Levoglucosan and phenols in Antarctic marine, coastal and plateau aerosols

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HIGHLIGHTS
- Levoglucosan and phenolic compounds were detected in remote Antarctic aerosols.
- Antarctic samples had different levoglucosan/PC ratios than biomass burning aerosol.
- Coastal PCs were less oxidized in comparison to those collected on the plateau.
- The results suggest that PCs have sources other than biomass burning in Antarctica.

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.
1. Introduction

Biomass burning encompasses the combustion of living and dead vegetation, and includes wildfires, prescribed burning (deforestation, shifting cultivation, agriculture waste) and domestic bio-fuel combustion (such as in fireplaces, stoves) (Cheng et al., 2013). Humans intentionally and accidentally ignite fires although volcanic activity and lightning also lead 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 et al., 2011).

Biomass burning aerosols influence the climate system by affecting the Earth’s solar balance (IPCC, 2013; Hobbs et al., 1997), acting as cloud condensation nuclei (Novakov and Corrigan, 1996; Vestin et al., 2007) and influencing snow albedo (IPCC, 2013; Flanner et 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-β-D-glucopyranose) as it is an unambiguous product of cellulose combustion produced at temperatures of approximately 250 °C (Kuo et al., 2011). Here, we use levoglucosan as a reference biomass burning tracer due to its specificity and high emission factors (Inumaa et al., 2007; Oros et al., 2006; Oros and Simoneit, 2001a; Oros and Simoneit, 2001b). Although levoglucosan can degrade in the atmosphere by reacting with OH (Hennigan et al., 2010; Hoffmann et al., 2010; Kessler et al., 2010), NO3 and SO4 (Hoffmann et al., 2010), the high concentrations injected into smoke plumes suggest that enough remains to allow using levoglucosan as a biomass burning tracer (Hoffmann et al., 2010). In Arctic aerosols levoglucosan was determined both in conditions influenced by (Stohl et al., 2006; Stohl et al., 2007) and not influenced (Fu et al., 2009; von Schneidemesser et al., 2009; Yttri et al., 2014; Zangrando et al., 2013) by wildfires, while in Antarctica studies only observe levoglucosan in marine aerosols (Hu et al., 2013). Ice core (Gambaro et al., 2008; Kawamura et al., 2012; Legrand et al., 2007; Yao et al., 2013) and snow pit (Hegg et al., 2010; Kehrwald et al., 2012) studies demonstrate that levoglucosan can reconstruct past biomass burning over annual to millennial timescales (Zennaro et al., 2014) in polar locations.

While levoglucosan records cellular burning, this marker alone cannot determine what type of vegetation burned to produce the smoke aerosols. PCs in atmospheric aerosols may indicate the types of burned plants. Methoxy phenols derive from lignin combustion. Lignin is a biopolymer comprised of three different aromatic alcohols; p-coumaryl, coniferyl and sinapyl alcohols where their proportions differ between the major plant classes. The degradation products from oxidation or burning of lignin are classified as coumaryl, vanillyl and syringyl moieties (Simoneit, 2002). Hardwood (angiosperm) lignin (Oros and Simoneit, 2001b) is enriched in sinapyl alcohol precursors so burning these plants principally produces syringyl and vanillyl moieties. In deciduous tree smoke the main PCs produced include homovanillic acid, vanillic acid, vanillin, and syringic acid. Softwoods (gymnosperms) (Oros and Simoneit, 2001a) contain high proportions of coniferyl alcohol with minor components from sinapyl alcohol and burning produces primarily vanillyl moieties. The dominant phenolic biomarkers in conifer smoke include vanillin, homovanillic acid, vanillic acid, and homovanillyl alcohol. In grasses (gramineae) (Oros et al., 2006) p-coumaryl alcohol is the dominant lignin unit not prevalent in softwood and hardwood. Other significant products from burning grasses are acetosyringone, syringic acid, vanillin and vanillic acid. Methoxy phenols degrade in the atmosphere, where 2-methoxyphenol (guaiacol) and its isomers in the gas-phase react with OH hydroxylradicals (Coeur-Tournaire et al., 2010), while phenols react with 3C (acrylic carbonyl) (Smith et al., 2014) and some methoxy phenols in particulate matter react with O3 (Net et al., 2011), NO3 (Liu et al., 2012), 3C (Yu et al., 2014), OH (Li et al., 2014; Yu et al., 2014), and UV (Li et al., 2014). Most previous determinations of PCs in aerosols were performed in zones close to residential areas using biomass burning in domestic heating (Bari et al., 2010, 2011; Dutton et al., 2009, 2010; He et al., 2010; Simpson et al., 2005; Ward et al., 2011) or else in zones heavily impacted from wildfire smoke (Ward et al., 2006). PCs occur in high concentrations near these biomass burning sources, ranging from 10 s to greater than 10,000 pg m−3 (Bari et al., 2010, 2011; Dutton et al., 2009, 2010; He et al., 2010; Simpson et al., 2005; Ward et al., 2011). In the Arctic, PCs have considerably lower concentrations with mean values (for particle sizes of 10 μm to <0.49 μm) of 14 pg m−3 (Zangrando et al., 2013). Several studies determine PCs in ice and snow collected in Arctic areas (Hegg et al., 2010; Kawamura et al., 2012; Mcconnell et al., 2007), suggesting their applicability to Antarctic sites.

