1    **Levoglucosan and phenols in Antarctic marine, coastal and plateau aerosols**

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## **Abstract**

Due to its isolated location, Antarctica is a natural laboratory for studying atmospheric aerosols and pollution in remote areas. Here, we determined levoglucosan and phenolic compounds (PCs) at diverse Antarctic sites: on the plateau, a coastal station and during an oceanographic cruise. Levoglucosan and PCs reached the Antarctic plateau where they were observed in accumulation mode aerosols (with median levoglucosan concentrations of 6.4 pg m$^{-3}$and 4.1 pg m$^{-3}$, and median PC concentrations of 15.0 pg m$^{-3}$and 7.3 pg m$^{-3}$). Aged aerosols arrived at the coastal site through katabatic circulation with the majority of the levoglucosan mass distributed on larger particulates (24.8 pg m$^{-3}$), while PCs were present in fine particles (34.0 pg m$^{-3}$). The low levoglucosan/PC ratios in Antarctic aerosols suggest that biomass burning aerosols only had regional, rather than local, sources. General acid/aldehyde ratios were lower at the coastal site than on the plateau. Levoglucosan and PCs determined during the oceanographic cruise were 37.6 pg m$^{-3}$ and 58.5 pg m$^{-3}$ respectively. Unlike levoglucosan, which can only be produced by biomass burning, PCs have both biomass burning and other sources. Our comparisons of these two types of compounds across a range of Antarctic marine, coastal, and plateau sites demonstrate that local marine sources dominate Antarctic PC concentrations.

## **Keywords**

Biomass burning

Levoglucosan

Phenolic compounds

Antarctica

Aerosols

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## Introduction

Biomass burning encompasses the combustion of living and dead vegetation, including wildfires, prescribed burning (deforestation, shifting cultivation, agriculture waste) and domestic bio-fuel combustion (such as in fireplaces, stoves etc) (Cheng at al., 2013). Humans intentionally and accidentally ignite fires although volcanic activity and lightning also leads to forest fires. (Taylor 2010). Biomass combustion is the largest source of primary fine carbonaceous particles and the second principal source of trace gases in the global atmosphere (Akagi at al., 2011).

Biomass burning aerosols influence the climate system by affecting the Earth's solar balance(IPCC 2013; Hobbs at al., 1997), acting as cloud condensation nuclei (Novakov and Corrigan, 1996; Vestin at al., 2007) and influencing snow albedo (IPCC 2013; Flanner at al., 2007; Ramanathan and Carmichael, 2008). However, the transport, evolution and sinks of many biomass burning aerosols are not well understood. Here, we examine two classes of biomass burning tracers (levoglucosan and phenolic compounds) in Antarctic plateau, coastal, and oceanic sites to determine how distance from biomass burning source regions and subsequent transport and aging affects their concentrations and size distribution.

Antarctica is surrounded by ocean, contains little to no biomass burning sources, lacks stable human settlements, and therefore presents a natural laboratory for investigating biomass burning aerosols after long range transport. We examine the specific biomarker levoglucosan (1,6 anhydro-$\beta$-D glucopyranose) as it is an unambiguous product of cellulose combustion produced at temperatures of approximately 250°C (Kuo at al., 2011). Here, we use levoglucosan as a reference biomass burning tracer due to its specificity and high emission factors (Iinuma at al., 2007; Oros at al., 2006; Oros and Simoneit 2001a; Oros and Simoneit 2001b). Although levoglucosan can degrade in the atmosphere by reacting with OH (Hennigan at al., 2010; Hoffmann at al., 2010; Kessler at al., 2010), $NO_3$ and

73    $SO_4^-$ (Hoffmann at al., 2010), the high concentrations injected into smoke plumes suggests that

74    enough remains to allow using levoglucosan as a biomass burning tracer (Hoffmann at al., 2010). In

75    Arctic aerosols levoglucosan was determined both in conditions influenced by (Stohl at al., 2006;

76    Stohl at al., 2007) and not influenced (Fu at al., 2009; von Schneidemesser at al., 2009; Yttri at al.,

77    2014; Zangrando at al., 2013) by wildfires, while in Antarctica studies only observe levoglucosan in

78    marine aerosols (Hu at al., 2013). Ice core (Gambaro at al., 2008; Kawamura at al., 2012; Legrand at

79    al., 2007; Yao at al., 2013) and snow pit (Hegg at al., 2010; Kehrwald at al., 2012) studies demonstrate

80    that levoglucosan can reconstruct past biomass burning over annual to millennial timescales (Zennaro

81    at al., 2014) in polar locations.

82         While levoglucosan records cellulose burning, this marker alone cannot determine what type

83    of vegetation burned to produce the smoke aerosols. PCs in atmospheric aerosols may indicate the

84    types of burned plants. Methoxy phenols derive from lignin combustion. Lignin is a biopolymer

85    comprised of three different aromatic alcohols; *p*-coumaryl, coniferyl and sinapyl alcohols where

86    their proportions differ between the major plant classes. The degradation products from oxidation or

87    burning of lignin are classified as coumaryl, vanillyl and syringyl moieties (Simoneit 2002).

88    Hardwood (angiosperm) lignin (Oros and Simoneit 2001b) is enriched in sinapyl alcohol precursors

89    so burning these plants principally produces syringyl and vanillyl moieties. In deciduous tree smoke

90    the main PCs produced include homovanillyl alcohol, vanillic acid, vanillin, and syringic acid.

91    Softwoods (gymnosperms) (Oros and Simoneit 2001a) contain high proportions of coniferyl alcohol

92    with minor components from sinapyl alcohol and burning produces primarily vanillyl moieties. The

93    dominant phenolic biomarkers in conifer smoke include vanillin, homovanillic acid, vanillic acid, and

94    homovanillyl alcohol. In grasses (*gramineae*) (Oros at al., 2006) *p*-coumaryl alcohol is the dominant

95    lignin unit not prevalent in softwood and hardwood. Other significant products from burning grasses

96    are acetosyringone, syringic acid, vanillin and vanillic acid. Methoxy phenols degrade in the

97    atmosphere, where 2-methoxyphenol (guaiacol) and its isomers in the gas-phase react with OH

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98  hydroxyradicals (Coeur-Tourneur at al., 2010), while phenols react with $^3C^*$ (aromatic carbonyl)

99  (Smith at al., 2014) and some methoxy phenols in particulate matter react with $O_3$ (Net at al., 2011),

100  $NO_3$ (Liu at al., 2012), $^3C^*$(Yu at al., 2014), OH (Li at al., 2014; Yu at al., 2014), and UV (Li at al.,

101  2014).

