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## Levoglucosan indicates high levels of biomass burning aerosols over oceans from the Arctic to Antarctic

Qi-Hou Hu<sup>1\*</sup>, Zhou-Qing Xie<sup>1\*</sup>, Xin-Ming Wang<sup>2</sup>, Hui Kang<sup>1</sup> & Pengfei Zhang<sup>1,3</sup>

<sup>1</sup>Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China, <sup>2</sup>State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China, <sup>3</sup>Department of Earth and Atmospheric Sciences, City College of New York, New York, NY 10031, USA.

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Correspondence and requests for materials should be addressed to Z.-Q.X. (zqxie@ustc.edu.cn)

\* These authors contributed equally to this work.

Biomass burning is known to affect air quality, global carbon cycle, and climate. However, the extent to which biomass burning gases/aerosols are present on a global scale, especially in the marine atmosphere, is poorly understood. Here we report the molecular tracer levoglucosan concentrations in marine air from the Arctic Ocean through the North and South Pacific Ocean to Antarctica during burning season.

Levoglucosan was found to be present in all regions at ng/m<sup>3</sup> levels with the highest atmospheric loadings present in the mid-latitudes (30°–60° N and S), intermediate loadings in the Arctic, and lowest loadings in the Antarctic and equatorial latitudes. As a whole, levoglucosan concentrations in the Southern Hemisphere were comparable to those in the Northern Hemisphere. Biomass burning has a significant impact on atmospheric Hg and water-soluble organic carbon (WSOC) from pole-to-pole, with more contribution to WSOC in the Northern Hemisphere than in the Southern Hemisphere.

**B**iomass burning, such as straw burning, biomass fuel combustion, and wildfires, discharges numerous kinds of gases and aerosols, such as CO<sub>2</sub>, CO, CH<sub>4</sub>, black carbon (BC), alcohols, organic acids and persistent organic pollutants (POPs)<sup>1,2</sup>, and plays an important role on air quality<sup>3</sup>. As an important component of atmospheric aerosols<sup>4</sup>, biomass burning aerosols affect earth's radiation budget and thus climate. In addition, biomass burning accounts for 4.4% of the total carbon loss in terrestrial ecosystems<sup>5</sup>, and thereby has an effect on the global carbon cycle. A suitable tracer is needed to estimate the influence of biomass burning.

Levoglucosan (1,6-anhydro-β-D-glucopyranose), derived from pyrolysis of cellulose and hemicellulose at high temperatures (>300°C)<sup>6</sup>, is a superior molecular tracer of biomass burning aerosols compared to traditional tracers (e.g. K<sup>+</sup> and BC) because of its single source. Although levoglucosan can be degraded in the atmosphere, especially oxidized by OH radicals as reported in some simulation experiments and model studies<sup>7,8</sup>, it was still considered as an ideal tracer for biomass burning due to its relative stability and high emission factors<sup>7</sup>. Levoglucosan as the tracer of biomass burning aerosols had been well applied in many studies in continents and coastal regions<sup>9–16</sup>. Information about levoglucosan as a biomass burning tracer in the marine boundary layer was gained through samples collected over oceans in the low and middle latitudes of the Northern Hemisphere during a round-the-world cruise from October 1989 to March 1990<sup>17</sup>, over the western North Pacific, the East China Sea and the Sea of Japan during an Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) campaign from March to April 2001<sup>18</sup>, and over the southern Beaufort Sea during a France–Canada–USA joint Arctic campaign (MALINA) in summer 2009<sup>19</sup>, as well as samples over remote islands in the North Atlantic Ocean<sup>20</sup> and the western North Pacific Ocean<sup>21</sup> (Table S1). Nevertheless, these studies were all confined to the Northern Hemisphere. More studies over oceans on larger scales are needed for a better understanding of the influence of biomass burning on marine aerosols.

During the 3<sup>rd</sup> Chinese Arctic Research Expedition (CHINARE 08) and the 26<sup>th</sup> Chinese Antarctic Research Expedition (CHINARE 09/10), aerosol samples were collected in the marine boundary layer from the Arctic to the Antarctic, across more than 150° latitudes. Biomass burning has a strong seasonal cycle. The peak burning time is summer, i.e., August–October, June–October, and September–December for boreal regions, Equatorial Asia, and Australia/South America, respectively<sup>5,22,23</sup>. Therefore, most of our samples were collected during the burning season in corresponding regions. We analyzed levoglucosan as well as WSOC, inorganic ions and



elements in the samples, and estimated the influence of biomass burning emissions on marine aerosols on a global scale, especially in the Southern Hemisphere for the first time.