This work determines levoglucosan and PCs including vanillic acid (VA), isoavamic acid (IVA), homovanillic acid (HA), syringic acid (SyA), vanillin (VAN), syringaldehyde (SyAH), ferulic acid (FA), p-coumaric acid (PA) and coniferyl aldehyde (CAH) in three different Antarctic environments in order to investigate how transport affects the concentrations, evolution and sinks of these compounds in aerosols. We examine the concentrations and particle size distributions of biomass burning tracers in remote aerosols at the Concordia Station (Dome C) on the East Antarctic plateau during 2011–2012, 2012–2013, the coastal Mario Zucchelli Station in 2010–2011, and marine aerosol samples collected during the R/V Italica oceanographic cruise in the Southern Ocean in 2012 (Fig. 1).

2. Experimental section

2.1. 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%), isoavamic 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 13C6 (98% isotopic enriched, ≥98% chemical purity) from Cambridge Isotope Laboratories Inc. (Andover, MA), vanillic acid 13C4 (98% isotopic enriched, ≥98% chemical purity) and vanillin 13C6 (98% isotopic enriched, ≥98% chemical purity) from Sigma Aldrich.

2.2. Aerosol sampling

Aerosols were collected using a TE-6070, PM10 high volume air sampler (average flow 1.21 m3 min−1) with a Model TE-235 five stage high volume cascade impactor (Tisch Environmental Inc., Cleves, OH) equipped with a high volume back-up filter (Quartz Fiber Filter Media 8″ × 10″ and 5.625″ × 5.375″ Slotted Quartz Fiber) for collecting particles in the following size ranges: 10.0–2.2 μm, 2.2–0.5 μm, 0.5–0.4 μm, 0.4–0.3 μm, 0.3–0.2 μm, 0.2–0.1 μm. Using this aerosol sampler, five size segregated aerosol samples were collected at the Faraglione Camp (74° 42′ 5″–164° 06′ E, 57 m asl), approximately 3 km south of the Mario Zucchelli Station in Victoria
Land, from November 29, 2010 to January 18, 2011. In the East Antarctic plateau (75° 06′ S–123° 20′ E) approximately 1 km south-west of the Dome C building, four aerosol samples were acquired from December 19, 2011 to January 28, 2012 while five airborne samples were collected from December 7, 2012 to January 26, 2013. At both terrestrial sampling sites impactors were fixed directly on the ground. Sampling details are in Table S1.

A TE 5000 High Volume Air Sampler (Tisch Environmental Inc., OH) attached to the ship deck was used to collect thirteen TSP (Total Suspended Particles) samples on a circular quartz fiber filter (SKC Inc., Eighty Four, To-13 model). Seven samples were collected over the Ross Sea (Antarctica) on the R/V Italica from January 13 to February 19, 2012 (Table S2). In order to avoid contamination from the ship’s exhaust during the oceanographic cruise, the air samples were automatically controlled by a wind sector to start sampling only when the relative wind direction ranged from $-135°$ to $135°$ of the bow and the relative wind was more than $1 \text{ m s}^{-1}$. Collection time was approximately five days and varied due to wind direction and the cruise events resulting in air sampling volumes between 511 and 2156 m$^3$.

All filters were pre-combusted (4 h at 400 °C in a muffle furnace) and wrapped in two aluminum foils before sampling and stored in aluminum at $-20 \text{ °C}$ after sampling until analysis. Blank samples were collected by loading, carrying and installing the filter holder in the instrument with a closed air pump.

2.3. Sample processing, instrumental analysis and quality control

Our aim was to determine all phenolic compounds and levoglucosan in the Antarctic samples using an extraction in water. In the previous method proposed by Zangrando et al. (2013) levoglucosan, VA, IVA, HA, Sya and FA were extracted in water while SyAH and PA were extracted in methanol. VAN was not present in the previous PCs method. In this work we modified the preanalytical protocol by using ice during the extraction in the ultrasonic bath in order to reduce the volatility and degradation of phenolic compounds. This modification allowed extracting levoglucosan and all phenolic compounds plus VAN in water.