102     Most previous determinations of PCs in aerosols were performed in zones close to residential

103  areas using biomass burning in domestic heating (Bari at al., 2010; Bari at al., 2011; Dutton at al.,

104  2010; Dutton at al., 2009; He at al., 2010; Simpson at al., 2005; Ward at al., 2011) or else in zones

105  heavily impacted from wildfire smoke (Ward at al., 2006). PCs occur in high concentrations near

106  these biomass burning sources, ranging from 10s to greater than 10,000 pg m$^{-3}$ (Bari at al., 2010; Bari

107  at al., 2011; Dutton at al., 2010; Dutton at al., 2009; He at al., 2010; Simpson at al., 2005; Ward at

108  al., 2011). In the Arctic, PCs have considerably lower concentrations with mean values (for particle

109  sizes of 10 μm to <0.49 μm) of 14 pg m$^{-3}$ (Zangrando at al., 2013). Several studies determine PCs in

110  ice and snow collected in Arctic areas (Hegg at al., 2010; Kawamura at al., 2012; McConnell at al.,

111  2007), suggesting their applicability to Antarctic sites.

112     This work determines levoglucosan and PCs including vanillic acid (VA), isovanillic acid

113  (IVA), homovanillic acid (HA), syringic acid (SyA), vanillin (VAN), syringaldehyde (SyAH), ferulic

114  acid (FA), *p*-coumaric acid (PA) and coniferyl aldehyde (CAH) in three different Antarctic

115  environments in order to investigate how transport affects the concentrations, evolution and sinks of

116  these compounds in aerosols. We examine the concentrations and particle size distributions of

117  biomass burning tracers in remote aerosols at the Concordia Station (Dome C) on the East Antarctic

118  plateau during 2011-2012, 2012-2013, the coastal Mario Zucchelli Station in 2010-2011, and marine

119  aerosol samples collected during the R/V Italica oceanographic cruise in the Southern Ocean in 2012

120  (Fig. 1).

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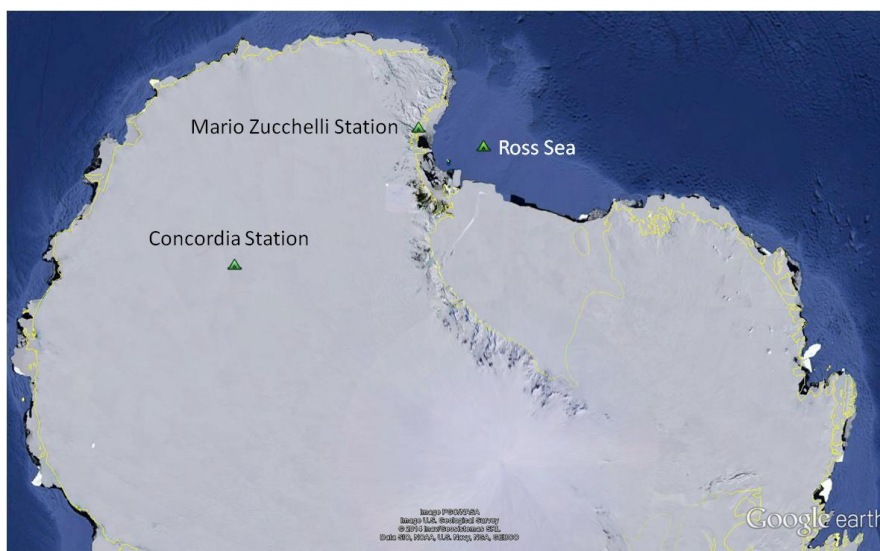
Fig 1. Map reporting the Antarctic sites studied.

## Experimental Section

### Reagents and standard solutions

HPLC/MS-grade methanol (MeOH) and acetonitrile (ACN) were purchased from Romil LTD (Cambridge, U.K.). The ultrapure water (18.2 MΩ cm, 0.01 TOC) was produced by a Purelab Flex (Elga, High Wycombe, U.K.) and formic acid (98%) was obtained by Fluka (Sigma Aldrich, Buchs, Switzerland). Levoglucosan (purity 99%), vanillin (VAN) (≥ 98%), syringic acid (SyA) (≥ 95%), homovanillic acid (HA) (≥ 98%), isovanillic acid (IVA) (97%), *p*-coumaric acid (PA) (≥ 98%), coniferyl aldehyde (CAH) (98%), were purchased from Sigma Aldrich, vanillic acid (VA) (≥ 97%), syringaldehyde (SyAH) (≥ 97%), ferulic acid (FA) (≥99%) from Fluka. Levoglucosan$^{13}C_6$(98% isotopic enriched, ≥ 98% chemical purity) from Cambridge Isotope Laboratories Inc. (Andover, MA), vanillic acid $^{13}C_1$(98% isotopic enriched, ≥ 98% chemical purity) and vanillin $^{13}C_6$(98% isotopic enriched, ≥ 98% chemical purity) from Sigma Aldrich.

### Aerosol sampling

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140    Aerosols were collected using a TE-6070, PM10 high volume air sampler (average flow 1.21 $m^3$ $min^-$

141    $^1$) with a Model TE-235 five stage high volume cascade impactor (Tisch Environmental Inc., Cleves,

142    OH) equipped with a high volume back-up filter (Quartz Fiber Filter Media 8" x 10"and 5.625" x

143    5.375" Slotted Quartz Fiber) for collecting particles in the following size ranges: 10.0 – 7.2 µm, 7.2

144    – 3.0 µm, 3.0 – 1.5 µm, 1.5- 0.95 µm, 0.95 – 0.49 µm, < 0.49 µm. Collection time was 10 days

145    resulting in a total air volume of ~15,000 $m^3$ per sample. Using this aerosol sampler, five size

146    segregated aerosol samples were collected at the Faraglione Camp (74° 42′ S – 164° 06′ E, 57 m asl),

147    approximately 3 km south of the Mario Zucchelli Station in Victoria Land, from November 29, 2010

148    to January 18, 2011. In the East Antarctic plateau (75° 06' S – 123° 20' E) approximately 1 km south-

149    west of the Dome C building, four aerosol samples were acquired from December 19, 2011 to January

150    28, 2012 while five airborne samples were collected from December 7, 2012 to January 26, 2013.

151    A TE 5000 High Volume Air Sampler (Tisch Environmental Inc., OH) was used to collect thirteen

152    TSP (Total Suspended Particles) samples on a circular quartz fiber filter (SKC Inc., Eighty Four, To-

153    13 model).Seven samples were collected over the Ross Sea (Antarctica) on the R/V Italica from

154    January 13 to February 19, 2012 (Table S1). In order to avoid contamination from the ship's exhaust

155    during the oceanographic cruise, the air samples were automatically controlled by a wind sector to

156    start sampling only when the relative wind direction ranged from -135° to 135° of the bow and the

157    relative wind was more than 1 m $s^{-1}$. Collection time was approximately five days and varied due to

158    wind direction and the cruise events resulting in air sampling volumes between 511 and 2156 $m^3$.

