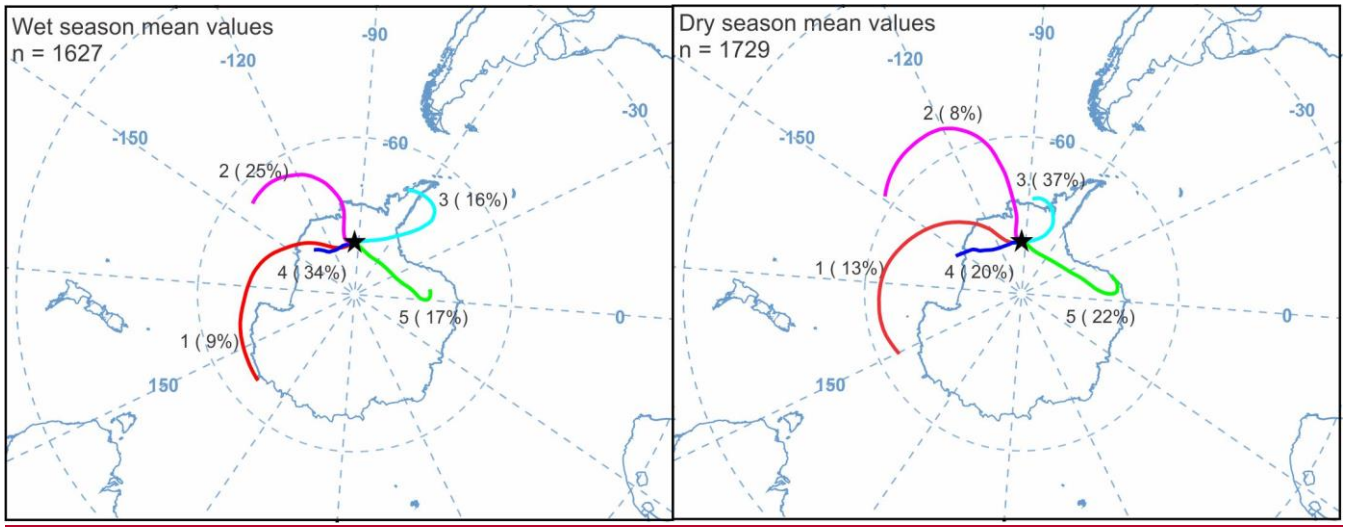


Figure 9. HYSPLIT clusters of 10-day back-trajectories ran every 5 days from 1968 to 2015 arriving at the TT07 drilling site. Results are separated by wet and dry season, and grouped in five clusters (percentage of trajectories for each cluster is shown in parenthesis). Number of trajectories (n) used for the cluster algorithm is shown at the top, on the left side.