The HPLC/(−)ESI–MS/MS analytical methods for PCs determination are reported in Zangrando et al. (2013) while the levoglucosan methods are presented in Perrone et al. (2012). Briefly, the samples were analyzed by HPLC/ESI–MS/MS using an Agilent 1100 Series HPLC system (Agilent, Waldbronn, Germany) coupled to an API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada).

In order to chromatographically separate PCs, we used a Zorbax Extend C18 column (150 mm × 4.6 mm, 3.5 μm, Agilent) with an eluent flow rate of 500 μL min$^{-1}$. A binary elution was used, eluent A was 0.01% formic acid in water and eluent B was of methanol/acetonitrile (80/20) mixture. Details on the chromatographic run and gradient program used are in Zangrando et al. (2013). Data were collected in negative ion mode by Multiple Reaction Monitoring. A summary of transitions monitored are reported in Table S3. We upgraded the instrumental method by also including transitions for vanillin.

For levoglucosan determination, the sample was injected onto two connected Zorbax SB-Aq columns (150 mm × 2.1 mm, 3.5 μm, Agilent); with eluent flow of 80 μL min$^{-1}$, where the mobile phases were included water (solvent A) and acetonitrile (solvent B). Details of the chromatographic separation are reported in Perrone et al. (2012). In the tandem mass spectrometer, negative ions produced in the ion source were analyzed by monitoring the transitions reported in Table S3. We upgraded the instrumental method by also including transitions for vanillin.

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The preanalytical steps in this paper also differ from the methods in Zangrando et al. (2013) and Perrone et al. (2012) in that ultrasound extraction is carried only in water in an ice bath. In order to avoid contamination from laboratory air particles, samples were handled under a class 100 laminar flow bench. Each quartz fiber filter was cut in half using stainless steel scissors that were previously washed with methanol. Filter pieces were placed into 50 mL conical flacks and spiked.
with internal standard solutions. Slotted quartz fiber supports and circular quartz fiber filters were spiked with 140 μL of isotopically-labeled $^{13}$C$_6$ levoglucosan (4 μg mL$^{-1}$), 70 μL of $^{13}$C$_6$ vanillin (1 μg mL$^{-1}$) and $^{13}$C$_6$ vanillin acid (1 μg mL$^{-1}$) standard solutions and extracted with 5 mL and then 2 mL of ultrapure water by ultrasonication in an ice bath. Each piece of background filter was spiked with 500 μL of labeled levoglucosan and 300 μL of labeled VA and VAN. Vanillin was determined using $^{13}$C$_6$ vanillin as internal standard. The filters were then extracted with 25 mL and then 5 mL of ultrapure water. The extracts were combined and filtered through a 0.45 μm PTFE filter in order to remove particulates before instrumental analysis.

Quantification was performed using internal standards. We used labeled $^{13}$C$_6$ levoglucosan to determine levoglucosan and we used $^{13}$C$_1$ vanillin acid and $^{13}$C$_6$ vanillin for determining PCs (Table S4). In order to quantify the concentrations, we compared the peak areas of the native compounds with the labeled internal standard. Results were corrected for the instrumental response factors. During the validation methods for each PC, the linearity of response was in the range of 0.01–100 pg mL$^{-1}$, and between 0.1 and 1000 pg mL$^{-1}$ for levoglucosan. Good linearity was obtained for all compounds and the R$^2$ values were always above 0.99. The concentrations found in Antarctic sample extracts were always within the calibration range.

Due to the change in the preanalytical procedure from the previously published work, the analytical methods for each PC were validated using each type of sampling filter (round, backup and slotted). The true-linearity, reproducibility and efficiency of the sample preparation procedure (yield %) resulted in a percent error and CV% less than 10% and a yield% in general greater than 50% for each compound (Table S4).

Before analyzing Antarctic samples, we evaluated the analytical accuracy of the levoglucosan determination method through the repeated analysis (n = 3) of the SRM 1649a for each type of sampling support (round, backup and slotted). These analyses resulted in values of $159 \pm 1$ μg g$^{-1}$ for round quartz filters, $161 \pm 8$ μg g$^{-1}$ for filters and $164 \pm 8$ μg g$^{-1}$ for back up filters. The obtained results are similar to published values in Perrone et al. (2012) and references therein.

During the sampling periods, field blanks for each station were taken at the beginning, during and end of the sampling campaign: six at Dome C (three for each sampling campaign), four at Mario Zucchelli and eight during the R/V Italica research cruise. In Table S5 is reported the mean absolute blank amount which was subtracted from the analytical results. The method detection limit for each station (MDL) was evaluated as 3 times the standard deviation of these field blanks.