159    All filters were pre-combusted (4 h at 400°C in a muffle furnace) and wrapped in two aluminum foils

160    before sampling and stored in aluminum at −20°C after sampling until analysis. Blank samples were

161    collected by loading, carrying and installing the filter holder in the instrument with a closed air pump.

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163    **Sample processing, quality control and instrumental analysis**

164    Our aim was to determine all phenolic compounds and levoglucosan in the Antarctic samples using

165    an extraction in water proposed by Zangrando et al. (Zangrando at al., 2013). However, we modified

166    the preanalytical protocol by using ice during the extraction in the ultrasonic bath in order to reduce

167    the volatility and degradation of phenolic compounds. This modification allowed the extracting

168    levoglucosan and all phenolic compounds plus VAN in water. In the previous version of method

169    (Zangrando at al., 2013) SyAH and PA were extracted in methanol and VAN was not present.

170    In order to avoid contamination from laboratory air particles, samples were handled under a class 100

171    laminar flow bench. Each quartz fiber filter was cut in half using stainless steel scissors that were

172    previously washed with methanol. Filter pieces were placed into 50 mL conical flacks and spiked

173    with internal standard solutions. Slotted quartz fiber supports and circular quartz fiber filters were

174    spiked with 140 µL of isotopically-labelled $^{13}C_6$ levoglucosan (4 µgmL$^{-1}$), 70 of $^{13}C_6$vanillin (1µgmL$^-$

175    $^1$) and $^{13}C_1$vanillic acid (1µgmL$^{-1}$) standard solutions and extracted with 5 mL and then 2 mL of

176    ultrapure water by ultrasonication. Each piece of background filter was spiked with 500 µL of labeled

177    levoglucosan and 300 µL of labeled VA and VAN. Vanillin was determined using $^{13}C_6$vanillin as

178    internal standard. The filters were then extracted with 25 mL and then 5 mL of ultrapure water. The

179    extracts were combined and filtered through a 0.45 µm PTFE filter in order to remove particulates

180    before instrumental analysis.

181    Each type of sampling filter (round, backup and slotted) and each analyte were validated. The

182    trueness, reproducibility and efficiency of the sample preparation procedure (yield %) resulted in a

183    percent error of 10%, CV% less than 10% and a yield% greater than 50% for each compound. This

184    unique procedure permits determining levoglucosan and PCs. For PCs determination the instrumental

185    method in Zangrando et al. (Zangrando at al., 2013) was upgraded to add monitored transitions for

186    VAN: *m/z* 150.9/135.8 (used for quantification) and *m/z* 150.9/92.0. Good linearity was observed for

187    vanillin between 0.01 and 100 pg µL$^{-1}$, $R^2$ =0.99. For both Declustering Potential and Entrance

188    Potential Declustering potential were -50 V and -10 V. Collision Energy and Cell Exit Potential were

189    -18 V and  -11 V for *m/z* 150.9/135.8  and  -27.5 V and -6 V for *m/z* 150.9/92.0 respectively.

190    Instrumental analysis of levoglucosan compounds was performed by HPLC/(-)ESI-MS/MS as

191    described in Perrone et al. (Perrone at al., 2012).

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**Back-trajectory calculation**

194    Back-trajectories for Mario Zucchelli Station, Dome C and R/V Italica were computed using the

195    Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) transport and dispersion

196    model(Draxler and Rolph, 2013). All back-trajectories use NCEP/NCAR Global Reanalysis Data.

197    The vertical velocity model used for Mario Zucchelli Station data incorporated vertical motion while

198    we employed the isoentropic model for Dome C air mass analyses, as suggested by Stohl et al (Stohl

199    and Sodemann, 2010).

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201    In order to highlight the main pattern of air masses, 240-hour normal back-trajectories beginning 500

202    m above ground level (AGL) at Mario Zucchelli Station and Dome C were calculated during each

203    sampling campaign period. Four runs were computed for every sampling day starting every six hours

204    and the resulting trajectories were mean-clustered into 6 groups. We evaluated how altitude

205    influences the HYSPLIT back trajectories by calculating  the cluster mean back trajectories at Mario

206    Zucchelli Station and Dome C for four different heights: 10 m, 100 m, 500 m and 1000 m. Regardless

207    of the atmospheric height, the resulting air mass clusters have similar geographical trajectories (Fig.

208    S1A-1C) but where the percentages of air masses in each cluster change. Because the aim of this

209    work is to study long range transport we used an atmospheric height of 500 m (NOAA) The mean

210    mixed layer height is 200-400 m agl at Dome C (Argentini at al., 2005) and at the coastal Halley site

211    the boundary layer height is usually up to 200 m (Saiz-Lopez at al., 2008). For the oceanographic

212    cruise, we performed trajectory matrices in order to simulate the ship track. We computed 5-day back-

213    trajectories for each oceanographic 24-h sampling event.