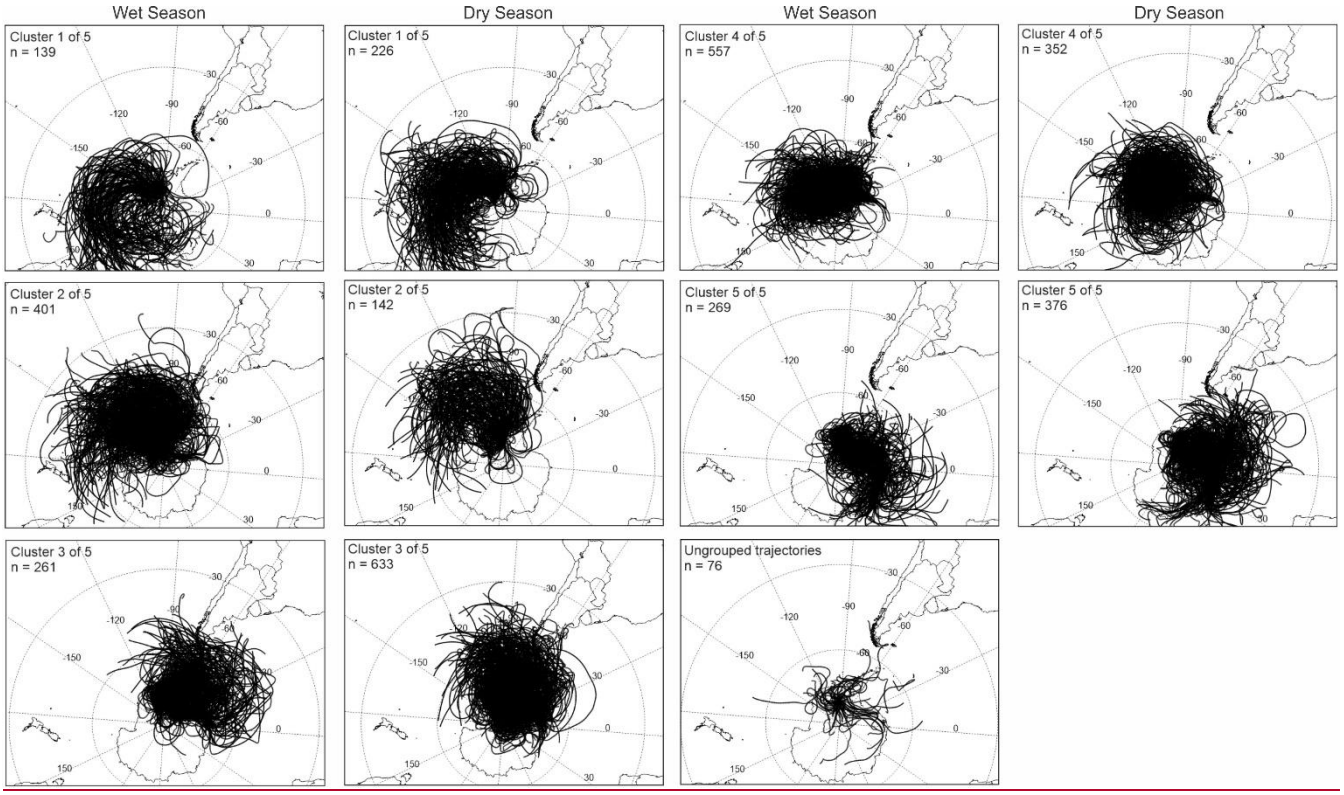


Figure 10. Individual trajectories used for the cluster analysis in figure 8. Number of trajectories (n) used for each cluster is shown at the top, on the left side. Clusters 1, 2 and 4 show air masses arriving from Australia and New Zealand to the TT07 drilling site,

while clusters 2, 3 and 4 show the (limited) contribution of South American air parcels to the site. Similar clusters from wet and dry season are side by side for comparison. Wet season presented 76 ungrouped trajectories, while dry season presented none.

Table 1. Parameters used to calculate albedo changes in snow for the TT07 site.

Incident-Flux	Diffuse
Surface spectral distribution	Summit Greenland clear-sky
Snowpack effective grain size	150 μm
Snowpack thickness	20 m
Snowpack density	400 kg/m^3
Visible albedo of underlying surface	0.2
Near-IR albedo of underlying surface	0.4
Uncoated black carbon concentration	Varied, see text
Sulfate-coated black carbon concentration	0 ppb
Dust concentration	0 ppm
Volcanic ash concentration	0 ppm
Experimental particle 1 concentration	0 ppb
MAC scaling factor	1.0

Table 2. Datasets used for the REDFIT spectral analysis.

Dataset	Data points	Range	Observation	Source
rBC	860	January 1969 December 2014	raw data[a]	TT07 core
ENSO[b]	576	January 1967 December 2014	Monthly data	Bureau of Meteorology, Australia[c]
AAO	432	January 1979 December 2014	Monthly data	NOAA[d]
ASL	432	January 1979 December 2014	Monthly data	BAS, Hosking *et al.* (2016)[e]
GFED4s	216	January 1997 December 2014	Monthly data	Global Fire Emission Database
Sentinel Hotspots	150	August 2002 December 2014	Monthly data	Geoscience Australia

Programa Queimadas	200	May 1998 December 2014	Monthly data	INPE	

[a] Not resampled, only dated by year and separated by dry/wet season.
[b] Here we use the Southern Oscillation index – SOI as the ENSO indicator.
[c] http://www.bom.gov.au/climate/current/soihtm1.shtml
[d] https://www.cpc.ncep.noaa.gov/products/precip/CWlink/
[e] https://legacy.bas.ac.uk/data/absl/