At Dome C where the concentrations were the lowest, to demonstrate that the concentrations found are significant, the mean absolute blank for levoglucosan and VAN has been calculated as a percentage of the absolute total found in each sample. The field blanks found represented on average 20% of the concentration found in the back up filters and 24% found in the slotted filters for levoglucosan, and 26% and 30% respectively for VAN.

2.4. Back-trajectory calculation

Back-trajectories for Mario Zucchelli Station, Dome C and R/V Italica were computed using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYPLIT) transport and dispersion model (Draxler and Rolph, 2013). All back-trajectories use NCEP/NCAR Global Reanalysis Data. The vertical velocity model used for Mario Zucchelli Station data incorporated vertical motion while we employed the isentropic model for Dome C air mass analyses, as suggested by Stohl et al. (Stohl and Sodemann, 2010).

In order to highlight the main pattern of air masses, 240-hour normal back-trajectories beginning 500 m above ground level (AGL) at Mario Zucchelli Station and Dome C were calculated during each sampling campaign period. Four runs were computed for every sampling day starting every 6 h and the resulting trajectories were mean-clustered into 6 groups. Because the aim of this work is to study long-range transport we used an atmospheric height of 500 m (NOAA) as this height is above the mean mixed layer height of 200–400 m agl at Dome C (Argentini et al., 2005) and up to 200 m at the coastal Halley site (Saiz-Lopez et al., 2008). We calculated back trajectories at 10 m, 100 m, 500 m and 1000 m. The comparison of the resulting clustered air mass demonstrated similar trajectories for all of these heights (Fig. S1A,B,C). As we examined long-range transport we used the trajectories for 500 m as it is close to, but above, the mixed height and therefore eliminates some of the local sources that contribute to the air masses of the mixed layer. For the oceanographic cruise, we performed trajectory matrices in order to simulate the ship track. We computed 5-day back-trajectories for each oceanographic 24-h sampling event.

3. Results and discussion

3.1. Levoglucosan and phenolic compounds in total suspended particles over the Southern Ocean

We determined levoglucosan and PCs in aerosol samples collected over the Southern Ocean during the R/V Italica research cruise from January 13 to February 19, 2012 during the trip to and from Mario Zucchelli Station. Sample summaries, and sampling details in Table S2, while Table 1 records atmospheric concentrations of levoglucosan and PCs. Median levoglucosan concentrations were 37.6 pg m$^{-3}$, ranging from BDL to 224.1 pg m$^{-3}$ (Fig. S2 and Table S6) and the median phenolic compound concentrations for all samples was 58.5 pg m$^{-3}$ (Fig. S3 and Table S6).

The January 13–18 sample has the highest levoglucosan concentrations of the marine samples, and also contains high total PC concentrations (Table 1). Back trajectories demonstrate that these high concentrations may be due to the influence of fires occurring in New Zealand (Figs. S4A and S5) during this time period, where the smoke plumes were transported to the sampling area. Low concentrations were determined in samples collected mainly in the Antarctic convergence (January 18–23 and February 12–18). The February 18–19 sample, which is located near New Zealand coastal areas, registered levoglucosan BDL and low PC concentrations of 16.6 pg m$^{-3}$. In this last case low levels can be explained by the short sampling time (only two days for this sample versus five days for the other samples).

January 25–29, January 31–February 6, and February 7–9 samples were collected over the Ross Sea (Fig. S6), and have a mean levoglucosan concentration of 73.5 pg m$^{-3}$. Recently Hu et al. (2013) reported levoglucosan concentrations recorded during Southern Ocean research cruises of 4.8 ng m$^{-3}$ (range of 1.1–18 ng m$^{-3}$) near the East Antarctica coast and 3.4 ng m$^{-3}$ (range of 0.18–11 ng m$^{-3}$) near the West Antarctica shore. These data together with black carbon studies from the Antarctic stations Syowa (Hara et al., 2010), Troll (Fiebig et al., 2009), Ferraz (Pereira et al., 2006), Halley (Wolff and Cachier, 1998) and Ross Island (Murphy and Hogan, 1992) demonstrate that South American biomass burning is a possible source of aerosols reaching Antarctica (Hara et al., 2010). However, 5-day back trajectories demonstrate that katabatic winds transport material from the interior of West Antarctica during the time period comprised by samples January 25–29, January 31–February 6, and February 7–9 (Fig. S4C–E). The major influence of katabatic winds conveying fine particles (Asmi et al., 2010; Pant et al., 2011) originating from the interior of the continent (Fig. S7A), appears during the February 7–9 sample when we record low levoglucosan concentrations in the Ross Sea.