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## Results and discussion

**Levoglucosan and Phenolic Compounds in size segregated particles over the Antarctic plateau**

In order to investigate background levoglucosan levels over the central Antarctic plateau, we determined levoglucosan concentrations during sampling campaigns in 2011-2012 and 2012-2013 resulting in respective median values of 6.4 pg m$^{-3}$ and 4.1 pg m$^{-3}$ (Fig 2A, 2B). Dome C levoglucosan concentrations were primarily present in accumulation mode aerosols (< 1 μm), accounting for 76% (2011-2012) and 77% (2012-2013) of the total levoglucosan concentrations determined in PM$_{10}$. The Dome C levoglucosan concentrations are significantly lower than mean Summit, Greenland (lat 72° 36' N lon 38° 25' W, 3231 m asl) atmospheric levoglucosan concentrations of 320 pg m$^{-3}$ (ranging from 170 to 830 pg m$^{-3}$)(von Schneidemesser at al., 2009). This order of magnitude difference in central Antarctic versus central Greenland levoglucosan concentrations may be due to the greater distance of Dome C from any biomass combustion source.
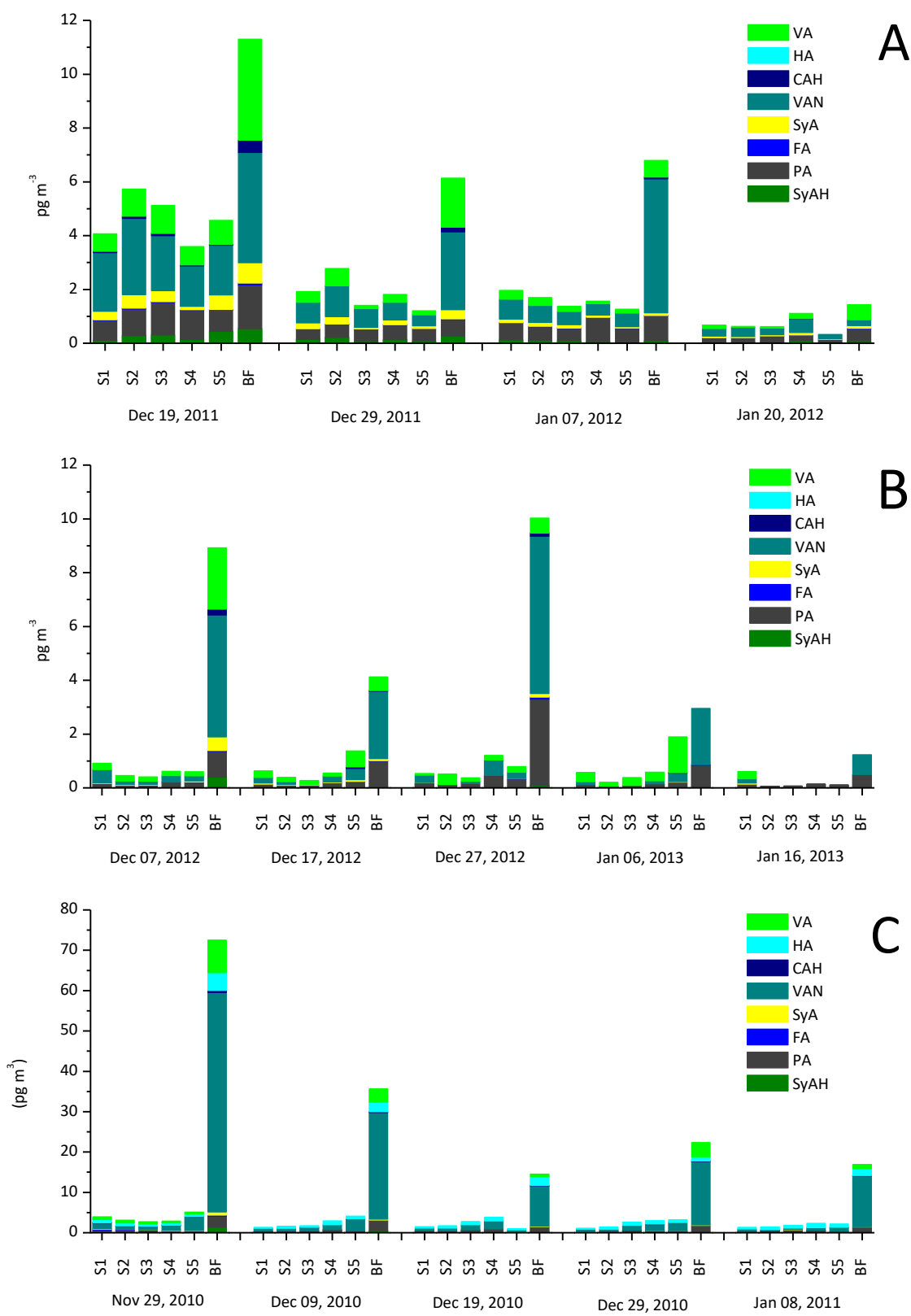
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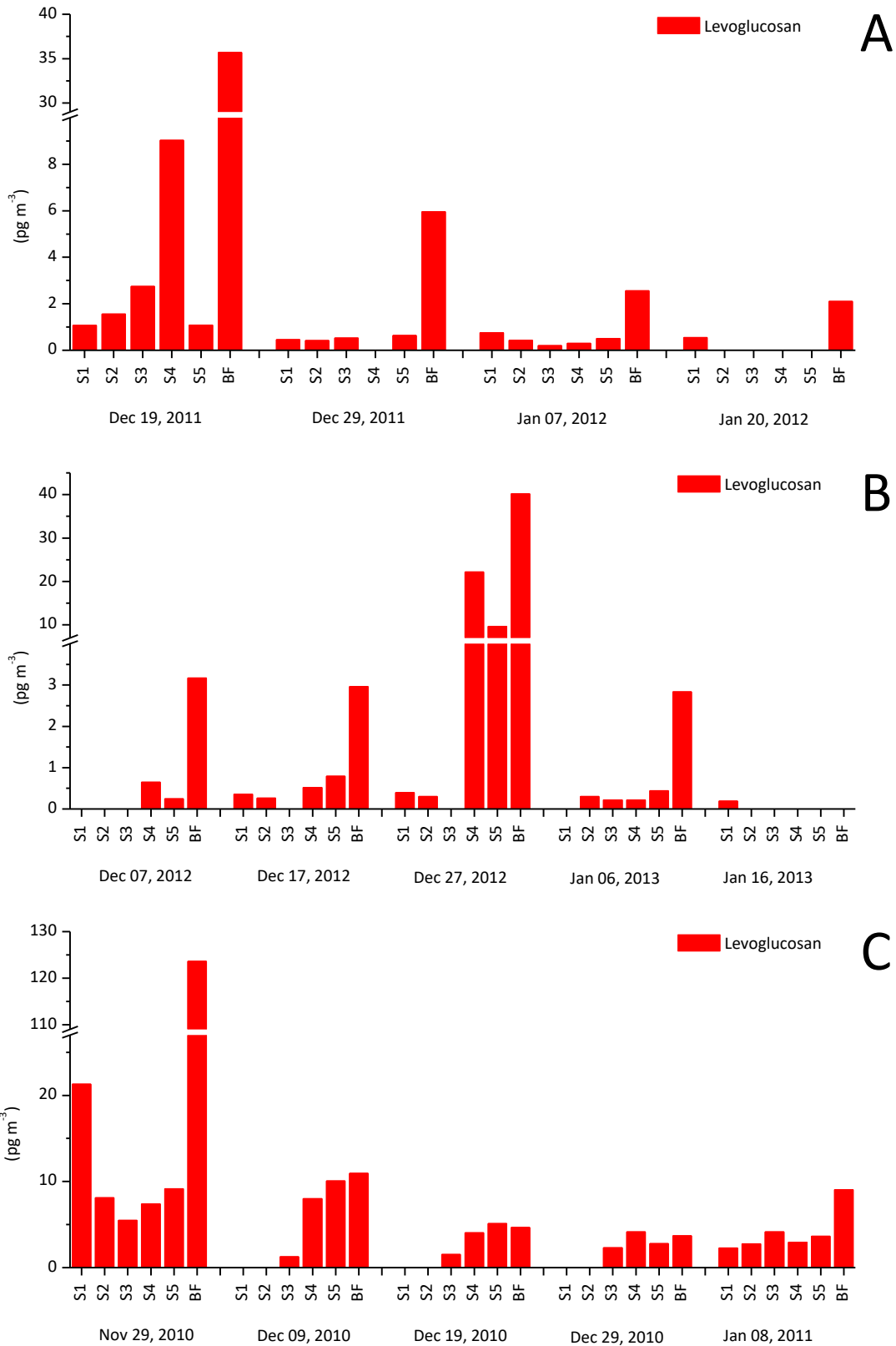
Fig 2: Size distributions of levoglucosan concentrations in samples collected at the Concordia Station during the austral summers 2011-12 (A) and 2012-13 (B) at the Mario Zucchelli Station (Antarctica) during 2010-2011 (C). Particle size dimesions (S1: 10-7.2 μm; S2: 7.2-3.0 μm; S3: 3.0-1.5 μm; S4: 1.5- 0.95 μm; S5: 0.95-0.49 μm; Backup Filter (BF): <0.49 μm).