## Results

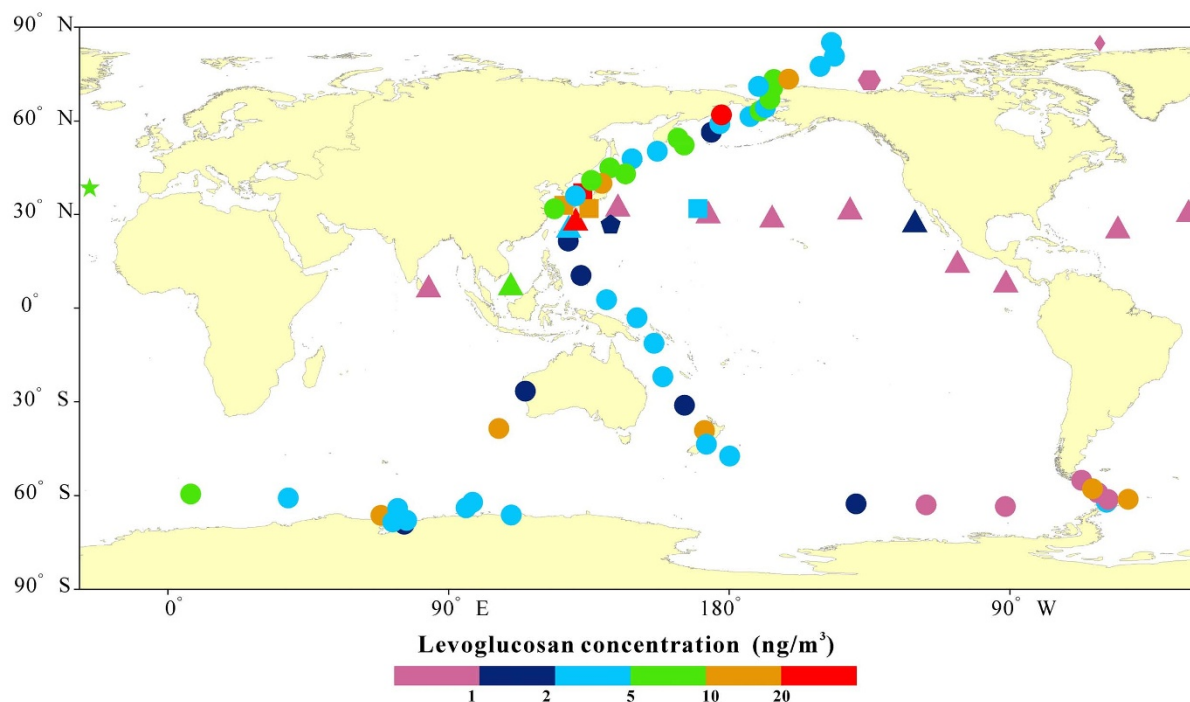
Levoglucosan and WSOC varied over a wide range during the cruises (Figure S1). Levoglucosan ranged from 0.18 to 41 ng/m<sup>3</sup>, with a mean of  $5.4 \pm 6.2$  ng/m<sup>3</sup>. There was no significant difference between levoglucosan concentrations in the Northern Hemisphere and those in the Southern Hemisphere ( $P = 0.2$ ). WSOC ranged from 86 to 3850 ng/m<sup>3</sup>, with an average of  $859 \pm 673$  ng/m<sup>3</sup>. WSOC from biomass burning (WSOC<sub>BB</sub>), calculated by the levoglucosan/WSOC conversion factor of 0.10 μg/μgC according to the biomass burning plume in Georgia, US<sup>24</sup>, ranged from 1.8 to 414 ng/m<sup>3</sup>, with an average of  $54 \pm 62$  ng/m<sup>3</sup>. Combined with results reported in the literature, the global distribution of levoglucosan in the marine boundary layer is summarized in Figure 1 and discussed in detail below.

**Levoglucosan in low latitude samples.** The concentration of levoglucosan in the atmosphere is influenced by emissions, atmospheric circulation, and deposition and degradation during transport. Although Equatorial Asia is one of the main sources of biomass burning emissions<sup>5</sup> and big fires during our cruises were evident on fire maps from NASA satellites (Figure S2a), levoglucosan concentrations in the low latitude (30° S–30° N) samples ( $2.7 \pm 1.1$  ng/m<sup>3</sup>, Table 1) were lower than those in middle latitude regions of the Northern Hemisphere and the Southern Hemisphere ( $P = 0.05$ ). The concentration variation in this region was relatively narrow and the minimum value was relatively high (Figure S1a), revealing its stable and local source. One possible reason for low levoglucosan levels is intense wet deposition in equatorial regions. Torrential rain often struck when our ship

sailed in the tropical oceans. The average precipitation in Southeast Asia in October is about 6–9 mm day<sup>-1</sup>, much higher than that in other regions (Figure S3). In Aparri, Philippines (18°19' N, 121°43' E), rainfalls from Oct. 3 to Oct. 13, 2009 (10 days before the sampling of Sample N1) were as high as 265 mm (<http://www.weatheronline.co.uk>). Wet deposition would remove large amounts of particles and particle-bound levoglucosan.