In addition to katabatic circulation, during individual days of the sampling periods January 25–27 and February 1, 2, and 5 the wind blew from the Ross Sea to the Ross Ice Shelf (Fig. S7B). In the January 25–29 and January 31–February 6 samples, the higher levoglucosan concentrations can be explained by the intrusion of air masses passing the Southern Ocean (versus originating from the Antarctic interior) where these air masses may contain biomass burning aerosols (Hu et al., 2013).
PC concentrations are relatively high for the time periods when the cruise traveled near the Ross Ice shelf (January 25–29, 2012 and January 31–February 6, 2012) and are especially high when the research vessel sailed through the Ross Sea polynya (February 7–9, 2012). These marine coarse fraction aerosols help interpret the coastal influence of marine aerosols on coastal particles. The TSP sampler demonstrates that air masses reaching Dome C much more quickly in 2011–2012, requiring only approximately 36 h to reach Dome C, versus the 2012–2013 air masses that traveled 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 and 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, B). 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$^{-3}$) 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. S10) demonstrate that air masses reaching Dome C originated over the ocean and the back trajectory paths are similar to others occurring during times with low levoglucosan and PCs concentrations. However, unusual combustion sources may influence this sample. The time interval of December 19–29, 2011 encompasses holiday festivities at the Dome C base, possibly accounting for the increased biomass burning concentrations. The December 27, 2012–January 6, 2013 sample also contains a plausibly particular source. An Antarctic traverse team arrived at Dome C December 31, 2012 (PNRA). The traverse used smoke bombs that incorporate lactose to produce the smoke. Lactose is a saccharide sugar composed from glucose and galactose, which can produce levoglucosan during combustion (here at 36.4 pg m$^{-3}$), but due to the lack of lignin in smoke bombs, these bombs do not produce phenolic compounds. The low concentration of PCs (13.4 pg m$^{-3}$) in this sample supports this conclusion of a particular source (Fig. 3B).

### 3.3. Levoglucosan and phenolic compounds in size segregated particles on the Antarctic coast

We sampled at the Faraglione Camp near Mario Zucchelli Station during austral summer 2010–2011 using a high volume impactor. Particulate matter collected at the coastal site during 2010–2011 contains median atmospheric levoglucosan concentrations of 24.8 pg m$^{-3}$ (ranging between 12.9 and 175.0 pg m$^{-3}$), with a particle size distribution that is relatively enriched in the coarse fraction (Fig. 2C). Due to the distance from biomass burning sources, Antarctic levoglucosan concentrations are substantially lower than concentrations determined in central Antarctic versus central Greenland levoglucosan concentrations may be due to the greater distance of Dome C from any biomass combustion source.

To the best of our knowledge, this study represents the first time PCs were determined in Antarctic plateau aerosols. We determined nine PCs: VAN, VA, HA, PA, SyA, SyAH, IVA, CAH, FA. Isovanillin acid concentrations were below detection limits in all samples in each campaign. The Antarctic plateau samples from Dome C in 2011–2012 and 2012–2013 resulted in median total PC atmospheric concentrations of 15.0 pg m$^{-3}$ and 7.3 pg m$^{-3}$ respectively (Fig. 3A, B). The main compounds present in all sample size fractions were VAN, VA and PA. In 2011–2012 these compounds respectively represented 47%, 26% and 14% of the total PCs in the <0.49 μm size fraction while in 2012–2013 these compounds accounted for 58%, 12% and 24%. HA was absent in all Dome C samples.

### Table 1

Atmospheric concentration of levoglucosan and PCs determined during the R.V Italica research cruise.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Levoglucosan (pg m$^{-3}$)</th>
<th>PCs (pg m$^{-3}$)</th>
<th>Sampling area</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 13–18</td>
<td>224</td>
<td>107.4</td>
<td>Littleton Harbor — Southern Ocean</td>
</tr>
<tr>
<td>January 18–23</td>
<td>22</td>
<td>5.4</td>
<td>Southern Ocean — Mario Zucchelli Station</td>
</tr>
<tr>
<td>January 25–29</td>
<td>103</td>
<td>64.9</td>
<td>Ross Sea</td>
</tr>
<tr>
<td>January 31–February 6</td>
<td>103</td>
<td>58.5</td>
<td>Ross Sea</td>
</tr>
<tr>
<td>February 7–9</td>
<td>15</td>
<td>113.9</td>
<td>Ross Sea</td>
</tr>
<tr>
<td>February 12–18</td>
<td>38</td>
<td>9.7</td>
<td>Mario Zucchelli Station — Southern Ocean</td>
</tr>
<tr>
<td>February 18–19</td>
<td>BDL</td>
<td>16.6</td>
<td>Southern Ocean — Littleton Harbor</td>
</tr>
</tbody>
</table>

Table 1: Atmospheric concentration of levoglucosan and PCs determined during the R.V Italica research cruise.
other polar coastal sites such as summer concentrations in Ny Alesund (Svalbard) at Gruvebadet with mean concentrations of 65 pg m$^{-3}$ (ranging from 4 to 682 pg m$^{-3}$) (Zangrando et al., 2013), summer and winter concentrations at the Zeppelin observatory (Yttri et al., 2014) (1020 pg m$^{-3}$ and 130 pg m$^{-3}$), and Alert (Canada) (Fu et al., 2009) which has mean concentrations of 147 (ranging between 3 and 1076 pg m$^{-3}$).