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235    To the best of our knowledge, this study represents the first time PCs were determined in Antarctic

236    plateau aerosols. We determined nine PCs: VAN, VA, HA, PA, SyA, SyAH, IVA, CAH, FA.

237    Isovanillic acid concentrations were below detection limits in all samples in each campaign. The

238    Antarctic plateau samples from Dome C in 2011-2012 and 2012-2013 resulted in median total PC

239    atmospheric concentrations of 15.0 pg m$^{-3}$and 7.3 pg m$^{-3}$ respectively (Fig 3A, 3B). The main

240    compounds present in all sample size fractions were VAN, VA and PA. In 2011-2012 these

241    compounds respectively represented 47%, 26% and 14% of the total PCs in the < 0.49 µm size

242    fraction while in 2012-2013 these compounds accounted for 58%, 12% and 24%. HA was absent in

243    all Dome C samples.

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Fig 3: Size distributions of phenolic compound concentrations in samples collected during the austral summers 2011-12 (A) and 2012-13 (B) at the Dome C and 2010-2011 (C) at the Mario Zucchelli Station (Antarctica). Particle size dimension s(S1: 10-7.2 μm; S2: 7.2-3.0 μm; S3: 3.0-1.5 μm; S4: 1.5- 0.95 μm; S5: 0.95-0.49 μm; Backup Filter (BF): <0.49 μm).

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The majority of PCs in Dome C occur in the fine fraction, where this distribution is consistent with long range transport (Roiger at al., 2012; Fattori at al., 2005; Jarvinen at al., 2013; Udisti at al., 2012) (Figs 3A-B). PCs in fine particles (< 1 μm) accounted for the 47% of total concentration in the 2011-2012 samples and 75% of the 2012-2013 samples. Even though the majority of PCs in the Dome C aerosols occur in the fine fraction, PCs are also present in the coarse fraction in 2011-2012. This behavior is consistent with their  physico-chemical properties: PCs are semivolatile species (Hawthorne at al., 1992; He at al., 2010) that can volatilize and recondense on coarse particles (Herckes at al., 2006; Wang at al., 2011) during long-range transport.

Cluster mean back trajectories help determine why PCs may be more present in the coarse fraction in 2011-2012 (Fig. S2 and S3). The majority ,71% (2011-2012) and 68% (2012-2013), of the air masses reaching Dome C only travelled over plateau locations during the sampling periods. The remaining air masses travelled over the Southern Ocean (29% in 2011-2012 and 32% in 2012-2013). The air masses originating over the Southern Ocean reached Dome C much more quickly in 2011-2012, requiring only approximately 36 hours to reach Dome C, versus the 2012-2013 air masses that travelled between the Southern Ocean and Dome C in four to seven days. This difference in transport time may have influenced the particle size distribution. The slower-moving air masses in 2012-2013 likely deposited PCs during transport as tropospheric particles between 5 -10 μm have atmospheric lifetimes of only 1-2 days (Petzold and Karcher, 2012)

Although the majority of the Dome C samples contain levoglucosan concentrations less than 10 pg m$^{-3}$, two samples (December 19-29, 2011 and December 27, 2012 – January 6, 2013) have relatively high levoglucosan concentrations and different size distribution patterns (Fig. 2A, 2B). Both of these samples may be influenced by particular sources. The December 19 - 29, 2011 sample simultaneously contains high levoglucosan (25.6 pg m$^{-3}$) and PCs (34.4 pg m$^{-3}$) (fig 2A-3A) compared to levoglucosan concentrations in all other 2011-2012 of 1.3 and 4.0 pg m$^{-3}$ and PC concentrations of 4.8-15.3 pg m$^{-3}$. The circulation patterns during this time period (Fig. S4) demonstrate that air masses

276  reaching Dome C originated over the ocean and the back trajectory paths are similar to others

277  occurring during times with low levoglucosan and PCs concentrations. However, unusual combustion

278  sources may influence this sample. The time interval of December 19-29, 2011 encompasses holiday

279  festivities at the Dome C base, possibly accounting for the increased biomass burning concentrations.

280  The December 27, 2012 – January 6, 2013 sample also contains a plausible particular source. An

281  Antarctic traverse team arrived at Dome C December 31, 2012 (PNRA). The traverse used smoke

282  bombs that incorporate lactose to produce the smoke. Lactose is a disaccharide sugar composed from

283  glucose and galactose, which can produce levoglucosan during combustion (here at 36.4 pg m$^{-3}$), but

284  due to the lack of lignin in smoke bombs, these bombs do not produce phenolic compunds. The low

285  concentration of PCs (13.4 pg m$^{-3}$) in this sample supports this conclusion of a particular source (Fig.

286  3B).

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288  **Levoglucosan and Phenolic Compounds in size segregated particles on the Antarctic coast**

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290  We sampled at the Faraglione Camp near Mario Zucchelli Station during austral summer 2010-2011

291  using a high volume impactor. Particulate matter collected at the coastal site during 2010-2011

292  contains median atmospheric levoglucosan concentrations of 24.8 pg m$^{-3}$ (ranging between 12.9-

293  175.0 pg m$^{-3}$), with a particle size distribution that is relatively enriched in the coarse fraction (Fig

294  2C). Due to the distance from biomass burning sources, Antarctic levoglucosan concentrations are

295  substantially lower than concentrations determined in other polar coastal sites such as summer

296  concentrations in Ny Alesund (Svalbard) at Gruvebadet with mean concentrations of 65 pg m$^{-3}$

297  (ranging from 4 to 682 pg m$^{-3}$) (Zangrando at al., 2013), summer and winter concentrations at the

298  Zeppelin observatory(Yttri at al., 2014) (1020 pg m$^{-3}$ and 130 pg m$^{-3}$), and Alert (Canada)(Fu at al.,

299  2009) which has mean concentrations of 147 (ranging between 3-1076 pg m$^{-3}$ ).