However, wet deposition alone would not result in such a large decrease of levoglucosan levels. The average concentration of levoglucosan in the low latitudes was about 50% less than the overall mean during the two cruises, while the average level of WSOC was slightly higher than the overall mean. Further, the ratios of WSOC<sub>BB</sub> to WSOC over this region were also low (Table 1). This might be due to an abundance of WSOC compounds other than the biomass burning origin in the tropical region, such as biogenic primary and secondary organic aerosols<sup>17</sup>. Alternatively, degradation may be an important mechanism causing the low levoglucosan concentrations and carbon fraction of WSOC<sub>BB</sub>. The annual average concentration of hydroxyl radicals from 5° S to 5° N is about  $1.6 \times 10^6$  molecules cm<sup>-3</sup>, much higher than that in other regions<sup>25</sup>. If we apply the levoglucosan-OH reaction rate constant of  $1.1 \times 10^{-11}$  cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> according to the smog chamber experiment<sup>8</sup>, 78% of initial levoglucosan would be depleted for one day. However, such oxidation reactions would not reduce carbon amount, but rather enhance the water-solubility of organic compounds due to the increase of oxygen fraction.

Another probable cause is interrelated with the intensive moist convection in the tropical region. Biomass burning emissions such as CO, CO<sub>2</sub>, O<sub>3</sub> and aerosols were found at an altitude of over 10 km by deep convection in the equatorial region of Amazon<sup>26</sup>. Levoglucosan was likely to be also lofted to the upper atmosphere, instead of staying in the boundary layer. Furthermore, Africa is the most important source of biomass burning emissions in the low latitudes and con-



**Figure 1 | Global distribution of levoglucosan in the marine boundary layer.** Circles represent data from this study; triangles represent data obtained from an around-the-world cruise<sup>17</sup>; four squares are average levels over East China Sea, Sea of Japan, Pacific (west of 140° E) and Pacific (east of 140° E) during the Aerosol Characterization Experiment campaign<sup>18</sup>; the diamond is the mean level at Alert (82.5° N, 62.3° W) from winter to spring<sup>27</sup>; the hexagon is the average level over the southern Beaufort Sea in summer 2009<sup>19</sup>; the pentagon is the annual mean level on the island of Chichi-jima in the western North Pacific (27°4' N, 142°13' E)<sup>21</sup>; the star is the annual mean level on the island of Azores in the North Atlantic (38°38' N, 27°2' W)<sup>20</sup>. Base map is from ArcGIS software.



Table 1 | Ranges and means of levoglucosan and WSOC at different locations

Location	Levoglucosan (ng/m <sup>3</sup> )		WSOC (ng/m <sup>3</sup> )		WSOC <sub>BB</sub> /WSOC (%)	
	Range	Mean	Range	Mean	Range	Mean
East Antarctica	1.1–18	4.8	252–2000	912	1.8–17	6.4
West Antarctica	0.18–11	3.4	267–1380	670	0.35–9.8	3.8
Southern Ocean	3.5–10	6.9	413–2230	1320	4.6–8.6	6.6
Austrian adjacent sea	1.9–14	5.0	559–2500	1060	0.75–13	6.0
Southeast Asia	1.2–4.3	2.8	468–1120	684	2.0–7.8	4.6
western North Pacific	2.0–6.6	4.8	618–1410	863	3.2–9.5	5.8
East China Sea	-*	6.4	-	1640	-	3.9
Sea of Japan	4.0–16	8.8	854–3850	1730	4.1–8.8	5.7
Sea of Okhotsk	-	3.1	-	753	-	4.1
Bering Sea	1.1–41	10	428–1980	844	2.7–21	8.4
the Arctic Ocean	2.4–11	5.2	86–883	373	8.0–45	19
90°S–60°S	0.18–18	3.9	252–2000	819	0.35–17	4.8
60°S–30°S	0.41–14	5.8	267–2230	831	0.83–13	6.5
30°S–30°N	1.2–4.3	2.7	468–2500	917	0.75–7.8	4.1
30°N–60°N	1.1–16	6.0	430–3850	1170	2.7–9.5	5.5
60°N–90°N	2.4–41	8.0	86–1980	581	5.4–45	16.0
Southern Hemisphere	0.2–18	4.4	252–2502	851	0.35–17	5.4
Northern Hemisphere	1.1–41	6.5	86–3849	866	2.0–45	9.9

\*“-” indicates only one sample in the location.

tributes to about 49% of the global amount<sup>5</sup>. However, studies over oceans adjacent to Africa were still scarce, thereby limiting our overall understanding of biomass burning aerosols over oceans in the low latitudes.