In the five samples collected in 2010–2011, PCs were predominantly present in the fine fraction ($<0.49\ \mu m$). The median concentration of PCs in the $<0.49\ \mu m$ fraction was 22.3 pg m$^{-3}$ (range of 14–73 pg m$^{-3}$) while the total median concentrations in the particle size $<10\ \mu m$ was 33.7 pg m$^{-3}$ (range 25–90 pg m$^{-3}$) (Table S6 and Fig. 3C). The only other concentrations of PCs in polar aerosols available in the literature were obtained at the coastal Arctic site of NyAlesund (Zangrando et al., 2013). In order to compare the data collected in coastal Arctic and Antarctic sites, we excluded vanillin from the Antarctic data as it was not determined at NyAlesund. The PC concentrations in $<0.49\ \mu m$ represent 36% of the total PCs determined in the NyAlesund samples with a median concentration of 19.0 pg m$^{-3}$ (range of 3.6–132.8 pg m$^{-3}$) (Zangrando et al., 2013). The main PCs present in the Ny Alesund samples were VA, HA, PA and SyAH which represented 28%, 27%, 39% and 3.5% of the total PC concentrations, respectively (Zangrando et al., 2013). The Faraglione Camp samples contained 54% of the total PC concentrations in the $<0.49\ \mu m$ fraction with a median total concentration of 6.6 pg m$^{-3}$ (range 4.2–18.1 pg m$^{-3}$). The composition of the PCs in the $<0.49\ \mu m$ fraction of the Antarctic aerosol

![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 dimensions (S1: 10–7.2 \mu m; S2: 7.2–3.0 \mu m; S3: 3.0–1.5 \mu m; S4: 1.5–0.95 \mu m; S5: 0.95–0.49 \mu m; backup filter (BF): <0.49 \mu m).](image-url)
samples contained VAN (74%), VA (10%), HA (7%), PA (6%), while SyA, CAH, SyAH represented only 4% of the total. The coastal samples contain HA (7%) which was not present in Dome C particulate matter.

Mario Zucchelli Station samples contained relatively consistent concentrations and particle size distributions of levoglucosan (Fig. 2C) and PCs (Fig. 3C), except for the November 29, 2010 sample that contains the highest concentrations (levoglucosan 175.0 pg m\(^{-3}\) and PCs 90.3 pg m\(^{-3}\)) of the season. In this sample the majority of the levoglucosan is present in the fine fraction, where this high concentration and size fraction distribution is similar to fresh particulate matter produced from biomass burning. In wood combustion aerosols levoglucosan is often associated with particles less than 1.1 \(\mu\)m (Agarwal et al., 2010; Herckes et al., 2006; Kleeman et al., 2008; Schkolnik et al., 2005) and aggregates range from 120 nm to 1 \(\mu\)m (Mavrocordatos et al., 2002). Similarly PCs were observed in fresh smoke mainly in fine particles (Herckes et al., 2006; Iinuma et al., 2007). This combination of factors suggests the influence of a particular biomass burning source such as the neighboring Italian base where an incinerator was used to burn waste such as paper, cardboard, and unvarnished wood, especially during November and December 2010–2011, as personally witnessed by the author.

At Mario Zucchelli Station in 2010–2011, 36% of the total levoglucosan concentrations were present in the coarse fraction (>1 \(\mu\)m). However, the Dome C plateau levoglucosan concentrations occurred mainly in accumulation mode particles where levoglucosan on coarse particles represented only 24% of the total in 2010–2011 and...
23% of the total in 2012–2013. This enhancement of levoglucosan concentrations in the coarse fraction at Mario Zucchelli Station may result from the hygroscopic growth of particles. More than 95% of air masses descend from the cold, dry Antarctic plateau (King and Turner, 1997), to reach the relatively more temperate and humid Mario Zucchelli Station coastal site (Fig. S11).