300      In the five samples collected in 2010-2011, PCs were predominantly present in the fine

301  fraction (<0.49 µm). The median concentration of PCs in the <0.49 µm fraction was 22.3 pg m$^{-3}$

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302   (range 14-73 pg m$^{-3}$) while the total median concentrations in the particle size <10 μm was 33.7 pg

303   m$^{-3}$ (range 25-90 pg m$^{-3}$) (Table S2 and Fig 3C). The only other concentrations of PCs in polar

304   aerosols available in the literature were obtained at the coastal Arctic site of NyAlesund (Zangrando

305   at al., 2013). In order to compare the data collected in coastal Arctic and Antarctic sites, we excluded

306   vanillin from the Antarctic data as it was not determined at NyAlesund. The PC concentrations in

307   <0.49 μm represent 36% of the total PCs determined in the Ny Alesund samples with a median

308   concentration of 19.0 pg m$^{-3}$ (range 3.6-132.8 pg m$^{-3}$) (Zangrando at al., 2013). The main PCs present

309   in the Ny Alesund samples were VA, HA, PA and SyAH which represented 28%, 27% , 39% and

310   3.5% of the total PC concentrations, respectively (Zangrando at al., 2013). The Faraglione Camp

311   samples contained 54% of the total PC concentrations in the <0.49 μm fraction with a median total

312   concentration of 6.6 pg m$^{-3}$ (range 4.2-18.1 pg m$^{-3}$). The composition of the PCs in the < 0.49 μm

313   fraction of the Antarctic aerosol samples contained VAN (74%), VA (10%), HA (7%), PA (6%),

314   while SyA, CAH, SyAH represented only 4% of the total. The coastal samples contain HA (7%)

315   which was not present in Dome C particulate matter.

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317   At Mario Zucchelli Station in 2010-2011, 36% of the total levoglucosan concentrations were present

318   in the coarse fraction. However, the Dome C plateau levoglucosan concentrations occurred mainly in

319   accumulation mode particles where levoglucosan on coarse particles represented only 24% of the

320   total in 2010-2011 and 23% of the total in 2012-2013. This enhancement of levoglucosan

321   concentrations in the coarse fraction at Mario Zucchelli Station may result from the hygroscopic

322   growth of particles. More than 95% of air masses descend from the cold, dry Antarctic plateau (King

323   and Turner, 1997), to reach the relatively more temperate and humid Mario Zucchelli Station coastal

324   site (Fig S5).

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326   The literature demonstrates that hygroscopic properties exist in mixed organic and inorganic aerosols

327   containing levoglucosan (Svenningsson at al., 2006). Recent studies establish that VA and SyA do

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328 not hygroscopicaly grow (Mochida and Kawamura 2004), although the reaction of phenols with $^3C^*$

329 and OH produce highly oxygenated species (Li at al., 2014; Smith at al., 2014; Yu at al., 2014) with

330 higher hygroscopicity (Li at al., 2014). At Aboa (Antarctica) Asmi et al.(Asmi at al., 2010) reported

331 the high hygroscopicity of aerosols from continental air due to the presence of chemically evolved

332 species carried by particulate matter.

333

334 Our results are surprising as we mainly observe PCs in fine particles (Fig 3C) while the volatility of

335 PCs suggests that they should be distributed on coarse particles (Herckes at al., 2006) during long-

336 range transport. In addition, degradated hygroscopic compounds (Asmi at al., 2010) should also

337 increase particle size. The presence of PCs primarily in the fine fraction suggests a local Antarctic

338 source. Faraglione Camp is located on a cliff above the Ross Sea, where the ocean supplies humidity

339 and marine aerosols. The ocean is a possible local source of PCs by ejecting fine particles (<1µm)

340 containing organic compounds into the atmosphere primarily during periods of high biological

341 activity but also during periods of low primary productivity(Ault at al., 2013; O'Dowd and De Leeuw

342 2007; Schmitt-Kopplin at al., 2012).

343

344 PC ratios further support the idea that the coastal samples derive from a local source. The VA/VAN

345 and SyA/SyAH (Table 1) ratios indicate of the oxidation of PCs (Net at al., 2011) and consequently

346 the degree of aerosol transformation. Student t-tests demonstrate that mean VA/VAN and SyA/SyAH

347 ratios were significantly lower at the coastal site than at the Dome C plateau location. These results

348 were consistent for both sampling seasons with VA/VAN (p=0.0095 2011-2012; p=0.014 2012-

349 2013), and SyA/SyAH (p=0.00019 2011-2012; p=0.00012 2012-2013) demonstrating the presence

350 of more oxidized aerosols at Dome C.

351

352 Comparing PCs with levoglucosan in Antarctic aerosols helps determine if the PCs in particulate

353 matter are affected by biomass burning. Dry wood mass is composed of 25-30% lignin, while

17

354    cellulose and hemicellulose account for the remaining 40-50% and 20-30%, respectively(Oros and

355    Simoneit 2001a). As levoglucosan derives from the pyrolysis of cellulose and PCs derive from the

356    combustion of lignin, the larger proportion of cellulose in wood results in biomass burning injecting

357    more levoglucosan than PCs into smoke plumes. In general levoglucosan/VA, levoglucosan/VAN,

358    levoglucosan/SyA and levoglucosan/SyAH ratios (calculated for atmospheric aerosols affected by

359    biomass burning) range from approximately 10 to 1000 demonstrating higher concentrations of

360    levoglucosan with respect to PCs (Table 1 and references therein). In Antarctic sites, Mario Zucchelli

361    Station and Dome C, these ratios were up to 100-1000 times (Table 1) less indicating higher

362    concentrations of PCs than biomass combustion aerosols

363

364    Mario Zucchelli Station samples contained relatively consistent concentrations and particle size

365    distributions of levoglucosan (Fig 2C) and PCs (Fig 3C), except for the November 29, 2010 sample

366    that contains the highest concentrations (levoglucosan 175.0 pg m$^{-3}$ and PCs 90.3 pg m$^{-3}$) of the

367    season. In this sample the majority of the levoglucosan is present in the fine fraction, where this high

368    concentration and size fraction distribution is similar to fresh particulate matter produced from

369    biomass burning. In wood combustion aerosols levoglucosan is often associated with particles less

370    than 1.1 µm (Agarwal at al., 2010; Herckes at al., 2006; Kleeman at al., 2008; Schkolnik at al., 2005)

371    and aggregates range from 120 nm to 1 µm (Mavrocordatos at al., 2002). Similarly PCs were observed

372    in fresh smoke mainly in fine particles (Herckes at al., 2006; Iinuma at al., 2007). This combination

373    of factors suggests the influence of a particular biomass burning source such as the neighbouring

374    Italian base where an incinerator was used to burn waste such as paper, cardboard, and unvarnished

375    wood, especially during November and December 2010-2011, as personally witnessed by the author.