**Levoglucosan in middle latitude samples.** High levoglucosan concentrations were found in the middle latitudes of both the Northern Hemisphere ( $6.0 \pm 3.7$  ng/m<sup>3</sup>) and the Southern Hemisphere ( $5.8 \pm 5.0$  ng/m<sup>3</sup>). The average levels of WSOC were  $1170 \pm 911$  ng/m<sup>3</sup> and  $831 \pm 594$  ng/m<sup>3</sup>, respectively (Table 1; Figure S1). Most of the sampling sites were near continents, boreal forests in the Northern Hemisphere, and Australia and South America in the Southern Hemisphere, where main sources of biomass burning were found. Although samples were collected in the summer, i.e., the burning season, levoglucosan concentrations over the Sea of Japan, the East China Sea and the western North Pacific were comparable or even lower than previous results during winter and spring<sup>17,18</sup> (Table S1). This region is under the influence of the Asian monsoon system. In the summer, prevailing winds originate from the Pacific anticyclone, whereas in the winter, air masses are transported from the East Asian continents. Relative to emissions, monsoon may be a more important factor influencing levoglucosan concentrations in this region<sup>21</sup>. The concentrations over the eastern North Pacific and the western North Atlantic were much less than those over the western North Pacific on similar latitudes (Figure 1). It revealed larger biomass burning emissions in Eurasia than in North America, in accordance with previous estimated results<sup>5</sup>.

**Levoglucosan in High latitude samples.** The average concentration of levoglucosan in the high latitudes (60° ~ 90°) of the Northern Hemisphere was  $8.0 \pm 11$  ng/m<sup>3</sup>, while that of WSOC was  $581 \pm 522$  ng/m<sup>3</sup> (Table 1). Such a high average value of levoglucosan was caused by Sample B30, which was collected over the Bering Sea and had an especially high levoglucosan concentration of 41 ng/m<sup>3</sup>. The median level (4.5 ng/m<sup>3</sup>) of levoglucosan was much less than the average level (Figure S1). According to the air mass back trajectories (BTs) for Sample B30 (Figure S4a), the high-level levoglucosan was probably associated with some big fires in East Siberia and Alaska (Figure S2b). Samples collected over the Arctic Ocean also had high levoglucosan concentrations with a mean of  $5.2 \pm 2.8$  ng/m<sup>3</sup>. Those were much higher than the results in previous

studies at Alert in the Canadian high Arctic<sup>27</sup> and over the southern Beaufort Sea<sup>19</sup> (Table S1). The samples at Alert were collected during winter to spring, while our samples were collected during summer to autumn, which is the main burning season for boreal regions. In addition, the weaker circumpolar vortex in the summer favored air mass transported from surrounding continents. Moreover, levoglucosan over both Alert and the southern Beaufort Sea were mainly derived from biomass burning in high latitudes of Canada, whereas our samples were significantly influenced by air mass from Siberia. Compared with high latitude regions of Canada, Siberia is a much larger biomass emission source<sup>5</sup>. The carbon fraction of WSOC<sub>BB</sub> in WSOC over the Arctic Ocean ( $19 \pm 12\%$ ) was much greater than the overall mean during the two cruises ( $7.6 \pm 7.5\%$ ). The Pearson correlation coefficient of levoglucosan and WSOC was as high as 0.72 over the Arctic Ocean, compared to the value of 0.49 for all samples. It indicated that compared to other regions biomass burning was a more important source of WSOC in aerosols over the Arctic Ocean and dominated the variation of WSOC in this region. BTs indicated that levoglucosan originated from boreal forest fires in Siberia and Canada (Figure S4b and S4c). Recently, levoglucosan derived from fire smoke in boreal forests had been detected in snow in Greenland<sup>28</sup> and ice core in the Kamchatka Peninsula<sup>29</sup>.

The average concentration of levoglucosan over oceans in the high latitudes of the Southern Hemisphere was  $3.9 \pm 4.6$  ng/m<sup>3</sup>, slightly higher than the level in the low latitudes (Table 1; Figure S1a). The levoglucosan concentrations over the West Antarctic adjacent oceans (including samples collected over the Drake Passage) ranged from 0.18 to 11 ng/m<sup>3</sup>, with a mean of  $3.4 \pm 4.3$  ng/m<sup>3</sup>; whereas the concentrations over the East Antarctic adjacent oceans ranged from 1.1 to 18 ng/m<sup>3</sup>, with an average of  $4.8 \pm 5.1$  ng/m<sup>3</sup>. This suggests that despite the absence of local biomass burning emissions, the Antarctic region is evidently affected by biomass burning. Although previous studies discovered the impact of biomass burning on Antarctica by BC<sup>30,31</sup>, the disturbance of local pollution could not be absolutely eliminated. Our result here provided direct evidence of intensive influence of biomass burning on the Antarctic.

Biomass burning aerosol components such as BC emitted in South America could cross over the Drake Passage and reach West Antarctic and Antarctic Peninsula through both upper-level and lower-level flows<sup>30</sup>, especially in summer when the circumpolar vortex broke down and surface inversions were weaker<sup>31</sup>. The degressive





gradient of BC concentrations from the coast to the South Pole supported the meridional transport<sup>32</sup>. BTs also proved that our samples with high levoglucosan contents were affected by the South America continent (Figure S4d). Samples with quite low levoglucosan concentrations were contacted with frequent rainfalls and snowfalls during the sampling episodes. For example, in November 2009, there were rainfalls or snowfalls in 19 days in Bellingshausen Station (62°12' S, 58°58' W) and the total precipitation was about 50 mm in the month (<http://www.weatheronline.co.uk>).