The literature demonstrates that hygroscopic properties exist in mixed organic and inorganic aerosols containing levoglucosan (Svenningsson et al., 2006). Recent studies establish that VA and SyA do not hygroscopically grow (Mochida and Kawamura, 2004), although the reaction of phenols with $^{3}$C and OH produce highly oxygenated species (Li et al., 2014; Smith et al., 2014; Yu et al., 2014) with higher hygroscopicity (Li et al., 2014). At Aboa (Antarctica) Asmi et al. (2010) reported the high hygroscopicity of aerosols from continental air due to the presence of chemically evolved species carried by particulate matter.

Our results are surprising as we mainly observe (66% of the total) PCs in particles $<$0.49 μm (Fig. 3C) while levoglucosan in the $<$0.49 μm fraction was only 33% of the total. Considering the more temperate coastal temperature and the volatility of PCs, we would expect the PCs to be distributed on coarser particles (Herckes et al., 2006). In addition, degraded hygroscopic compounds (Asmi et al., 2010) should also increase particle size. The presence of PCs primarily in the fine fraction suggests that PCs and levoglucosan have different sources where PCs may also incorporate a local Antarctic source. Faraglione Camp is located on a cliff above the Ross Sea, where the ocean supplies humidity and marine aerosols. The ocean is a possible local source of PCs by ejecting the reaction of phenols with $^{3}$C while levoglucosan in the $<$0.49 μm fraction is sequestered.

Table 2

<table>
<thead>
<tr>
<th>Category</th>
<th>Sampling period</th>
<th>VA/VAN</th>
<th>SyA/SyAH</th>
<th>LG/VA</th>
<th>LG/VAN</th>
<th>LG/SyA</th>
<th>LG/SyAH</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Missula (MT, USA) Smoke</td>
<td>Wild fire Winter 2003–2004</td>
<td>343</td>
<td>51.3</td>
<td>1568</td>
<td>2031.7</td>
<td>490.4</td>
<td></td>
<td>Ward et al. (2006)</td>
</tr>
<tr>
<td>Libby (MT, USA) Urban aerosol (PM2.5)</td>
<td>Winter 2008–2009</td>
<td>30.1</td>
<td>4117.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ward et al. (2011)</td>
</tr>
<tr>
<td>Nanjing (China) Size segregate urban aerosol (PM10)</td>
<td>Biomass burning haze</td>
<td>252 (haze)</td>
<td>408, 246 (none-haze)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ward et al. (2011)</td>
</tr>
<tr>
<td>Rodônia (Brazil) Forest aerosol (PM2.5)</td>
<td>Biomass burning period</td>
<td>6.9 (pasture site)</td>
<td>6.2 (forest site)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ward et al. (2011)</td>
</tr>
<tr>
<td>Rodônia (Brazil) Forest aerosol (PM10)</td>
<td>Biomass burning period</td>
<td>6.9 (pasture site)</td>
<td>6.2 (forest site)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ward et al. (2011)</td>
</tr>
<tr>
<td>Jeju Island (Korea) Aerosol (TSP)</td>
<td>Spring Nov 2005–Mar 2006</td>
<td>134.4</td>
<td>2441.0</td>
<td>363</td>
<td></td>
<td></td>
<td></td>
<td>Wang et al. (2009)</td>
</tr>
<tr>
<td>Dittausen (Germany) Urban aerosol (PM10)</td>
<td>Winter</td>
<td>1.3</td>
<td>112.0</td>
<td>83.0</td>
<td>54.1</td>
<td></td>
<td></td>
<td>Fu et al. (2010)</td>
</tr>
<tr>
<td>Chennai (India) Urban aerosol (PM10)</td>
<td>Summer</td>
<td>0.9</td>
<td>140.5</td>
<td>198.2</td>
<td>179.0</td>
<td></td>
<td></td>
<td>Fu et al. (2010)</td>
</tr>
<tr>
<td>Seattle (WA, USA) Urban aerosol (PM10, PM2.5)</td>
<td>Winter</td>
<td>102.5 (PM10)</td>
<td>135.5 (PM2.5)</td>
<td>71.2</td>
<td>185.1 (PM10)</td>
<td>228.9 (PM2.5)</td>
<td>338.4</td>
<td>Simpson et al. (2004)</td>
</tr>
<tr>
<td>Ny-Alesund (Svalbard) Size segregate aerosol (PM10)</td>
<td>25 Apr–14 Sep Boreal summer</td>
<td>5.0</td>
<td>4.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zangrando et al. (2013)</td>
</tr>
<tr>
<td>MZS (Svalbard) Aerosol size segregated (PM10)</td>
<td>29 Nov–18 Jan Austral summer</td>
<td>0.1</td>
<td>0.5</td>
<td>1.0</td>
<td>162.3</td>
<td>69.7</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>DC 2011–2012 Size segregate aerosol (PM10)</td>
<td>Dec 2011–Jan. 2012 Austral summer</td>
<td>0.4</td>
<td>1.3</td>
<td>1.1</td>
<td>10.3</td>
<td>12.9</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>DC 2012–2013 Size segregate aerosol (PM10)</td>
<td>Dec 2012–Jan. 2013 Austral summer</td>
<td>0.5</td>
<td>1.3</td>
<td>1.7</td>
<td>1.0</td>
<td>14.3</td>
<td>18.2</td>
<td>This work</td>
</tr>
</tbody>
</table>