376

377    **Levoglucosan and Phenolic Compounds in total suspended particles over the Southern Ocean**

378    We determined levoglucosan and PCs in aerosol samples collected over the Southern Ocean during

379    the R/V Italica research cruise (Table S1) from January 13 to February 19, 2012 during the trip to and

380    from Mario Zucchelli Station. The January 13-18 and January 18-23 samples were collected during

381    the journey from Littleton Harbor, New Zealand to Mario Zucchelli Station. The January 25-29,

382    January 31- February 6, and February 7-9 samples were collected over the Ross Sea near the Antarctic

383    continent. The February 12-18 and February 18-19 samples were collected during the return trip to

384    New Zealand. We used a TSP sampler to collect fine particles, and the coarse fraction resulting

385    particles with a marine origin(O'Dowd and De Leeuw, 2007; O'Dowd at al., 2004) and from

386    hygroscopic growth(Petzold and Karcher, 2012; Raes at al., 2000). Median levoglucosan

387    concentrations were 37.6 pg m$^{-3}$, ranging from BDL to 224.1 pg m$^{-3}$ (Fig S6 and Table S2) and the

388    median phenolic compound concentrations for all samples was 58.5 pg m$^{-3}$ (Fig S7 and Table S2).

389

390    The January 13-18 sample has the highest levoglucosan concentrations (224.1 pg m$^{-3}$ ) of the marine

391    samples, and also contains high total PC concentrations of 107.4 pg m$^{-3}$ Back trajectories demonstrate

392    that these high concentrations may be due to the influence of fires occurring in New Zealand (Fig

393    S8A and S9) during this time period, where the smoke plumes were transported to the sampling area.

394    Low concentrations in the February 18-19 sample, which is also located in New Zealand coastal areas,

395    registered levoglucosan BDL and low PC concentrations of 16.6 pg m$^{-3}$. These low levels can be

396    explained by the short sampling time (only two days for this sample versus five days for the other

397    samples).

398

399    The January 18-23 and February 12-18 samples were collected mainly in the Antarctic Convergence

400    area distant from both New Zealand and Antarctica, with a marked presence of sea ice. Levoglucosan

401    has atmospheric concentrations of 22.4 and 37.6 pg m$^{-3}$ and PCs of 5.4 pg m$^{-3}$ and 9.7 pg m$^{-3}$

402    respectively.

403

404        January 25-29, January 31- February 6, and February 7-9 samples were collected over the

405    Ross Sea (Fig S10), and have a mean levoglucosan concentration of 73.5 pg m$^{-3}$. Recently Hu et al.

406    (Hu at al., 2013) reported levoglucosan concentrations recorded during Southern Ocean research

407    cruises of 4.8 ng m$^{-3}$ (range 1.1-18 ng m$^{-3}$) near the East Antarctica coast and 3.4 ng m$^{-3}$ (range 0.18-

408    11 ng m$^{-3}$) near the West Antarctica shore. These data together with black carbon studies from the

409    Antarctic stations Syowa (Hara at al., 2010), Troll (Fiebig at al., 2009), Ferraz (Pereira at al., 2006),

410    Halley (Wolff and Cachier 1998) and Ross Island (Murphey and Hogan 1992) demonstrate that South

411    American biomass burning is a possible source of aerosols reaching Antarctica (Hara at al., 2010).

412    However, 5-day back trajectories demonstrate that katabatic winds transport material from the interior

413    of West Antarctica during the time period comprised by samples January 25-29, January 31- February

414    6, and February 7-9 (Fig. S8C-E). The major influence of katabatic winds conveying fine

415    particles(Asmi at al., 2010; Pant at al., 2011) originating from the interior of the continent (Fig S11A),

416    appears during the February 7-9 sample when we record low levoglucosan concentrations in the Ross

417    Sea.

418

419        In addition to katabatic circulation, during individual days of the sampling periods January

420    25-27 and February 1, 2, and 5 the wind blew from the Ross Sea to the Ross Ice Shelf (Figs S11B).

421    In the January 25-29 and January 31- February 6 samples, the higher levoglucosan concentrations

422    can be explained by the intrusion of air masses passing the Southern Ocean (versus originating from

423    the Antarctic interior) where these air masses may contain biomass burning aerosols (Hu at al., 2013).

424

425        PC concentrations are relatively high for the time periods when the cruise traveled near the

426    Ross Ice shelf (January 25-29, 2012 and, January 31-February 6 2012) and are especially high when

427    the research vessel sailed through the Ross Sea polynya (February 7-9, 2012), (Fig S7). HA (67%)

428    was the most abundant phenolic compound in the Ross Sea samples followed by PA (22%), VA (8%),

429    and FA (1%) and SyA (3%). We did not determine the aldehydes VAN and SyAH as field blanks for

20

430    these compounds were higher than the amount sampled, suggesting high levels of these aldehydes in

431    marine aerosols. The TSP sampler demonstrates that HA and PA are prevalent in marine aerosols,

432    even including the coarse fraction. These marine coarse fraction aerosols help interpret the coastal

433    coarse fraction data where HA and PA increased to 29% and 26%, showing an influence of marine

434    aerosols on coastal particles.

435

436    **Conclusion**

437

438    Here, we determined that levoglucosan can be detected in remote areas, even in sites as distant

439    from biomass burning sources as Dome C, East Antarctica. Our results indicate that the biomass

440    burning tracer levoglucosan reached the inner Antarctic plateau through long-range transport and was

441    present in accumulation-mode aerosols. At the coastal site levoglucosan was substantially present on

442    coarse particles created by hygroscopic growth. During an oceanographic cruise on the Ross Sea

443    when winds arrived to the Ross Sea from the Southern Ocean, levoglucosan was present in higher

444    concentrations in comparison to levels observed during prevailing katabatic winds.