Compared to West Antarctic, East Antarctic is even further away from fire emissions grounds. In a previous study, BC was detected over Maitri (70°S, 12°E) and Larsemann Hills (69°S, 77°E)<sup>33</sup>. The authors recognized that the BC was derived from pollution of stations instead of biomass burning, because the 7-day air mass back trajectories arriving at the measurement sites were all confined to either continental Antarctic or coastal oceanic regions of the Antarctic. Likewise, 10-day air mass back trajectories of our samples collected over oceans adjacent to East Antarctic (Figure S4e and S4f) also did not pass through nearby lower latitude continents (Africa and Australia). However, highly elevated levoglucosan levels in aerosols revealed influence of biomass burning rather than only contamination from anthropogenic activities at stations. Where did the levoglucosan originate from? The back trajectories indicated that the air mass was derived from West Antarctic and arrived here through oceans or continental Antarctic. Fundamentally, the levoglucosan in East Antarctic originated from biomass burning in South America, too. The atmospheric circulation of the Antarctic is separated into two portions by the circumpolar trough around Antarctica at approximately 64°S. Westerly winds are predominant north of 64°S, while easterly winds prevail south of 64°S<sup>34</sup>. Levoglucosan in Sample N32 (62.21°S, 97.77° E) was directly transported from West Antarctic through the westerly winds over oceans (Figure S4e), while levoglucosan in Sample N26 (66.40°S, 68.39° E) was transported through the easterly winds over the continental Antarctic (Figure S4f). The air mass in West Antarctic was lifted near the trough, transferred at a high elevation, and then reached the surface as the form of katabatic winds over the coastal regions of East Antarctic<sup>35</sup>. Thus we speculate that there would be even higher levoglucosan levels over continental Antarctica. Indeed, levoglucosan had been directly detected at picogram per milliliter levels in the ice core collected at Dome C (75°6' S, 123°21' E), Antarctic inland<sup>36</sup>.

## Discussion

The influence of biomass burning on the chemical composition of aerosols was illustrated by factor analysis (Table 2). About 84% of the variance can be explained by five factors. A shipboard study over the seas of Russian Arctic suggested that Fe, Ni, Cu, Cr, Zn, Mn, Pb and other heavy metals originate from anthropogenic emissions<sup>37</sup>. NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are partly associated with combustion of fossil fuels<sup>38</sup>. In this study, these elements and ions were separated into three factors (Factors 1, 3 and 4), indicating three potential anthropogenic sources. Besides, crustal sources may also have contributed to Factor 4 owing to the indicator Fe<sup>39</sup>. Factor 2 was loaded significantly with K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup>, indicating a sea salt source. Levoglucosan was substantially loaded in Factor 5, revealing this factor represented the influence of biomass burning emissions. It is interesting that K<sup>+</sup>, a conventional tracer for biomass burning in continents, gathered with other sea salt ions instead of levoglucosan. Because of the disturbance by massive sea salt, K<sup>+</sup> cannot be used as an indicator for biomass burning over oceans. In order to estimate the relative influence of biomass burning on each sample, the factor scores were calculated. If a sample had a high score for Factor 5, then the sample was heavily affected by biomass burning. The scores for Factor 5 showed similar spatial variations with levoglucosan (Figure S5), e.g., high levels in the middle latitudes and low levels in the low latitudes. As presented in Figure 2, the factor score was significantly