PC ratios further support the idea that the coastal samples derive from a local source. The VA/VAN and SyA/SyAH (Table 2) ratios indicate the oxidation of PCs (Net et al., 2011) and consequently the degree of aerosol transformation. Student t-tests demonstrate that mean VA/VAN and SyA/SyAH ratios were significantly lower at the coastal site than at the Dome C plateau location. These results were consistent for both sampling seasons with VA/VAN (p = 0.0095 2011–2012; p = 0.014 2012–2013), and SyA/SyAH (p = 0.00019 2011–2012; p = 0.00012 2012–2013) demonstrating the presence of more oxidized aerosols at Dome C.

Comparing PCs with levoglucosan in Antarctic aerosols helps determine if the PCs in particulate matter are affected by biomass burning. Dry wood mass is composed of 25–30% lignin, while cellulose and hemi-cellulose account for the remaining 40–50% and 20–30%, respectively (Oros and Simonet, 2001a). As levoglucosan derives from the pyrolysis of cellulose and PCs derive from the combustion of lignin, the larger proportion of cellulose in wood results in biomass burning injecting more levoglucosan than PCs into smoke plumes. In general levoglucosan/VA, levoglucosan/VAN, levoglucosan/SyA and levoglucosan/SyAH ratios (calculated for atmospheric aerosols affected by biomass burning) range from approximately 10 to 1000 demonstrating higher concentrations of levoglucosan with respect to PCs (Table 2 and references therein). In Antarctic sites, Mario Zucchelli Station and Dome C, these ratios were up to 100–1000 times (Table 2) less indicating higher concentrations of PCs than biomass combustion aerosols.

The differences between levoglucosan and PCs, regardless of sampling time or location, suggest that PCs have sources other than biomass.
burning. Such a non-biomass burning source is consistent with the literature including results from Ny Aalesund (Arctic) (Zangrando et al., 2013) and in Alert (Canadian Arctic) (Fu et 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 et al., 2012), and are present in soils (Cecchi et al., 2004), natural waters (Louchouarn et al., 2000), rivers (Benner and Opsahl, 2001; Lobbes et al., 2000; Onstad et al., 2000), in oceans both as dissolved organic matter and particulate organic matter (Hedges et al., 1997; Opsahl and Benner, 1997; Opsahl and Benner, 1998) and aerosols (Shakya et 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; Kell et al., 2011). Other oceanic sources of PCs include the aging of Emiliana Huxleyi (Seyedsayamdost et 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.

4. Conclusions

Here, we determined that levoglucosan can be detected in remote areas, even in sites as distant from biomass burning sources as Dome C, East Antarctica. Our results indicate that the biomass burning tracer levoglucosan reached the inner Antarctic plateau through long-range transport and was present in accumulation-mode aerosols. At the coastal site levoglucosan was substantially present on coarse particles created by hygroscopic growth. During an oceanographic cruise on the Ross Sea when winds arrived to the Ross Sea from the Southern Ocean, levoglucosan was present in higher concentrations in comparison to levels observed during prevailing katabatic winds. PCs on the Antarctic plateau were mainly observed in fine particles although the coarse fraction was considerable in the 2011–2012 Dome C samples. PCs in coastal Mario Zucchelli Station particle matter were primarily observed in fine particles, unlike levoglucosan that was also present in the coarse fraction. The Antarctic samples had different levoglucosan/PC ratios from aerosols directly affected by biomass burning. PCs in coastal samples were less oxidized in comparison to those collected on the plateau, as demonstrated by low acid/aldheyde ratios at the coastal site. These results suggest that PCs in Antarctic aerosols include other sources than just biomass burning. 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.

Acknowledgments

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Appendix A. Supplementary data

Meteorological conditions, navigation details and cruise tracks are available in Tables S1, S2 and Fig. S10. In Table S3 instrumental details, in S4 results of PCs validation and S5 and blands and MDL. The atmospheric concentrations (Table S6) and distributions (Figs. S2, and S3) of molecular tracers for all Antarctic campaigns are reported. Back-trajectories, CMBT and vector wind plots are reported in Figs. S1A–IC, S4A–C, S7A–B, S8–S11. The NASA, FIRMS Web Fire Mapper data is reported in S5, and Google map Ross Sea cruise in S6. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2015.11.166.

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