445    PCs on the Antarctic plateau were mainly observed in fine particles although the coarse

446    fraction was considerable in the 2011-2012 Dome C samples. PCs in coastal Mario Zucchelli Station

447    particle matter were primarily observed in fine particles, unlike levoglucosan that was also present in

448    the coarse fraction. The Antarctic samples had different levoglucosan/PC ratios from aerosols directly

449    affected by biomass burning. PCs in coastal samples were less oxidized in comparison to those

450    collected on the plateau, as demonstrated by low acid/aldehyde ratios at the coastal site.

451

452    The differences between levoglucosan and PCs, regardless of sampling time or location, suggests that

453    PCs have sources other than biomass burning. Such a non-biomass burning source is consistent with

454    the literature including results from Ny Alesund (Arctic) (Zangrando at al., 2013) and in Alert

455    (Canadian Arctic) (Fu at al., 2009). The lack of vegetation in Antarctica excludes plant debris as a

possible source of PCs and suggests that the ocean is a likely source, especially as lignin is present in marine environments. Lignin compounds account for one third of terrestrial plant biomass, are produced in vascular plant tissues (Li at al., 2012), and are present in soils (Cecchi at al., 2004), natural waters (Louchouarn at al., 2000), rivers (Benner and Opsahl 2001; Lobbes at al., 2000; Onstad at al., 2000), in oceans both as dissolved organic matter and particulate organic matter(Hedges at al., 1997; Opsahl and Benner 1997; Opsahl and Benner 1998) and aerosols (Shakya at al., 2011). Lignin contains methoxyphenols (Opsahl and Benner 1997) and degrades photochemically (Opsahl and Benner 1998) and microbiologically (Edelkraut 1996). Although the degradation of lignin in water is described in the literature, only a limited number of publications determine free PCs in water (Opsahl and Benner 1995), where these studies are limited to free vanillin in rivers and sounds (Edelkraut 1996; Keil at al., 2011). Other oceanic sources of PCs include the aging of *Emiliana Huxleyi* (Seyedsayamdost at al., 2011), an ubiquitous marine microalga present in tropical to polar waters that produces PA as an algal lignin breakdown product, which may then be transferred to the atmosphere. In addition, the relatively high percentage of HA at the Mario Zucchelli Station coastal site (29% of the coarse fraction) and in marine aerosols collected during the oceanographic cruise indicates that this compound is a possible marine biomarker.

We determined that PCs are reliable tracers close to their source, yet their atmospheric concentrations may be influenced by other sources after long-range transport. Further studies on the geographical variations of PCs at their source and after transport are essential in order to fully understand their applicability as environmental markers

495  **Supporting Information Available**

496  Navigation details and cruise tracks are available in Table S1 and Figure S10. The atmospheric

497  concentrations (Table S2) and distributions (Figures S6, and S7) of molecular tracers for all Antarctic

498  campaigns are reported. Back-trajectories, CMBT and vector wind plots are reported in Figures S1A-

499  1C, S2-S5, S8A-G, S11A-B. The NASA, FIRMS Web Fire Mapper data is reported in S10.

500
501  **References**
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| | Category | Sampling period | VA/VAN | SyA/SyAH | LG/VA | LG/VAN | LG/SyA | LG/SyAH | Ref |
|---|---|---|---|---|---|---|---|---|---|
| Missula (MT, USA) | Smoke | Wild fire | | | 343 | | 1568 | | (Ward at al., 2006) |
| Libby (MT, USA) | Urban Aerosol (PM2.5) | Winter 2003-2004 | | | 51.3 | | 2031.7 | 490.4 | (Ward at al., 2011) |
| Libby (MT, USA) | Urban Aerosol (PM2.5) | Winter 2008-2009 | | | 30.1 | | 4117.2 | | (Ward at al., 2011) |
| NanJing (China) | Size segregate urban Aerosol (PM9) | Biomass burning Haze | | | | 252 (Haze) 408, 246 (none-Haze) | | | (Ward at al., 2011) |
| Rodônia (Brazil) | Forest Aerosol (PM2.5) | Biomass burning period | 8.2 (day) 4.9 (night) | 1.9 (day) 1.0 (night) | 75.9 (day) 66.0 (night) | 622.0 (day) 324.7 (night) | 64.2 (day) 46.5(night) | 123.8(day) 47.2 (night) | (Kundu at al., 2010) |
| Rodônia (Brazil) | Forest Aerosol | Biomass burning period | 6.9 (Pasture site) 6.2 (Forest site) | 1.5 (Pasture site) 5.5 (Forest site) | 115.4 (Pasture site) 344.6 (Forest site) | 796.9 (Pasture site) 2125.0 (Forest site) | 65.9 (Pasture site) 149.1 (Forest site) | 101.2 (Pasture site) 822.6 (Forest site) | (Graham at al., 2002) |
| Jeju Island (Korea) | Aerosol (TSP) | spring | | | 134.4 | | 363 | | (Wang at al., 2009) |
| Dittausen (Germany) | Urban Aerosol (PM10) | Nov 2005-Mar 2006 | | | | 2441.0 | | 53.0 | (Bari at al., 2009) |
| Chennai (India) | Urban Aerosol (PM10) | Winter | 1.3 | | 112.0 | 83.0 | 54.1 | | (Fu at al., 2010) |
| Chennai (India) | Urban Aerosol (PM10) | Summer | 0.9 | | 140.5 | 198.2 | 179.0 | | (Fu at al., 2010) |
| Seattle (WA, USA) | Urban Aerosol (PM10, PM2.5) | Winter | | | | 122.5 (PM10) 135.5 (PM2.5) | | 185.1 (PM10) 228.9 (PM2.5) | (Simpson at al., 2004) |
| NyAlesund (Svalbard) | Size segregate Aerosol (PM10) | 25 Apr-14 Sep Boreal summer | | 5.0 | 4.3 | | 71.2 | 338.4 | (Zangrando at al., 2013) |
| MZS | Aerosol size sequestred (PM10) | 29 Nov- 18 Jan Austral summer | 0.1 | 0.5 | 10.1 | 1.0 | 162.3 | 69.7 | this work |
| DC 2011-2012 | Size segregate Aerosol (PM10) | Dic 2011-Jan 2012 Austral summer | 0.4 | 1.3 | 3.9 | 1.1 | 10.3 | 12.9 | this work |
| DC 2012-2013 | Size segregate Aerosol (PM10) | Dic 2012-Jan 2013 Austral summer | 0.5 | 1.3 | 1.7 | 1.0 | 14.3 | 18.2 | this work |

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845 **Table 1**: LG/VA, LG/VAN, LG/SyA and LG/SyAH ratios calculated using means reported in the literature and in this work, as well as VA/VAN
846 and SyA/SyAH, ratios which indicate the oxidation of PCs. LG is the abbreviation for levoglucosan.

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