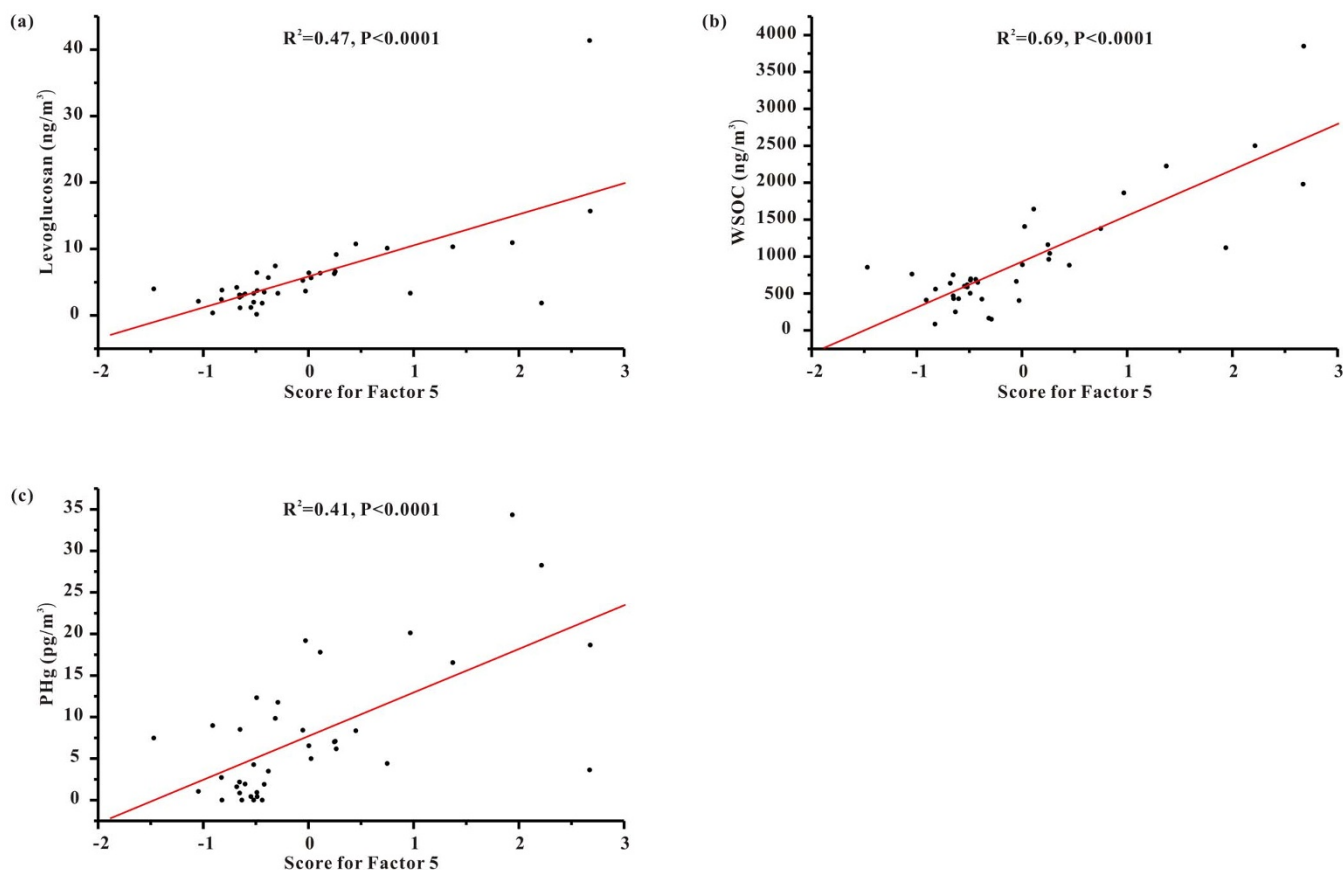
**Table 2 | Loadings for factor analysis of chemical compositions of aerosols over oceans\***

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Levoglucosan	0.079	-0.299	-0.02	0.228	0.686
WSOC	0.353	0.197	-0.066	-0.023	0.831
K <sup>+</sup>	-0.085	0.955	-0.018	-0.101	0.127
Na <sup>+</sup>	0.161	0.964	-0.032	-0.011	0.039
Ca <sup>2+</sup>	0.179	0.883	0.115	0.192	0.082
Mg <sup>2+</sup>	0.071	0.982	-0.031	-0.004	0.045
Cl <sup>-</sup>	0.103	0.554	-0.098	-0.188	-0.282
NO <sub>3</sub> <sup>-</sup>	0.887	0.152	0.091	0.134	0.256
SO <sub>4</sub> <sup>2-</sup>	0.725	0.463	0.046	0.266	-0.058
Al	0.815	-0.036	-0.004	0.075	0.044
Cr	0.015	-0.089	0.981	0.003	0.031
Mn	0.321	0.093	-0.084	0.862	0.017
Fe	0.106	0.023	0.239	0.926	0.041
Ni	-0.167	0.031	0.964	0.003	-0.006
Cu	0.158	-0.296	0.04	0.581	-0.018
Zn	0.849	0.113	0.017	0.419	0.154
Sr	0.407	0.853	-0.05	0.044	0.14
Ba	0.949	0.073	0.036	0.158	0.103
Pb	0.502	-0.063	0.774	0.294	0.025
Co	0.079	0.264	0.616	0.684	0.144
Cd	0.117	-0.046	0.967	0.045	0.032
As	0.576	-0.017	-0.08	0.682	0.153
Se	0.864	0.357	0.131	0.089	0.167
Hg	0.14	0.332	0.194	-0.063	0.642
% of variance	23.0	22.6	16.6	14.2	7.8
Cumulative %	23.0	45.6	62.1	76.3	84.1

\*Factor loadings with varimax rotation.

correlated with levoglucosan ( $R^2 = 0.47$ ,  $P < 0.0001$ ), WSOC ( $R^2 = 0.69$ ,  $P < 0.0001$ ) and Hg ( $R^2 = 0.41$ ,  $P < 0.0001$ ), indicating the impact of biomass burning on WSOC and Hg in marine aerosols. However, the factor score could not entirely interpret the variations of levoglucosan levels. In addition to biomass burning emissions, some physical and chemical processes during transport, such as diffusion, dry and wet deposition, degradation by hydroxyl radicals, also affect levoglucosan concentrations in the atmosphere. These processes could explain the inconspicuous relationship between levoglucosan and Hg, and the significant correlation between the factor score and Hg. In addition, as discussed above, the reactions in the atmosphere would not cause the depletion of WSOC. This may be the reason why WSOC had even better correlations with the factor score than levoglucosan. Relative to the single index levoglucosan, the factor score may better indicate the influence of biomass burning.