Table 3. Main results from the core rBC analysis. All values in μg L^{-1}, except fluxes, that are in μg m^{-2} yr^{-1}. Geomean = geometric mean and 1σ* = multiplicative standard deviation, representing 68.3% of the variability (Bisiaux et al., 2012b; Limpert et al., 2001)**.**

Total samples	860
Annual geomean	0.03
1σ* interval	0.020 / 0.041
Lowest/highest	0.012 / 0.080
Dry season geomean	0.057
1σ* interval	0.031 to 0.105
Lowest/highest	0.005 / 0.332
Wet season geomean	0.015
1σ* interval	0.009 to 0.027
Lowest/highest	0.001 / 0.053
rBC flux geomean	6.25
Lowest/highest	2.67 / 14.61

Table 4. Coordinates, elevation, period covered and rBC information for this study and previous studies in Antarctica with time overlap with this study. We show only studies that used the SP2 in snow/ice to have a direct comparison between them.

		Location in Antarctica	Lat/ Long	Elev. (m)	Period Covered	Annual rBC conc. (μg L^{-1})	rBC conc. range (2σ)[a]	Annual accum. (w eq m)	Annual rBC fluxes (μg m^{-2})	rBC flux range (2σ)[a]
This study	TT07	West	82°40'S 89°55'W	2122	1968-2015	0.03	0.01 to 0.06	0.21	6.25	2.7 to 14.6
Pasteris et al. (2014)	DIV2010	West	76°48'S 101°42'W	1329	1867-2010	0.17	-	0.41[b]	-	-
	PIG2010		78°00'S 96°00'W	1593	1917-2010		-	0.42[b]	-	-
	THW2010		76°46'S 121°13'W	2020	1867-2010		-	0.28[b]	-	-
Bisiaux *et al.*, 2012b	WAIS	West	79°46'S 112°08'W	1766	1963-2001[c]	0.08	0.05 to 0.12	0.2	16	9.8 to 24.4
	Law Dome	East	66°73'S 112°83'E	1390	1963-2001[c]	0.07	0.04 to 0.15	0.15	13.5	7.3 to 30.6
Bisiaux *et al.*,	NUS07-1	East	73°43'S 07°59'E	3174	1963-2006[c]	0.14	0.08 to 0.27	0.05	7.8	4.0 to 15.8

2012b	NUS07-2		76°04'S 22°28'E	3582	1963-1993[c]	0.14	0.08 to 0.24	0.03	3.9	2.4 to 7.3
	NUS07-5		78°39'S 35°38'E	3619	1963-1989[c]	0.18	0.14 to 0.24	0.02	3.62	2.6 to 5.2
	NUS07-7		82°49'S 54°53'E	3725	1963-2008[c]	0.19	0.13 to 0.29	0.02	5	3.1 to 8.0
	NUS08-4		82°49'S 18°54'E	2552	1963-2004[c]	0.15	0.08 to 0.26	0.04	5.4	2.7 to 10.0
	NUS08-5		82°38'S 17°52'E	2544	1963-1993[c]	0.12	0.08 to 0.20	0.04	4.5	2.7 to 8.0
Casey *et al.*, 2017	Clean air sector	South Pole	90°S	2835	Surface snow (2014-2015)	0.24[d]	-	0.08[e]	-	-
	Upwind of generator					0.48[d]	-		-	-
Khan *et al.*, 2018	Snowpit 1 m deep	McMurdo Dry Valleys	77°31'S 163°E	650	2006-2013	0.35[d]	-	0.05[f]	-	-

[a] Multiplicative standard deviation representing 95.5% of the interval of confidence.
[b] From Criscitiello et al. (2014).
[c] Core goes back to ~1800, we present only from 1963 on to have time overlap between these and this study.
[d] Not annual.
[e] From Mosley-Thompson et al. (1999)
[f] From Witherow and Lyons (2008)

Table 5. Albedo changes due to rBC concentrations in TT07 site (from SNICAR-online).

Concentration (μg L^{-1})	Reference	Albedo variation (relative to clean snow)
0.015	Wet season geomean	0
0.057	Dry season geomean	-0.41%
0.105	Highest seasonal geomean	-0.48%