Hg is a ubiquitous toxic element and its major pathway of transport is through the atmosphere<sup>40</sup>. Ocean emissions, biomass burning and anthropogenic emissions are main sources of global atmospheric mercury<sup>41</sup>. It is notable that in most studies, Hg is referred to gaseous elemental mercury (GEM) due to the predominant amount in the atmosphere. Very little is known about Hg in aerosols, i.e., particulate Hg (PHg), compared to GEM, especially over oceans. During our cruises, the average concentration of PHg was  $7.4 \pm 8.0$  pg/m<sup>3</sup>, comparable to the results at Okinawa Island, Japan ( $3.0 \pm 2.5$  pg/m<sup>3</sup>)<sup>42</sup> and Appledore Island, US ( $7.6$  pg/m<sup>3</sup> during daytime and  $3.1$  pg/m<sup>3</sup> during nighttime)<sup>43</sup>. According to previous studies, PHg is formed from GEM and reactive gaseous mercury (RGM) through condensation on primary particles and gas-particle transformation<sup>43,44</sup>. Biomass burning may also be a source of PHg in continents<sup>45</sup>, similar to the case over oceans according to the factor analysis. WSOC can enhance the hygroscopic property of particles in the atmosphere and serves as cloud condensation nuclei<sup>46</sup>. Biomass burning emits many species of water-soluble organic compounds<sup>47</sup> and is one of the most important sources of WSOC in the atmosphere<sup>24</sup>. During the two cruises, WSOC<sub>BB</sub> accounted for  $7.6 \pm 7.5\%$  of WSOC. It is noted that



**Figure 2** | Relationships between the score for Factor 5 (see Table 2) and atmospheric (a) levoglucosan, (b) WSOC and (c) PHg during the CHINARE08 and CHINARE09/10 cruises.

the calculation probably underestimated the fraction of  $WSOC_{BB}$  in WSOC due to the degradation of levoglucosan in the atmosphere. The fractions of  $WSOC_{BB}$  in WSOC in the Northern Hemisphere ( $9.9 \pm 9.5\%$ ) were significantly higher ( $P < 0.05$ ) than those in the Southern Hemisphere ( $5.4 \pm 4.1\%$ ). More oxidation reactions during transport may have caused the low fractions. The highest fraction reached 45%, which was found over the Arctic Oceans. The fractions over coastal regions of Antarctica ranged from 0.35% to 10%, with a mean of  $3.9 \pm 3.9\%$ . Clearly, biomass burning is an important source of WSOC in the marine boundary layer, even over remote oceans.

Up to now, there has been no estimate about the contribution of biomass burning to organic carbon in continental Antarctica. Here, through the sample collected in the coastal region of Antarctica, we attempt to assess such a contribution. We estimated  $WSOC_{BB}$  over continental Antarctica as  $11 \text{ ng/m}^3$ , with the concentration of Sample N26 whose BTs passed through continental Antarctica (Figure S4f). If we use the dry-deposition velocity of  $0.33 \text{ cm s}^{-1}$  measured at snow-covered area of Dronning Maud Land ( $73^{\circ}3' \text{ S}$ ,  $13^{\circ}25' \text{ W}$ ), Antarctica<sup>48</sup>, the deposition fluxes of  $WSOC_{BB}$  in Antarctic inland are  $1180 \mu\text{g m}^{-2} \text{ yr}^{-1}$ . Furthermore, if we apply the average snow accumulation rate from Zhongshan station to Dome A from 2005 to 2008 ( $74 \text{ kg m}^{-2} \text{ yr}^{-1}$ )<sup>49</sup>, the concentration of  $WSOC_{BB}$  in snow is  $16 \mu\text{g L}^{-1}$ . Compared with the mean levels of total organic carbon (TOC) in snow samples in Dronning Maud Land and Princess Elizabeth Land, East Antarctica ( $140 \mu\text{g L}^{-1}$  and  $259 \mu\text{g L}^{-1}$ , respectively)<sup>50</sup>,  $WSOC_{BB}$  accounted for about 6% to 11% in TOC in snow. Therefore, biomass burning may be a significant source of organic compounds in snow in continental Antarctica. It is noted however, that this estimation may not well reflect the true deposition flux of biomass burning aerosols due to the temporal and spatial limitations on our sampling. Because the

samples were collected in a burning season of the South America and the circumpolar vortex was weak in summer, this estimation may represent the upper limit of the contribution of biomass burning. Further studies at more locations with longer periods are needed to gain an accurate estimate of the contribution of biomass burning on organic carbon in Antarctica.

## Methods

**Sampling.** Twenty-four total suspended particles (TSP) samples and three field blanks were collected between the East China Sea and the Arctic Ocean ( $33^{\circ} \text{ N}$ – $85^{\circ} \text{ N}$ ) during the CHINARE 08 from July to September, 2008<sup>51</sup>. Thirty-one TSP samples and three field blanks were collected between the East China Sea and Antarctica ( $26^{\circ} \text{ N}$ – $69^{\circ} \text{ S}$ ) during the CHINARE 09/10 from November 2009 to April 2010. A high volume air sampler was placed on the upper-most deck of the icebreaker *Xuelong*, and TSP samples were collected with a flow of  $1.05 \text{ m}^3/\text{min}$  by glassfiber filters ( $8 \times 10$  inches) that were prebaked at  $450^{\circ} \text{ C}$  for 4 h. Each sampling lasted for 1–3 days, and the air volumes ranged from 372 to 2752  $\text{m}^3$  (at  $0^{\circ} \text{ C}$  and 1 atm). Samples were then wrapped with aluminum foil, zipped in plastic bags, and stored in freezers at  $-20^{\circ} \text{ C}$  until analysis. Details of sampling information were presented in Table S2 in the supporting information.

**Chemical analysis.** A punch ( $9 \times 11.5 \text{ cm}$ ) of each filter was taken and analyzed for levoglucosan. The detailed method was described elsewhere<sup>52,53</sup>. Briefly, each sample was extracted by sonication with 30 mL of mixed solvent (dichloromethane : hexane 1 : 1, V/V) twice, and then extracted with 30 mL of another mixed solvent (dichloromethane : methanol 1 : 1, V/V) twice. Before extraction, levoglucosan-<sup>13</sup>C was spiked as the internal standard. The four extracts of each sample were combined, filtered and concentrated. The concentrated extracts were silylanized by *N,O*-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) and then analyzed by a gas chromatograph–mass selective detector (GC-MSD). The method detection limits (MDLs) were  $0.051 \text{ ng/m}^3$  for samples collected during the CHINARE 08 calculated by three times of the standard deviation of field blanks under the average sampling volume of 1311  $\text{m}^3$ , and  $0.008 \text{ ng/m}^3$  for samples collected during CHINARE 09/10 under the average volume of 2189  $\text{m}^3$ . Levoglucosan concentrations in real samples were one to two orders of magnitude more than field blanks.



Another punch (2.5 cm diameter) was taken from each filter and extracted with 20 mL of 18-Mohm Milli-Q water by sonication for 60 minutes in an ice-water bath. Then the extract was analyzed for WSOC with a total organic carbon analyzer (Shimadzu TOC-VCPH). The MDLs were 30 and 143 ng/m<sup>3</sup> for CHINARE 08 and CHINARE 09/10 samples, respectively. Some of these samples were selected to determine 7 ions and 15 elements. Details of analytical procedures were described by Kang, et al.<sup>54</sup>.

**Quality assurance/quality control (QA/QC).** Levoglucosan and WSOC were analyzed in the State Key Laboratory of Organic Geochemistry (KLOG), Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Field blank samples and laboratory blank samples were extracted and analyzed in the same way as ambient samples for quality assurance and quality control (QA/QC) according to procedures described by Ding, et al.<sup>53</sup>. All the data reported in this study were corrected for the field blanks. Recovery of levoglucosan in six spiked samples (authentic standard spiked into solvent with prebaked filter) was 87 ± 4%. The relative differences for the target compound in paired duplicate samples (n = 6) were all < 15%. The results in this study were not recovery corrected.

**Air mass BTs and fire maps.** Air mass BTs were calculated for the cruise samples using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) transport and dispersion model from the NOAA Air Resources Laboratory (<http://www.arl.noaa.gov/ready/hysplit4.html>). Ten-day BTs for the start and end of each sampling episode were traced with 6 h steps at 100, 500, and 1000 m above the sea level. Global fire maps were obtained by using the Moderate Resolution Imaging Spectroradiometer (MODIS) from NASA satellites (<http://lance-modis.eosdis.nasa.gov/cgi-bin/imagery/firemaps.cgi>).

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## Author contributions

Q.H.H. and Z.Q.X. contributed equally to the design of the study and preparation of the manuscript. X.M.W. and P.F.Z. contributed to the discussion of results and manuscript refinement. Q.H.H., Z.Q.X. and H.K. contributed to the sample collection and analysis.

## Additional information

**Supplementary information** accompanies this paper at <http://www.nature.com/scientificreports>

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